Update in Alloy Selection for Ammonia Furnaces

Cast tubulars with high stress rupture properties, good ductility, adequate stability, and a low coefficient of thermal expansion offer the highest reliability in steam methane reformers. For the past 15 years, the design and operation of high severity ammonia furnaces have improved significantly to provide long-term reliable performance. Here are new technology trends and challenges.

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Introduction

Ammonia is the primary feedstock for the nitrogenous fertilizer industry. Designs of ammonia plants in the early 1950s had the capacities of 300 metric tons a day (MTD), increasing later in the 1960s to 600 MTD and further to 1,000 MTD with breakthroughs in design. Advanced ammonia technologies have led to worldwide acceptance with an average growth rate of 3.6% per annum.

Now, as we approach the threshold of the new millennium, big units up to 1,800 MTD sound more and more convincing. Most new ammonia plants required in the next ten years will be built in countries that have abundant and inexpensive gas. In the U. S. we will see retrofits aimed at cutting energy consumption, improving efficiency through debottlenecking, innovative techniques to increase production, and fixing up equipment that has contributed to repeat failures. This will provide plants with a higher safety factor, fewer shutdowns, and a service factor exceeding 90%.

Figure 1 shows the basic steps utilized in making ammonia. Note how a majority of steps are designed to remove impurities such as sulfur, CO, CO\textsubscript{2} and water from the feed, the hydrogen, and syngas streams. Discussion will center chiefly on the primary reformer, furnace tube alloys, and steps to prevent the metal dusting problem. Materials of construction play a major role in optimum performance and reliability.

Primary Reformer

Squeezing BTUs starts with the primary reformer, our single largest energy consumer. The heat released by the burners is transferred to the reformer tubes. Preheat of combustion air by stack gases and of the hydrocarbon feedstock in the radiation section are now standard practice. The optimum design and operation of the tubular steam-hydrocarbon reformer is critical for reliability and economy of the ammonia plant. Figure 2 shows a typical ammonia reformer section.

The designs of the early 1950s had relatively small horizontally-tubed furnaces with predominately Type 304 tube material. As temperatures reached 735°C to
At 815°C (1,350°F to 1,500°F), we saw the introduction of Type 310 stainless steel and Incoloy Alloy 800. When furnaces became larger, centrifugally cast HK-40 alloy (25Cr/20Ni) was introduced in 1965-1970, first as horizontal and later as vertical tubing, allowing design parameters of 953°C (1,750°F) tube temperatures and 350 psi operating pressure.

**HK-40 tubulars**

In many cases, HK-40 tube life was short due to overheating. Figure 3 (first published by Schillmoller in 1968) clearly shows that operation at 55°C (100°F) above design can shorten tube life from 10 years to approximately 1.4 years. Successful control of temperature depends on conscientious adjustment of burners for uniform tube metal temperature throughout the furnace. Also, note that the changes in pressure in the newer furnaces, for example, by going from 350 to 450 psi (2.4 to 3.1 MPa), could result in shortening the tube life to 3.2 years. Longitudinal splitting due to overheating did override all other tube performance factors, and this became very significant in cases of maloperation, causing unanticipated failures in one out of five furnaces every year.

Other failure modes included weld cracking due to the lower strength of the weld compared to the parent alloy, and stresses from thermal cycling (low thermal fatigue) chiefly during startup and shutdown. The latter was responsible for many failures in risers, manifolds, transfer headers and other components.

**Operational control**

Inadequate control of temperatures in the tube rows adjacent to radiant walls have caused nonuniform tube performance, with temperatures 30°C (50°F) hotter in the end rows than in the middle rows. Also, flame impingement, localized hot spots, carbon formation, and catalyst “hot banding” have contributed to overheating. The difficulty of proper furnace control has led to conservative operation with HK tubulars at 30°C to 55°C (50°F to 100°F) below design.

**HP-Mod alloys**

Since the early 1980s, the ammonia industry has used the HP-45 Nb alloy with its numerous modifications. Many of the modifications are considered proprietary, but they are copied with minor variations by other suppliers. In our judgment, there was no great difference between the HP+Mo, HP+Nb, HP+W, and HP+W+Nb+Mo alloys of which HP+Nb is the most commonly used variation, and is firmly established. One advantage of niobium over molybdenum is its tendency to form finer, better distributed carbides.

Figure 4 shows that HP-Mod has a 40% incremental stress rupture strength over HK-40, and a capability of operating at 55°C (100°F) higher temperature. The thermal fatigue life is at least twice as long. The use of stronger alloys has allowed tube volumes to grow without increases in tube wall thickness, producing capacity increases of 30% or more for the same tube count with only marginally higher cost.

