# In-plant corrosion testing in chlorine dioxide environments

Johan Nordström and Arne Bergquist

*ABSTRACT: Welded coupons of stainless steels, nickel-base alloys, and titanium were exposed in process equipment used to produce or to bleach with chlorine dioxide. Test locations included tanks for spent acid from chlorine dioxide production, bleach-plant scrubbers, bleaching tower inlets, and bleach washers. The results of ten exposures are discussed in connection with descriptions of the process environments. All tested alloys—except for titanium and stainless steel S32654—suffered corrosion in at least one test environment.*

*KEYWORDS: Alloy, alloy steel, chlorine dioxide, corrosion tests, environments, light metals, materials testing, nickel, oxides, stainless steel, steel, test methods, titanium, transition metals.*

## Corrosion in chlorine dioxide environments

Chlorine dioxide, $ClO_2$, is the main corrosive constituent in many of the most aggressive environments encountered during production of pulp and paper. Stainless steels have seen only limited use in these aggressive $ClO_2$ environments. Other construction materials—titanium, nickel-base alloys, bricks, and polymers—are often used instead. However, the most highly alloyed stainless steels have been used successfully in the washing equipment of $ClO_2$ bleaching stages *(1, 2)*.

Chlorine dioxide is such a strongly oxidizing agent that the corrosion potential of many stainless steels is often raised above their pitting or crevice-corrosion potentials when exposed to $ClO_2$-containing solutions. The stainless steels' insufficient resistance to localized corrosion has been the main reason for choosing other construction materials. However, under certain conditions, the oxidizing power is also high enough to cause uniform transpassive corrosion of stainless steels and some other metallic materials. This phenomenon has recently been much discussed as a problem for nickel-base alloys *(3–8)*. Glass-fiber reinforced plastics (GRP) also are attacked by $ClO_2$ *(9)*.

**Nordström, technical manager, pulp and paper business segment, and Bergquist, project engineer, research and development, are affiliated with Avesta Sheffield AB, S-774 80 Avesta, Sweden.**

In laboratory tests, a new stainless steel, Avesta Sheffield 654 SMO® (S32654), showed superior resistance to localized corrosion compared with that of other stainless steels, and it appeared to be less prone to transpassive corrosion than nickel-base alloys *(1, 10)*. These results prompted us to test the corrosion resistance of this material in process equipment containing chlorine dioxide.

## Coupon-testing method

In-plant exposure of test coupons has proved to be a good method for predicting long-term service experiences within a given environment. Materials resisting 3–7 months of in-plant testing have performed well in actual service for many years *(2)*.

In this work, welded test coupons were mounted on an insulated bolt with serrated polytetrafluoroethylene (PTFE) crevice washers separating the coupons from each other. The resultant test rack is illustrated in **Fig. 1**. The crevice washers had 20 plateaus on each side, making contact with only the base metal, not with the weld or the heat-affected zone around the weld. Fasteners were put on each end of the bolt, and the rack was assembled with nuts torqued to 1.58 N·m. Double nuts were used to prevent loosening during the exposure.

After exposures for 4.5–13.6 months each rack was dismantled, and all coupons were cleaned and dried. In some cases, brushing in ordinary tap water was sufficient to

**I.** Typical chemical composition of the tested alloys, wt.%

| Alloy | C | Cr | Ni | Mo | N | Cu | Other |
|---|---|---|---|---|---|---|---|
| Stainless steels | | | | | | | |
| S31803 | 0.02 | 22 | 5.5 | 3 | 0.17 | ... | ... |
| N08904 | 0.01 | 20 | 25 | 4.5 | 0.06 | 1.5 | ... |
| S32750 | 0.02 | 25 | 7 | 4 | 0.27 | ... | ... |
| S31254 | 0.01 | 20 | 18 | 6.1 | 0.20 | 0.8 | ... |
| S32654 | 0.01 | 24 | 22 | 7.3 | 0.50 | 0.5 | 3 Mn |
| Nickel-base alloys | | | | | | | |
| N06625 | 0.02 | 22 | Balance | 9 | ... | ... | Fe, Nb |
| N10276 | 0.008 | 16 | Balance | 16 | ... | ... | Fe, W |
| N06022 | 0.008 | 22 | Balance | 13 | ... | ... | Fe, W |
| Titanium * | ... | ... | ... | ... | ... | ... | ... |

* Grade 2, commercially pure

**II.** Welding techniques and typical composition of the filler metals

| | Welding | Filler | Filler metals, wt.% | | | | | |
|---|---|---|---|---|---|---|---|---|
| Alloy | method [a] | name | C | Cr | Ni | Mo | N | Other |
| Stainless steels | | | | | | | | |
| S31803 | SMAW | 2205 | 0.02 | 22.5 | 9.5 | 3.1 | 0.14 | ... |
| N08904 | SMAW | 904L | 0.03 | 20 | 25 | 4.5 | ... | 1.5 Cu |
| S32750 | SMAW | 2507/P100[b] | 0.03 | 25 | 9.5 | 3.6 | 0.22 | ... |
| S31254 | SMAW | P12[b] | 0.02 | 21.5 | Balance | 9 | ... | 2 Nb, 4 Fe |
| S32654 | GTAW | P16[b] | 0.02 | 25 | Balance | 15 | ... | ... |
| Nickel-base alloys | | | | | | | | |
| N06625 | SMAW | P12[b] | 0.02 | 21.5 | Balance | 9 | ... | 2 Nb, 4 Fe |
| N10276 | SMAW | C-276 | 0.015 | 16 | Balance | 16 | ... | 3 W |
| N06022 | SMAW | C-22 | 0.015 | 21 | Balance | 13 | ... | 3 W |
| Titanium [c] | ... | ... | ... | ... | ... | ... | ... | ... |

