

## Corrosion in Chlorine Dioxide Bleach Environments—Experiences with Stainless Steels and Nickel-Base Alloys

by

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### Abstract

In this paper, the corrosion resistance of highly alloyed stainless steels and nickel-base alloys in chlorine dioxide environments is discussed. According to published experiences, 6Mo austenitic steels have been the most corrosion resistant among stainless steels in D stage environments. Published results from field coupon exposure tests are reviewed as well as a survey of service experiences from Finnish and Swedish bleach plants. Special attention is given to grade S31254. The performance of this grade in filter washer components has in general been very satisfying, while damages from localised corrosion have occurred in pulp pipes between ClO<sub>2</sub> mixer and bleaching tower. Because of their well-known resistance to localised corrosion, nickel-base alloys, such as N10276 and N06022, are sometimes chosen for use in such environments which are too aggressive for 6Mo stainless steels. In some recent papers, however, uniform corrosion thinning of nickel-base alloys in D stage environments is reported. These papers are briefly reviewed. Laboratory tests on a new stainless steel, S32654 (24Cr-22Ni-7.3Mo-0.5N-0.5Cu), are also reported. This new steel is considerably more resistant to localised corrosion than other stainless steels and also seems to be more resistant to uniform corrosion than the nickel-base alloy N10276 under typical D stage conditions.

### Introduction

In recent years it has become a trend in European and North American bleach plants to partly or completely replace chlorine with chlorine dioxide in order to reduce the amount of chlorinated species in the mill effluent. The corrosion resistance of different construction materials in ClO<sub>2</sub> environments has thus attracted increasing interest. The combined effect of a high redox potential, the presence of chloride ions formed during the reduction of chlorine dioxide, a high service temperature and a pH value in most cases ranging from about 2 to neutral, make D stage bleaching environments aggressive to most conventional construction materials. The group of materials which has shown satisfactory resistance in D stage environments includes stainless steels, nickel-base alloys, titanium and glass-fibre reinforced plastic, GRP. In this paper high alloy austenitic stainless steels and nickel-base alloys will be discussed.

# Experiences with Stainless Steels and Nickel-Base Alloys

## Stainless Steels

Introduction of wash water recycling some 25 years ago made C and D stage bleach plant washer environments considerably more aggressive. Extensive corrosion failures were experienced with stainless steels containing 2-4 per cent of molybdenum, e.g. grades 316L and 317L, which at that time were predominating as washer construction materials. Among higher alloyed materials, the 6Mo austenitic stainless steels performed well in field coupon tests as reported by Henriksson (1). One of the first commercially available 6Mo steels was Avesta Sheffield 254 SMO (UNS 31254) which was chosen as construction material for a large number of bleach plant installations, starting in the late seventies. A study of experiences from installations in Swedish and Finnish bleach plants was performed in 1989 by Olsson and Frigren (2). Most installations in C/D and D stage washers were successful although in some cases pitting corrosion had taken place, often in weld areas exposed to the gas phase. Lack of post weld cleaning and welding with a filler metal not overalloyed with regard to molybdenum were suggested (2) as possible reasons for the weld attacks. The survey (2) also showed grade S31254 to be insufficiently resistant for use in ClO<sub>2</sub> mixer to tower piping, where severe pitting occurred in six out of seven installations.

Also experiences from an extensive exposure programme in North American bleach plants (3) showed 6Mo stainless steel welded with Alloy 625 or higher Mo content filler metals to be "excellent candidates for many bleach plant applications". However, at coupon exposure tests in D stage filter washers, 6Mo steels suffered pitting and crevice corrosion under certain conditions, e.g. when no "antichlor" was added between tower and vat (4). In a 14 month exposure of pipe sections in a chlorine dioxide filtrate line (3), 6Mo stainless steels pitted along the circumferential welds. Residual ClO<sub>2</sub> ranged between 20 and 50 ppm and pH between 3.0 and 4.7.

Willis and Johnson (5) reported on coupon tests in three D stage bleach washers. The environments contained 130-600 ppm Cl<sup>-</sup> and ≤ 20 ppm chlorine dioxide residual (as active chlorine). pH ranged between 3 and 3.3 and the temperature between 60 and 79°C (140-175°F). In the washer with the lowest temperature, three out of four tested 6Mo steels were more or less attacked by crevice corrosion in the liquid phase. In the other two tests all four 6Mo steels showed crevice corrosion attack.

