

Corrosion Resistance of Stainless Steels in Soils and in Concrete

Paper presented at the Plenary Days of the Committee on the Study of Pipe Corrosion
and Protection

Ceacor, Biarritz, October 2001

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1. Abstract

Corrosion by soil is a complex phenomenon due to the great number of variables involved.

In principle, stainless steels should be in the passive state in soils, but the presence of water and aggressive chemical species such as chloride ions, sulphates and as well as types of bacteria and stray current, can cause localised corrosion.

In such aggressive environments, stainless steel piping buried in soils should therefore be coated.

In concrete structures with high levels of chlorides e.g. in marine environments, stainless steels generally offer an excellent alternative where other metallic materials are subjected to corrosion.

1. Résumé

La corrosion dans les sols est un phénomène complexe car elle met en jeu un grand nombre de variables.

En principe, les aciers inoxydables sont à l'état passif dans les sols mais l'humidité et la présence de certaines espèces chimiques agressives telles que les chlorures, les sulfates aussi bien que certaines bactéries et les courants vagabonds peuvent conduire à des formes de corrosion localisée. Dans de tels environnements très agressifs, il est prudent de protéger les conduites enterrées par un revêtement.

Dans des structures en béton pouvant contenir des teneurs élevées en chlorures, comme c'est le cas dans les environnements marins, les aciers inoxydables offrent généralement une excellente solution alors que d'autres matériaux métalliques se corrodent.

1. Zusammenfassung

Korrosion in Erdböden ist ein komplexes Phänomen, an dem eine Vielzahl von Variablen beteiligt ist.

Im Regelfall befinden sich nichtrostende Stähle im Erdreich im passiven Zustand. Allerdings können Feuchtigkeit und aggressive chemische Substanzen wie Chloride oder Sulfate sowie bestimmte Bakterien und Streuströme zu Lokalkorrosion führen. Unter solchen besonders korrosiven Umgebungsbedingungen ist es empfehlenswert, die im Erdreich verlegten Leitungen durch eine Beschichtung zu schützen.

In Betonbauteilen, die erhöhte Anteile von Chloriden enthalten können – etwa in Meeresatmosphäre – und in denen andere metallische Werkstoffe korrodieren, stellen nichtrostende Stähle eine ausgezeichnete Lösung dar.

2. Introduction

Generally, buried steel pipelines and tanks suffer from soil corrosion because one or more of the following conditions:

- High moisture content
- A pH value less than 4.5
- A resistivity less than 1000 $\Omega \cdot \text{cm}$
- Presence of chlorides, sulphides and bacteria
- Presence of stray currents.

Steel reinforcing not protected by large concrete covers or not protected by a coating, of which the long term performance is a concern, is susceptible to corrosion and thus spalling of the concrete.

Stainless steels have been successfully used in limited applications in soil. Based on tests in Europe, Japan and the U.S., stainless steels have performed well in a variety of soils, they also offer an excellent alternative where reinforcing is subject to corrosion especially in marine environments and in chlorine environments which exist on bridge where de-icing salts are used.

3. Classification and Corrosivity of Different Types of Soils

Soils classification refers to their physical properties, chemical composition and their resistivity and can be summarised as follows in table 1.

Table 1: Soils classification based on their physical properties, chemical composition, and their resistivity

Type of Soil	Physical Properties (Particle size, plasticity, moisture,)	Chemical Composition (Main constituents and contaminants)	Resistivity ($\Omega \cdot \text{cm}$)
Sand	Particle sizes: Fine : 0.02 / 0.06 mm Medium : 0.06 / 0.2 mm Coarse : 0.2 / 0.6mm Good drainage	SiO_2 , ...	10,000 to 500,000
Gravel	Particle sizes: Fine : 2 / 6 mm Medium : 6 / 20 mm Coarse : 20 / 60 mm Excellent drainage	SiO_2 , ...	20,000 to 400,000
Loam	Plastic mixture High moisture	SiO_2 , Al_2O_3 , ... Dissolved species: H^+ , Cl^- , SO_4^{2-} , HCO_3^- , ...	3,000 to 20,000
Clay	Very plastic mixture High moisture	SiO_2 , Al_2O_3 , ... Dissolved species: H^+ , Cl^- , SO_4^{2-} , HCO_3^- ,	500 to 2,000
Silt	Coarse clay High moisture	SiO_2 , Al_2O_3 , ... Dissolved species: H^+ , Cl^- , SO_4^{2-} , HCO_3^- ,	1,000 to 2,000

Soils with the poorest drainage are the most corrosive while drained soils are the least corrosive. Backfilling pipe ditches with sand offers quite good, long-term protection in corrosive plastic clay soils.

