Selection and use of stainless steels in water systems

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1. Background

Stainless Steel is being used for water treatment and supply systems. It is used for numerous applications (table 1) controlled by strict regulations and standards.
With attention to material quality, joining techniques and fabrication practices, excellent performance have been achieved within the range of drinking water conditions and chemistry defined by European Regulations. From European Standard EN 10088, sixteen grades are normally used for the vast range of drinking water applications. These grades which are divided into four families (Austenitic, Ferritic, Duplex and Martensitic can contain:

- 16-30% Chromium
- 1.5-18.5% Nickel
- up to 7.0% Molybdenum
- up to 1.0% Copper
- up to 0.8% Titanium

according to *table 2*.

2. Electrochemical investigations (Ref. 1, 2 and 3)

2.1. Passivity phenomenon

The passivity phenomenon is extremely important since it is the basic mechanism in the corrosion resistance of stainless steels. It involves the formation in fine barrier layer at alloy surface of the order of 1.0 to 2.0 nm, which reduces the corrosion rate to negligible levels. This passive layer or film adheres strongly to the metal substrate and prevents virtually all contact between the alloy and the surrounding medium. For passivation to occur and remain stable, the Fe-Cr alloy must have a minimum chromium content of about 11 weight per cent. There is thus threshold chromium content above, which passivity can occur and below which is impossible. More ever, if the passive layer is locally destroyed due to accidental damage in a media, it has the capacity to heal spontaneously by self-passivation. Chloride ions can be a problem, because of specific ions effect, which can lead to pitting corrosion. For a given system defined by an alloy composition, a microstructure, a surface condition, and a specific corrosion medium at a given temperature, pitting may appear, if at all, above a certain potential which is an effective criterion, for evaluating the resistance of stainless steel (and all passivable metal alloys) to pitting corrosion.

2.2. The critical pitting potential

Electrochemical investigations were carried out to compare the stability of different grades in chloride containing waters. If the potential is varied slowly to determinate the resulting variation in current density, it is found that in the vicinity of the critical pitting potential E_{pit}, the current density rises steeply, usually preceded by the series of instabilities caused by the formation of pits that repassivate after the dissolution of certain types of inclusion.

The pitting potential decreases, when the temperature rises and/or when the chloride concentration increases. An increase in the chromium and molybdenum contents increases the pitting potential. Nitrogen has also a beneficial influence in the austenitic alloys. In order to quantify these composition effects, empirical indices have been derived to describe the resistance to pitting corrosion, in the form of a Pitting Resistance Equivalent (PRE).

For ferritic and martensitic grades (Fe-Cr-(Mo) alloys), the formula employed is:
$PRE = \%Cr + 3.3(\%Mo)$
Where the concentrations are in weight (%).

For austenitic and duplex grades (Fe-Cr-Ni-(Mo,N) alloys), the formula becomes:
$PRE = \%Cr + 3.3(\%Mo) + x(\%N)$
Where $x=16$ for duplex stainless steels
$x=30$ for austenitic stainless steels

Experience shows that there is a good correlation between the PRE value (***Table 5***) and pitting potential (expressed in mV/SCE or mV/SHE). ***Table 6*** gives values of pitting potential (mV/SCE) for a number of representative stainless steels used in drinking water systems. Within the passivity domain (passive state) i.e. up to the pitting potential, the current density is very low ($I \leq 1\mu A/cm^2$) and from these experiments it can be concluded that there is no corrosion and corresponding negligible cation migration for the grades having a minimum PRE value of the order of 17.

2.3. The Open Circuit Potential (OCP)

Localised corrosion model for metallic alloys is based on the fact that localised attack would occur only if the open circuit corrosion potential exceeds a critical potential for a given environmental condition. The ***open circuit potential*** also referred to as the ***equilibrium potential*** or the ***rest potential*** is the potential at there is a negligible current density (µA/cm2), that is, experiments based of the open circuit potential are potentiometric experiments. The OCP test is close to actual using conditions of the material. Medium and duration are chosen according to the specific application. The corrosion potential of various metallic materials can be detected directly by OCP measurements done during the immersion of each coupon into the test water. The experiment consists of the open circuit potential (OCP) during a long period of time (of the order of 50 hours). If there is no or a slight variation of potential, there is no pitting initiation which means that the material is in the passive state.