[a] SMAW = shielded metal arc welding; GTAW = gas tungsten arc welding
[b] Trademarks of Avesta Welding (Sweden)
[c] Unknown

get a clean surface, while coupons from other test racks had to be cleaned in dilute nitric acid or an oxalic acid solution. After the weight losses of the coupons had been determined, they were examined in a stereo microscope at 20X magnification. The maximum depth of any pitting or crevice-corrosion attack was measured by a needle-point micrometer or a microscope equipped with a calibrated fine-focus knob.

## Tested materials

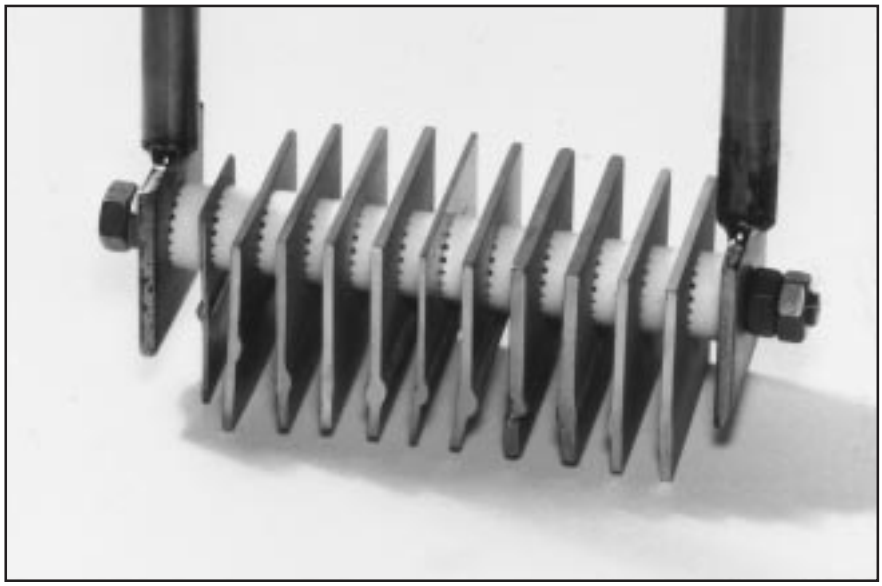
Welded coupons of stainless steels and nickel-base alloys were included in all test racks, while titanium was included only in some racks. After welding, the weld beads were blasted with aluminum oxide, and the coupons were finally pickled. All test coupons were cut from cold-rolled sheet, with most measuring 60 mm x 60 mm x 3mm. **Table I** shows the typical chemical compositions of the base metals. **Table II** shows the compositions of the filler metals and the welding methods.

## Test locations, environments, and results

### General

The process environments in each of the ten test locations are described either in a table or within the text. The test results for the coupons exposed to these ten environments are presented in tables and discussed in

**1.** Test rack

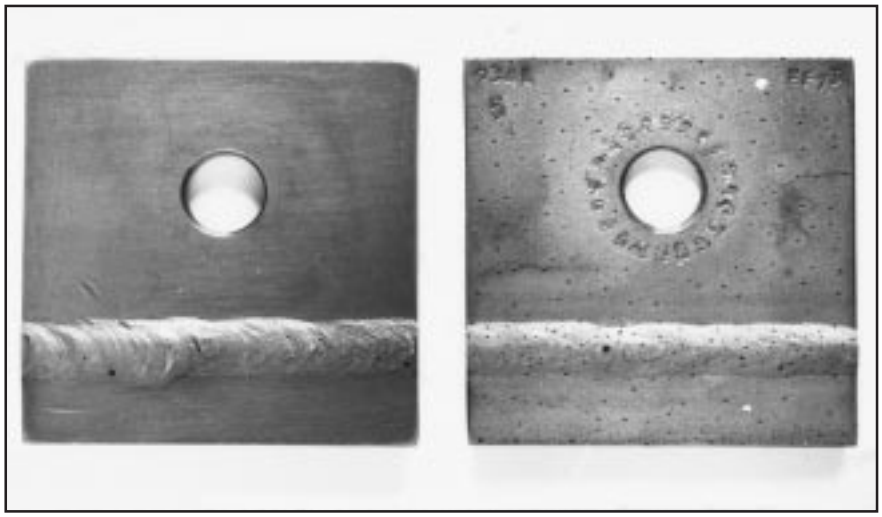


**III.** Test environment, Rack 1 (spent-acid tank)*

| | |
|---|---|
| $H_2SO_4$, g/L | 480 |
| $NaClO_3$, g/L | 6 |
| NaCl, g/L | 0.6 |
| $ClO_2$ (as active chlorine), g/L | 2.9 |
| pH | <0 |
| Temperature, °C | 35 |

* Coupons exposed for 138 days

**2.** Two samples from Rack 1—stainless steels S32750 and N08904



the text. Results are expressed in terms of corrosion rate, the number of crevice-corrosion sites (out of a possible total of 40), the maximum depth of crevice corrosion, the location of pitting-corrosion sites, and the maximum depth of pitting corrosion.