Corrosivity of soils to buried structures, such as pipelines and tanks, is commonly identified to be related to several key factors.

3.1 Acidity of the Soil

Soils usually have a pH range of 4.5 – 8.0. In this range, pH is generally not considered to be a problem for stainless steels. More acidic soils may represent a serious risk to common construction materials including some stainless steel grades. Soils acidity is produced by mineral leaching, decomposition of acidic plants, industrial wastes, acid rain and certain forms of micro-biological activity.

3.2 Resistivity of the Soil

Resistivity is a broad indicator of soil corrosivity since corrosivity is associated with electrochemical reaction in soils, high soil resistivity (see table 1), slow down corrosion reactions. Soil resistivity generally decreases with increasing moisture and the concentration of chemical species. Based on limited experience to soil conditions, stainless steel could be subject to corrosion if the soil resistivity is less than $700 \Omega \cdot \text{cm}$ indicative of a wet soil containing chlorides. Sandy soils have a high resistivity (more than $20,000 \Omega \cdot \text{cm}$) and therefore considered the least corrosive. On the opposite, clay soils with a resistivity of the order of $1,000 \Omega \cdot \text{cm}$ are considered to be highly corrosive. The soil resistivity is widely used and generally considered to be the dominant parameter in the absence of micro-biological activity. On a practical standpoint, well-drained soils are recognised to be less corrosive than poorly drained ones.

A generally accepted corrosivity index for soils according to resistivity is:

- Very corrosive under $1,00 \Omega \cdot \text{cm}$
- Aggressive from $1,000$ to $5,000 \Omega \cdot \text{cm}$
- Mildly corrosive from $5,000$ to $10,000 \Omega \cdot \text{cm}$
- Slightly corrosive from $10,000$ to $20,000 \Omega \cdot \text{cm}$
- Progressively less corrosive over $20,000 \Omega \cdot \text{cm}$
- Not corrosive from $30,000$ to $100,000 \Omega \cdot \text{cm}$

To sum, it can be said that soil resistivity determines the reciprocal of conductivity for a particular soil. Low resistivity indicates that a soil will be a good electrolyte. Soil moisture plays a large part in resistivity.

3.3 Presence of Chlorides, Sulphates and Other Dissolved Species

It is generally agreed that with stainless steel, one of the most important factors is the chloride ion (Cl^-) concentration in the soil and the soil moisture, which can contain different dissolved species such as sulphate ions (SO_4^{2-}) and some others e.g.: H^+ , HCO_3^- , etc...

Chloride ions are harmful, as they participate directly in pitting initiation of stainless steels and their presence tends to decrease the soil resistivity. They may be found naturally in soils as result of brackish groundwater and historical geological sea beds or from external sources such as de-icing salts applied to roadway. The chloride ion concentration in the corrosive soil electrolyte will vary, as soil conditions alternate between wet and dry.

Compared to the aggressivity of chloride ion levels, sulphates are generally considered to be less aggressive. The presence of sulphates may pose a risk for some stainless steels in the sense that sulphates can be converted to highly corrosive sulphides by anaerobic sulphate reducing bacteria.

3.4 Microbiologically Induced Corrosion (MIC)

Microbiologically induced corrosion (MIC) refers to corrosion that is induced by the presence and activities of microorganisms and the products produced in their metabolism.

Especially the sulphate reducing bacteria (SRB), which occur under anaerobic conditions can play a major part in soil corrosion. The reaction product of SRB metabolism is sulphide ions, which react with the metal surface allowing a corresponding corrosion. The environmental conditions under which these microorganisms normally operate are:

Temperatures: from 20 to 30 °C

pH: from 6 to 8

Soil resistivities: from 500 to 20,000 $\Omega \cdot \text{cm}$

3.5 Oxygen Concentration Cells

Oxygen takes part in the cathodic reaction and a supply of oxygen is therefore, in most circumstances, a prerequisite for corrosion in soil. The supply of oxygen changes with the type of soil and the different oxygen levels may lead to corrosion problems due to the creation of oxygen concentration cells. The oxygen concentration of the soil moisture generally will determine its redox potential. The higher the oxygen content the higher the redox potential. Low redox values may provide an indication that conditions are conducive to anaerobic microbiological activity.

