**Pickling of stainless steels in a mixture of HNO$_3$ + HF and the use of alkaline potassium permanganate**

During the hot rolling and annealing of alloyed stainless steels and acid-proof steels an oxide coating is created on the surface which if formed by approximately 50% of mixed spinel oxides (Fe, Cr), approximately 30% of iron oxides and approximately 20% of oxides of other alloying elements. Their proportion depends on the steel composition, annealing conditions (temperature, heating duration and furnace atmosphere), the rolling temperature and the speed of cooling. In addition to simple oxides (Fe$_2$O$_3$, Fe$_3$O$_4$, FeO, CrO$_2$, Cr$_2$O$_3$, NiO, MoO$_3$, SiO$_2$), the iron scale layer also contains mixed oxides (FeO.NiO, FeO.Fe$_2$CrO$_3$, NiFe$_2$O$_4$, FeCr$_2$O$_4$, Fe(Cr$_2$O$_7$)$_3$, Fe$_2$SiO$_4$).

Most of the metal oxides contained in the iron scale layer form a spinel structure which is particularly difficult to dissolve in acids. Apart from this fact, a small chromium-depleted layer of a different composition and thickness is created under this layer. To maintain identical surface properties the concentration of chromium on the surface and inside the steel must be equal.

The iron scale layer and the chromium-depleted layer removal from the steel surface requires pickling or additional pickling in acids. The mixture of nitric acid and hydrofluoric acid is mainly used for the pickling of highly alloyed steels.

The pickling of stainless and acid-proof steels may be described as a double-step procedure which is shown in its simplified form in the overview of chemical reactions. Metal oxides and the thin chromium-depleted layer of the basic metal are dissolved under the effect of strongly oxidizing nitric acid. In addition to divalent and trivalent metal oxides, nitrogen oxides and water are generated. The completeness of the pickling procedure however requires the separation of these metals. Hydrofluoric acid serves for such purpose, as it transforms these metal ions into stable fluoride complexes.

The solubility of individual fluoride complexes changes with the pickling solution temperature. During the pickling process the concentration of reaction generating products increases and when a certain threshold value is reached, mainly fluorides and partly also metal nitrates come out from the solution. The solubility of metals in the mixture of nitric acid and hydrofluoric acid mainly depends on the temperature and content of the free hydrofluoric acid. As an example supporting this hypothesis, the solubility of iron in the mixed acid with 150 g.l$^{-1}$ of nitric acid, temperature of 50°C and various concentrations of hydrofluoric acid are given below.

<table>
<thead>
<tr>
<th>Free HF in g.l$^{-1}$</th>
<th>Fe solubility in g.l$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>44</td>
</tr>
<tr>
<td>10</td>
<td>36</td>
</tr>
<tr>
<td>20</td>
<td>29</td>
</tr>
<tr>
<td>30</td>
<td>23</td>
</tr>
<tr>
<td>40</td>
<td>19</td>
</tr>
<tr>
<td>50</td>
<td>16</td>
</tr>
</tbody>
</table>

Sludge created on the bottom of the pickling bath contains difficult to dissolve compounds, the separation of which is a necessary prerequisite e.g. for any type of regeneration. Examples of potential compounds contained in the sludge include: FeF$_3$, FeF$_3$.4.5 H$_2$O, Fe(NO$_3$)$_3$.6 H$_2$O, Fe(NO$_3$)$_3$.9 H$_2$O, NiF$_2$, CrF$_3$, Ni(NO$_3$)$_2$.6 H$_2$O, Cr(NO$_3$)$_3$.6 H$_2$O, Cr(NO$_3$)$_3$.7,5 H$_2$O, Cr(NO$_3$)$_3$.9 H$_2$O, MoF$_6$, TiF$_4$, etc. During the pickling process the concentration of metals in
the bath grows and the content of the free acid falls accordingly. The pickling effect decreases and the pickling bath has to be renewed or strengthened. The acid concentration in the pickling bath may be maintained by the addition of acid until the concentration of metals exceeds the value of approximately 40 g.l\(^{-1}\). Then further strengthening is non-economical. Therefore, the bath is drained and newly created at a concentration of metals of approximately 40 g.l\(^{-1}\). An optimum effective level satisfactory both for technological reasons and for the needs of regeneration procedures is at approximately 30 g.l\(^{-1}\) of dissolved metals. The pickling procedure effectiveness of course depends on the content of the used free acid which is approximately 130 g.l\(^{-1}\) of the free nitric acid and 25 g.l\(^{-1}\) of the free hydrofluoric acid for the value of 30 g.l\(^{-1}\).