The corrosion rate—calculated from the weight loss of each coupon—is presented as the average rate of thinning, expressed in millimeters per year. Corrosion rate was calculated for all coupons, even in cases where localized attack was the main cause of weight loss. Maximum depths of localized attacks are given in millimeters, and the degree of crevice corrosion is presented as the number of corroded crevice sites, out of 40 possible sites. The location of pitting corrosion is denoted "A" if all surfaces are attacked and "W" if mainly the weld is attacked. Uniform corrosion was not always evenly distributed over a coupon but, rather, was concentrated in certain spots. This explains why uniform corrosion is sometimes noted, even though the weight loss is low.

## Chlorine dioxide production

Rack 1 was tested in a tank containing spent acid from chlorine dioxide production in a Mathieson generator. **Table III** shows the chemical composition of the acid. The tank is made of carbon steel lined with 40-mm-thick tiles and a 4-mm GRP membrane in between the steel and the tiles. No corrosion of the tank has been reported.

After 138 days of testing, only two of the stainless steels were attacked. Stainless steel N08904 suffered severe localized corrosion, and stainless steel S32750 exhibited pitting in the weld, as seen in **Fig. 2**. No sign of corrosion was found on the stainless steels S31254 and S32654 nor on the nickel-base alloys or the titanium specimen. More detailed results are presented in **Table IV**.

Racks 2 and 3 were tested in another tank containing spent acid from chlorine dioxide production in a Mathieson generator. This tank is made of solid GRP, and no corrosion of the tank material has been reported. The chemical composition of the acid is shown in **Table V**. The Rack 2 samples were immersed in the acid, and the Rack 3 samples were kept above the liquid surface. Both racks were exposed for 182 days.

**IV.** Test results, Rack 1 (spent-acid tank)

| Alloy | Corrosion rate, mm/year | Crevice corrosion: No. of sites [a] | Crevice corrosion: Max. depth, mm | Pitting corrosion: Location [b] | Pitting corrosion: Max. depth, mm |
|---|---|---|---|---|---|
| Stainless steels | | | | | |
| N08904 | 0.039 | 40 | 0.7 | A | 1.0 |
| S32750 | 0.017 | ... | ... | W | 0.7 |
| S31254 | 0.006 | ... | ... | ... | ... |
| S32654 | 0.003 | ... | ... | ... | ... |
| Nickel-base alloys | | | | | |
| N06625 | 0.006 | ... | ... | ... | ... |
| N10276 | 0.006 | ... | ... | ... | ... |
| N06022 | 0.002 | ... | ... | ... | ... |
| Titanium | 0.002 | ... | ... | ... | ... |

[a] Out of 40 possible sites
[b] A = all surfaces; W = weld area

**V.** Test environment, Racks 2 and 3 (spent-acid tank)*

| | |
|---|---|
| $H_2SO_4$, g/L | 420–450 |
| $NaClO_3$, g/L | 3 |
| NaCl, g/L | 1–3 |
| $ClO_2$ (as active chlorine), g/L | 1–3 |
| pH | <0 |
| Temperature, °C | 25 |

