Number: 2005/20 December 2005

PICKLING METHODS FOR DUPLEX STAINLESS STEEL
Surface treatment without nitric acid

Duplex stainless steel is mainly used in the chemical, petrochemical and offshore industries because of its mechanical properties and high resistance to corrosion. As a result of this high resistance to many types of corrosion, especially stress corrosion, Duplex is preferred to austenitic stainless steel. Yet, practice has shown that Duplex becomes sensitive for stress corrosion under certain critical environmental conditions. This is certainly the case under conditions of high temperatures in combination with chlorides and low pH. The corrosion resistance of Duplex, just like other highly alloyed chromium steels, is governed by the presence of a chromium oxide film that is formed as a result of the reaction between the chromium and the oxygen in the air. This chromium oxide is strong, passive and homogeneous, resulting in the underlying material being protected by the passive film.
This chromium oxide film can be disturbed by the presence of contaminants on the surface and especially by the presence of thermal oxides. The thermal oxides are formed during processes such as welding and annealing. There is no adhesion between the thermal oxides and the underlying material. The thermal oxides are porous and interfere with the formation of the passive chromium oxide film. This stops the underlying material from being protected in certain places and, hence, lowers the corrosion resistance of the material

Surface treatment
A surface treatment is necessary to remove these undesired thermal oxides from the stainless steel and the most common one is a chemical surface treatment. It is known that the corrosion resistance of the stainless steel (and Duplex) after a chemical pickling process will completely be restored. All undesirable contaminants, such as thermal oxides and foreign iron particles, are removed by means of the pickling treatment, so that a homogeneous passive chromium oxide film can be formed at the interface with the air. The standard pickling process consists of the treatment of the stainless steel with a mixture of nitric acid and hydrofluoric acid.

Research has shown that the removal of thermal oxides from Duplex SS by means of the conventional pickling process on basis of nitric acid and hydrofluoric acid is not fast enough. This is certainly the case, for instance, for thermal oxides that were formed in the annealing process of Duplex piping during bending. Besides, hazardous nitrogen oxides (NOx) fumes will be formed as a result of the chemical reaction of nitric acid during this pickling process (see Figure 1). Certain chemical substances, accelerators, can be added to the conventional bath to prevent the formation of NOx-fumes. The accelerators react during the pickling process with the decay products of the pickling reaction whereby nitric acid is partially regenerated and inert nitrogen is formed. This causes a less rapid decrease of the acid concentration. The formation of nitrogen gas during the pickling causes micro-agitation. This form of agitation allows a faster change of the pickling fluid at the SS interface with pickling fluid from the bulk of the solution. Hence, the action of the accelerators is twofold:
I. Decreasing the pickling time, and, II. Decreasing the NOx discharge. (Figure 2)

Pickling without nitric acid
Another technique is pickling without nitric acid. In this process, the nitric acid, which has an oxidising action and acts as an acid donor, is replaced by a mixture of hydrogen peroxide and sulphuric acid.
For the pickling process without nitric acid, a number of parameters are important for the proper functioning of the bath. The dissolved iron in the pickling fluid may be present as the ferrous (Fe^{2+}) or the ferric (Fe^{3+}) ion. The ferric iron participates in the pickling process and will therefore be converted to ferrous iron. This reaction takes place at a specific potential that will be obtained as a result of the presence of hydrogen peroxide. The second function of hydrogen peroxide is the conversion of ferrous iron to ferric iron (see Figure 3). However, hydrogen peroxide stabilisers will be required because hydrogen peroxide has a limited life in an acidic environment. Despite the addition of stabilisers, it is necessary to regularly add hydrogen peroxide as a result

of its consumption during the pickling process. Hence, the maintenance of such a bath is significantly more intensive than a conventional bath, in which only the saturation of the acids and dissolved metals need to be determined with some regularity.
The corrosion rate (or material loss per certain surface area in a set time) is indicative for the action of the pickling process. A high loss of material means a shorter pickling time. Various tests have been carried out on pulsed MIG welded AISI 316L and TIG welded Duplex 1.4462 SS material. The results are shown in Table 1.
This shows that adding accelerators has no influence on the pickling time of Duplex stainless steel. Only the method without nitric acid gives a significant increase in corrosion rate and hence a decrease in pickling time.
Analyses of the pickling fluids also show that the increase of dissolved metals in the pickling fluid (iron, chromium and nickel) occur in a certain ratio in the various pickling fluids. Besides the increase in the iron concentration in the conventional pickling fluid, there is a proportional increase in the chromium and nickel concentrations. The increase in the chromium and nickel concentrations in pickling fluids based on sulphuric acid/hydrogen peroxide is significantly less. Under the influence of ferric iron, the sulphuric acid pickling process will mainly remove undesirable oxides and 'etch' the basic material to a lesser degree.
This immediately explains the visual difference between the pickled SS when the two methods are compared. These findings are confirmed by the measurement of the surface roughness.