Potential chemical reactions during pickling in the mixed acid:

1) Dissolution of the basic material:
   \[
   \begin{align*}
   \text{Fe} + 4\text{H}^+ + \text{NO}_3^- & = \text{Fe}^{3+} + \text{NO} + 2\text{H}_2\text{O} \\
   \text{Cr} + 4\text{H}^+ + \text{NO}_3^- & = \text{Cr}^{3+} + \text{NO} + 2\text{H}_2\text{O} \\
   \text{Fe} + 6\text{H}^+ + 3\text{NO}_3^- & = \text{Fe}^{3+} + 3\text{NO} + 3\text{H}_2\text{O} \\
   \text{Cr} + 6\text{H}^+ + 3\text{NO}_3^- & = \text{Cr}^{3+} + 3\text{NO} + 3\text{H}_2\text{O} \\
   3\text{Ni} + 8\text{H}^+ + 2\text{NO}_3^- & = 3\text{Ni}^{2+} + 2\text{NO} + 4\text{H}_2\text{O}
   \end{align*}
   \]

2) Dissolution of the iron scale
   \[
   \begin{align*}
   3\text{FeO.(Fe,Cr)}_2\text{O}_3 + 28\text{H}^+ + 14\text{NO}_3^- & = 6\text{Fe}^{3+} + 3\text{Cr}^{3+} + \text{NO} + 14\text{H}_2\text{O} \\
   3\text{FeO.Fe}_2\text{CrO}_3 + 28\text{H}^+ + 14\text{NO}_3^- & = 6\text{Fe}^{3+} + 3\text{Cr}^{3+} + \text{NO} + 14\text{H}_2\text{O} \\
   3\text{FeNiO} + 16\text{H}^+ + 8\text{NO}_3^- & = 3\text{Fe}^{3+} + 3\text{Ni}^{2+} + \text{NO} + 8\text{H}_2\text{O} \\
   \text{NiO} + 2\text{HNO}_3 & = \text{Ni(NO}_3)_2 + \text{H}_2\text{O} \\
   \text{SiO}_2 + 4\text{HF} & = \text{SiF}_4 + 2\text{H}_2\text{O}
   \end{align*}
   \]

3) The creation of complexes with HF:
   \[
   \begin{align*}
   6\text{HF} + \text{Fe}^{3+} + \text{Cr}^{3+} & = \text{FeF}_3 + \text{CrF}_3 + 6\text{H}^+ \\
   4\text{HF} + \text{Fe}^{3+} + \text{Cr}^{3+} & = \text{FeF}_2 + \text{CrF}_3 + 4\text{H}^+ \\
   2\text{HF} + \text{Fe}^{3+} + \text{Cr}^{3+} & = \text{FeF}_2 + \text{CrF}_2 + 2\text{H}^+ \\
   \text{HF} + \text{Ni}^{2+} & = \text{NiF}^+ + \text{H}^+
   \end{align*}
   \]

4) Temperature intervals of stability of the complexes:
   \[
   \begin{align*}
   20 – 45^\circ\text{C} & \quad \text{FeF}_3, \text{FeF}_2^+, \text{CrF}_3, \text{CrF}_2^+ \\
   46 – 65^\circ\text{C} & \quad \text{CrF}_2, \text{FeF}_2^+, \text{CrF}_2^+, \text{FeF}_2^+ \\
   65 – 75^\circ\text{C} & \quad \text{CrF}_2^+, \text{FeF}_2^+, (\text{CrF}_3^+, \text{FeF}_3^+) 
   \end{align*}
   \]

The described system of the mixture of nitric acid and hydrofluoric acid is usually used for pickling and additional pickling of anti-corrosive and special steels with minimum deviations from the composition described herein. It is also applied for additional pickling of titanium and its alloys.

The mixed acid is able to remove compounds such as silicon and boron oxides from metal surfaces. This is important for silicon-alloyed steels (e.g. high-speed cutting and tool steels) or for grades alloyed with boron (nuclear power industry).