3. Metal Leaching Experiments (Ref. 4, 5 and 6)

Several recent studies have looked at metal release in water.

In the "Co-normative research on test methods for materials in contact with drinking water" (4), three types of stainless steel were used for the pipe work simulation in cold water system, i.e: ***X5CrNi18-10/1.4301*** containing 18% chromium and 10% nickel, ***X5CrNiMo17-12-2/1.4401*** containing 17% chromium, 12% nickel and 2% molybdenum and ***X2CrMoTi18-2/1.4521*** containing 18% chromium and 2% molybdenum, which is stabilised with titanium. The pipe work system (rig system) was designed to investigate leaching over a period 5 months. The flow regime was designed to simulate actual conditions at a kitchen tap (flushing and stagnation periods). Leaching data were obtained for chromium, molybdenum, iron, titanium, and the results were as follows:

- ***Chromium***
  Concentrations range from detection limit of 1µg/l to 2µg/l (with the exception of one result of 25µg/l after 1 hour stagnation on day 637 with nanofiltration concentrate). As trivalent chromium (Cr^{3+}) is one of the components of the passive layer, these values clearly show that alloys where in the passive state, implying that no corrosion occurred.

- ***Molybdenum***
  Concentrations were less than 1µg/l.

- ***Iron***
  As Fe^{3+}, is, with chromium, a major constituent element of the passive film. It was leached in small quantities (less than 50µg/l) but release decreased with time. The explanation for this result is that passive film is mainly composed of Fe and Cr oxides and hydroxides and that the Fe components are less stable than the Cr components. Thus they are dissolved preferentially. This leads to a Cr-enrichment of the passive film and a corresponding increased corrosion resistance of the material.

- ***Nickel*** concentrations were, in most cases, less than 2µg/l. Only two results exceeded 10µg/l, both with nanofiltration concentrate. In this context, it should be noticed that Ni-release was very low and this result confirms the absence of this element the passive film.

- ***Titanium*** is added to the ferritic grade X2CrMoTi18-2/1.4521 to prevent intergranular in welded zones. Its concentration was always less than 5µg/l. Titanium also improves the pitting corrosion resistance of this material.

In the "Interlek Testing Services" (ITS) study (5) three grades of stainless steel:

- X2CrNi18-9/1.4307 (304L)
- X2CrNiMo17-12-2/1.4404 (316L)
- X2CrNiMoN22-5-3/1.4462 (2205)

have been tested according to the method set out in BS 7766:2001. The detection limit for each element analysed was 8µg/l for iron, 1.0µg/l for nickel and 1.0 µg/l for chromium.
The chemical composition of test water, in metallic elements, at the beginning of the leaching test was: Fe<8.0µg/l; Cr<1.0µg/l and Ni<1.0µg/l. The concentration of relevant elements of the materials (Fe, Cr and Ni) in final extracts where found to be, for all grades, as follows: Fe<8.0µg/l, Cr<1.0µg/l and Ni<1.0µg/l and it can be concluded that all grades comply with the acceptance criteria within BS7766:2001.

In the third survey (6), release rates of chromium and nickel from X5CrNi18-10/1.4301 (304) and X5CrNiMo17-12-2/1.4401 (316) have been determinate during a one-year field exposure of panels in an urban environment (Stockholm) and through complementary exposures in artificial rain. The field exposure was performed during one year, which the run-off water was collected approximately every second week depending on the frequency, quantity and duration of rain events. A rainwater volume corresponding to approximately 500 mm was collected during the exposure period. In parallel, an experimental set-up to simulate rain events was constructed for laboratory investigations. The released ***chromium*** quantity (*table 3*) varied during different periods from less than 0.5 ng/cm^2 (chromium detection limit) to 3ng/cm^2 (<0.5-1.6µg/l) and from less than 0.5 to 5 ng/cm2 (<0.5-2.2µg/l) for the X5CrNi18-10/1.4301 and the X5CrNiMo17-12-2/1.4401, respectively. The released ***nickel*** quantity (*table 4*) varied from less than 0.1 ng/cm^2 (nickel detection limit) to 12 ng/cm^2 (<0.1-3.5µg/l) and from 0.5 to 31 ng/cm^2 (0.2-11µg/l) for the X5CrNi18-10/1.4301 and the X5CrNiMo17-12-2/1.4401, respectively.

