Eco⁴ – an ecological and economical stainless steel pickling process

Eco⁴ is a new stainless steel pickling process that avoids formation of hexavalent chromium, reduces NOx and nitrates in the waste water, reduces consumption of HF and HNO₃ acids, reduces overall energy consumption and reduces the investment and operating costs for spent acid regeneration, treatment and disposal.

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Pickling removes surface oxides and cleans surfaces to expose the bare metal. Pickling operations are very important in the manufacture of stainless steel and provide the transition between hot plant and cold plant, coming after the annealing operations. It is carried out in one or more reactors, involves multi-step chemical reactions, and is one of the most polluting and costly chemical processes in the steel industry due to the presence of the highly corrosive acids and hazardous substances such as hexavalent chromium and NOx.

The most common processes used include electrochemical and chemical operations to remove oxide scale as well as the chromium-depleted layer generated on the strip surface during high temperature steel annealing.

In recent years, Tenova has addressed its research activities to develop new pickling technologies aimed at reducing both the polluting effects of the chemicals used and the overall process operational costs.

After some years of intense research at CSM, a new pickling process has been successfully developed and tested up to pilot scale. This new process not only has a reduced environmental impact, but also a much lower operational costs thanks to a dramatic reduction of expensive acids (such as HF and HNO₃) used and, as a consequence, the energy and fuel consumption in the treatment of relevant wastes.

TRADITIONAL STAINLESS STEEL PICKLING

The pickling of stainless steel after annealing is performed by a series of chemical reactions to dissolve the metal oxides and the chromium depleted layer generated during hot rolling, continuous annealing and cooling. In a hot annealing and pickling line (H-APL) for hot rolled coils, it is used mainly after mechanical shot-blasting, using a sequence of processes using a de-scaling tank with high temperature H₂SO₄ (up to 100°C), followed by chemical pickling in mixed acid baths (HNO₃ + HF or HNO₃-free) (see Figure 1).

In a cold annealing and pickling line (C-APL) for cold rolled coils, the traditional pickling process uses Na₂SO₄ electrolytic treatment, followed by mixed acid chemical pickling (HNO₃ + HF) in same way as hot rolled coils but with different recipes (see Figure 2).

The scale formed during the annealing of cold rolled steel is compact and richer in chromium than the steel bulk, so the sodium sulphate (Na₂SO₄) electrolytic treatment is to dissolve the chromium oxide into solvable chromates so that the mixed acid liquor can easily remove remaining scale.

In both cases, the conventional pickling process is based mainly on HF and HNO₃ as pickling agents; these two acids are expensive and hazardous, the process produces spent liquors and fumes are extremely dangerous to
the main pickling process innovation is the new AC electrolytic pickling tank (AC BOOSTER) specifically designed to use the strong descaling and pickling effects of the AC current applied onto the strip by means of a series of grids. Compared to traditional DC electrolytic treatments, the continuous reversal of polarity produces a transient polarisation regime which does not allow the stabilisation of the reaction products and greatly increases the kinetics of the dissolution of the oxidised layer.

As the AC current is very effective in scale removal as well as on the chromium-depleted layer dissolution, the majority of mass loss is in the H₂SO₄ acid solution (see Figure 4). This significantly reduces the pickling load on the HF/HNO₃ mixed acids bath and consequently, acid consumption is minimised, and spent liquor and NOx in the fumes produced for surface unit are reduced.

The cost saving has been estimated at 1.5-2€/t of produced steel considering the chemicals costs (with acid purification unit to recover the free acid from the waste solution in both cases) the neutralisation costs, NOx reduction cost and electrical energy.

If an Acid Regeneration Plant (ARP) is installed, the relevant investment and operating cost (natural gas, ammonia for NOx reduction) are dramatically reduced.

THE ECO⁺ PICKLING PROCESS

The new ECOlogical and ECOnomial eco⁺ pickling process (patent pending) developed by Tenova and CSM has been designed significantly to reduce the pollution risks to the environment and the operator and to reduce the operational costs both for production and for waste treatment. It is based on the following steps:

For hot rolled coils (see Figure 3):
- Mechanical descaling using shot blaster
- Optimised H₂SO₄ de-scaling tank
- Electrolytic pickling fed with AC current in an H₂SO₄ acid bath to complete the de-scaling of metal oxides and to dissolve a large portion of the chromium depleted layer
- Final pickling and passivation with HF and HNO₃, or with a nitric-free mix of acids
- Re-oxidation of the mixed acid solution to continuously regenerate the HNO₂ back to HNO₃, through the O₂ re-oxidation unit or, in case of nitric-free acid solutions, re-oxidation of the Fe ions to the 3-valent form.

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in fact a plant designed for one traditional line, in the case of the innovative sequence, can be utilised for three lines.