In addition, the good ductility and weldability of HP-Mod deserve mention. It has in the as-cast condition about 8% elongation. After prolonged service, this drops to about 4%. If field repairs are required on HP-Mod after aging, a solution anneal for about two hours is recommended which will restore much of the elongation.

Lighter tubing also allows lighter tube supports. Thinned walls result in better heat transfer and increase the resistance to thermal cycling. Consequently, running and maintenance costs are lowered and service life is extended. With the thinner wall, the cost per foot of catalyst tubing is comparable to HK-40, even though the cost of HP-Mod by weight is substantially higher. HP-Modified has the best economics for either revamps or new projects.

**HP microalloys**

This category of HP-Mod Nb has become more established in recent years. During casting, microalloys use trace quantities of Ti, Zr, and rare earth elements (believed to be cesium). There is a broad range of compositions. The addition of Ti/Zr up to about 0.6% maximum is claimed to improve high temperature stress rupture resistance by promoting the forma-
Table 1. Chromium Equivalents of Various Wrought and Cast Alloys (Cr eq = Cr% + 3 x (Si% + Al%))

<table>
<thead>
<tr>
<th>Alloy Nominal</th>
<th>Cr</th>
<th>Ni</th>
<th>Si</th>
<th>Al</th>
<th>Cr eq</th>
<th>Performance Expected</th>
</tr>
</thead>
<tbody>
<tr>
<td>AISI 304 SS</td>
<td>18</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>18</td>
<td>poor</td>
</tr>
<tr>
<td>Incoloy 800/800H</td>
<td>20</td>
<td>32</td>
<td>.3</td>
<td>.3</td>
<td>22</td>
<td>poor</td>
</tr>
<tr>
<td>Incoloy 803</td>
<td>25</td>
<td>35</td>
<td>.3</td>
<td>.3</td>
<td>27</td>
<td>fair</td>
</tr>
<tr>
<td>AISI 310 SS</td>
<td>25</td>
<td>20</td>
<td>.3</td>
<td>-</td>
<td>26</td>
<td>fair</td>
</tr>
<tr>
<td>Inconel 600</td>
<td>15</td>
<td>72</td>
<td>-</td>
<td>-</td>
<td>15</td>
<td>fair</td>
</tr>
<tr>
<td>Inconel 601</td>
<td>22</td>
<td>60</td>
<td>-</td>
<td>1.5</td>
<td>27</td>
<td>good</td>
</tr>
<tr>
<td>Inconel 617</td>
<td>22</td>
<td>52</td>
<td>-</td>
<td>1.2</td>
<td>26</td>
<td>good</td>
</tr>
<tr>
<td>Haynes 214</td>
<td>16</td>
<td>76</td>
<td>-</td>
<td>4.5</td>
<td>30</td>
<td>good</td>
</tr>
<tr>
<td>Kanthal APM</td>
<td>22</td>
<td>-</td>
<td>-</td>
<td>6.0</td>
<td>40</td>
<td>best</td>
</tr>
<tr>
<td>Cast</td>
<td>25</td>
<td>20</td>
<td>1.0</td>
<td>-</td>
<td>28</td>
<td>good</td>
</tr>
<tr>
<td>ACI HK-40</td>
<td>26</td>
<td>35</td>
<td>1.5</td>
<td>-</td>
<td>30</td>
<td>good</td>
</tr>
<tr>
<td>ACI HP-Mod</td>
<td>35</td>
<td>48</td>
<td>1.5</td>
<td>-</td>
<td>40</td>
<td>best</td>
</tr>
</tbody>
</table>

Figure 1. Basic principles of producing ammonia.

Figure 2. Typical reformer section ammonia production.
tion of more finely dispersed carbides. The parallel addition of rare earth elements appears to enhance the carburization resistance by encouraging the formation of more stable, continuous oxides. The microalloys also appear to retain 10% ductility after aging, which is significantly better than the standard HK and HP alloys.

The average stress-to-rupture value, based on data from several vendors, is shown in Figure 4. Long-term experience is limited. While some users question the extra stress rupture performance to be obtained at temperatures over 1,000°C (1,850°F), there is little to lose in experimentation since microalloy additives are offered at little or no extra cost and there are no downside risks in performance. Until further proven, it is suggested that no credit should be taken for the extra strength that may be claimed.

