New Tubes Solve Reformer Heat Problem

Supertherm alloy replacements for original tubing in radiant section provide satisfactory performance in California ammonia plant.

C.P. Leyel Collier Carbon and Chemical Corp. Brea, Calif.

An installation of "Supertherm" tubes, replacing HK-40 in the radiant section of a reformer at Collier's Brea, Calif., ammonia plant, has performed completely satisfactorily since January, 1971, in spite of the unit operating at as much as 12% over design production rate.

Supertherm is a patented alloy manufactured by Abex Corp. Its composition is: chromium 26%, nickel 35%, carbon 0.50%, manganese 0.70% (max.), silicon 1.6%, cobalt 15%, and tungsten 5%.

The reformer, part of a 750-ton/day ammonia plant, is conventional Foster-Wheeler design, shown in Figure 1. It has two cells, staggered tube rows, and two burner terraces on each side. Figure 2 is a view of the radiant tubes in the bottom burner terrace. Among interesting design features are:

1. The combustion air is provided by the exhaust gases from a gas turbine. Figure 1 shows the large exhaust gas duct. The turbine thus acts as a forced draft fan. The ex-



Figure 1. Primary reformer at Brea, Calif.

haust gases are at around 930° F and contain approximately 17% oxygen.

2. The ammonia plant is a C.F. Braun design. (1) The plant thus operates with a high methane leakage from the primary reformer and a hydrogen to nitrogen ratio about 2:1 out of the front end. Excess nitrogen is then removed, with most of the methane and argon, by cryogenic distillation before going to the synthesis loop. Thus reforming conditions are less severe than those encountered in a "conventional" plant. The Brea reformer is operated at an exit temperature of $1,270^{\circ}F$, as measured by thermocouple.

3. There is no outside source of process steam. Thus when the front end has to be shut down, the reformer has to be shut down all the way. This, of course, creates more thermal cycling than in a plant where process steam can be added from an offsite source.



Figure 2. Radiant tubes, showing bottom burner terrace.



Figure 3. Typical tube temperature profile.

Before switching to Supertherm, the furnace radiant tubes were HK-40 with a 0.75-in. wall thickness. The tube internal diameter was 5 in. The reformer has always exhibited a rather unusual radiant tube skin temperature profile, shown in Figure 3. This profile is only approximate. Accurate measurement of tube skin temperatures is considered very difficult, although Collier has extensive experience with both optical and infra-red pyrometers. In this case, there is considerable evidence to indicate that the hot spot is opposite the upper burner terrace, the most convincing indication being that this is where all the tube failures have occurred. Much work has been done trying to smooth this profile by adjusting the firing split between the upper and lower burners, and also the proportioning of the air between the two levels.

When it became apparent that the HK-40 tubes were in third-stage creep and the furnace would have to be retubed, a considerable investigation was made, covering the following items:

1. Even by switching to smaller size catalyst (5/8-in. x 1/4-in. in the hottest section of the tube), firing the reformer to stay below the design tube skin maximum of the previous tubes, which was $1,650^{\circ}$ F for 100,000 hr. of life, could not be assured. The maximum tube skin temperature was thus increased to $1,700^{\circ}$ F.

2. The high tube skin temperature was required because it was found necessary to operate at an average heat flux of 30,000 Btu/hr.sq.ft., which was above design for the reformer. Expanding the reformer was quickly ruled out as prohibitively expensive.

3. A design with HK-40 tubes with a maximum tube skin temperature of $1,700^{\circ}$ F was ruled out because this would have required a tube thickness of over one inch. Collier's metallurgists were concerned about the stresses set up by the high thermal gradiant across the tubes, although they say there is no way of calculating these stresses accurately. There were indications that thermal stresses were a major factor in the failure of the previous set of tubes. A one-third increase in tube thickness would greatly magnify this problem.

4. It was calculated that Supertherm was able to meet the tube skin maximum design temperature of $1,700^{\circ}$ F for 100,000 hr. life with a 0.55-in. tube wall thickness. This involved a certain amount of judgment, because the manufacturer had data only for 10,000 hr.; thus the 100,000-hr. figure was obtained by extrapolation. Collier was more conservative in their extrapolation than curves provided by the manufacturer.