4. *Stray Current Corrosion in Soils*

Stray current can be caused by local direct current (DC) electric transportation systems. Typical examples of this type of systems are:

- Railways, tram or trolley bus systems
- Cathodic protection systems for underground natural gas pipeline
- DC welding equipment
- DC power supply systems

The development of stray current can be suppressed with a proper electrical insulation of the pipe (coatings or wrappings) and / or cathodic protection. The most common types for cathodic protection are impressed current cathodic protection and sacrificial anode cathodic protection.

5. The Corrosion Resistance of Stainless Steels in Soils

In principle, stainless steels should be in the passive state in soils, but the presence of water and aggressive chemical species such as chloride ions, sulphates and as well as types of bacteria and stray current can cause localised corrosion. This probability increases with increasing chloride ion content and higher redox potential. Chloride ions can be a primary problem, because of specific ions effect (pitting corrosion). They are also prone to being absorbed or chemisorbed in films on the material surface (silicates, aluminates, calcareous deposits) with attendant adverse effects. Because of this, the chloride concentration of the soil is a first indication of the corrosive nature of the soil vis-à-vis stainless steel. As a first approximation, one may use the values given in table 2.

Table 2: Critical value of C_l for a number of stainless steels in aqueous chloride containing environment

Stainless Steel			Critical Cl ⁻ (ppm)
Type	Grade		
	Name	Number	
Austenitic	X5CrNi18-10	1.4301	500
Austenitic	X5CrNiMo17-12-2	1.4401	1.500
Ferritic	X2CrMoTi18-2	1.4521	1.700

In order to quantify the material composition effects to pitting corrosion in chloride containing environments, empirical indices have been derived to describe the corrosion resistance, in the form of a Pitting Resistance Equivalent (PRE). For ferritic grades, the formula employed is:

$$PRE = \% Cr + 3.3 (\% Mo)$$

where the concentration is in weight, while for austenitic and duplex (austenitic-ferritic) grades, it becomes:

$$PRE = \% Cr + 3.3 (\% Mo) + x (\% N)$$

Where $x = 16$ for duplex (austenitic – ferritic) stainless steels
 $x = 30$ for austenitic stainless steels.

Table 3: Pitting Resistance Equivalent (PRE) of various stainless steel

Stainless Steel			PRE
Type	Grade		
	Name	Number	
Austenitic	X5CrNi18-10	1.4301	19
Austenitic	X5CrNiMo17-12-2	1.4401	25
Ferritic	X2CrMoTi18-2	1.4521	25
Duplex (Austenitic-Ferritic)	X2CrNiMoN22-5-3	1.4462	34

6. Selecting the Appropriate Grade of Stainless Steel for Buried Structures

For selection purposes it is recommended to consider corrosion resistances of buried stainless steels firstly in relation to the presence of chloride ions (inland and marine locations) and secondly according to their resistivities and pH, assuming poorly drained soils in all cases.

6.1 Inland Locations

Locations away from the sea are generally low in chloride concentration. Several surveys and experiences have been carried out in different countries throughout the world (1, 2) draw the conclusion that type X5CrNi18-10 / 1.4301 is resistant to uniform and pitting corrosion. In some countries, such as Sweden, type X5CrNiMo17-12-2 / 1.4401 has however been used in inland locations (2).

6.2 Marine Locations

6.2.1. Non-Tidal Zone

In these zones the chloride concentrations are higher than in inland locations (up to 1,500 ppm Cl). It is recommended for these aggressive environments to use molybdenum containing stainless steels such as types X5CrNiMo17-12-2 / 1.4401 (austenitic) or X2CrMoTi18-2 / 1.4521 (ferritic).

6.2.2. Tidal Zone

For this zone, it was concluded than 2% molybdenum containing stainless steels (austenitic and ferritic) was unsatisfactory but found that X1CrNiMoCu20-18-7 / 1.4547 (super-austenitic) and X2CrNiMoN25-7-4 / 1.4410 (duplex: austenitic-ferritic) showed no signs of corrosion.

6.3 Recommendations

The following recommendations are based on the results of different experiments in soils. In a soil for which the resistivity is less than $1.000 \Omega \cdot \text{cm}$, the chloride content is higher than 500 ppm, and the pH less than 4.5 should be considered as an aggressive one.