## Nickel-Base Alloys

Compared to stainless steels, nickel-base alloys with high contents of chromium and especially of molybdenum are known to have better resistance to pitting and crevice corrosion. They have thus been among the potential candidates for installation in such equipment where high amounts of residuals imply too large a risk for localised corrosion on stainless steels. Besides being used for filter washer components, these alloys

have performed satisfactorily in such equipment as C stage mixers and tower top scrapers. Also in several D stage environments nickel-base alloys such as Hastelloy C-276 (N10276) and Inconel 625 (N06625) have performed well. Tuthill (4) reports good resistance to pitting and crevice corrosion of test coupons exposed in D stage filter washers, also when 6Mo stainless steels suffered corrosion. However, recently there have been some reports of uniform corrosion on nickel-base alloys in ClO<sub>2</sub> environments.

One of the first reports on corrosion of nickel-base alloys in D stages came in 1990, when Wensley et al (6) reported results from test coupons exposed in a chlorine dioxide pulp bleach washer. Caustic soda was used as an "antichlor" before this washer and the test environment thus had a pH of 6-7. The chloride content was 600 ppm, the temperature 70°C and the ClO<sub>2</sub> content was 20-200 ppm as active chlorine. In these tests nickel-base alloys were attacked by general corrosion of rather high rates (max 0.48 mm/y), while stainless steels and high nickel alloys (30-50 % Ni) did not suffer from general corrosion but rather from crevice corrosion attack. From corrosion potential monitoring and polarisation curves, obtained in washer filtrate, it was concluded that transpassive corrosion caused thinning of the nickel-base alloys.

In 1991 Arlt et al (7) reported laboratory tests aimed at simulating the conditions reported by Wensley et al (6). Tests were performed at the free corrosion potential in environments containing ClO<sub>2</sub> as well as under potentiostatic control on both base material and welded specimens of nickel-base alloys and high alloy stainless steels. In the simulated chlorine dioxide medium at free corrosion potential, high alloy austenitic stainless steels DIN 1.4529 and DIN 1.4565 suffered no corrosion, while stainless steel N08904 suffered crevice and pitting corrosion and nickel-base alloys N06022, N10276 and N06625 were attacked by uniform corrosion. In potentiostatic tests without ClO<sub>2</sub>, uniform corrosion of nickel-base alloys N10276 and N06625 took place at +700 mV<sub>SCE</sub> and above, while stainless steel S31254 suffered pitting corrosion at +800 mV<sub>SCE</sub> and above. Weld joints of nickel-base materials welded with nickel-base filler were prone to general corrosion but showed no signs of localised attack. Weld joints of stainless steel DIN 1.4565 with nickel-base filler were attacked by a special form of localised corrosion, primarily at the solidification fronts.

The TAPPI coupon exposure tests (4) originally only focused on localised corrosion, but the test data was later reexamined with respect to uniform corrosion rates for nickel-base alloys (8). A maximum corrosion rate of 0.1 mm/y (4.3 mpy) in neutral D stage environments was reported for alloy N10276. This rate is considerably lower than those reported by Wensley et al (6). It is suggested that lower corrosion rates are obtained at longer exposure times (8).

Nadezhdin et al (9) reported on coupon immersion tests in laboratory environments simulating mixer conditions at various levels of ClO<sub>2</sub> substitution. Typical environmental parameters were: pH between 1.7 and 3.5, 50°C, total active chlorine concentration 1.6 g/l. The corrosion rate of nickel-base alloys was found to increase with increased proportion of ClO<sub>2</sub>. An example of nickel-base alloy performance in an environment where ClO<sub>2</sub> partly substituted Cl<sub>2</sub> is also given. A high shear mixer made from cast alloy C-4 performed well for nearly four

years at 25 % ClO<sub>2</sub> substitution. After switching to 50 % ClO<sub>2</sub> substitution the rotor had to be replaced because of cracking, pitting and general corrosion with an estimated rate of 2.5 mm/y (100 mpy).

Bardsley (10) reported laboratory weight loss measurements in simulated mixer environments varying from 0% to 100% ClO<sub>2</sub> substitution. High alloy austenitic steels AL6XN, Alloy 24 and Alloy 31 showed high corrosion rates in these environments. N10276, which performed well in a straight 100% Cl<sub>2</sub> bleach environment, showed high corrosion rates in ClO<sub>2</sub> substituted environments. The corrosion rate of high alloy stainless steels was found to decrease with increasing ClO<sub>2</sub> concentration while the corrosion rate of nickel-base alloys increased with increasing ClO<sub>2</sub> concentration.

