In Japan, especially, the development of new austenitic material started 20 years ago and since the end of the 90s power plants with steam temperatures of around 600°C have been in operations.

Raising efficiency in order to lower CO₂ emission requires the use of austenitic materials in the final stages of the superheaters and reheaters. In the selection of the materials high temperature corrosion and steam side oxidation need to be considered as important as creep strength. Hitachi Power Europe (HPE) has gained considerable know how from the operational results and experiences of Japanese and German power plants and also from its own test rig investigations together with utilities. HPE has developed a life time calculation tool which considers the growth of the magnetite layers and the high temperature corrosion rate. This paper gives some theoretical background of steam-side oxidation and high temperature corrosion and how to calculate the life time and operational results for power plants. Recommendations for operational limits for different austenitic materials are given in conclusion.

### Development of steam parameters

Progress in the development of materials for steam generators, turbines and piping has led to new power plants being built with higher steam parameters in recent years. This process started in Denmark, Japan and Germany when building new lignite fired power plants. The driving forces for this development were the wish to hold the price of electricity down and the growing discussion about climate change through CO₂ emission. Fig. 1 shows specific CO₂ emission as a function of plant efficiency.

Between 1950 and 1980 around 30 industrial power plants were built where austenitic materials were used in several components (Fig. 2). Reports based on long-time operation,
mostly from steam generators producing steam and electricity in chemical fabrication plants (base load operation), show positive results for super heaters and re-heater tubes. Steam-side oxidation layer thicknesses in the range of 0.09 – 0.25 mm, which is uncritical under these operational conditions [Ref. 1] were found.

Steam-side oxidation and corrosion behaviour play as important a role as the creep strength in super-heater materials (Fig. 3). There is literature regarding the exfoliation behaviour of the magnetite layers, that is to say, of the outer steam side epitaxial layer of austenitic super heater tubes, which shows that the growing magnetite layers at higher temperatures will see compressive stress during cooling resulting in partial exfoliation of the epitaxial layer. The topotaxial layer remains fixed to the tube surface. In Germany up to the late 1990s only X20CrMoV11-1, AC66 and X3CrNiMoN17-13 were considered as super-heater materials. Surface preparation technologies, such as shot peening, were not considered in Germany and the use of Japanese materials was not permitted at that time in terms of the relevant design rules of TRD and AD.
As a result of this, and with the higher steam temperatures required, the use of X3CrNiMoN17-13 material was decided upon. No serious problems in final stage heating surfaces with steam temperatures up to 583°C have been reported up to now. In one plant, with temperatures up to 600°C, serious problems occurred. Fig. 4 shows exfoliated magnetite from this plant.

After mechanical cleaning of the slag layer from the heating surfaces exfoliated magnetite accumulated in the tube bends after a pressure test, and after starting the boiler again overheating and bursting of tubes occurred in the super heater (Fig. 5). In the re-heater tubes exfoliated material blocked the tube bends from sufficient steam flow and highly elevated steam temperatures were measured.

The re-heater material was finally changed to 310N, a 25% chromium austenite.

Fig. 7 shows typical operational results from Japanese power plants before using fine grain material or shot peened material. The definition of the deposit rate (Fig. 7) is the percentage of the tube inner diameter covered with exfoliated material measured on X-ray film. The bends in Japan were checked by X-ray periodically and in case of severe indications the bends were cut and cleaned.

**Oxidation behaviour**

Literature and in house operational tests show that the growth of the steam-side oxidation layer follows, and can be forecast, on the basis of the Tamman law of scaling:

\[ d^2 = K \times t \]

where \( d \) = metal loss ~ 0.5 x scale thickness in mm
\( K \) = scale constant in mm²/h
\( t \) = time in h

Fig. 9 shows, as an example, the relationship between the logarithm of the K scale constant and the steam temperature at the wall for an 18/8 austenitic material. The available documented operational results of conventional steels are much higher than for the new martensitic and austenitic materials. Knowledge of the oxidation behaviour of a heated steam tube leads to an acceptable lifetime design.

Thicker magnetite layers hinder cooling of the material by the steam. The severity of this depends on the porosity of the magnetite layer. As mentioned in the literature, tube wall temperature rises according to magnetite layer thickness and depends on the existing heat flux. The higher temperature influences the high temperature corrosion rate negatively. Fig. 9 shows the rising temperature as a function of the inner layer thickness at common heat fluxes.

**High temperature corrosion behaviour**

At higher wall temperature, high temperature corrosion plays an important role. Beside the concentration of aggressive corrosive substances in the flue gas, the tube material temperature plays the most important role. Fig. 10 shows, in principal, the material loss rate as a function of the temperature of HR3C. The rate of material loss by high temperature corrosion is mainly influenced by the chromium content. Fig 11 shows, in theory, this influence. The rates of corrosion were checked by laboratory testing of synthetic ash composition.

**Austenitic tube materials**

Fig. 12 shows the creep strength behaviour of different austenitic super-heater materials and Fig. 13 shows the associated chemical analysis for the assessment of their corrosion and oxidation behaviour. The 18% chromium steels show higher creep strength than the 12% chromium steel X20CrMoV12-1, but no better oxidation behaviour.
in laboratory and field tests. Only when using fine grain material like TP347 H FG or shot peened material like Super 304H can good oxidation resistance characteristics be reached.