For cold rolled coils (see Figure 5):

- Electrolytic pickling operated with H$_2$SO$_4$ fed with DC and AC (according to steel grade) current to convert the chromium oxides of the scale and to realise Cr-depleted layer dissolution (up to 60% of standard metal losses).
- Final pickling and passivation with mixed acid solution (HF and HNO$_3$ or nitric-free mix of acids).
- Re-oxidation of the mixed acid solution to continuously regenerate the HNO$_3$ back to HNO$_2$, through the O$_2$ re-oxidation unit or, in case of nitric free mix of acids, re-oxidation of the Fe ions to the 3-valent form.

As for HR coils, the main pickling process innovation is the new AC BOOSTER. In such a way, the majority of the mass loss is in the H$_2$SO$_4$ acid solution, thus strongly reducing the pickling load of the HF/HNO$_3$ acids and then the relevant consumption and wastes (see Figure 6).

Using the new pickling process, the overall cost saving for a C-APL is 4-6€/t on a total pickling cost of 9-12 €/t steel depending on local rates. (Costs refer to electrical energy, chemicals, Cr conversion, acid recovery via acid purification unit and neutralisation treatment.)

H$_2$SO$_4$ VERSUS Na$_2$SO$_4$

Another important contributor in achieving this more environmental friendly process/technology is the adoption of a H$_2$SO$_4$ bath (working at specific temperature ranges for each steel grade) instead of the traditional Na$_2$SO$_4$ in the electrolytic tank.

By using H$_2$SO$_4$ (sulphuric acid) in the electrolytic process instead of Na$_2$SO$_4$ (sodium sulphate), Cr(VI) (as chromates) formed during the electrolytic scale dissolution are immediately transformed to Cr(III): thanks to the chemical reaction with Fe(II) ions that are produced during electrolytic bulk dissolution. Consequently, the Cr(VI) is eliminated at source.

The development of this electrolytic tank technology and the relevant bath recirculating system has been helped by means of 3D CFD calculations, used to obtain accurate cell fluid-dynamics to ensure gas removal and to avoid surface areas with reduced electrolytic pickling activity and consequently current localisations. In fact, between the electric grids, where the process is performed, the heat power released by Joule effect as well as the H$_2$ and O$_2$ coming from water electrolysis are rapidly evacuated. Furthermore, thanks to the continuous renewal of the solution on the strip surface, the new tank guarantees enhanced pickling efficiency and steel surface quality especially with ferritic steel grades. Moreover, higher strip quality in terms of roughness and brightness is obtained (see Figures 7 and 8).

A further big advantage of the Tenova process for C-APLs is the significant reduction in electrical energy consumption (-40%) due to:

- Lower electrical resistivity of H$_2$SO$_4$ compared to Na$_2$SO$_4$ allowing the process to operate at lower voltage for the same total current.
- Specific cell design and submerged roll positioning allowing a significant reduction of lost current inside the cell between electrodes connected to different poles.
- Higher pickling efficiency (due to shorter treatment times) of the AC treatment compared to DC.
As a direct consequence of the reduced pickling load of the mixed acid pickling, further big advantages are:

- Lower fresh acid consumption (HF + HNO₃) and, if an acid regeneration plant is adopted, reduced natural gas necessary to regenerate spent acids
- Lower energy and chemicals (urea or ammonia) necessary to treat the fumes containing NOx when a conventional selective catalytic reactor is used
- The possibility of eliminating the SCR by adopting a reduced operating maintenance cost de-NOx system based on the above-mentioned O₂ acid re-oxidation units suitable to convert most of the HNO₂ (unstable acids) generated by the pickling reactions to HNO₃.

In such an approach, a final Tenova fume scrubbing system composed by scrubbing tower in series is sufficient to eliminate the residual NOx and to filter HF and H₂SO₄ vapours.

**CONCLUSIONS**

Steel producers usually have two main concerns:

- To dramatically reduce investment costs necessary to minimise environmental problems
- To reduce operating costs required to achieve higher product quality and line productivity.

The new eco⁴ pickling process meets these concerns and, compared to the traditional technology, has the following main advantages:

- Avoids formation of hexavalent chromium and hence the need for conversion and neutralisation treatment plant
- Reduces about 90% of the NOx and 40% of the nitrates in the waste water
- Reduces consumption of the most pollutant and costly HF and HNO₃ by 40-70%
- Reduces the overall energy consumption for a C-APLs pickling section by 40%
- Reduces the investment and operating costs for spent acids regeneration, treatment and disposal.

The new eco⁴ pickling process can be considered as the best currently available technology to be used in the new annealing and pickling lines for stainless steel or to modernise existing pickling plants. **MS**

**Fig 7** AISI 304 cold rolled, pickled with the traditional process (left) and with eco⁴ pickling (right)

**Fig 8** SEM Views of surface, sample pickled with eco⁴ – x 1000

No oxide residues
No over-pickling
Roughness
Ra 0.12-0.34µm

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