The figures show that the release of chromium and nickel is significantly higher from X5CrNiMo17-12-2/1.4401 compared to X5CrNi18-10/1.4301. This is surprising since it is generally believed that the corrosion resistance of X5CrNiMo17-12-2 is superior to that of X5CrNi18-10. The X5CrNiMo17-12-2 is primarily designed for chloride –rich environments, whereas the performance in more acidic atmospheres may not fully utilise the presence of molybdenum.

4. Conclusions

The ***leaching*** results obtained from testing stainless steel types :

X5CrNi18-10 / 1.4301 (304)
X2CrNi18-9 / 1.4307 (304L)
X5CrNiMo17-12-2 / 1.4401 (316)
X2CrNiMo17-12-2 / 1.4404 (316L)
X2CrMoTi18-2 / 1.4521 (444)
X2CrNiMo22-5-3 / 1.4462 (2205)

In various water solutions showed that the release of ***chromium, nickel, molybdenum*** and ***iron*** is negligible and these stainless steel grades comply with European regulations on the quality of water intended for human consumption (Council Directive 98 / 83 / EC).

Electrochemical investigations based on the determination of ***pitting potential*** and / or ***open circuit potential*** (OCP) were also carried out to compare the stability (passive state) of these alloys in synthetic waters at pH of the order of 6.6 therefore, slightly acidic. The result of these electrochemical tests show, for the alloys containing at least ***17% chromium***, a large passive domain in which current density is less than 1µA / cm^2.

Table 1: Examples of Stainless Steel Applications in Drinking Water Treatment and Supply Systems

Application End Use	Stainless Steel		
	Type	Grade	
		Name	Number
Pipelines, Tubes, Storage Tanks, Taps, Valves	Austenitic	X5CrNi18-10 (*)	1.4301 (*)
		X2CrNi18-9(*)	1.4307 (*)
		X6CrNiTi18-10	1.4541
		X5CrNiMo17-12-2 (*)	1.4401 (*)
		X2CrNiMo17-12-2 (*)	1.4404 (*)
		X6CrNiMoTi17-12-2	1.4571
		X1CrNiMoCuN28-18-7	1.4547
	Duplex	X2CrNiN23-4	1.4362
		X2CrNiMoN22-5-3	1.4462
		X2CrNiMoN25-7-4	1.4410
	Ferritic	X3Cr17	1.4016
		X3CrTi17	1.4510
		X2CrMoTi18-2 (*)	1.4521 (*)
	Martensitic	X17CrNi16-2	1.4057
Hot Water Tanks	Austenitic	X5CrNiMo17-12-2	1.4401
		X2CrNiMo17-12-2	1.4404
		X6CrNiMoTi17-12-2	1.4571
	Ferritic	X2CrTi17	1.4520
		X3CrTi17	1.4510
		X2CrMoTi18-2	1.4521
Boilers, Heat Exchangers	Austenitic	X5CrNiMo17-12-2	1.4401
		X2CrNiMo17-12-2	1.4404
		X6CrNiMoTi17-12-2	1.4521
	Duplex	X2CrNiN23-4	1.4362
		X2CrNiMoN22-5-3	1.4462
		X2CrNiMo N25-7-4	1.4410
	Ferritic	X3CrTi17	1.4510
		X2CrMoTi18-2	1.4521
Tubing for seawater Desilination plants	Ferritic	X2CrMoCuTi29-4	1.4592