Results from laboratory tests and field coupon exposures as well as service experiences show that 6Mo austenitic stainless steels can be used successfully in many D stage bleach environments. Their weak point is the susceptibility to pitting and crevice corrosion under the most aggressive conditions. Nickel-base alloys with high contents of chromium and molybdenum are very resistant to pitting and crevice corrosion in these environments but may be attacked by transpassive corrosion.

## Laboratory Tests with the New Stainless Steel S32654

A new stainless steel has now been developed which could also be a candidate for such components in which the environment is too aggressive for the stainless steel grades previously available. This grade, Avesta Sheffield 654 SMO (S32654), has the typical composition: 24% Cr, 22% Ni, 7.3% Mo, 0.5% Cu and 0.5% N. The very high contents of chromium, molybdenum and especially nitrogen, make this new steel superior to the 6Mo steels in terms of its resistance to pitting and crevice corrosion. This is illustrated by the high critical pitting and

crevice corrosion temperatures (CPT, CCT) obtained in 6% FeCl<sub>3</sub>, see Table 1 (11). There are obvious similarities between the oxidising, acid, FeCl<sub>3</sub> solution and the environments found in C and D stage equipment. FeCl<sub>3</sub> was characterised by Tuthill et al (3) as "particularly appropriate for predicting corrosion performance in the bleach plant". The resistance of this new material in simulated D stage environments has been studied.

**Table 1:** Critical temperatures determined in 6 % FeCl<sub>3</sub> (ASTM G48), unwelded specimens (11).

Alloy	Critical temperature, °C	
	CPT	CCT*
S31254	75	37.5
S32654	>BP	≥60
N06625	<85-> BP	≥20
N10276	>BP	60

\* CCT determined according to the MTI-2 procedure, although crevice formers mounted by a torque of 1.58 Nm.

## Experiments

### Potentiostatic tests

Potentiostatic tests were performed according to the method described by Arlt et al (7). The test solution was a sodium chloride solution, containing 600 ppm of chloride. The test temperature was 70°C (158°F) and the specimens were exposed under potentiostatic control at +900 mV<sub>SCE</sub> for a test period of 20 hours. The first exposure was performed at a pH of 6.5 to simulate the conditions when sodium hydroxide is added as antichlor, as described by Wensley et al (6). Another exposure was performed at pH 2 to study the behaviour under acidic conditions. The pH of the test solution was adjusted by adding H<sub>2</sub>SO<sub>4</sub>. Test materials were the austenitic stainless steels, S32654 and S31254, and the nickel-base alloy N10276. The chemical composition of the test materials is presented in Table 2. Both exposures included welded as well as unwelded specimens. The welding procedures were GTAW (one pass) or SMAW (two passes). The heat input was 1-1.4 kJ/mm for GTAW-welds and around 0.5 kJ/mm for each pass of the SMAW-welds. The chemical composition of the filler material and the shielding gases used in GTAW welding are presented in Table 3. Postweld cleaning was performed by immersion in a conventional pickling bath.

**Table 2:** Chemical composition of the tested materials, wt %.

Alloy	%C	%Cr	%Ni	%Mo	%Cu	%N	%Mn	%Fe	%W
S31254	0.017	20.2	17.9	6.1	0.7	0.198	-	Bal.	-
S32654	0.017	24.3	22.0	7.3	0.5	0.460	3.0	Bal.	-
N10276	0.006	15.9	Bal.	16.5	-	-	-	7.6	3.1

**Table 3:** Chemical composition of nickel-base filler materials.

Alloy	Filler (Method)	Shielding gas		C max.	Composition of filler, wt %			
		Top side	Root side		Cr	Ni	Mo	Other
S31254	A (SMAW)	-	-	0.025	21	Bal.	9	2Nb
S32654	- (GTAW)	Ar + 10% N <sub>2</sub>	N <sub>2</sub>	-	-	-	-	-
S32654	B (GTAW)	Ar + 10% N <sub>2</sub>	N <sub>2</sub>	0.025	23	Bal.	16	-
S32654	B (SMAW)	-	-	0.025	25	Bal.	14	-
N10276	C (GTAW)	Ar	N <sub>2</sub> + 10% H <sub>2</sub>	0.020	16	Bal.	16	3W

### Potentiodynamic tests

Anodic potentiodynamic scans were performed on unwelded materials, starting from -350 or -300 mV<sub>SCE</sub> using a scan rate of 20 mV/min. The same basic electrolyte as in the potentiostatic exposures was used and tests were performed at three different pH levels, besides pH 6.5 and 2, a pH of 3.5, typical of D stage filter washers when no sodium hydroxide is added, was also chosen.

### Results and Discussion

Results from the potentiostatic tests are summarised in Tables 4 and 5. Neither S32654 nor N10276 were attacked by localised corrosion while welded S31254 suffered pitting corrosion in the weld area in both environments.

