Editorial

Stainless Steel – The Safe Choice
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1. Introduction

The aim of this paper is to show that stainless steels which have been used in a wide range of applications such as cooking utensils, sinks, food and drink industry equipment, hospital and medical equipment, prothetic human implants, etc... are safe for human health.

2. What are Stainless Steels ?

Stainless steels are defined as iron based alloys containing at least 10.5 % chromium and a maximum of 1.2 % carbon.

One of the most important properties of stainless steels is their resistance to corrosion. Corrosion resistance in stainless steels is provided by a passive surface film which acts as a barrier between the alloy and the surrounding medium. The passive film is a continuous, non-porous and insoluble film which, if broken, is self-healing under normal conditions.

Chromium plays an essential role in the formation and the stabilisation of the passive film. Other elements can influence the effectiveness of chromium in forming or maintaining the film, but no other element can, by itself, create the properties of stainless steels.

Increasing the chromium content from 10.5 % to the 18 % level typical of the austenitic stainless steels, provides increased stability of the passive film. In austenitic stainless steels, the nickel content does not contribute directly to the composition of the passive film, but does promote repassivation, especially in reducing atmospheres.

Molybdenum in combination with chromium is very effective in stabilising the passive film in the presence of chlorides. It also considerably improves the resistance to pitting and crevice corrosion in neutral chloride solutions.

3. What is harmful to health ?

Everything taken in by the body or affecting it in excess can have a negative influence, whether it be the level of nutrition, special foodstuffs, drugs, metallic trace elements or even vitamins.

The reasonings of Paracelsus (1493 - 1541) are valid still today :

> “What is not poisonous ?
> Everything is poisonous.
> Only the dose makes a thing not
> poisonous.”

Following this definition no material could be regarded as toxic “a priori”. One has also to notice that the toxicological behaviour of metallic alloys depends strongly on the valence state of the metal.

4. The essential character of metals

Metals are naturally occurring components of the environment albeit often in small quantities. Most of them are required for plant, animal and human health and development. For many of them the dose-response relationship in figure 1 illustrates the concept of deficiency-sufficiency-toxicity.

Various metal compounds or trace nutrients have been recognised to be essential. The main criteria used for establishing the essential character of metals and metal compounds are :

a) The metal or the metal compound must be present in the soil and water environment
b) The metal or the metal compound must be present in the normal diet
c) The metal or the metal compound must be present in body tissues and biological fluids
d) A biological activity or metabolic activity must be associated with the metal.

4.1 The essential character of Chromium

Chromium is the 24th element on the periodic chart, situated between vanadium and manganese, and has an atomic weight of 52. Chromium is the 13th most abundant element in the Earth's crust at about 400 ppm.

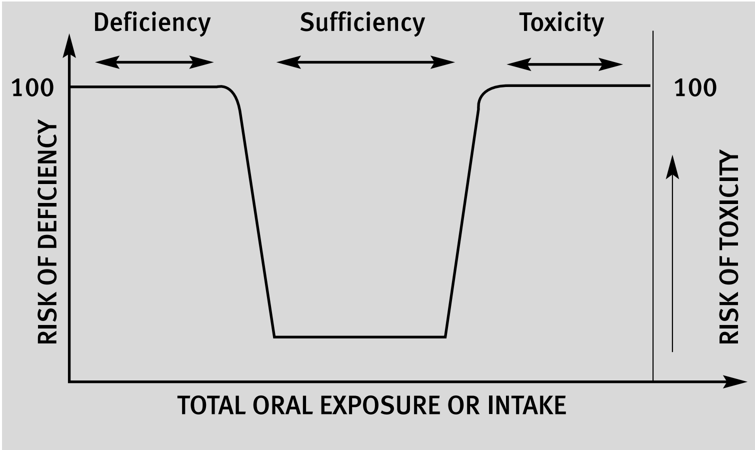

Figure 1 : Typical dose - response curve for an essential trace element

Chromium may occur in several valent states :

- Metallic form (valent state 0)
- Trivalent form (Cr III) and
- Hexavalent form (Cr VI).

Trivalent chromium (Cr III) occurs naturally in the environment. It is an essential nutrient required by the human body to promote the action of insulin in body tissues so that glucose, protein and fat can be used (1,2,3). Cases of chromium deficiency resulting in impaired glucose tolerance have been reported, which have been corrected by an addition of chromium to the daily diet. As Trivalent chromium (Cr III) is an essential nutrient, a daily intake of 50 to 500 µg of Cr III is recommended for adults.

