Technical paper: The possibilities & limitations of austenitic and duplex stainless steels in chlorinated water systems

Stainless steel is extensively used in systems carrying chlorinated water. Depending on the chemistry and temperature of the water a wide range of steel grades can be applied.

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One attractive feature of stainless steel is the ability to maintain the passive layer in contact with water and thus resist thinning by uniform corrosion. The corrosion risks for stainless steel in contact with water at moderate temperatures are mainly chloride-induced, localized corrosion, typically pitting or crevice corrosion. When deciding what stainless steel grade to use for a water system, the main parameters to consider are the chloride concentration of the water, the steel wall temperature, and the level of chlorination. Chlorine is typically added to e.g. cooling waters to minimize biofilm formation and biofouling. The main effect of chlorine on the construction material is that being a strong oxidant, significantly stronger than oxygen, it tends to shift the open circuit potential of stainless steel to more positive values (Figure 1), thereby increasing the risk that the pitting or crevice corrosion potential is exceeded, resulting in localized attack on the stainless steel.

Material selection

Different guidelines for material selection in water systems can be found in literature. The example in Table 1 is presented by Nickel Institute (1). It is common to suggest suitable steel grades for different levels of chloride in the water, but less common to also include the effect of chlorination. Residual chlorine has a significant influence on the corrosion behavior of stainless steels and is thus an important factor to consider in material selection and corrosion control. In the following the combined effect of residual chlorine level, water temperature and chloride concentration is discussed for the range of stainless steel

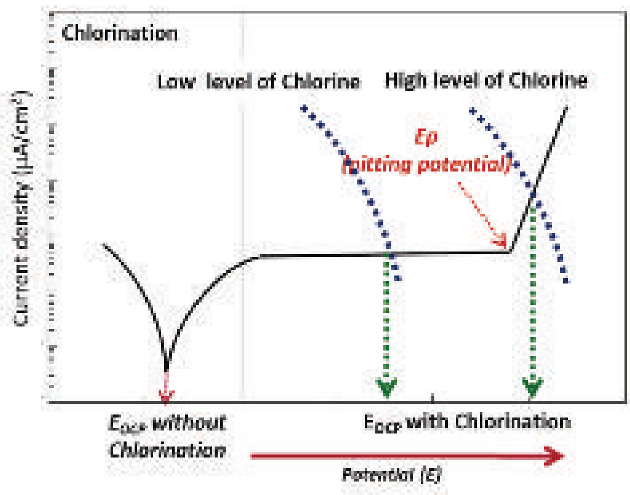

Figure 1. The effect of chlorination on the open circuit potential of stainless steel (schematic)

Table 1. Chloride level guidelines for waters at ambient temperatures (1)

Chloride level (ppm, mg/L)	Suitable grades
<200	1.4301 (304), 1.4307 (304L), 1.4404 (316L)
200-1000	1.4304 (316L), 1.4462 (duplex 2205)
1000-3600	1.4462 (duplex 2205), 6% Mo Superaustenitic, Superduplex
>3600 and sea water	6% Mo Superaustenitic, Superduplex

Table 2. Chemical compositions of austenitic (red) and duplex (grey) stainless steel grades

Outokumpu	EN/W.nr	ASTM/UNS	C	N	Cr	Ni	Mo	Others
4307	1.4307	304L	0.02	-	18.1	8.1	-	-
4404	1.4404	316L	0.02	-	17.2	10.1	2.1	-
LDX 2101®	1.4162	S32101	0.03	0.22	21.5	1.5	0.3	5Mn
LDX 2404®	1.4662	S82441	0.02	0.27	24	3.6	1.6	3Mn
2205	1.4462	S31803/S32205	0.02	0.17	22	5.7	3.1	-
2507	1.4410	S32750	0.02	0.27	25	7	4	-
254 SMO®	1.4547	S31254	0.01	0.20	20	18	6.1	Cu
4529	1.4529	N08926*	0.01	0.20	20.5	24.8	6.5	Cu
654 SMO®	1.4652	S32654	0.01	0.50	24	22	7.3	3Mn,Cu

*also meeting UNS S08367

grades listed in Table 2. Steels with an austenitic microstructure are represented by the well-known 304 and 316 types as well as 6Mo "super austenitic" grades and the 7Mo super austenitic grade 654 SMO®. Duplex stainless steels are represented by the common 2205 grade and also by 25Cr "super duplex" grades and the leaner LDX 2101® and LDX 2404®.

