

How to Avoid Quick Deterioration of Paints Applied to Oxidized Steel

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Nowadays, the anti-corrosive protection of a non-oxidized steel surface with a suitable paint no longer raises any problem. Due to the use of modern polymers, protection of 10 years can be assured, even under the severest conditions, by applying the correct paint system.

Surface rust, on the other hand, always creates problems and its presence should be strictly avoided. The reasons are that rust does not provide a firm mechanical base, but, more important, that rust is electrochemically unstable under a paint film. A satisfactory result can only be obtained after removing the rust and after stabilizing the residual oxides. Fe_2O_3 should be removed from the metal surface or at least electrically isolated from it.

KELATE® completely eliminates the dangerous oxides and, in addition transforms them into an organo-metallic layer, which guarantees an almost perfect anodic passivation of the surface.

1. The Nature of Rust

Under atmospheric conditions, iron can yield 3 different types of oxides, representing 3 different stages of iron oxidation:

FeO : wüstite

Fe_3O_4 : magnetite

Fe_2O_3 : haematite

FeO is only stable above 550°C and quickly turns to Fe_3O_4 and to Fe_2O_3 .

Fe_3O_4 is only stable under neutral to alkaline conditions and in the absence of any oxidant whatsoever (e.g. O_2).

Fe_2O_3 may assume 2 forms:

- α haematite, formed by direct iron oxidation
- γ haematite, formed by oxidation of the magnetite.

Fe_3O_4 and $\gamma \text{Fe}_2\text{O}_3$ can afford a passivating action provided that they are formed “in situ” on the ferrous surface γ and constitute a sealed micro-crystalline layer. This happens only under certain pH conditions and with precise electrode potentials, as shown in the Pourbaix diagram (1). Under normal atmospheric conditions, these are not realised and the $\gamma \text{Fe}_2\text{O}_3$ and Fe_3O_4 present in the rust have no passivating action.

2. Rust-Metal Interaction

Numerous studies on weight loss have shown that, under normal atmospheric conditions, rust growth follows a logarithmic law. The reason is to be found in the complexity of electrochemical reactions and in the role that rust itself plays in the corrosion process.

The presence of rust on metal fundamentally changes the mechanism of the electrochemical reactions. Herzog (2) has demonstrated that the potential of rusted steel is from 0.3 to 0.4 volt more positive than that of non rusted steel, this being associated with a considerable reduction in the speed of the attack. Herzog has also measured electric currents between an iron electrode and an electrode of rust, both in the presence of oxygen and in without oxygen.

Pourbaix's diagram shows that, with a pH below 8, iron corrodes even without oxygen. But, with a neutral pH, the rate of corrosion is extremely slow due to the hydrogen over-voltage of the ferrous surface.

In the presence of oxygen, the potential of iron is considerably increased and an important galvanic element accumulates. The difference of potential may be as high as 1.4 volt and rapid corrosion results.

The situation is completely different when the iron is covered with a layer of rust. In this case, iron, oxygen and different forms of oxides are all present simultaneously. All have well determined electrode potential and all play the role of an oxidant vis-à-vis the iron or of a reducer vis-à-vis the oxygen.

Between iron with an electrode potential of ± 0.6 volt* and oxygen with an electrode potential of ± 0.8 volt, there are the oxides with increasing electrode potential in the order: FeO, Fe₃O₄, Fe₂O₃.

The electrode potentials of FeO and Fe₃O₄ are very close to that of iron and differences are almost negligible. On the other hand, apart from the galvanic element formed between iron and oxygen, which is about 1.4 volt, the following galvanic elements are also formed:

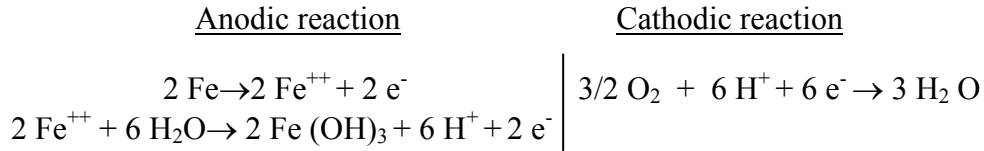
Fe – Fe₂O₃ with a $\Delta E = \pm 0.4$ volt
FeO – Fe₂O₃ with a $\Delta E = \pm 0.3$ volt
FeO - O₂ with a $\Delta E = \pm 1.3$ volt
Fe₃O₄ – O₂ with a $\Delta E = \pm 1.2$ volt

* The electrode potentials are measured with reference to a standard hydrogen electrode, i.e. vis-à-vis the equilibrium potential of the reaction $\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\text{e}^-$ in a solution where the pH is 0 under a pressure of one atmosphere.