Even if present in very large amounts, trivalent chromium (Cr III) has very little toxic effect. Chromium as a pure metal has no adverse effect.

Both acute and chronic toxicity from chromium are mainly caused by hexavalent chromium compounds (Cr VI). If taken orally, soluble hexavalent chromium would be reduced to the desirable trivalent chromium before being absorbed in the small intestine.

In the case of stainless steel utensils or food process equipment, any chromium released from the cooking processes will be in the trivalent state and no toxicity is to be expected. Not only it is non toxic but it can be beneficial to health.

4.2 The essential character of Nickel

Nickel is the 28th element on the periodic chart and is situated between cobalt and copper. It is a metallic element belonging to the group of "transition metals" (Group VIII) like iron and cobalt, and has an atomic weight of 59. Nickel is the 24th most abundant element in the Earth's crust at about 80 ppm.

The need for nickel in the diet of animals has been proven (4,5) but the ubiquitous nature of nickel makes it difficult to establish its need in the human diet. However, a nickel dietary requirement for humans of 50 µg/kg of diet has been proposed by Nielsen (6).

It is impossible to be skin-sensitised to nickel by the ingestion of nickel compounds, but some investigators have shown that ingested nickel may cause exacerbation of hand eczema in those people who are already sensitised to nickel. Although only a minority of people react to oral nickel doses below 1250 µg (7), it has been concluded that a reduction of the dietary intake of nickel may be beneficial for some already nickel sensitised people (8).

In contrast, it has been found that oral exposure to nickel prior to sensitisation results in a reduced frequency of nickel hypersensitivity. That conclusion was reached from a survey (9) of persons who had oral contact with nickel at an early age prior to ear piercing, a common cause of nickel sensitisation. The effectiveness of nickel ingestion as a way of promoting tolerance to sensitisation by nickel was subsequently demonstrated (10).

5. Hazard or risk?

It is worth defining these items. The hazard of a metal or a metallic alloy is its "potential" to cause harm and it is one way of expressing the (adverse) "intrinsic properties" of a metal or a metallic alloy. Hazard identification for a metallic alloy, (i.e. the determination of adverse effects which an alloy has a potential capacity to cause) must be based on the physical, chemical and toxicological properties of the alloy. Consequently, hazard identification should take into account the physical forms of an alloy (massive form or powdered form) and its chemical properties paying particular attention to its corrosion resistance in a different set of media.

The risk posed by a metallic alloy is a probability function and is the likelihood of harm occurring. It depends on the exposure to the (hazardous) metallic alloy. For simplicity :
Risk = Hazard x Exposure

Consequently, most metallic alloys in the “massive” form (which represents more than 99 % of total metallic alloy production in the world) are considered to present no risk to human health.

5.1 Stainless steel in contact with skin

Although Nickel release from nickel-plated materials may induce allergic contact dermatitis, for nickel-containing stainless steels (i.e. austenitic stainless steels) the effect is much different.

The aim of recent studies (11,12,13) was to define the risk of nickel contact dermatitis from AISI 304 (1.4301), AISI 316L (1.4404) and AISI 430 (1.4016) grades as well as a high sulphur containing stainless steel grade AISI 303 (1.4305) and a nickel-plated steel. Methods included nickel release in synthetic sweat, electrochemical investigations, and clinical patch tests on already sensitised persons. Table 1. gives the chemical composition of the different materials used in the studies. These grades will be identified using the AISI and the European standards.

Leaching experiments were performed mainly in artificial sweat solutions at pH 4.5 at room temperature for one week. Composition of the artificial sweat solution was as follows : 0.3 % NaCl, 0.1 % Na_2SO_4, 0.2 % urea and 0.2 % lactic acid. The stainless steels were also tested according to the standardised test (pr EN 1811). The method described therein was developed for implementation of the 12[th] amendment (Directive 94/27/EC) to Directive 76/769/EEC relating the restrictions of the marketing and use of certain dangerous substances and preparations. The composition of the artificial sweat solution was as follows : 0.5 % NaCl, 0.1 % urea, 0.1 % lactic acid, and NH_3 to adjust the pH at 6.6.