The steel grades in Table 2 may all be suitable for use in systems carrying chlorinated waters but there is a large difference in corrosion resistance between the standard austenitic 304 grade and the highest alloyed grade 654 SMO®, which is why a thorough understanding of the corrosivity of the water to be carried is essential for an optimal material selection. In the following, results from laboratory and field tests will be used to illustrate what service conditions each stainless steel grade can tolerate.

Waters with moderate chloride content

Figure 3 shows results from laboratory tests carried out in water containing either 200 mg/l or 500 mg/l of chloride (2). Tests were performed at two temperatures; 30°C and 50°C and with three different levels of residual chlorine; 0.2 ppm, 0.5 ppm and 1 ppm. Plain sheet specimens as well as specimens with welds and artificial crevices were evaluated.

The test results illustrates clearly that crevices are the part of a water system most vulnerable to corrosion. The two least resistant grades in this study 304L and LDX 2101® suffered from crevice corrosion also at the mildest conditions and even 316L suffered crevice corrosion when the residual chlorine level was 0.5 ppm or higher. Crevice corrosion is a risk e.g. in all kinds of connections where water may penetrate such as flanged or threaded connections. Crevices may form also under deposits formed in a water system.

Without crevices present, pitting is the main corrosion risk in water systems. The steel grades 304L, LDX 2101® and 316L all performed better when tested without artificial crevices, indicating that systems with good quality, well cleaned butt welded connections can tolerate somewhat more corrosive conditions than systems with e.g. flange connections.

LDX 2101® generally performed better than 304L when crevices were not present and 316L was resistant in all but the most aggressive test (500 ppm chloride, 50°C and 1 ppm of residual chlorine).

The duplex grades LDX 2404® and 2205 were resistant to both pitting and crevice corrosion even under the most corrosive conditions represented in this laboratory test.

Challenges of seawater systems

Despite the excellent corrosion resistance demonstrated by 2205 in laboratory test in waters with up to 500 ppm of residual chlorine, the grade is hardly suitable for use in water systems carrying chlorinated seawater. That is illustrated by the results in Table 3

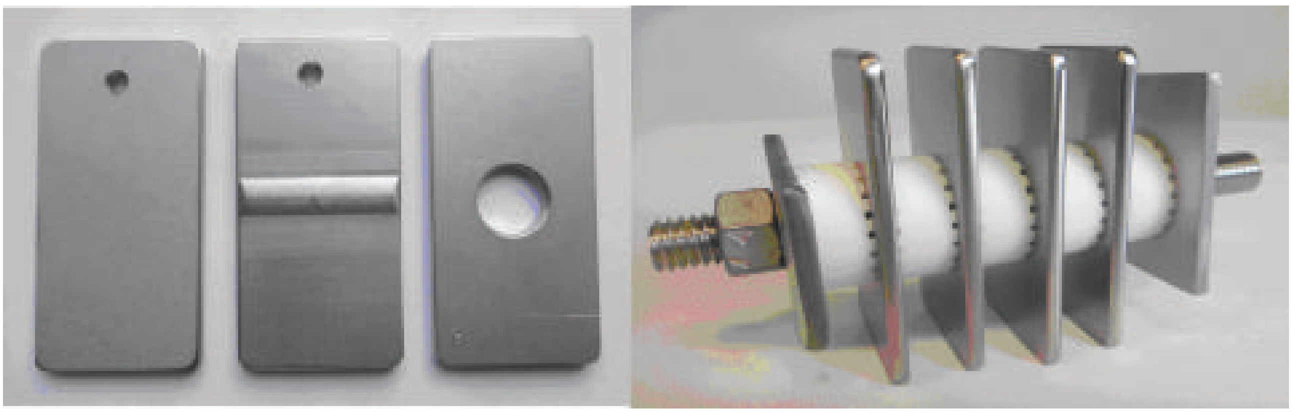

Figure 2. Specimens used for laboratory tests in water with 200 ppm or 500 ppm of chlorides.