Fig. 14 shows a manufacturing process for shot peening that is used by Babcock Hitachi Kure. During this process the inner surfaces of the tubes are plasticized and condensed to a depth of 100 µm by peening with austenitic wire particles at high velocity. This treatment supports the diffusion of chromium in this layer and therefore the oxidation resistance behaviour. Because the prices of these higher alloyed materials are much higher they are only used at higher material temperatures and/or in corrosive flue gas atmospheres. Fig. 15 shows comparisons of laboratory results. Materials used in the latest Japanese high temperature steam generators were also applied in Germany, from the middle of the 1990s, in several tests (Fig. 16, 17).

**Operational results with shot peened Super 304H**

HPE has developed a life time calculation programme which considers the increase of material temperature due to the formation of the oxide layers on the inner surface of the tubes as well as the loss of material due to fire-side corrosion. The life time calculation is done in accordance with the standard EN 12952-4: 2001 Annexure A. Time intervals have been defined and the consumption of life time is added over the intervals up to 100%. The method of calculating by intervals is necessary because the wall temperature and wall thickness change over the life-span. Different corrosion laws can be applied within this programme. Verification of the calculation results was carried out by means of a series of operational test cycles. The programme is applicable for the materials X3, 347 H FG, Super 304H, with and without shot peening, and HR3C. Fig. 18 shows life time calculation results for 347H FG at several steam temperatures.

As a result of the overall material investigation the maximum material temperature recommendation as shown in Fig. 19 can be stated with confidence. The life time calculation programme shows what wall thickness margin, if any, has to be added in order to reach the expected life time of the steam generator.

### Power Station | Material | Component | Temperature | Installation
---|---|---|---|---
PS Vestkraft Unit 3 | X6CrNiMoV12.1, X10CrNiMoW25-10, NF 616, TP 347 H FG, TP 310 N, HR 3 C | 97 H3 fast Superheater, each 4 loops | 497 - 580°C steam, 251 bar, 527 - 620°C steam, 251 bar | July 1995
PS Weisweiler Unit G | Super 304H, TP 347 H FG, NF 709, HR 3 C, AC 54, Alloy 617 | 2 loops | 700°C steam, 160 bar | May 1998
PS Westfalen Unit B | HCM 12 A, E 911, 792, Super 304H, NF 709, TP 347 H FG, HR 3 C, X10CrNiMoW17.13, X10CrNiW18.10, AC 66, Alloy 617 | 9 loops | 650°C steam, 180 bar | August 1998

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**Figure 15:** Effect of temperature on steam oxide scale of stainless steel tubes.

**Figure 16:** Field tests of superheater materials.

**Figure 17:** Expected life time.

**Figure 19:** Materials for superheater.
<table>
<thead>
<tr>
<th>Power station</th>
<th>Material</th>
<th>Dimension</th>
<th>Component</th>
<th>Temperature</th>
<th>Installation</th>
</tr>
</thead>
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<tr>
<td>PS Weisweiler Unit G</td>
<td>Super 304H TP 347 H FG NF 709 HR 3 C AC 66 Alloy 617</td>
<td>38 x 5.6 38 x 6.3 38 x 6.6 38 x 6.6 38 x 6.3</td>
<td></td>
<td>700 °C steam, 160 bar</td>
<td>May 1998 2001 Decommissioning December 2002</td>
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<tr>
<td>PS Weisweiler Unit G</td>
<td>X20CrMoV12-1 Ac 66 Alloy 617 Thermie 740 Alloy 623 Alloy 617</td>
<td>38 x 5.0 38 x 6.3 38 x 6.3 42 x 7 38 x 6.3</td>
<td></td>
<td>720 °C steam, 160 bar</td>
<td>June 2001 Decommissioning March 2004</td>
</tr>
<tr>
<td>PS Weisweiler Unit G</td>
<td>X20CrMoV12-1 TP347HFG DMV SB 1.4910 DMV SB S304HDV SB S304HSM1 SB HR3C SMO DMV310N SB HR6W SMI</td>
<td>38 x 5.0 38 x 6.3 38 x 6.3 38 x 6.3 38 x 6.3 38 x 6.3</td>
<td></td>
<td>650 °C steam, 160 bar</td>
<td>August 2004</td>
</tr>
<tr>
<td>PS Weisweiler Unit G</td>
<td>X20CrMoV12-1 TP347HFG DMV SB 1.4910 DMV SB S304H DMV SB S304H SMI SB HR3C SMO DMV310N SB Sanicro 25 HR6W SMI Alloy 617 Alloy 740 Alloy 617</td>
<td>38 x 5.6 38 x 6.3 38 x 6.6 38 x 6.6 38 x 6.3 38 x 6.3 38 x 6.3 38 x 6.3 38 x 6.3 38 x 6.3 38 x 6.3 38 x 6.3</td>
<td></td>
<td>720 °C steam, 160 bar</td>
<td>August 2004</td>
</tr>
</tbody>
</table>

Fig. 17: Field tests of superheater materials.

Summary

HPE has examined and tested all the necessary know-how in order to ascertain the correct material selection, necessary design margins and manufacturing procedures to be used in the manufacture of steam generators for highest steam parameters. This has mainly been based on operational and laboratory results from Japan and in house investigations. All new power plants under contract in Germany will be based on these experiences.

References


Contact Robin Duff, Hitachi Power Africa, Tel (011) 656-3601, r_duff@hitachi-power.co.za