Table 1: Material loss for the different pickling methods

Type pickledSS material	Nitric acid/ hydrofluoric acid	HF/HNO_3 with accelerators	Nitric acid-free HF/H_2O_2/ H_2SO_4
Duplex (1.4462) Loss in $g/m^2/24h$	5,2	5,6	17
AISI 316L (1.4404) Loss in $g/m^2/24h$	132	275	127

Waste

In the pickling fluid based on sulphuric acid, the iron concentration can become higher before saturation occurs and changing of the bath becomes necessary. For the nitric acid containing baths, this becomes necessary at approx. 25 g/l iron, but for sulphuric acid baths it will be necessary at up to 100 g/l iron. The reason for this is that the iron ions take part in the pickling process, as mentioned above. Hence, the standing time of a sulphuric acid bath is an averaged 4 times longer. It must be taken into account in the processing stage that this high iron concentration will also require more of the neutralising agent in the form of lime. Furthermore, gypsum (calcium sulphate) is formed during this neutralising process. with a subsequent increased amount of sludge in relation to the processing of a nitric acid containing bath. These sulphates must be taken into account for the waste water treatment, especially in places where there are often strict discharge requirements with respect to sulphate. The neutralisation of sulphate containing streams with lime (calcium hydroxide) is not in all cases sufficient to satisfy the requirements and additives will be necessary to actually fulfil these standards.

Conclusions

The removal of the annealing skin of Duplex pipes is significantly faster with the nitric acid–free developed method when compared with the conventional pickling agents. Other types of austenitic stainless steel can also be pickled using this method. This method can be a good alternative pickling method if the discharge of nitrogen oxides, resulting from pickling agent that contains nitric acid, is a problem.
Despite a number of great advantages of the pickling of stainless steel on basis of sulphuric acid/hydrogen peroxide, there are also a number of disadvantages in comparison with the conventional method. The cost of acquisition and processing are higher and the bath requires more maintenance. In addition, even though no more nitrogen oxides can be formed with the alternative method, a strongly acidic solution is still required for the process.

Table 2: Comparison of stainless steel pickling methods

	Conventional HF/HNO_3 method	Method without nitric acid
Acquisition costs	Relatively low	Approx. 3 x conventional
Waste disposal costs	Relatively low	Approx. 3 x conventional
Rinsing water/neutralisation	Relatively easy to treat with calcium hydroxide	Requires additives, besides calcium hydroxide
Analysis frequency	Monthly or less	At least once a week
Indication standing time	Approx. 1-2 years	Approx. 4-10 years
Appearance after pickling	Mat, silvery grey, somewhat roughened	Less mat
Environment/ Working conditions / Safety	NOx and HF fumes	SO_4^{2-} and HF fumes, working with peroxide