200 ppm Chloride

Temperature (°C)	Chlorine (ppm)	BM		Weld		Crevice	
50	1	304L LDX 2101®	316L LDX 2404® 2205	304L LDX 2101®	316L LDX 2404® 2205	(304L) (LDX 2101®)	316L LDX 2404® 2205
50	0.5	304L LDX 2101®	316L LDX 2404® 2205	304L LDX 2101®	316L (LDX 2404®) 2205	304L LDX 2101®	316L (LDX 2404®) (2205)
50	0.2	304L LDX 2101®	316L LDX 2404® 2205	304L LDX 2101®	316L (LDX 2404®) 2205	304L LDX 2101®	316L (LDX 2404®) (2205)
30	1	304L LDX 2101®	316L LDX 2404® 2205	304L LDX 2101®	316L LDX 2404® 2205	304L LDX 2101®	316L LDX 2404® 2205
30	0.5	304L LDX 2101®	316L (LDX 2404®) 2205	304L (LDX 2101®)	(316L) (LDX 2404®) (2205)	304L LDX 2101®	(316L) (LDX 2404®) (2205)
30	0.2	304L LDX 2101®	316L (LDX 2404®) 2205	(304L) (LDX 2101®)	(316L) (LDX 2404®) (2205)	304L LDX 2101®	(316L) (LDX 2404®) (2205)

500 ppm Chloride

Temperature (°C)	Chlorine (ppm)	BM		Weld		Crevice	
50	1	304L LDX 2101®	316L LDX 2404® 2205	304L LDX 2101®	316L LDX 2404® 2205	(304L) (LDX 2101®)	316L LDX 2404® 2205
50	0.5	304L LDX 2101®	316L LDX 2404® 2205	304L LDX 2101®	316L (LDX 2404®) (2205)	(304L) (LDX 2101®)	316L (LDX 2404®) (2205)
50	0.2	304L LDX 2101®	316L LDX 2404® 2205	304L LDX 2101®	316L (LDX 2404®) (2205)	304L LDX 2101®	316L (LDX 2404®) (2205)
30	1	304L LDX 2101®	316L LDX 2404® 2205	304L LDX 2101®	316L LDX 2404® 2205	(304L) (LDX 2101®)	316L LDX 2404® 2205
30	0.5	304L LDX 2101®	316L (LDX 2404®) 2205	304L LDX 2101®	(316L) (LDX 2404®) (2205)	(304L) LDX 2101®	316L (LDX 2404®) 2205
30	0.2	304L LDX 2101®	316L (LDX 2404®) 2205	304L LDX 2101®	(316L) (LDX 2404®) (2205)	304L LDX 2101®	(316L) (LDX 2404®) 2205

Red-corrosion,

(Red)-possibly corrosion, not tested in this study

Green-no corrosion,

(Green)-possibly no corrosion, not tested in this study

Figure 3. Results of laboratory tests in water with 200 ppm or 500 ppm of chlorides, base material (BM), welded and creviced specimens.

from a field test where 2 inch pipes with flanges welded on them were tested in loops with continuously chlorinated seawater at 30°C for 85 days (3,4). Two different levels of residual chlorine were tested; 0.5 ppm and 1.5 ppm. 2205 suffered crevice corrosion on about 50% of the flanges tested, while the higher alloyed super duplex grades and the 6 Mo super austenitic grades were un-attacked on all but one flange at the lower chlorine content but showed some crevice attacks at 1.5 ppm of residual chlorine. The super duplex grade also showed some pitting in the weldment.