Table 4 summarises the stainless steel selection criteria and indicates the types of stainless steel that can be employed without any coating and / or cathodic protection in the absence of stray current.

Table 4: Stainless steel selection criteria according to soil conditions

Stainless Steel Grade		Soil conditions
Name	Number	
X5CrNi18-10	1.4301	Cl ⁻ < 500 ppm Resistivity > $1,000 \Omega \cdot \text{cm}$ pH > 4.5
X5CrNi17-12-2	1.4404	
X2CrMoTi18-2	1.4521	
X5CrNi17-12-2	1.4404	Cl ⁻ < 1,500 ppm Resistivity > $1,000 \Omega \cdot \text{cm}$ pH > 4.5
X2CrMoTi18-2	1.4521	
X2CrNiMoN25-7-4	1.4410	Cl ⁻ < 6,000 ppm Resistivity > 500 ohm $\Omega \cdot \text{cm}$ pH > 4.5
X1CrNiMoCu20-18-7	1.4547	

7. Stainless Steel in Concrete

7.1 Introduction to Concrete

Concrete is a compound of cured Portland cement, aggregate and various admixtures. Cement consists of four constituents: tricalcium silicate, dicalcium silicate, tricalcium aluminates and tetracalcium aluminate ferrite. In the presence of water, these four constituents react to produce concrete gel: $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ and free lime $\text{Ca}(\text{OH})_2$. The free lime is partly soluble in aqueous solution and it further reacts with various salts to give calcium sulphate: CaSO_4 and hydroxide ions: NaOH – Hydroxide ions are very soluble in water that contributes to the initial high pH (pH greater than 12). Under these conditions both carbon steel and stainless steel will be in the passive state. However, decrease in pH can be caused by the diffusion of CO_2 in the air and SO_3 in the rain. The penetration of CO_2 in the pores partially filled with water will produce the carbonation reaction, which is at the origin of steel corrosion. Once the oxide film is broken down, the oxygen acts as oxidizing agent and corrodes the steel (4).

Chloride ions can be introduced into the concrete via two ways:

- contaminates in the original mixture
- exposure to de-icing salts and / or chloride ions in marine environments (5, 6)

7.2 The Corrosion Resistance of Stainless Steels in Concrete

Pitting corrosion could be the most risk of stainless steel corrosion in concrete. Because of the critical role of chloride ions, pitting resistance is a particular factor in concrete with high chloride ion concentration. The risk of pitting increases when the chloride concentration increases and / or when the temperature rises. An increase in the chromium and molybdenum contents increases the resistance to pitting and is particularly effective in the ferritic grades. In austenitic and duplex stainless steels, nitrogen has also a beneficial influence. In order to quantify these composition effects, the Pitting Resistance Equivalent (PRE) is used (see section 5).

The main stainless steel grades which can be used in concrete and their PRE are shown in table 5.

Table 5: Pitting resistance Equivalent (PRE) of various stainless steels tested in solutions simulating exposure in concrete.

Stainless Steel			PRE
Type	Grade		
	Name	Number	
Martensitic	X12Cr13	1.4006	13
Austenitic	X5CrNi18-10	1.4301	19
Austenitic	X5CrNiMo17-12-2	1.4401	25
Duplex	X2CrNiMoN22-5-3	1.4462	34

The results of these different tests (15) show:

- Martensitic type X12Cr13 / 1.4006 can be used in carbonated concrete, provided a low chloride content (no more than 0.5%) is expected
- For higher chloride contents (up to 5%) austenitic or duplex grades are necessary at pH values typical of alkaline or carbonated concrete.

No pitting corrosion was observed on austenitic types X5CrNi18-10 / 1.4301 and X5CrNi17-12-2 / 1.4401 and in duplex (austenitic – ferritic) grade X2CrNiMoN22-5-3 / 1.4462.

8. General Conclusion

In soils and for selection purposes it is recommended to consider corrosion resistance of buried stainless steels firstly in relation to the preserve of chloride ions and secondly according to their resistivity and pH. Specific stainless steel grade must be carefully selected according to soil conditions.

In concrete, most of stainless steels with a PRE greater than 19 should be satisfactory in many cases. Type X5CrNiMo17-12-2 / 1.4401 gives excellent performances in carbonate or in chloride containing concrete.

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