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

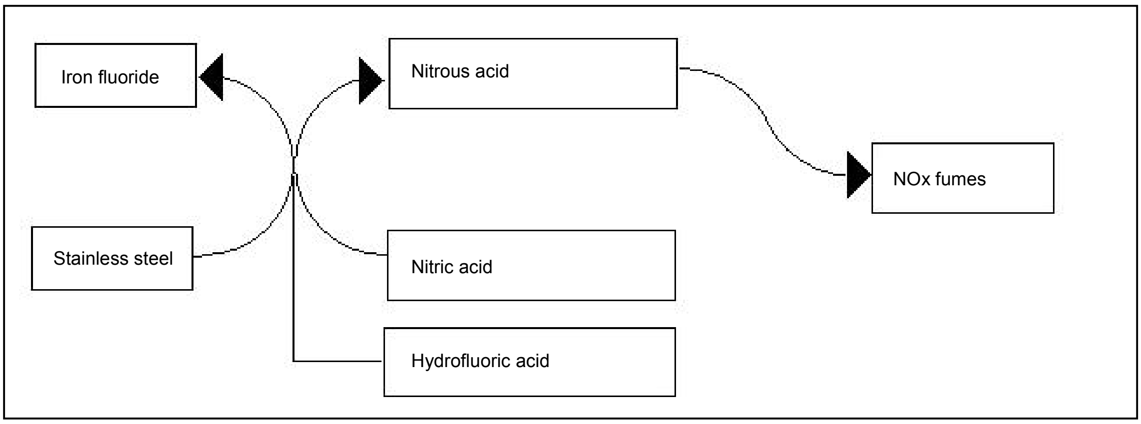

Figure 1*: Schematic representation of pickling with nitric acid/hydrofluoric acid*

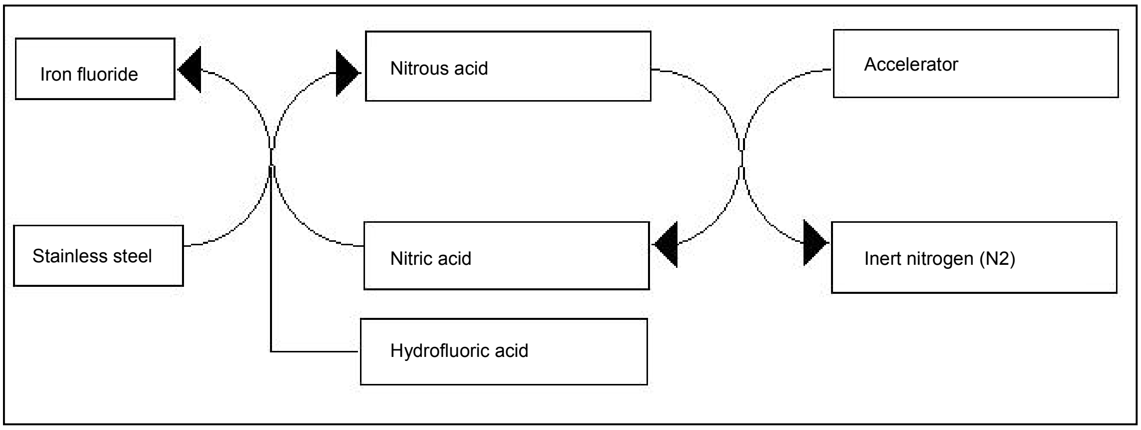

Figure 2*: Schematic representation of the decreased discharge of nitrogen oxides as a result of adding accelerators*

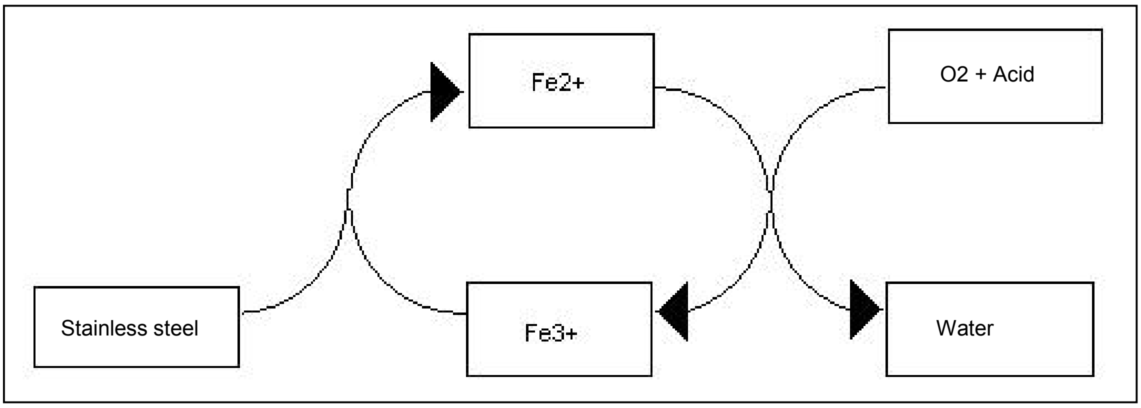

Figure 3*: Schematic representation of pickling with sulphuric acid/hydrogen peroxide and the influence of ferric iron*