Grade	AISI 303 1.4305	AISI 304 1.4301	AISI 316L 1.4404	AISI 430 1.4016	Nickel
C	0.064	0.036	0.021	0.037	
Si	0.54	0.49	0.61	0.33	0.01
Mn	1.79	0.81	1.67	0.43	
Ni	8.45	8.65	11.29	0.11	99.8
Cr	17.25	18.18	17.87	16.59	
Mo	0.26	0.26	2.15	0.11	
S	0.2753	0.0069	0.0018	0.0010	0.0020

Table 1: Chemical composition (wg %) of the stainless steel grades and nickel used in the Ni allergy study

Electrochemical investigations were carried out to compare the stability (passivity/activity) of materials in different solutions. Corrosion (activity) and corrosion resistance (passivity) of metals and metallic alloys are basically electrochemical processes. Electrochemical tests were conducted in synthetic sweat solutions at pH 4.5 and 6.6. Samples were tested in the as received conditions or wet-polished.

Clinical patch tests were performed on 50 already Ni-sensitised persons, with circular samples of the four stainless steel grades and of the Ni-plated steel in the as received conditions. The patch tests were removed after 2 days of exposure, and readings were carried out 30 min after.

The results of leaching experiments in the synthetic sweat-solutions show three groups of materials characterised by three different levels of nickel migration:

1. A very low nickel release (less than 0.05 µg/cm^2/week at pH 4.5 and 6.6) close to the detection limit and which must be considered as harmless according to the European Directive 94/27/EC. This group includes the three low-sulphur stainless steel grades (AISI 430, 304 and 316L).

2. An intermediate nickel release, close to the 0.5 µg/cm^2/week value which is considered as the limit for a positive reaction in already Ni-sensitised persons, following a prolonged contact with skin. This was for the resulphurised grade (AISI 303).

Grade	Domain of passivity	Current density	Grouping
AISI 304/1.4301 AISI 316L/1.4404	Yes	‹ 1µA/cm^2	1
AISI 303/1.4305	No	› 1mA/cm^2	2
Ni-plated steel	No	›› 1mA/cm^2	3

Table 2: Electrochemical behaviour in a synthetic sweat solution of pH 4.5 at 23°C

3. A high release (75 µg/cm^2/week) which probably will be harmful in case of prolonged contact of the material with skin. The Ni-plated steel belongs to that group.

The results of leaching experiments correlate with those from the electrochemical (polarisation) tests which show that in synthetic sweat solutions:

1. The low-sulphur stainless steel AISI 304 and 316L grades (i.e. standard austenitic grades) have excellent corrosion resistance, characterised by the presence of a passive domain.

2. By comparison the resulphurised stainless steel (AISI 303) and Ni-plated steel have poor corrosion resistance. They present no passive domain in this medium of synthetic sweat.

From these experiments it can be concluded that there is no corrosion and correspondingly negligible cation migration for AISI 304 and 316L grades. In comparison for AISI 303 grade and even more for the Ni-plated steel the current density is high (more than 1 mA/cm^2) indicating an active state and consequently cation migration. The result of electrochemical investigations are summa-rised in Table 2.

Results of clinical patch tests clearly show that standard austenitic stainless steel (AISI 304/1.4301 and 316L/1.4404) and the ferritic grade (AISI 430/1.4016 : Ni-free 17 % Cr) stainless steel are harmless since no allergic reaction was seen on the 50 already Ni-sensitised persons. In contrast, the resulfurised austenitic stainless steel (AISI 303/1.4305) induces allergic reaction for a few persons (14 %) and the Ni-plated steel for nearly all the persons (96 %).

The correlation between leaching experiments, electrochemical investigations and clinical patch test validate the value of 0.5 µg/cm^2/week as a limit of nickel release in a synthetic sweat solution. Table 3 summarises the situation.

Grade	Corrosion resistance (passivity)	Ni release in synthetic sweat (µg/cm2/week)	Clinical test (allergic reactions) (%)	Grouping
AISI 430/1.4016 AISI 304/1.4301 AISI 316L/1.4404	Yes	‹ 0.05	0	1
AISI 303/1.4305	Weak	≈ 0.5	14	2
Ni-plated steel	No	› 70	96	3

Table 3: Stainless steel in prolonged contact with skin and the Ni contact dermatitis issue.

5.2 Stainless steels in contact with food

Stainless steel plays a vital role in the production and processing of food and beverages. For over 70 years stainless steel has been used in the preparation, processing and transport of food products to ensure a high standard of quality. It does not affect the taste of food and drink. Stainless steel has a high resistance to cleaning agents, disinfectants and sterilising agents such as pressurised steam.

