Number: 2007/05

PRE-COMMISSION CLEANING OF A POLYPROPYLENE PLANT

Installations (boilers, heat exchangers, cooling water systems, etc.) are often cleaned before they are taken into service. This is called “pre-commission cleaning”. The system is contaminated with grease/oil, welding scale and suchlike by various operations on the installation, such as welding, grinding, etc. The temporary protective layer of the steel will also be corroded so that (flash) rust occurs.
A chemical-technical cleaning is therefore usually carried out to obtain a clean and passive steel surface. This Technical Bulletin will examine the pre-commission cleaning, the pickling and passivation of an ethylene installation.

Ethylene is used in petrochemistry as the raw material for the production of polymers (plastics). The ethylene is obtained for example from naphtha via a cracking process. Such a process occurs in a furnace at high temperatures. ABB Lummens Global develops and builds such ethylene production installations. The ABB installations are known for their good performance and energy efficiency. ABB has completed 175 Ethylene projects throughout the world, which is 40% of the worldwide ethylene production capacity. One of these projects, the replacement of old furnaces, is being carried out at the SNOS (Salavat Neft Org Sintez) refinery in Salavat, Russia. The second installation will be completed at the end of 2007, and for this purpose Vecom, on the orders of ABB, carried out a chemical cleaning before commissioning.

The cleaning consists of the removal of organic pollutants, such as grease/oil and atmospheric precipitation, by means of a degreasing. Corrosion products (rust) are removed using a pickling agent with an organic acid base. Ultimately the steel surface is preserved by then performing a passivation.

Degreasing

The degreasing step in a pickling process is essential. Oil, grease and atmospheric contaminations, all caused by different circumstances, can be present on the steel surface. Such contaminations interfere with the pickling action; the steel surface is sealed by this contamination so that that the acid cannot do its work well enough in the pickling phase. Degreasing can be done with a (slightly) alkaline solution and surfactants, at higher temperatures, so that the oil/grease can be saponified or emulsified.

Pickling

The pickling process aims at the removal of all corrosion products (rust) from the steel surface. An acid is used to remove corrosion products (or iron oxides). The acid will undergo a chemical reaction with the iron oxides, which then dissolve. The art is to dissolve only the oxides and not to attack the base material, the steel surface of the installation, and therefore to prevent corrosion by the acid used.

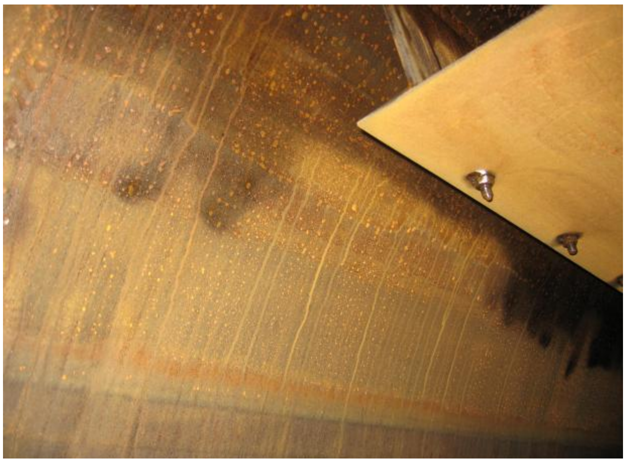
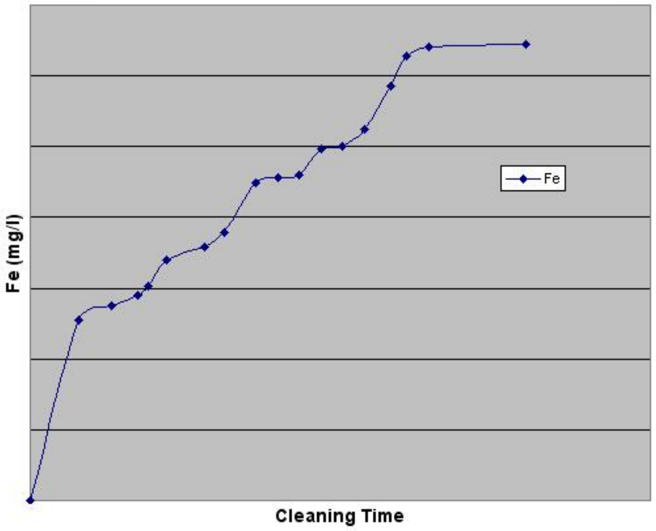


Figure 1: Steam drum before pickling and passivation

Figure 2: Steam drum after pickling and passivation

The acid corrosion can be limited by several factors: choice of the acid and addition of inhibitors. The pickling of this installation is therefore done with a mild acid; a partially neutralised and inhibited, diluted citric acid solution. Analyses were performed in order to follow the pickling process, including the increase of the iron concentration. The iron concentration will increase because the corrosion products (iron oxides) are dissolved. All corrosion products will have been dissolved once the iron concentration remains stable for several measurements, and the cleaning will be finished. The iron values are plotted on a graph to give an idea of the course of the pickling (see graph 1).