A certain disadvantage of the specified system is the generation of NO\(_x\) during the pickling process. This must be either collected in a suitable way or catalytically removed from the exhausted air. Another disadvantage is the increase of nitrates content in waste waters.
The use of alkaline solution of KMnO₄ for cleaning of special steels

Generally: The use of alkaline solution of potassium permanganate is clearly destined for the surface cleaning of steels, wires and profiles at pickling and removal of carbon residuals and other non-soluble residuals on the pickled material. This is not news. This procedure has been used with good results in the United States and Canada since 1953. In Europe and especially in Germany the procedure with alkaline potassium permanganate had not been known until 1968. Only after publication in magazines, and the practical use of the method with potassium permanganate in relevant European magazines and an intensive technical promotion by Goldschmit, the procedure went through in a relatively short time in Germany and other European steelworks.

Chemical procedures and working conditions:
Potassium permanganate belongs to the strongest oxidizing agents we know. It represents a simple form of active oxygen in a solid state. The use of this active oxygen depends on the oxidized substance and more or less on the reaction conditions. The following formula may be considered an optimum reaction condition of reactions in progress:

\[ 2 \text{KMnO}_4 + \text{H}_2\text{O} = 2 \text{KOH} + 2 \text{MnO}_2 + 3 \text{O} \]

During the oxidation process intensively violet permanganate gradually changes to brown non-soluble manganese dioxide MnO₂ – black manganese under the influence of the oxidized substance. The generated black manganese comes out in the bath as sludge. The most economical operating procedure of the bath is recommended under the following conditions. Manganese 50 - 100 g.l⁻¹, sodium hydroxide 50 – 100 g.l⁻¹, temperature 80 – 100°C.

The same results are achieved with sodium hydroxide as with potassium hydroxide.

As far as the reaction temperature is concerned, we may say that the speed of oxidation is higher, the higher the selected bath temperature is. Preferably, the temperature of 90 – 95°C is used. With regard to the given formula, we may generally ask what is oxidized during the surface cleaning of wires and profiles. Carbonized remains, organic materials such as fats or organic portions of drawing means and old soaps, which get on the surface during the production processing of wire from carbon and alloyed steels, are disintegrated and removed in the potassium permanganate solution due to oxidation. These materials are particularly difficult to clean without permanganate when organic portions are transferred by cracking due to the annealing process to substances non-soluble in acids. During annealing or heat processing under a protective atmosphere, drawing fats of organic origin and mainly carbon-rich substances are cracked.

Carbon residuals on the surface of metals may form components of annealing atmospheres during annealing, if they contain carbon. As softly diffused carbon remains on wire surface give the wire a black appearance and are difficult to remove by mechanical methods, they are non-soluble in pickling acids and non-removable, only under the risk of the material over-pickling, and not fully. Professionals in the field of wire production give the following advantages especially of the alkaline permanganate:

1. The gaining of a clean surface without residuals and perfect degreasing of the metal surface.
2. The shortening of the pickling time and thus decreasing of potential over-pickling due to the basic material attack with the occurrence of shiny surfaces.
3. The reduction of occurrence of residuals after pickling, especially after using sulphuric acid.
4. The reduction of hydrogen fragility and general reduction of all pickling defects which incur as a result of acid exposure.
5. The prolongation of the lifetime of drawing jaws (dies) due to the processing of metal-clean surfaces. Highly hard metal carbides are partly created mainly on alloyed steels under annealing conditions which cause fast wear and tear of dies.
   The use of permanganate also has its importance during the pickling of anti-corrosive steels and highly alloyed or tool and high-speed cutting steels where this bath is able to create oxides of Cr, Mo and W otherwise non-soluble in acids to alkaline solution.

The same applies to the processing of steels alloyed with Ti.
   Analytical procedures have been processed for optimum use of the permanganate solution to determine active substances.

Conclusions:
The use and advantages of permanganate may be briefly summed up as follows:
- the use for wires and profiles from carbon and alloyed steels to remove carbonized residuals generated during annealing from the drawing materials and annealing atmosphere.
- removal of residuals after pickling in acids and disintegration of hard iron scales on high-quality and alloyed steels before and during pickling
- with the use of permanganate metal-clean and shiny surfaces without residuals and perfectly degreased are achieved
- reduction or removal of hydrogen brittleness and elimination of defects caused by over-pickling in acids.