Chromium and nickel release from stainless steel in contact with food or during its processing, storage and during meal preparation and cooking is, in most cases, negligible. Experiments on pick-up of chromium and nickel from stainless steel utensils have been conducted using acid fruit (14). Experiments using AISI 430Ti/1.4510 and AISI 444/1.4521 (ferritic grades) and AISI 304/1.4301 (austenitic grade) in a boiling acetic acid solution showed that chromium and nickel release is very low. The concentration observed were close to the detection limits i.e. 30 µg/l for chromium and 10 µg/l for nickel.

A recent field investigation (15) of actual operation using meals cooked in glass, ferritic (AISI 436/1.4526) and austenitic (AISI 304/1.4301) stainless steel pans showed that the levels of nickel and chromium fall either within or very close to the range of chromium and nickel reported in the literature.

Statistical tests showed that nickel and chromium intake from meals cooked in stainless steel utensils (in austenitic 18.2 % Cr - 8.6 % Ni/304 grade and in ferritic 16.6 % Cr - 1.0 % Mo niobium stabilised/436 grade) was insignificant.

It is clear that the use of stainless steel cooking utensils does not provide a significant source of dietary chromium or nickel and there is no advantage to be gained by nickel-sensitive persons who suffer from contact allergy by avoiding the use of stainless steel utensils.

5.3 Stainless steel in contact with drinking water

Several surveys of performance of stainless steel in drinking water systems were carried out from 1997 to 1999. Three types of stainless steel were used for the pipework simulation (17) in a cold water system, i.e. stainless steel X5CrNi18-10/1.4301 containing 18 % chromium and 10 % nickel, X5CrNiMo17-12-2/1.4401 containing 17 % chromium, 12 % nickel and 2 % molybdenum and X2CrMoTi 18-2/1.4521 containing 18 % chromium and 2 % molybdenum.

Electrochemical investigations (18, 19) were also carried out to compare the stability of alloys in de-aerated synthetic water at pH 6.6 and at ambient temperature (23°C). The composition of the synthetic water solution was as follows : Cl^- = 200 mg/l, SO_4^{2-} = 250 mg/l, Mg^{3+}= 50 mg/l, Na^+ = 150mg/l and K^+ = 12 mg/l.

The results of the electrochemical tests show the presence of a large passive domain in which the current density is less than 0.5 μA/cm^2, which implies no corrosion having taken place.

The pipework system (rig system) was designed to investigate leaching over a period of several months. Leaching data were obtained for chromium, molybdenum, iron, titanium, and the results were as follows:

- Chromium species were detected in the solution as trivalent chromium (Cr^{3+}). The values range from detection limit of 1 μg/l to 2 μg/l. As trivalent chromium was one of the components of the passive layer, these values clearly show that the alloys were in the passive state, implying that no corrosion occured.

- Molybdenum concentrations were less than 1 μg/l. Molybdenum enhances the properties of the passive layer and makes all stainless steels more corrosion resistant, particularly to pitting in chloride environments. Pitting corrosion resistance can be expressed as pitting resistance equivalent number (PRE), taking into account the role of chromium and molybdenum, according to the emperical relationship to predict the pitting resistance of :

  · Ferritic stainless steels :
  PRE = % Cr + 3.3 (% Mo)
  · Austenitic and duplex stainless steels :
  PRE = % Cr + 3.3 (%Mo) + X (%N)

  with X = 16 for duplex stainless steels and X = 30 for austenitic stainless steels

- Iron, as Fe^{3+} , is, with chromium, a major constituent element of the passive film. It was leached in small quantities (less than 50 μg/l) but release decreased with time.

The explanation for the result is that the 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.

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

- Nickel concentrations were, in most cases, less than 2 µg/l. In this context, it should be noticed that Ni-release was very low and this result confirms the absence of this element in the passive film.

Following these results, it can be concluded that the three stainless steel grades

- X5CrNi18-10/1.4301 (Fe-Cr-Ni austenitic alloy)
- X5CrNi17-12-2/1.4401 (Fe-Cr-Ni-Mo austenitic alloy)
- X2CrTi18-2/1.4521 (Fe-Cr-Mo ferritic alloy)

comply with European regulations on the quality of water intended for human consumption (Council Directive 98/83/EC). The parametric values reported in the above directive are :

- 50 µg/l for chromium
- 200 µg/l for iron
- 20 µg/l for nickel

6. Conclusions

The wide range of stainless steel applications brings a large number of consumers into stainless steel contact be exposed (skin contact, ingestion of metal ions).