At pH 6.5 a very low corrosion rate was found for unwelded S32654 while N 10276 was attacked by uniform (transpassive) corrosion. The corrosion rate of auto-generously welded S32654 was the same as for the unwelded sheet, while higher weight loss values were found for the two specimens welded with nickel-base filler B. Considering the geometry of the weld bead, the surface area ratio between the base material and the weld was roughly estimated for each specimen. The corrosion rate of the weld metal was calculated from the specimen's total weight loss, considering the estimated surface area ratio and assuming that the base material of a welded specimen corroded at the same low rate as the unwelded base material. The calculated corrosion rates are presented in Table 6, together with the chemical composition of the weld metals, determined by microprobe analysis. The estimated corrosion rates range between 0.04 and 0.2 mm/y, which is significantly higher than for the base material, but never reaches the rate of the pure nickel-base alloy. In the weld metals, the nickel-base filler is diluted by the base metal, which is indicated by the relatively low contents of nickel and molybdenum and high contents of iron in the analysed weld metals. The dilution from base material was estimated from the content of nickel and molybdenum of the weld metal, expressed as a percentage of weld metal. The estimated values are presented in Table 6. A large dilution from base metal is favourable to resistance to transpassive corrosion in neutral D stage environments, as shown by the moderate corrosion rates of the nickel-base filler welds, compared to the pure nickel-base metal.

**Table 4:** Potentiostatic corrosion test in simulated D-stage environment, pH = 6.5.

Alloy	Welding		Corrosion rate, mm/y
	Method	Filler	
S31254	-	-	0.01
S31254	SMAW	A	0.10 <sup>1)</sup>
S32654	-	-	0.004
S32654	GTAW	-	0.004
S32654	GTAW	B	0.01
S32654	SMAW	B	0.04
N10276	-	-	0.47
N10276	GTAW	C	0.47

1) Pitting on edge in fusion zone, max. 0.4 mm

**Table 5:** Potentiostatic corrosion test in simulated D-stage environment, pH = 2.

Alloy	Welding		Corrosion rate, mm/y
	Method	Filler	
S31254	-	-	0.23
S31254	SMAW	A	0.32 <sup>1)</sup>
S32654	-	-	0.24
S32654	GTAW	-	0.24
S32654	GTAW	B	0.25
N10276	-	-	0.39
N10276	GTAW	C	0.38

1) Pitting in weld metal, max. 1.0 mm

It should be noted that the experimental potential +900 mV<sub>SCE</sub> is unrealistically high. According to Nadezhdin et al (9), the redox potential of pure ClO<sub>2</sub> environments is in the range +700 to +800 mV<sub>SCE</sub>. Wensley (6) measured corrosion potentials for stainless steels and nickel-base alloys in a D stage filter washer, where the chlorine dioxide content was 50 ppm (as active chlorine) and the pH was 7. The corrosion potentials for stainless steels ranged between +616 and +627 mV<sub>SCE</sub>, while transpassive corrosion limited the corrosion potentials for nickel-base alloys from +406 to +448 mV<sub>SCE</sub>.

**Table 6:** Weld metal, S32654 with nickel-base filler B. Chemical composition and estimated corrosion rate in potentiostatic test (+900 mV<sub>SCE</sub>) In 600 ppm Cl<sup>-</sup>, pH 6.5.

Welding method	Chemical composition, wt %				Dilution from base metal, %	Corrosion rate, mm/y
	Cr	Ni	Mo	Fe		
GTAW	24	27	8.4	37.5	87	0.04
SMAW	26	45	12	15	40	0.22

The anodic polarisation curves are presented in Figures 1-3. In the neutral environment the nickel-base alloy N10276 showed a transpassive behaviour at considerably lower potentials than did the stainless steels S31254 and S32654. At pH 2 only very small differences in transpassive behaviour were found. These results are consistent with the corrosion rates found in the potentiostatic tests. At pH 3.5 the polarisation curve for nickel-base alloy N10276 looks much the same as at pH 2 or 6.5 while the curve for stainless steel S32654 contains a "wave" at about the same potential at which transpassive corrosion initiates for the nickel-base alloy, although complete loss of passivity does not take place until about 200 mV higher potentials. This "wave", although smaller, is also present at pH 6.5 and was also observed by Wensley (6) in polarisation curves obtained for stainless steels and high nickel alloys in washer filtrate. It seems probable that the same reaction involved in transpassive corrosion of nickel-base alloys and of stainless steels at pH 2 also causes the wave in the polarisation curve of stainless steels at higher pH. A pH dependence of the transpassive potential, similar to that found for S32654 in solutions containing 600 ppm Cl<sup>-</sup>, has been found also for S31254 by Qvarfort (12), who performed tests in 1 M NaCl at different pH levels.

