Special Considerations for Primary Reformer Tube

Here's a discussion of some of the problems resulting from high reaction temperatures in catalyst tubes, and how they can be dealt with.

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In recent years there has been a rapidly developing trend towards large, single stream plants in the chemical and petrochemical industries, with considerable savings in both capital and manufacturing costs per ton of product. This trend has resulted in higher primary reformer pressures in ammonia, methanol, and hydrogen plants in order to reduce the size of vessels in the downstream gas conversion and purification systems, and to facilitate the use of centrifugal compressors.

Higher pressure reforming has required higher reaction temperatures in the catalyst tubes to achieve the required degree of methane conversion to hydrogen and carbon monoxide. The modern reformer is generally designed to operate in the 300 psig to 500 psig pressure range, with exit gas temperatures from 1,500°F for ammonia, and up to 1,750°F for hydrogen plants. Tube skin temperatures will normally exceed exit gas temperatures by 50°F or more and this, coupled with other factors such as reduced catalyst activity, catalyst voids channels, or high pressure drop due to fines or obstruction, will further increase temperatures of some tubes in service. High heat flux design and non-ideal thermal profile in the furnace are also factors which tend to accentuate high temperatures in catalyst tube walls.

Catalyst tubes are almost exclusively centrifugally cast A.C.I. HK 40, a 25% Cr – 20% Ni, 0.35% - 0.45% C heat resisting austenitic alloy. They are generally in the size range of 2.5 in. to 4.5 in. bore, 30 ft. to 40 ft. in length, and vertically arranged in the furnace. Effective wall thickness lies in the range of 0.5 in. to 1 in., depending upon size and duty. Wall thicknesses exceeding 1 in. are generally considered unlikely to provide useful increase in service life due to the increase in thermally induced stress in externally fired thick wall tubes.

A design stress in the range of 700 psi to 1,500 psi, depending upon a design skin temperature in the range of 1,650°F to 1,850°F, and the safety factor used, will be associated with HK 40 catalyst tubes. The design stress will normally be based upon the value of the 100,000 hr. mean creep-rupture stress for the material, with the hoop stress due to internal pressure as the major criterion.

Expectations

Industry experience with the earlier, lower pressure reformers has been very satisfactory with respect to catalyst tube life, which has frequently exceeded ten years. Present indications are that the new reformers are not going to do nearly as well, with initial failure expected in the first three to five years of service. It is also probable that the large plant will find a continuing series of unscheduled shutdowns due to random failures in a large population of catalyst tubes an intolerable situation economically. To offset this, complete tubing change-out may be undertaken after only ten per cent or so of the original tubing has failed. On this basis, relatively small failure percentages of total tube exposure assume increased significance. Even so, the present volume of replacement tubing on high pressure reformers commissioned since 1965 runs into several hundred tubes, and within the next two years is likely to be several thousand.

This dramatic change in experience is almost certainly due to the increased severity of service. Over 1,650°F, the creep strength of HK 40 diminishes at a precipitous rate. If the mean tube skin temperature is 1,650°F, which is quite normal, then "hot spots" or hot tubes may easily reach 1,850°F, and blocked tubes 2,000°F. At these temperatures, irreversible cumulative damage will occur, and the future service life of the tube will be shortened, even though the cause of overheating is corrected. In our plant, we use the very rough rule of thumb that sharply contrasting hot spots or hot tubes (gas cooled but catalyst inactive) will lose ten days of design life per day of use, and blocked tubes, with no gas flow, will lose 100 days per day of use in this condition.

Investigation of failed tubes will almost invariably result in a report that failure was due to overheating. In practical terms, it is almost impossible to maintain a large reformer furnace on-line for very long without developing tubes with some evidence of "overheating". In the low pressure (less than 200 psig) reformer, damaging overheating probably meant 400°F higher than the average tube temperature in the reformer. Today, it may mean little more than 100°F above the average tube before there is concern. This indicates that the tolerance or design reserve which accomodated operating variables and gave long life for earlier reformers is no longer available with HK 40 under present high pressure, high temperature reformer conditions. Realistically, the operator has to keep his large plant on line, and suffer the consequences; a shorter catalyst tube life.

Factors other than simple overheating may have signficance. Several premature tube failures have been caused by catastrophic bore oxidation. Evidence indicates that the mechanism of failure is highly specific to particular tubes in the same furnace, and may require specific environmental conditions. Tubes failing in this manner have generally had a service life of less than three years. Characteristically, a dense, adherent mass of magnetic oxide of iron is formed locally in the tube bore, invading the tube wall section until bulging and rupture occur. The local formation of a flux due to the absence of sulphur, sodium, or tramp element segregates in the tubing are possible causes.

The most disturbing mode of premature failure encountered has been creep to rupture. Considerable variation is found in the creep strength of a material such as HK 40. It changes from cast to cast, depending upon compositional variables (e.g., carbon content), grain size, pouring temperature, cooling rate, tramp elements, etc. This inherent variation in strength, when considered in conjunction with temperature variations in the tube length and the furnace generally, changes in wall thickness and soundness in the tubes, will generate a random pattern of failure in a large population of tubes. This means that once tube failures start, it is almost impossible to anticipate which one is going to fail next.