Graph 1: course of the iron concentration



Passivation

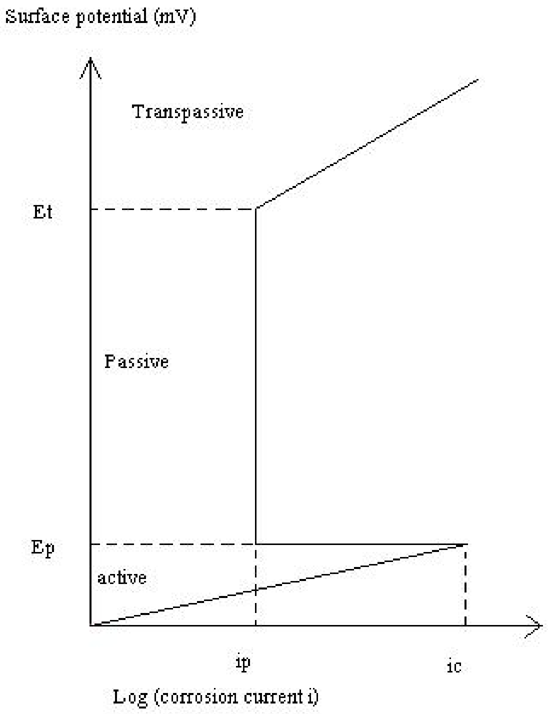
After the chemical removal of the oxide skin by means of a pickling process, the unprotected steel surface will be enormously active and will react directly with the oxygen in the air. These oxides are better known as “flash rust” and do not protect the steel. The activity of the steel surface can be resisted by treatment with certain chemicals, which form a passive, non-conducting iron oxide film. Passivity of steel can be achieved with strong oxidising substances, which can oxidise ferrous ions and thus convert metallic iron to ferric ions, so that a firm, uniform gamma-iron (III) oxide (γ -Fe_2O_3) is produced. The passive iron oxide layer is very thin (40-100 A) and if the grey passivated steel surface is examined, only the actual steel colour is seen. A passivated layer cannot be seen. Such chemical oxidation/reduction reactions, which occur during passivation, are complex processes. Briefly it means changing the surface potential of the steel by additions to the ammonium citrate solution, which is used for the passivation process. Addition of an oxidant increases the potential of the liquid, the potential of the steel surface becomes positive and oxidation of the surface is initiated. The potential is increased so that a minimum value of 0.6 V is reached (Ep in graph 2), the point at which the semi conducting γ-iron oxide is formed. This oxide layer is impermeable to ions (such as Fe^{2+} of Fe^{3+}) and therefore ensures that the underlying steel cannot be corroded.

Normally, different iron oxides (FeO, Fe_2O_3, etc.) can be formed together in corrosion processes (oxidation). Controlled oxidation in a certain medium can therefore chemically produce the desired type of iron oxide.

In practice this means that the passivation is begun with a citric acid solution in order to remove any flash rust after the pickling.
The use of citric acid is necessary because the solution is neutralised to an alkaline pH. Normally, iron would then precipitate by the formation of iron hydroxide. However, the iron forms a complex with the citrate (citric acid molecule) and the iron ions remain in solution. The addition of an oxidant to the ammonium citrate will increase the potential of the liquid. The passivation process is therefore also followed by means of potential measurements. The passivation is finished once the potential of the passivation liquid has risen by the addition of the oxidant; the gamma iron oxide layer will be formed on the steel surface and the passivation liquid can be drained off.

Sources:
1. McCoy, Industrial Chemical Cleaning, NY 1984
2. www.abb.com

Author: Ing. Thomas van Os
With thanks to Tony Kohlen (ABB)
Reactions and/or questions: e-mail: tb@vecom.nl
www.vecom-group.com



Graph 2: Diagram of the passivation of steel