The possible electrochemical reactions may be summed up as follows:

A. Reactions in the presence of oxygen

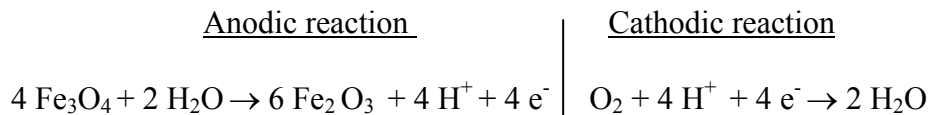
Since oxygen is a far more potent oxidant than the various forms of iron oxides, the determinant reaction will be as follows:



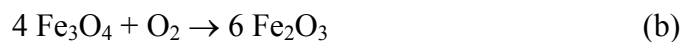
Total reaction



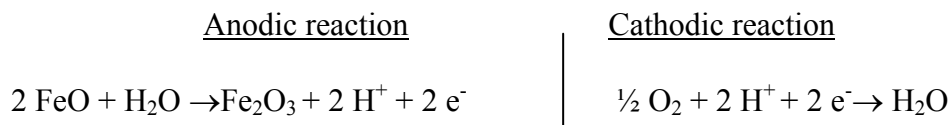
It follows from this that, according to the conditions (pH and aeration), the reaction may pass through various intermediate stages with the formation of FeO and Fe₃O₄. The Fe₃O₄ which can be present in the rust for various reasons (alkaline, pH and insufficient local aeration) is also oxidised.



Total reaction



The FeO is also oxidized.



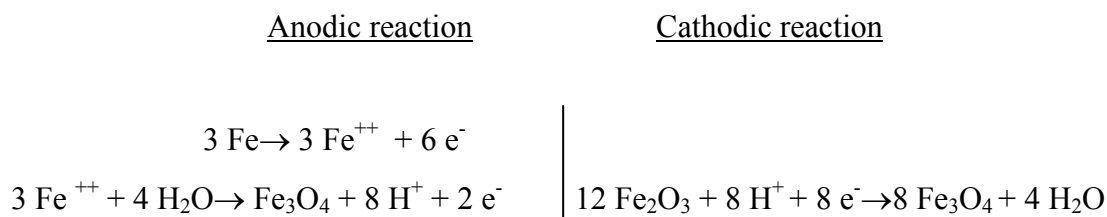
Total reaction



The oxidation of the steel continues and the final stage of oxidation is always Fe₂O₃.

B. Reactions without oxygen

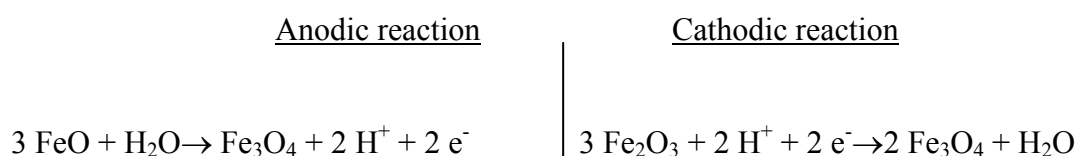
Fe₂O₃ is an oxidant vis-à-vis the iron and the FeO.



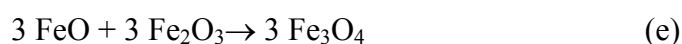
Total reaction



The FeO possibly present also oxidizes:



Total reaction



Hence, due to the presence of Fe₂O₃, the corrosion continues even in the absence of oxygen, because of the formation of magnetite.

Even when applied with maximum thickness, the most efficient low permeability paint systems cannot prevent corrosion, since rusting continues even in the complete absence of oxygen.

KELATE® is efficient both in the presence of oxygen and without oxygen, since it eliminates all possibility of galvanic element formation on the surface.

(1) Pourbaix: "Atlas of Electrochemical Equilibrium in Aqueous Solutions".- Pergamon 1966.

(2) Herzog: « Quelques expériences sur le rôle de la rouille dans le processus de la corrosion de l'acier en milieu aqueux ».

(Métaux – Corrosion – Industrie – Avril 1967).