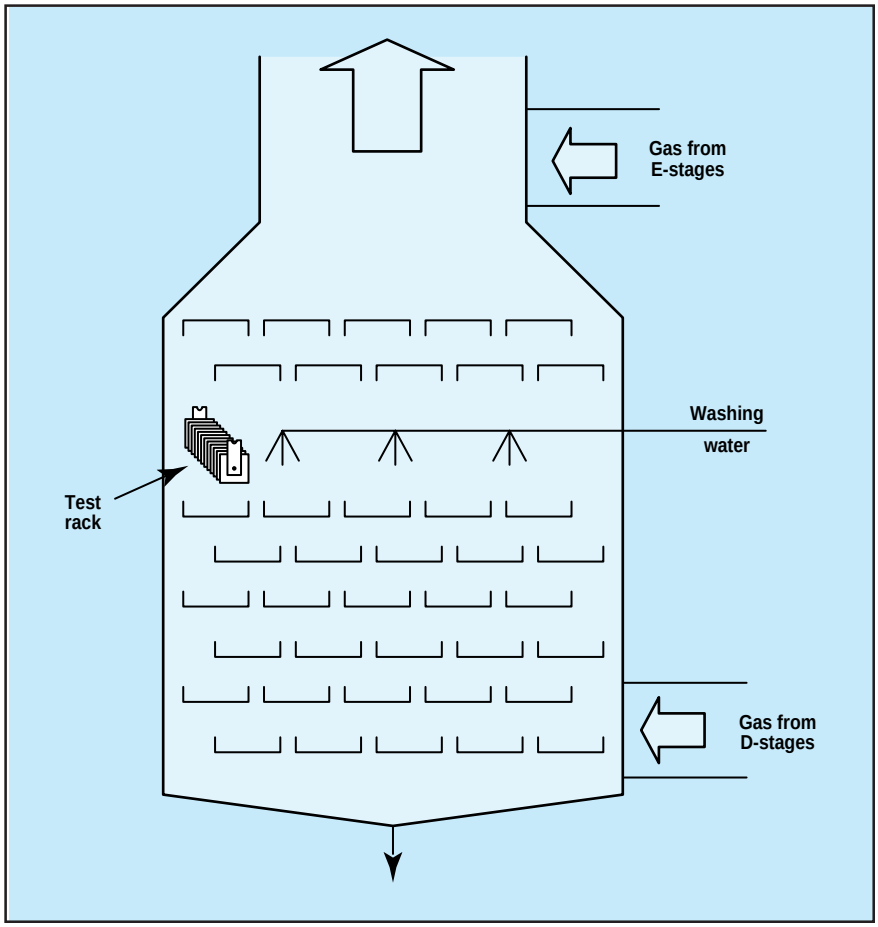
* Coupons exposed for 182 days

The results in **Table VI** show that stainless steel N08904 was the only nonresistant material. Both pitting and crevice corrosion were observed on N08904, and the degree of corrosion was higher in the gas phase than in the liquid.

## Bleach-plant scrubbers

Rack 4 was inserted in the inlet duct of a scrubber designed to clean exhaust gases from bleaching towers and washers (D stages). Both scrubber and duct are made of GRP, which is reported to be resistant. The gas temperature was about 50°C, and the content of chlorine and chlorine dioxide, as active chlorine, was 310 mg/$m^3$ (normal temperature and pressure (NTP), 0°C, 1.013 x $10^5$ Pa). The samples were not in contact with any washing liquid and were wetted only by condensate formed when the gas was cooled in the uninsulated outdoor duct. During the test period of 182 days, the ambient temperature was initially below the freezing point and gradually increased to a maximum of about 25°C during daylight hours. Pitting and crevice corrosion were found on stainless steel N08904, as seen in **Table VII**, but the more highly alloyed grades showed no sign of attack.

**3.** Location of Rack 5 in bleach-plant scrubber




Rack 5 was placed inside the bleach-plant scrubber at another pulp mill, as shown in **Fig. 3**. This scrubber also is made of GRP and has suffered no apparent corrosion problems. The gas temperature was

**VI.** Test results, Rack 2 (immersed in spent acid) and Rack 3 (suspended in spent-acid fumes)

| | Corrosion rate, mm/year | | Crevice corrosion | | | | Pitting corrosion | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | No. of sites [a] | | Max. depth, mm | | Location [b] | | Max. depth, mm | |
| Alloy | Rack 2 | Rack 3 | Rack 2 | Rack 3 | Rack 2 | Rack 3 | Rack 2 | Rack 3 | Rack 2 | Rack 3 |
| Stainless steels | | | | | | | | | | |
| N08904 | 0.015 | 0.077 | 14 | 36 | 0.2 | 0.4 | A | A | 0.4 | 0.7 |
| S32750 | 0.006 | 0.001 | ... | ... | ... | ... | ... | ... | ... | ... |
| S31254 | 0.002 | 0.001 | ... | ... | ... | ... | ... | ... | ... | ... |
| S32654 | 0.001 | 0 | ... | ... | ... | ... | ... | ... | ... | ... |
| Nickel-base alloys | | | | | | | | | | |
| N06625 | 0.003 | 0.002 | ... | ... | ... | ... | ... | ... | ... | ... |
| N10276 | 0.005 | 0.003 | ... | ... | ... | ... | ... | ... | ... | ... |
| N06022 | 0.002 | 0.001 | ... | ... | ... | ... | ... | ... | ... | ... |

[a] Out of 40 possible sites
[b] A = all surfaces

**VII.** Test results, Rack 4 (bleach-plant scrubber inlet)

| | | Crevice corrosion | | Pitting corrosion | |
|---|---|---|---|---|---|
| Alloy | Corrosion rate, mm/year | No. of sites [a] | Max. depth, mm | Location [b] | Max. depth, mm |
| Stainless steels | | | | | |
| N08904 | 0.011 | 13 | 0.2 | W | 0.7 |
| S32750 | 0 | ... | ... | ... | ... |
| S31254 | 0 | ... | ... | ... | ... |
| S32654 | 0 | ... | ... | ... | ... |
| Nickel-base alloys | | | | | |
| N06625 | 0 | ... | ... | ... | ... |
| N10276 | 0 | ... | ... | ... | ... |
| N06022 | 0 | ... | ... | ... | ... |

[a] Out of 40 possible sites
[b] W = weld area

approximately 50°C, and the content of chlorine and chlorine dioxide, as active chlorine, varied between 20 mg/m$^3$ and 4000 mg/m$^3$ (NTP). The samples were mainly exposed to the gas and condensate dripping from the droplet separators. However, some influence from the alkaline washing water (pH 10.8)—basically tap water with additions of NaOH and $SO_2$—cannot be excluded. After 138 days, stainless steel N08904 had one perforating attack starting in the drilled hole, but there was no attack of higher alloyed grades, as seen in **Table VIII**.