**Specialty alloys**

Alloys such as Supertherm (25Cr/35Ni/15Co/5W), NA22H (28Cr/48Ni/5W) and XTM (35Cr/45/Ni + Additional Elements) fall into this category. These strong alloys can provide either a higher operating temperature with better yield or offer as a substitute for HK-40 or HP-Mod an improvement in run length and in tube life. A life extension between five and ten years should be quite possible. Because of the excellent performance of the HP-Mod alloys and the microalloy introduction, there is presently little need for such specialty alloys in the primary reformer. However, it should be noted that such alloys with their high nickel content permit higher concentrations of chromium and silicon which both enhance the resistance to coking, carburization and metal dusting.

**Manifold Materials**

In the early stages many steam methane reformer furnaces had unanticipated failures of risers, manifolds and transfer headers made of HK, HT and HU alloys due to stresses from thermal cycling, chiefly during startup and shutdown. Welds in positions where thermal stresses and stress concentrations are highest should be avoided. These alloys lacked ductility and resistance to thermal shock. Wrought Alloy 800H, while not as strong as the cast alloys, had much greater ductility and thermal-shock resistance and became the alloy of choice.

There has been a reluctance to change what is generally seen as a satisfactory construction. Twenty years ago, the cast version of the Alloy 800H was developed. The 20/32 Nb alloy with 0.10 carbon and 0.5-1.5% Nb provides high strength below 900°C (1,650°F) and a low tendency for embrittlement. It is more extensively used in Europe today than in the U.S. The 20/32 Nb cast alloy is less expensive than Alloy 800H, because it has higher creep and rupture strength and permits the use of larger and fewer outlet headers. Weldability is excellent and no preheat and post weld heat-treatments are required. Elongation is 25% when the alloy is new and over 15% when aged. Figure 5 shows the mechanical properties of Alloy 20/32 Nb compared to HK-40. The incentive to change has not come for technical reasons, but for the need to be more competitive. Alloy 20/32 Nb is now more widely used for manifolds and has become the standard for high temperature piping.

**Metal Dusting**

**More widespread**

Metal dusting is governed by oxidation and carburization. Modern ammonia plants have reduced energy requirements and operate with a lower steam/H$_2$ ratio. Also, the higher front end pressures have increased the CO content and we have a more efficient CO$_2$ removal system. These are some of the reasons why metal dusting or catastrophic carburization seems to have become more a widespread phenomenon in ammonia plants than before.

**Temperature and CO/CO$_2$ ratio**

Metal dusting has been frequently observed in the outlet sections of the secondary reformer, as shown in Figure 6. When heat is being recovered in the waste heat boiler (WHB), metal wall temperatures here drop to or through the critical metal dusting temperature range, believed to be 500°C to 800°C (900°F to 1,500°F). Figure 7 shows how materials such as Type...
Figure 3. HK-40 tube in steam-methane reformer. Life is greatly affected by small changes in pressure and temperature.

Figure 4. Generalized comparison of allowable creep-rupture stress for HK-40. HP-Nb and HP-Mod Microalloyed.

Figure 5. Mechanical properties of HK-40 and cast alloy 20/32Nb.

Figure 6. Location of metal dusting found in the outlet portion of waste heat boilers.
304 stainless and Incoloy 800 are very susceptible to attack in this temperature zone. In addition to temperature, the reaction kinetics are controlled by the ratio of CO/CO\(_2\) in the gas, and the gas partial pressure. Figure 8 shows how a ratio of 0.5 and less yields insignificant attack, while with a ratio of 3 to 10 metal wasting rates can be catastrophic. In the past many ammonia plants operated with a CO/CO\(_2\) ratio of 0.5 to 1.0, where alloys such as Type 309 and 310 stainless steel, or sometimes even Type 304, have proven adequate.

The operating zone has now frequently moved from “intermediate attack” to the zones of “severe attack” or “catastrophic.” Recirculation of some CO\(_2\) into the primary reformer feedstock should be considered, as it is helpful in lowering the CO/CO\(_2\) ratio of the system and severity of attack.

**Alloy selection**

Resistance of an alloy to metal dusting is dependent on its ability to form an adequately protective chromium-oxide scale. Alloy performance can be ranked according to

\[
\text{Cr Equivalent} = \text{Cr\%} + 3 \times (\text{Si\%} + \text{Al\%})
\]

Table 1 shows how the alloy can be upgraded according to the guidelines and the severity of the attack, if metal dusting is experienced on channels, outlet cones, bypass or shell liners, ferrules, etc. in the waste heat boiler or between the WHB and steam superheater (SSH).