(*) Most suitable grades for plumbing

Tableau 2 : Stainless Steel Compositions for Drinking Water Service

Stainless Steel Grade EN 10088		Composition in Weight (%)						
Name	Number	C	Cr	Ni	Mo	Ti	Cu	N
X5CrNi18-10	1.4301	≤ 0.07	17-19.5	8.0-10.5	-	-	-	-
X2CrNi18-9	1.4307	≤ 0.03	17-19.5	8.0-10.0	-	-	-	-
X6CrNiTi18-10	1.4541	≤ 0.08	17-19	9.0-12.0	-	<0.7	-	-
X5CrNiMo17-12-2	1.4401	≤ 0.07	16.5-18.5	10.0-13.0	2.0-2.5	-	-	-
X2CrNiMo17-12-2	1.4404	≤ 0.03	16.5-18.5	10.0-13.0	2.0-2.5	-	-	-
X6CrNiMoTi17-12-2	1.4571	≤ 0.08	16.5-18.5	10.5-13.5	2.0-2.5	<0.7	-	-
X1CrNiMoCuN28-18-7	1.4547	≤ 0.02	19.0-21.0	17.5-18.5	6.0-7.0	-	-	0.18-0.27
X2CrNiN23-4	1.4362	≤ 0.03	22-24.0	3.5-5.5	0.1-0.6	-	0.1-0.6	0.05-0.09
X2CrNiMoN22-5-3	1.4462	≤ 0.03	21.0-23.0	4.5-6.5	2.5-3.5	-	-	0.1-0.2
X2CrNiMoN25-7-4	1.4410	≤ 0.03	24.0-26.0	6.0-8.0	3.0-4.0	-	-	0.2-0.3
X3Cr17	1.4016	≤ 0.08	16.0-18.0	-	-	-	-	-
X3CrTi17	1.4510	≤ 0.05	16.0-18.0	-	-	<0.8	-	-
X2CrTi17	1.4520	≤ 0.025	17.0-20.0	-	-	<0.8	-	-
X2CrTi18-2	1.4521	≤ 0.025	16.0-18.0	-	1.8-2.5	<0.6	-	-
X17CrNi16-2	1.4057	0.12-0.22	15.0-17.0	1.5-2.5	-	-	-	-

Table 3: Chromium release during rain exposure (one-year field exposure)

Stainless Steel Grade		Cr release (µg/l)
Name	Number	
X5CrNi18-10	1.4301	<0.5-1.6
X5CrNiMo17-12-2	1.4401	<0.5-2.2

Table 4: Nickel release during rain exposure (one-year field exposure)

Stainless Steel Grade		Ni release (µg/l)
Name	Number	
X5CrNi18-10	1.4301	<0.1-3.5
X5CrNiMo17-12-2	1.4401	<0.2-11

Table 5: Pitting Resistance Equivalent (PRE) of various stainless steels

Stainless Steel Grade			**PRE**
Family	**Name**	**Number**	
Ferritic	X6Cr17	1.4016	17
	X3CrTi17	1.4510	
	X2CrMoTi18-2	1.4521	25
Autenitic	X5CrNi18-10	1.4301	19
	X5CrNiMo17-12-2	1.4401	25

Table 6: Pitting potentials of various stainless steels in a deaerated 0.02 M NaCl solution at 23°C (pH = 6.6)

Stainless Steel Grade		**Pitting Potential (mV/SCE)**
Name	**Number**	
X6Cr17	1.4016	290
X3CrTi17	1.4510	400
X2CrMoTi18-2	1.4521	650
X5CrNi18-10	1.4301	420
X5CrNiMo17-12-2	1.4401	600

1. BAROUX B.: Further Insights in Pitting Corrosion of Stainless Steels: Metallurgical Effects, Stochastic Aspects, New Techniques of Investigation, Proceedings of the First Stainless Steel Congress in Thailand, 219 – 231, December 1997

2. SIRILUCK, N. and SIRIPORN D.: Effect of Water Chlorination Addition to the Stainless Steel Corrosion Resistance, Proceedings of the First Stainless Steel Congress in Thailand, 137 – 144, December 1997

3. ELFSTRÖM BROO, A., BERGHULT, B. and HEDBERG, T.: The Influence of Drinking Water Quality and the Corrosion of Stainless Steel EN 1.4401 (SS 2347), Proceedings of the Seminar on Pipe Material Selection in Drinking Water Systems, Göteborg, September 2000

4. BARON, J., et al: Metallic Materials in Contact with Drinking Water, Factors Influencing Migration, Outcomes of Co-normative Research-CEOCOR 5th International Congress, Brussels, 2000 and Co-normative Research on Test Methods for Materials in Contact with Drinking Water, European Commission, Brussels, 2000.

5. BICKNELL, W., et al: Preliminary Study on Reproductibility of BS7766:2001, Test Report on 3 Grades of Stainless Steel, Interlek Testing Services, November 2001.

6. WALLINDER, I. O., et al: Release Rates of Chromium and Nickel from 304 and 316 Stainless Steel During Urban Atmospheric Exposure- A Combined Field and Laboratory Study (to be published in “Corrosion Science”).