## Bleach-tower inlets

Rack 6 was placed in the bottom part of a $D_2$ tower for 365 days. (The bleach plant was running a $D_1(EOP)D_2D_3$ sequence after oxygen delignification.) The inside of the tower is tile-lined, while mixer and pulp pipes are made of titanium. No corrosion problems have been reported for this process equipment. The chemical environment at the test location is shown in **Table IX**. (Note that in this case, the amount of $ClO_2$ is given as the charge in the mixer.) No pitting or crevice corrosion were found on any material. The nickel-based weld of stainless steel S31254 suffered some uniform corrosion, mainly confined to a weld defect where the welding had been interrupted and then resumed without sufficiently remelting the previous pass and the base material. Severe uniform corrosion occurred on all

**VIII.** Test results, Rack 5 (bleach-plant scrubber)

| *Alloy* | *Corrosion rate, mm/year* | *Crevice corrosion* | *Pitting corrosion* |
|---|---|---|---|
| Stainless steels | | | |
| N08904 | 0.011 | One perforating attack starting in the drilled hole | |
| S32750 | 0.001 | ... | ... |
| S31254 | 0.001 | ... | ... |
| S32654 | 0 | ... | ... |
| Nickel-base alloys | | | |
| N10276 | 0.002 | ... | ... |
| N06022 | 0.004 | ... | ... |

**IX.** Test environment, Rack 6 (inlet of second D-stage bleach tower) [a]

| | |
|---|---|
| $ClO_2$ (as active chlorine), [b] g/L | 1.6–2.2 |
| pH | 5–6 |
| Pressure, bar | 3 |
| Temperature, °C | 70 |

[a] Coupons exposed for 365 days
[b] Charge to mixer

**X.** Test results, Rack 6 (bleach-tower inlet)

| *Alloy* | *Corrosion rate, mm/year* | *Crevice corrosion* | *Pitting corrosion* | *Remarks* |
|---|---|---|---|---|
| Stainless steels | | | | |
| S32750 | 0.001 | ... | ... | ... |
| S31254 | 0.002 | ... | ... | Uniform corrosion of inhomogeneities in weld |
| S32654 | 0.001 | ... | ... | ... |
| Nickel-base alloys | | | | |
| N06625 | 0.189 | ... | ... | Severe uniform corrosion |
| N10276 | 0.164 | ... | ... | Severe uniform corrosion |
| N06022 | 0.272 | ... | ... | Severe uniform corrosion |
| Titanium | 0 | ... | ... | ... |

**XI.** Test environment, Rack 7 (inlet of second D-stage bleach tower) [a]

| | |
|---|---|
| $ClO_2$ (as active chlorine),[b] g/L | 1.8–2.0 |
| pH | 3.5 |
| Pressure, bar | 3 |
| Temperature, °C | 70 |

[a] Coupons exposed for 413 days
[b] Charge to mixer

nickel-base alloys. **Figure 4** shows the N06022 coupon, the thickness of which locally had been reduced from 2.0 mm to 0.3 mm during one year. Stainless steels S32654 and S32750 and titanium were the only grades without any attack, as seen in **Table X**.

Rack 7 was exposed in the bottom part of another $D_2$-tower for 413 days. (This bleach-plant configuration is $D_1(EO)D_2D_3$, following oxygen delignification.) **Table XI** shows the chemical environment at testing, with the amount of $ClO_2$ again given as the charge in the mixer. Materials of construction and service experiences are the same as for Rack 6. None of the tested materials experienced pitting or crevice corrosion. All grades but titanium lost some weight because of slight uniform corrosion, but the corrosion rates were low and can be disregarded, as seen in **Table XII**.

## Bleach-tower tops

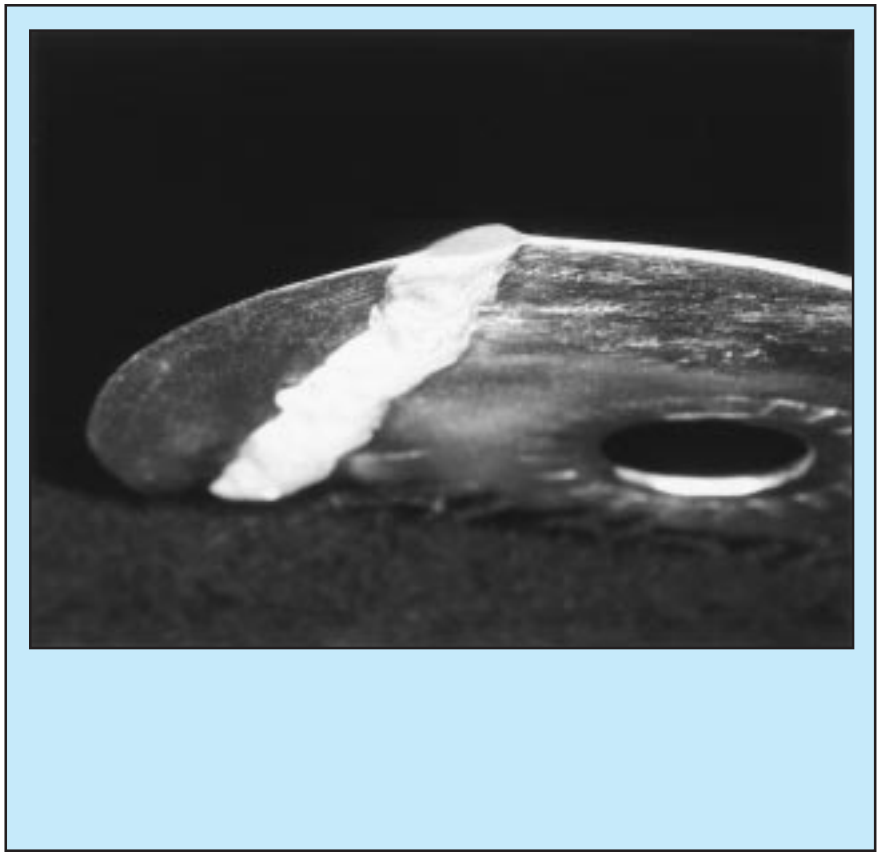
Rack 8 was exposed in the same bleach tower as Rack 7, but it was placed in the top of the tower, above the pulp suspension. The process parameters are very much the same, except for a slightly lower temperature (60°C), a lower chlorine dioxide content (0–10 mg/L as active chlorine), and a lower pressure (atmospheric). This rack was exposed for 399 days, which resulted in pitting and crevice corrosion of stainless steel S31803 but no visible attacks of the other alloys, as seen in **Table XIII**.

