

## THE PASSIVATION OF STEEL

### Introduction

It is known that the chromium content of stainless steel is important for the formation of a passive film, the chromium oxide skin. This chromium oxide skin is formed spontaneously in the air and in this way it protects the underlying material.

Construction steel (also called carbon steel) does not have this property, because of the absence of chromium as the alloying element. However, a reaction with the oxygen from the air does take place. The active iron reacts to give iron oxides. The underlying material is not protected, because, as a rule, iron oxides, which are bulky and hygroscopic, do not adhere to the underlying material. Furthermore, under the influence of moisture and oxygen, the oxidation continues until a red-brown rust has been formed.

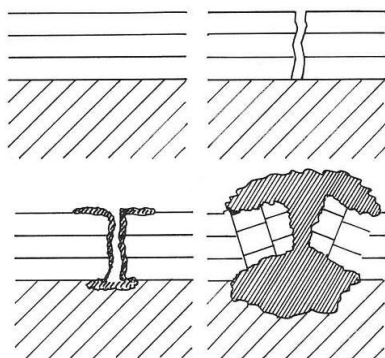
Hence, construction steel must be protected in order to prevent corrosion. Long-term protection on the outside is realised by the application of a permanent coating, a coating of lacquer, a metal coating etc.

The inside of piping made of construction steel must also be treated and protected. Depending on the application, there are several methods to apply temporary protection: phosphating, chromating and/or a chemical passivation. This Technical Bulletin gives more detailed information about the last method, the chemical passivation of construction steel.



### Mill and welding scales and annealing skin

During the production process of construction steel, the intermediate product is generally made by milling, casting or forging. High temperatures are used in all these processes that, consequently, involve an associated oxidation process, resulting in the formation of various iron oxides. During the milling process, these oxides will be compressed to a compacted mill scale that consists of ferrous oxide, magnetite and haematite. Unfortunately, the mill scales do not remain intact, because as a result of the cooling contraction cracks are formed right down to the steel surface. Rust is formed in these cracks causing the steel surface to be attacked (see fig. 1).



Other oxide films that can occur are annealing skins, which are formed as a result of the heat treatment of steel (for example for making bends), and welding scales, which are formed as a result of the heat input during the fusion-welding process. As a result of this short heat input, a relatively thinner oxide film is formed than in the case of mill scales.

Fig. 1: various stages of rust of mill scales.

The undesirable oxide film can be removed from the surface in a number of ways: mechanical (blasting) or chemical (pickling).

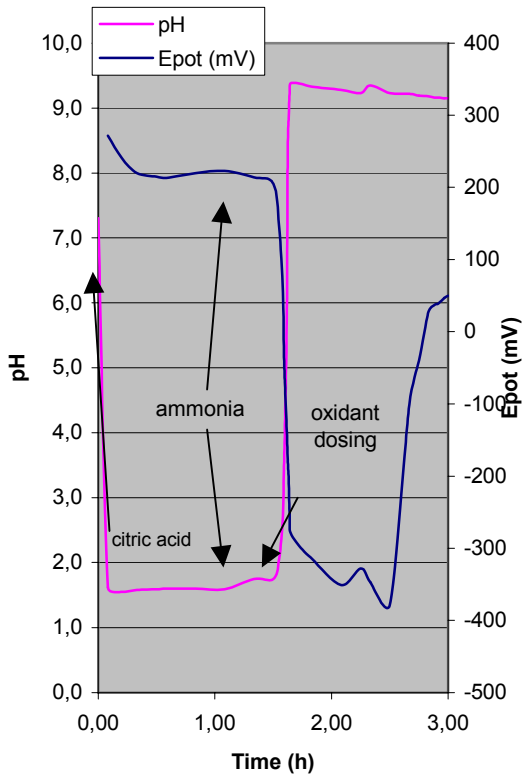
After the removal of the oxide film by means of the pickling process, the unprotected steel surface is very reactive and will react immediately with the oxygen from the air. These oxides are better known as flash rust and do not protect the steel. The activity of the steel surface can be counteracted by a treatment with certain chemicals that form a passive non-conducting iron oxide film. The passivity of steel can be achieved with strongly oxidising substances that are able to oxidise ferrous ions and, hence, convert metallic iron exclusively into a ferric state, allowing the formation of a solid uniform gamma-iron III oxide ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). This extremely thin and vulnerable passive film can temporarily protect the steel and does not have the property of autopassivation like chromium in stainless steel. However, the chemical passivation forms a good substrate for conversion systems such as chromating and phosphating processes. Alternatively, when it concerns the water side of a system, the passive film formed will be a good basis for the (boiler) water treatment programme.

## Passivation process

The standard treatment for the chemical passivation of steel consists of a number of steps. Often, a number of "pre-cleaning steps" are necessary before the actual passivation process can be started.

De-greasing to remove the organic material that might be present and that could possibly interfere with the process, and pickling to completely remove any corrosion products, mill scales, welding scales and annealing skin that might be present. As the steel is very reactive after a pickling treatment, flash rust will be formed very quickly. This is removed using citric acid and the passivation is started by adding ammonia and an oxidant.

Graph 1: Passivation ammonium citrate typical plot



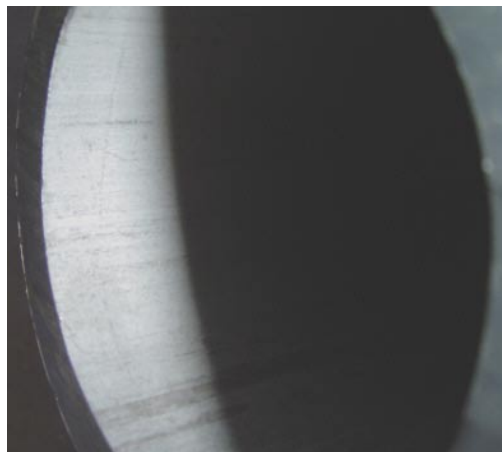
The use of citric acid is also necessary, because the solution is neutralised to an alkaline pH. Normally, the iron would precipitate due to the formation of iron hydroxide. However, as a result of the strong complex formation of iron with the citrate, the iron ions will remain in solution. The addition of an oxidising agent to the ammonium citrate will increase the potential of the solution. Hence, the passivation process is monitored by means of potential measurements (see graph 1). The passivation process is ready when the potential of the passivation liquid has increased sufficiently as the result of the addition of the oxidant. The gamma iron oxide film will then have formed on the steel surface. The passivation liquid can then be removed.

As mentioned before, a chemical passivation is suitable for a (boiler) water treatment programme and is therefore mainly applied after a pickling treatment of boiler systems by means of circulation. When circulation is impossible, it is also possible to carry out a chemical passivation by immersion. The only disadvantage is that the prepared chemical passivation bath can only be used once, because the dosage has to be carried out in a specific sequence. The steel goes through the whole phase, starting with the citric acid and to which all the chemicals are subsequently added.

The result is a beautiful silvery grey passive steel surface.



before



after

Author: ing. T. van Os (Head Laboratory)  
Reactions and/or questions: e-mail: [tb@vecom.nl](mailto:tb@vecom.nl)