Both S32654 and N10276 seem to be very resistant to pitting corrosion in this environment. Nickel-base alloy N10276 is attacked by transpassive corrosion at potentials exceeding 600-700 mV<sub>SCE</sub> independent of pH in the range 2-6.5. The transpassive corrosion of S32654 in this environment is dependent of the pH level. At pH 2 transpassive corrosion is initiated in the same potential range as for N10276, while at pH ≥3.5 significantly higher potentials can be tolerated without uniform corrosion attack.

## Conclusions

- 6Mo austenitic stainless steels are excellent materials for many D stage applications, including most filter washers, but might suffer localised corrosion in applications involving high contents of chlorine dioxide, such as mixer to tower piping.
- Nickel-base alloys with high contents of chromium and molybdenum show good resistance to localised attack in most D stage environments, but might under certain circumstances be attacked by uniform corrosion.
- Laboratory tests in simulated D stage environments on the new stainless steel S32654, indicate a resistance to localised corrosion on a level with that of highly alloyed nickel-base alloys and a better resistance to uniform (transpassive) corrosion at pH ≥3.5.

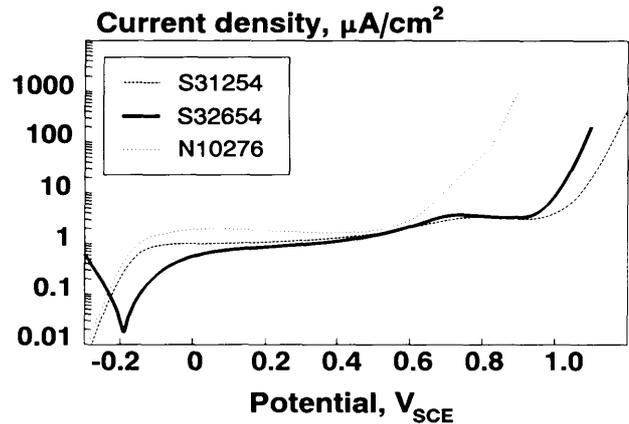


Figure 1  
Anodic polarisation curves (20 mV/min) determined in 600 ppm Cl<sup>-</sup>, 70°C, pH = 6.5.

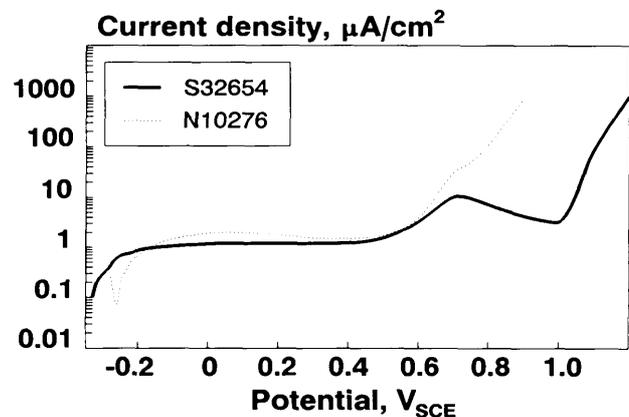


Figure 2  
Anodic polarisation curves (20 mV/min) determined in 600 ppm Cl<sup>-</sup>, 70°C, pH = 3.5.

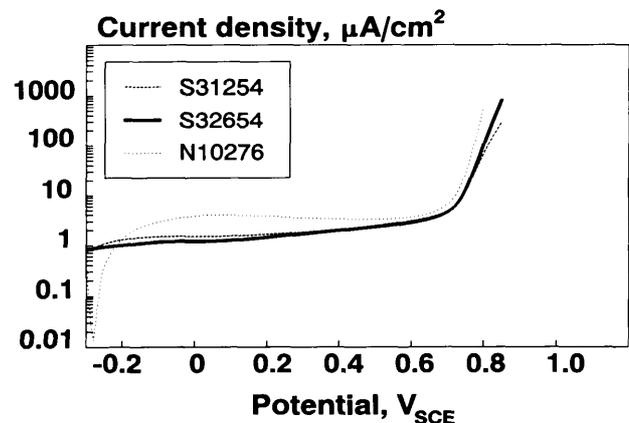


Figure 3  
Anodic polarisation curves (20 mV/min) determined in 600 ppm Cl<sup>-</sup>, 70°C, pH = 2.

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