Rack 9 was tested in another pulp mill that bleaches pulp in five stages after oxygen delignification, in a $D_1ED_2ED_3$ sequence. The samples hung in the top of the $D_3$-tower, above the pulp suspension, for 138 days. This tower is internally lined with titanium, and no corrosion problem has been reported. **Table XIV** shows the testing environment. Stainless steel N08904 was the only grade suffering from localized corrosion. All grades lost some weight because of slight uniform corrosion, but the corrosion rates were negligible, as seen in **Table XV**.

## Bleach washer

Rack 10 was exposed in the same bleaching stage as Rack 9, but Rack 10 was mounted just beneath the hood of the filter washer. The process parameters are much the same, except for a slightly lower temperature (60–70°C) and a lower chlorine dioxide content (<0.1 g/L as active chlorine). A dilution of the pulp suspension from 11% to 2% consistency contributes to the changed conditions, but one also must consider the presence of sulfur dioxide in the water added in the tower outlet. Provided the $SO_2$ addition is made, the amount of $ClO_2$ is probably far be-

**4.** Alloy N06022 from Rack 6, bleach tower inlet. The edge of the circular coupon is shown in the upper foreground, and the most corroded area is to the left.



low the upper limit specified. The filter drum is made of Type 316 stainless steel and suffers corrosion on the end walls. The vat also was originally made of 316 stainless steel and experienced corrosion until it was lined with S31254. No corrosion has been observed on the hood, which is fabricated from GRP. Rack 10 was exposed for 138 days, which resulted in pitting and crevice corrosion of stainless steel N08904 but no attack of the other alloys, as seen in **Table XVI**.

## Discussion of results

### Chlorine dioxide production

Three test racks were exposed in tanks for spent acid from chlorine dioxide production. Seven of the alloys were included in all three racks: the three nickel-base alloys and the stainless steels S32654, S31254, S32750, and N08904. Stainless steels S32654, S31254, and all nickel-base alloys, i.e., the most highly alloyed grades, were resistant. However, N08904 suffered pitting and crevice corrosion in all three locations. Stainless steel S32750 experienced pitting corrosion in one case (Rack 1). The attack of N08904 was also most severe in this location, as evidenced by the number of attacked crevice sites and the depth of corrosion. The temperature and the chlorate concentration in the Rack 1 location was slightly higher than in the other two locations, and the mean value for residual $ClO_2$ content was higher. All three factors contribute to an increased risk of localized corrosion.

Racks 2 and 3 were both exposed in the same tank, one above the liquid and one fully immersed. Stainless steel N08904 was the only grade attacked, and the extent of corrosion was clearly larger above the liquid. Field tests in bleach plants also have indicated that the gas phase is significantly more corrosive than the liquid phase. However, while a large difference has been found in most $Cl_2$ stages, this difference in corrosivity is not as apparent in $ClO_2$ stages *(11–13)*.

### Bleach-plant scrubbers

The stainless steel N08904 also showed inadequate resistance to localized attack in the two bleach-plant scrubbers. The amount and depths of attack were not as extensive as in the spent-acid tests, even though the temperature was higher. On the other hand, it is very hard to know exactly what chemical environment the coupons were exposed to, since both gaseous and liquid compounds were present, with transitions between the gas and liquid phases occurring.

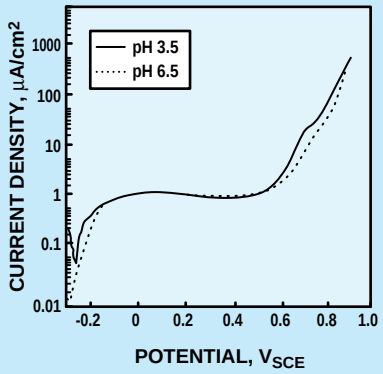
The higher alloyed grades—S32750, S31254, S32654, N06022, and N010276, as well as N06625 (only included in one rack)—were all resistant.

### Bleach-tower inlets

Other authors have suggested that the level of residual active chlorine is the single most important factor in determining the lifetime of stainless steels in bleaching equipment *(12, 13)*. However, in this study, the corrosion rates of alloys exposed in one bleach-tower inlet were much higher than those in another inlet, even though the reported environments—including $ClO_2$ levels—were about the same in both bleach-tower inlets, as seen in Tables IX and XI. The only difference between the two environments was pH, which was 5–6 for Rack 6 and 3.5 for Rack 7.

All of the nickel-base alloys in Rack 6 were severely attacked by uniform corrosion. Titanium was completely resistant, as were S32750 and S32654, while S31254 suffered uniform corrosion in a weld defect. The samples in Rack 7 also lost some weight, but the corrosion rates were negligible, and the alloys can be regarded as resistant.