These results indicate that 30°C is very close to the upper limit for use of 25 Cr superduplex and 6Mo superaustenitic grades in chlorinated seawater and that close control of the residual chlorine levels is essential in corrosion control.

For systems carrying seawater at higher temperatures and/or where a strict control of low residual chlorine levels are not possible, the 7 Mo superaustenitic stainless steel 654 SMO® is an alternative to e.g. titanium or nickel-base alloys. This is illustrated by the results in Table 4 from a field test in seawater with 10 ppm of residual chlorine at a temperature of 45°C (5). 654 SMO® showed no attack under these severe conditions, which caused crevice corrosion of some nickel-base alloys. 654 SMO is used for instance in condenser tubes in nuclear industry.

Table 3. Results of field test in continuously chlorinated seawater, 30 C, 85 days, after (3.4)

Alloy		0.5 ppm chlorine		1.5 ppm chlorine	
UNS	**Type**	**Flanges**	**Welds**	**Flanges**	**Welds**
S31803	22Cr duplex	7 out of 12	0 out of 12	6 out of 12	0 out of 12
S32750	25Cr superduplex	0 out of 12	1 out of 12	4 out of 12	1 out of 12
S32760	25Cr superduplex	0 out of 12	2 out of 12	3 out of 12	0 out of 12
S31254	6Mo super austenitic	0 out of 12	0 out of 12	3 out of 12	0 out of 12
N08367	6Mo super austenitic	1 out of 12	0 out of 12	2 out of 12	0 out of 12
N08925	6Mo super austenitic	0 out of 12	0 out of 12	3 out of 12	0 out of 12

Table 4. Results of field test in chlorinated (10 ppm) seawater at 45 C, 95 days. Welded coupons with aramide fibre crevice formers torqued to 40Nm

Alloy	Type	Crevice corrosion
254 SMO	6Mo superaustenitic	7 out of 8, 0.98 mm maximum depth
654 SMO	7Mo superaustenitic	0 out of 8
625	Nickel-base	8/8, 0.47 mm maximum depth
C-276	Nickel-base	7/8, 0.31mm maximum depth

Summary

Consider when selecting stainless steel for chlorinated waters with up to 500 ppm of chlorides:

- In systems with crevices present 304L and LDX 2101 are likely to suffer from crevice corrosion in water with a chloride content of 200 ppm and a temperature of 30°C, even at residual chlorine levels as low as 0.2 ppm.
- 316L may be useful in water with up to to 500 ppm at 30°C but with a significant risk of crevice corrosion if the residual chlorine concentration is 0.5 ppm or higher.
- 304L, LDX 2101® and 316L can all tolerate somewhat more corrosive conditions in systems which do not contain obvious crevices, provided all welds are of good quality and well cleaned.
- LDX 2101® is slightly more resistant than 304L in systems without severe crevices
- Residual chlorine levels as high as 1 ppm significantly increases the risk of pitting and crevice corrosion.
- LDX 2404® and 2205 show good resistance to both pitting and crevice corrosion in waters with ≤500 ppm of chlorides, ≤1 ppm chlorine and ≤50°C

Consider when selecting stainless steel for chlorinated seawater:

- 2205 or lower alloyed grades are usually not sufficiently corrosion resistant.
- 6Mo superaustenitic, 25 Cr superduplex or higher alloyed grades are required
- In systems containing crevices 30°C is a maximum limit for 6Mo and superduplex grades and the level of chlorination needs to be carefully controlled, preferably the residual chlorine level should not exceed 0.5 ppm.
- 6Mo superaustenitic grades may tolerate somewhat more corrosive conditions, e.g. a temperature somewhat exceeding 30° C in "crevice free systems", while 25Cr superduplex may suffer pitting in weldments.
- 654 SMO® is an option for systems with higher temperatures or residual chlorine levels.

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