Without detailing the economics, the choice was between retubing the furnace in kind with 0.75-in. wall HK-40 and taking a shorter tube life, or paying a premium for 0.55-in. wall Supertherm and extending the period between retubing. The cost premium for the new alloy was high. The installed cost was estimated at the time to be 80% more than for the HK-40. However, the cost was not much different than the cost of the thicker wall HK-40, which would have been necessary for the $1,700^{\circ}$ F temperature.

The new tubes were installed in January of 1971, and have operated satisfactorily to date at up to 12% over design production rates. The operating maximum tube skin temperature is held at or below $1,650^{\circ}F$, because only the temperature of the end tubes can be measured.

Collier plans to retube the reformer at its 1500-ton/day ammonia plant at Kenai, Alaska, with Supertherm. The reformer for the new ammonia plant at Kenai will be Manaurite 36X, which is manufactured by the French company, Pompey. #

Literature cited

1. Grotz, B.H., Hydrocarbon Proc., 46, April, 1967.



LEYEL, C. P.

DISCUSSION

MARTY FANKHANEL, Heat Research Corp.: I had two questions. Would you care to state the operating pressure of this reformer, number one; and, number two, what was the life actually achieved with HK-40 tubes in original service? **LEYEL**: Okay, operating pressure at the inlet to the tubes is 475 pounds and the ΔP across the tubes is about 40 pounds. The tube life of these tubes was only three years, "but this was complicated by the fact that we had a carbonyl sulfide problem in the plant, and our sulfur guards were not picking this up. So, we had severe catalyst poisoning, and damaged our tubes we think due to this—we probably overheated them during this time. So this may not be a fair assessment of the tube life under more normal operating conditions.

JAN BLANKEN, UKF, Holland: In one of our plants we have a sidewall fired furnace, not the terrace wall type, but the side burner type, and we experienced severe problems with bowing of the tubes to the extreme that the tubes are touching the sidewall. This furnace has a staggered row of tubes. We had two tubes which we had to nip off by the ICI technique. My question is: does your furnace have staggered rows, and if it has, do you experience bowing of the tubes?

LEYEL: Yes, we do get bowing. The tube bows towards either of the furnace walls (not necessarily the closest wall) which has always puzzled me as to why.

BLANKEN: And the rows are staggered?

LEYEL: The rows are staggered, right.

BLANKEN: If I may, I would like to make a comment. We are the company, mentioned by Salot in his paper who retubed a furnace with thin walled 36 X tubes. We decided to go to these larger inside diameter tubes because we could increase the catalyst quantity with about 30% and could

bring the maximum skin temperature down with about 50° C. Also we found that the cost of going to thin walled 36 X was about the same as using HK 40. The furnace is in operation now for about one and a half year and up till now—and I hope everybody will keep his fingers crossed—it looks fine.

LEYEL: The designers of our new plant would apparently agree with you, as they are going to the same thing, 36X.

Q. Have you yet removed any of these supertherm tubes from service for testing, and if so, has the much greater brittleness of the tubes caused you a problem?

LEYEL: Well we had to remove one tube because we plugged it by mistake. We were changing the gasket on the bottom flange during a shutdown. The catalyst support bullet slipped and was pushed back into place. On startup we found that we had plugged the tube, so we pinched it off on the run. We removed the tube during the next shutdown.

Q. You were able to remove it without breaking it? **LEYEL**: But it had ruptured in the furnace.

Q. The tube?

LEYEL: Yes, once it was pinched off, the tube was sitting in there at a very high temperature—it was glowing red hot. **ANON:** We have operated some supertherm tubes in a hydrogen reformer, and although we had no problem during the operation after a five-year period, in taking out a tube for testing, because of the brittleness, it had completely fractured.

LEYEL: We don't have any experience with this. We have heard that there could be trouble with brittleness, and we've always told our maintenance crews not to hit the tubes with hammers, or treat them roughly because of this brittle property, but we have not had a problem with it.