### Steam/hydrogen ratio

This is another factor controlling the degree of metal dusting attack. The oxidizing potential of a high steam-to-hydrogen ratio has shown to be effective in maintaining a protective oxide film on the stainless steels. However, new potassium-enhanced catalysts have offered a savings in energy consumption and this has resulted in requiring less steam. Figure 8 shows the negative effect of the much lower steam/hydrogen ratio. It is known that sulfur additions to the feedstock are beneficial in maintaining a protective chromium film and retards and suppresses the reaction mechanism of metal dusting. However, this is not practical for ammonia plants, as the sulfur poisons the activity of the nickel catalyst.
Summary

All alloys in H$_2$/CO/CO$_2$/H$_2$O systems in the 500°C to 800°C (900°F to 1,500°F) temperature range are suspect for metal dusting to take place when the CO/CO$_2$ ratio exceeds 0.5. One should consider the following to reduce the extent of attack or prevent the same. Economic and other factors may prevent their adoption, however, there is no substitute for using the right alloy in the first place.

1. Recycle CO$_2$ in the feedstock to the primary reformer to lower the CO/CO$_2$ ratio to 1.0 or less.
2. Use a steam/hydrogen ratio in excess of 1.0; preferably over 1.5.
3. Control the temperature outside the critical zone. Prevent hotspots in lower temperature areas and maintain good insulation in the higher temperature zones.
4. Never select an alloy using temperature as the only guide. If there is susceptibility to metal dusting, select an alloy with a high chromium equivalent for the critical temperature zone. Stay away from Type 304 stainless steel and Incoloy alloy 800H or similar low-chromium content alloys.

New Technology Trends and Challenges

During the past ten years, the HP-Mod alloys have been perfected and have made a great contribution to a more efficient and more profitable steam reforming operation. Plasma welding and electrobeam welding have been introduced to improve the stress rupture strength of welded parts. Initial acceptance has been obtained for the special Ni-Cr-Si alloys that have received their first application in millisecond ethylene furnaces and demanding short-residence-time furnaces.

Today’s greatest challenge is to ensure and monitor correct procedures for furnace operation, as well as for startup and shutdown. It is necessary to have a clear understanding of the limitations of materials and maintain good operational control and uniformity of firing. Alloys and design play an important role; however, proper operation, monitoring of the feedstock for contaminants, and control of the steam/carbon ratio to counteract persistent coking and metal dusting are the key to providing a high-efficiency, profitable operation with an extended tube life.

Literature Cited

DISCUSSION

Z. Anwar, Fauji Fertilizer Ltd.: We have a bit of metal dusting experience. You put Alloy 800 at an advantage compared to SS-304, but our experience is contrary to this. We experienced metal dusting downstream of our waste heat boiler and in the superheater. It resulted in an enlargement of baffle holes and consequent failure of the superheater tubes due to vibration. As a stop-gap arrangement, we reinforced the tube bundle by providing a crisscross rod baffles arrangement with the help of SS-304 tubes to avoid vibration of the tubes. The same were inserted on baffles at four different elevations and welded to a circumferential strip. We did some patchwork on shroud with plates of SS-304. After a year of operation, when our replacement in Incoloy 601 was ready, we took the bundle out and found that there was absolutely no attack on 304 material. The rod baffles and the patchwork were intact. Only Incoloy 800 was affected by metal dusting. About the steam gas ratio, as an interim arrangement, we introduced some extra steam through the secondary reformer to retard metal dusting. This does not limit the primary reformer, and you don’t lose much energy. In fact, practically more than 90% of the energy is recovered in a downstream heat recovery system with the advantage of a reduction in metal dusting.

Schillmoller: Thank you for sharing this information. I don’t think there was a specific question that I have to answer there. The relative attack on Type 304 stainless steel and Incoloy Alloy 800 depends very much on the temperature and range of the Cr/Si/Al content in Alloy 800. Of course, increasing the steam/gas ratio increases the oxidizing potential and is very helpful in reducing the degree of metal dusting. It must be considered if the system permits doing so.

G. Schlichthärle, BASF: You rated different materials with respect to resistance. Does the “best material” mean that there is no metal dusting to be expected at all or is the metal dusting with that particular material only remarkably reduced?

Schillmoller: This depends on the severity of the conditions that I showed in Figure 8. If conditions show “catastrophic,” you have to go to as high a Cr-equivalent number as possible and supplement the system with oxygen or sulfur compounds. If the attack is “intermediate,” which occurs in most cases at this time in ammonia plants, then the number 26 would probably be adequate to solve your problem. Under “severe” conditions, alloys with a Cr-equivalent of 40 would be expected to be resistant. I just listed a number of typical materials, but any other alloy with a high Cr/Si/Al level can be considered.