**5.** Anodic polarization curves at pH 3.5 and 6.5 for alloy N10276




**XII.** Test results, Rack 7 (bleach-tower inlet)

| Alloy | Corrosion rate, mm/year | Crevice corrosion | Pitting corrosion |
|---|---|---|---|
| Stainless steels | | | |
| S32750 | 0.008 | ... | ... |
| S31254 | 0.009 | ... | ... |
| S32654 | 0.014 | ... | ... |
| Nickel-base alloys | | | |
| N06625 | 0.020 | ... | ... |
| N10276 | 0.010 | ... | ... |
| N06022 | 0.012 | ... | ... |
| Titanium | 0 | ... | ... |

**XIII.** Test results, Rack 8 (bleach-tower top)

| | | Crevice corrosion | | Pitting corrosion | |
|---|---|---|---|---|---|
| Alloy | Corrosion rate, mm/year | No. of sites [a] | Max. depth, mm | Location [b] | Max. depth, mm |
| Stainless steels | | | | | |
| S31803 | 0.002 | 15 | 0.1 | A | 0.3 |
| N08904 | 0 | ... | ... | ... | ... |
| S32750 | 0 | ... | ... | ... | ... |
| S31254 | 0 | ... | ... | ... | ... |
| S32654 | 0 | ... | ... | ... | ... |
| Nickel-base alloys | | | | | |
| N06625 | 0.006 | ... | ... | ... | ... |
| N10276 | 0.001 | ... | ... | ... | ... |
| N06022 | 0.003 | ... | ... | ... | ... |
| Titanium | 0 | ... | ... | ... | ... |

[a] Out of 40 possible sites
[b] A = all surfaces

The high resistance of the stainless steel S31254 in these tests is somewhat surprising, since S31254 pipes between the mixer and tower usually have not been resistant in $ClO_2$ stages *(2)*. Stainless steels S32750 and S31254 have shown comparable corrosion resistance in laboratory tests *(10)*, so it was also expected that S32750 would not be resistant.

The uniform corrosion of nickel-base alloys in $ClO_2$ environments has received much attention recently. In this investigation, the high-alloy stainless steels were resistant in the near-neutral pH exposure, while the nickel-base alloys experienced uniform corrosion, which correlates to some earlier findings *(1, 4, 8)*. Laboratory tests have also shown that there may be a large difference in transpassive behavior between a nickel-base alloy (N10276) and a high-alloy stainless steel (S32654) at pH as low as 3.5, while the difference is very small at pH 2 *(1)*. A different behavior at a low pH compared with that at neutral pH was found for the stainless steel but not for the nickel-base alloy. Hence, it is difficult to explain why the nickel-base alloys suffered uniform corrosion at a rate 10–70 times higher in one tower, since the only reported difference between the test environments was that pH was 3.5 in one and 5–6 in the other.

Thermodynamically, the redox potential can be expected to rise when the pH decreases. Furthermore, Alfonsson *et al.* showed that N10276 has a similar transpassive behavior at pH 6.5 and 3.5, as seen in **Fig. 5** *(1)*. Thus the risk of transpassive corrosion should increase rather than decrease at lower pH.

It has been suggested that nickel-base alloys are less susceptible to transpassive corrosion at acidic pH *(7, 8)*, and the test results in this study support that point of view. However, we have not found any plausible explanation for why the pH and no other parameter should be the determining factor. Transpassive

**XIV.** Test environment, Rack 9 (bleach-tower top)*

| | |
|---|---|
| $ClO_2$ (as active chlorine), g/L | ≈0.5 |
| pH | 3 |
| Temperature, °C | 70–75 |

* Coupons exposed for 138 days

**XV.** Test results, Rack 9, (bleach-tower top)

| Alloy | Corrosion rate, mm/year | Crevice corrosion: No. of sites [a] | Crevice corrosion: Max. depth, mm | Pitting corrosion: Location [b] | Pitting corrosion: Max. depth, mm |
|---|---|---|---|---|---|
| Stainless steels | | | | | |
| N08904 | 0.017 | 4 | 0.4 | A | 0.6 |
| S32750 | 0.016 | ... | ... | ... | ... |
| S31254 | 0.013 | ... | ... | ... | ... |
| S32654 | 0.009 | ... | ... | ... | ... |
| Nickel-base alloys | | | | | |
| N10276 | 0.008 | ... | ... | ... | ... |
| N06022 | 0.009 | ... | ... | ... | ... |

[a] Out of 40 possible sites
[b] A = all surfaces

**XVI.** Test results, Rack 10, (bleach washer)

| Alloy | Corrosion rate, mm/year | Crevice corrosion: No. of sites [a] | Crevice corrosion: Max. depth, mm | Pitting corrosion: Location [b] | Pitting corrosion: Max. depth, mm |
|---|---|---|---|---|---|
| Stainless steels | | | | | |
| N08904 | 0.002 | 1 | 0.2 | W | 0.4 |
| S32750 | 0 | ... | ... | ... | ... |
| S31254 | 0 | ... | ... | ... | ... |
| S32654 | 0 | ... | ... | ... | ... |
| Nickel-base alloys | | | | | |
| N10276 | 0 | ... | ... | ... | ... |
| N06022 | 0 | ... | ... | ... | ... |

[a] Out of 40 possible sites
[b] W = weld area

corrosion of nickel-base alloys at lower pH has been observed both in simulated $ClO_2$-stage environments *(1, 6)* and in coupons exposed to process environments. In one in-plant test performed more than ten years ago, uniform corrosion was found on both nickel-base filler metals and stainless steels after exposure in a displacement bleach tower with a maximum $ClO_2$ content of 2.8 g/L (as active chlorine), a temperature of 60°C, and a pH occasionally as low as 1.8. Uniform corrosion was found also on a ferritic stainless steel containing no nickel, only 4% molybdenum, but 30% chromium *(12)*.