Nickel release from the widely used austenitic stainless steels (X5CrNi18-10/1.4301 and X5CrNi17-12-2/1.4401) in prolonged contact with skin is negligible and no allergic reaction was seen in already Ni-sensitised persons, while the lesser used high sulphur grade (X8CrNiS18-9/1.4305) could elicit reactions.

Release of chromium and nickel from stainless steel utensils is, in most cases, negligible. It is clear that the use of stainless steel cooking utensils does not provide a source of dietary chromium or nickel of any significance. There is no advantage to be gained by Ni-sensitised persons suffering from contact allergy, in avoiding the use of stainless steel utensils.

As a result of research carried out by international authorities it is clear that stainless steel in a material complying with the European regulations dealing with drinking water.

7. References

1) Anderson RA. Chromium and parenteral nutrition 1995; 11, 83-86
2) O'Flaherty EJ. Chromium as an essential and toxic metal. Scand J. Work Environ Health 1993; 19, 124-125
3) Anderson RA. Chromium, glucose tolerance and diabetes. Biol Trace Elem Res 1992, 32, 19-24
4) Nielsen FH, Myron DM, Givand SH, Zimmerman TJ, and Ollerich DA. Nickel deficiency in rats. Journal of Nutrition 1975; 105, 1620-1630
5) Anke M, Grun M, and Kronemann H. Distribution in nickel deficient goats and their offspring. Nickel toxicology, edited by SS. Brown and FW Sunderman (London : Academic Press) 1980, 69-72
6) Nielsen FH. Possible future implications of nickel, arsenic, silicon, vanadium and other ultratrace elements in human nutrition. Clinical, Biochemical and Nutritional Aspects of Trace Elements (New York : Alan R. Liss Inc) 1982, 379-404
7) Menne T and Maibach HI. Systemic contact-type dermatitis. Dermatotoxicology, 4th Edition, edited by FN Mazulli and HI Maibach (New York : Hemisphere Publishing Corp) 1991, 453-472
8) Veien NK, Hattel T, and Lauerberg G. Low nickel diet : an open prospective trial. Journal of the American Academy of Dermatology, 1993; 29 (6), 1002-1007
9) Van Hoogstraten IMW, Andersen KE, von Blomberg BM, Boden D, Bruynzeel DP, Burrows D, Camarasa JG et al. Reduced frequency of nickel allergy upon oral nickel contact at an early age. Clinical and Experimental Immunology 1991; 85, 441-445
10) Van Hoogstraten IMW, Boss C, von Blomberg ME, Scheper RJ, and Kraal G. Oral induction of tolerance to nickel sensitisation in mice. Journal of Investigative Dermatology 1993; 101 (1), 26-31
11) Haudrechy P, Foussereau J, Mantout B, and Baroux B. Nickel release from 304 and 316 stainless steels in synthetic sweat. Comparison with nickel and nickel plated metals. Consequences on allergic contact dermatitis. Corrosion Science 1993; 35 (1-4), 329-336

12) Haudrechy P, Foussereau J, Mantout B and Baroux B. Nickel release from nickel-plated metals and stainless steels. Contact Dermatitis 1994; 31, 249-255
13) Haudrechy P, Mantout B, Frappaz A, Rousseau D, Chabeau G, Faure M, and Claudy A. Nickel release from stainless steels. Contact Dermatitis 1997; 37, 113-117
14) Flint GN and Packirisamy S. Purity of food cooked in stainless steel utensils. Food Additives and Contaminants 1997; 14 (2), 115-126
15) Accominotti M, Bost M, Haudrechy P, Mantout B, Cunat PJ, Comet F, Mouterde C, Plantard F, Chambon P, and Vallon JJ. Contribution to chromium and nickel enrichment during cooking of foods in stainless steel utensils. Contact Dermatitis 1998; 38, 305-310
16) Büning-Pfaue H, Strompen C. Bestimmung der Gebrauchssicherheit von Edelstahl-Kochtöpfen – Nickelfreisetzung aus Kochtöpfen aus nichtrostendem Stahl. Institute for Food Science and Food Chemistry of the University of Bonn, 1999
17) Co-normative research on test methods for materials in contact with drinking water, CRECEP Report, July 1999
18) Baroux B and Baltenneck S, Critère de choix des aciers inoxydables pour emploi au contact des eaux chlorurées, de l'eau de ville à l'eau de mer, journées des aciers spéciaux et des eaux industrielles, XIIième Conférence Internationale des Arts Chimiques, Paris, 12 décembre 1980
19) Haudrechy P, Private Communication, Ugine, 1993