In another test, in a pulp pipe about one meter downstream from the $ClO_2$ mixer, a bolt of N10276 suffered extensive uniform corrosion, while a welded coupon of S32654 was resistant. The pH was approximately 3.5, the temperature 70–75°C, and the $ClO_2$ charge about 3 g/L (as active chlorine) *(14)*.

## Bleach-tower tops

Most of the oxidizing bleaching chemicals are consumed in the bleaching towers, and conditions are thus expected to be less aggressive in the tower top than in the inlet. Fear of rapid or severe corrosion attack—implying a risk of loose coupons damaging equipment or disturbing the process—prevented exposure of N08904 and less-resistant alloys in the tower inlets. Thus, stainless steels S31254 and S32750 were the lowest alloyed grades included in both tower inlets and tops. Since these grades were resistant in both the tops and the inlets (except for one attack in a weld defect), no comparison can be made between these two test locations.

The main difference between the two tower tops was the amount of residual chlorine dioxide. Stainless steel N08904 was resistant in the tower with the lower residual (<10 mg/L as active chlorine in the pulp suspension), but not in the one with a higher residual (≈ 500 mg/L). Based on service experience in bleach washers, even highly alloyed grades such as S31254 would run a large risk of suffering corrosion at a residual $ClO_2$ level of 500 mg/L as active chlorine. However, only N08904 was attacked in the tower with a residual of 500 mg/L. Given the earlier findings that residual $ClO_2$ is the single most important parameter governing corrosivity *(12, 13)*, this result is somewhat surprising. The results indicate that other factors also have a great influence on corrosivity.

## Bleach washer

The bleach-washer test rack was exposed in the filter of the same stage in which N08904 suffered corrosion in the bleach-tower top. The residual

chlorine dioxide content in the filter washer is less than 100 mg/L, compared with 500 mg/L in the tower top. The actual residual is probably far below this upper limit because of the $SO_2$ addition between the tower and the washer. Despite this much lower residual, the N08904 coupon in this rack also suffered corrosion. On the other hand, the depths of attack were shallower, and there were fewer creviced sites experiencing corrosion. The more highly alloyed grades were resistant and showed no sign of corrosion, which agrees with service experience from the use of S31254 in this and many other filter washers.

### Alloy performance

Titanium was included in four test racks but showed no sign of corrosion in any of these tests, which probably represented the most severe environments. Besides titanium, stainless steel S32654 was the only alloy resistant in the same four tests.

The three nickel-base alloys also performed well, with one exception. All three alloys experienced severe uniform corrosion in a bleach-tower inlet at pH 5–6.

Surprisingly good results were obtained for the stainless steels. S32654 has shown a corrosion resistance superior to that of other highly alloyed stainless steels in laboratory tests *(10)*, and it was the only material that was resistant in all ten tests.

Stainless steels S31254 and S32750 have shown comparable corrosion resistance in other tests. However, their performance differed in two of the test environments examined in this study. S31254 exhibited better corrosion performance in a spent-acid tank, while S32750 was more resistant in one of the bleach-tower inlets. Our interpretation of these results is that both alloys offer about the same resistance to $ClO_2$ environments. We believe that the tower inlet and the spent-acid tank offered conditions that are on the extreme limit of the corrosion resistance of these two stainless steels.

Stainless steel N08904 was only resistant in one rack, a bleach-tower top. This rack was also the only one containing S31803, which suffered pitting and crevice corrosion. All other alloys were resistant to the environment in the bleach-tower top. The corrosion of these two grades—both of which are much more resistant to chloride-induced corrosion than conventional grades of stainless steel such as 316L *(15)*—clearly demonstrates the aggressiveness of the environments included in this study.

## Summary and conclusions

Welded coupons of stainless steel, nickel-base alloys, and titanium were exposed in a variety of aggressive $ClO_2$ environments. Five grades were included in all ten test racks: the stainless steels S32654, S31254, S32750, and the nickel-base alloys N0276 and N06022. Only S32654 was resistant in all tests. Titanium was tested in the four most aggressive environments and also resisted attack.

None of the nickel-base alloys was attacked by localized corrosion in any test, but all experienced extensive uniform corrosion in the inlet of one bleaching tower. They withstood all other environments.

Stainless steel S31254 withstood all environments but one, a bleach-tower inlet, where it underwent uniform corrosion of inhomogeneities in the weld. Stainless steel S32750 suffered corrosion only in one spent-acid tank, where it underwent pitting corrosion in the weld area. However, both environments are believed to be borderline cases for both grades.

All chlorine dioxide environments included in this study were very corrosive. Two highly alloyed materials—N08904 and S31803—proved to be unsuitable for any of the environments included in this test program. TJ

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