A modern large reformer may have several hundred tubes in its radiant section. Initial failures may be spaced a few months apart, particularly if a few tubes have had an unusually adverse history of overheating due to blockage, etc. However, once the explainable casualties have developed and passed, the main pattern of failure will accelerate. Each failure may mean shutting down a large plant for tube replacement, or accepting damage to adjacent tubes due to process gas release through developing fissures. Operating uncertainties, and the possibility of damaging other tubes or process equipment by a series of start-ups and shutdowns, will probably dictate complete replacement before about 10% of the tubes have failed. Each shutdown for tubing replacement is likely to cost, with lost production, about 10% of the expense of complete furnace retubing.

Creep tests

Creep tests are carried out on sound, machined specimens, held at a uniform temperature in a clean, non-carburising environment, with simple uni-axial loads. We relate these tests, which are rarely full scale in either physical dimension or duration, to furnace tubes which are rough and porous in the region of maximum tension stress, may carburize in service, and are subject to multi-axial stress. The thermal gradient of approximately 50 °F across an 0.7 in. thick wall HK 40 tube would theoretically develop a stress gradient of about 20,000 psi, with the O.D. surface in 10,000 psi compression and the bore in 10,000 psi tension. These stresses cannot be sustained at operating temperatures, and are moderated by relaxation or plastic flow of the material.

After a week or so at temperature, this stress gradient will be reduced to a low value, but it may be seen that, on cooling, the stress gradient will be regenerated with reversed sign. Reheating back to operating temperature, but with reduced heat flux during start-up, will again tend to diminish the stress gradient and subsequently re-establish it when the full flow of cooling gas is restored. This type of cycle will impose a rachet-like demand upon the material's ductile reserve, and it would not seem unreasonable to expect a number of start-ups and shutdowns to have an adverse influence on the tube life. Considerations of this type suggest that, although high pressure reformer furnaces have been carefully designed using the best available data, one should not be unduly surprised if tube life in service does not correlate precisely with the predicted design life.

It could be contended that the many reformers built in the last five years for higher temperature, higher pressure

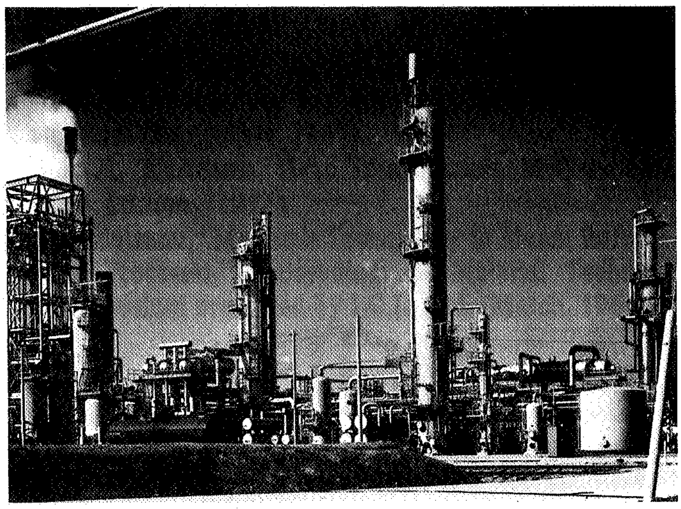

Figure 1. Modern 1,000 ton/day ammonia plant operated by Canadian Industries at Hamilton.

operation are providing many thousands of tubes as practical creep to rupture specimens. These are full scale, full duration, fully relevant tests in actual service, and the data developing from these sources is more directly useful and applicable than laboratory creep data. These tubes may fail prematurely due to "overheating" from the designer's viewpoint, but providing the furnace has been carefully and responsibly controlled consistent with established operating and production standards, the owner is entitled to consider such failures as unavoidable, and the design unrealistic.

Alternate materials to HK 40 involve considerable escalation in first cost. An approximate estimate is that fabricated assemblies will be twice the cost, at a given design pressure, to increase design temperature by 100°F over 1,700 °F. Fabrication is likely to be more difficult, aging effects more marked, and repair feasibility and creep ductility reduced. To some extent, problems may be transferred to exit pigtails or collection manifolds and headers. Great care in furnace design will be needed to avoid brittle fractures during start-up or shutdown.

Canadian Industries plans to make the best possible use of HK 40 tubing in reforming natural gas at 450 psig for ammonia manufacture. In order to do this, we propose to continue, and emphasize, careful operation and control of the furnace, and improve, where possible, the quality of HK 40 tubing purchased and fabricated for replacement by:

1. Maintaining the catalyst in optimum condition. This requires the best desulfurizing practice for feedstock, the use of de-mineralised water for generating process steam, avoidance of condensate formation in the reformer during shutdowns, and avoidance of thermal shock or shock depressurization of the catalyst tubes. In addition, tubes will be vibrated to rectify voids or channels formed by catalyst shrinkage. Catalyst losing activity will be changed out with minimum delay.

2. Maintaining steady state conditions in the reformer as far as possible to avoid thermal cycling of tubing. The reformer should be kept hot during shutdowns of less than seven days unless work has to be done in the reformer.

3. Optimum adjustment of the firing to provide uniformity from row to row of tubing, and the best feasible heat flux profile from top to bottom of the tube. Shift inspection and logging of furnace conditions, and recording of rogue tubes. Routine scan of temperature using good pyrometric equipment. Provision, if needed, of additional inspection ports to allow all tubes to be observed.

4. Maintaining support systems or other devices provided to accommodate thermal expansion of tubes, headers, risers, and collection manifolds in good calibration and condition.

5. Specifying and procuring HK 40 tubing of superior quality for catalyst tube service. Examination of numerous samples of failed tubing by colleagues and friends has repeatedly shown evidence of the damaging effects of local overheating, local carburization, and gross bore fissures and porosity. There is also considerable evidence that the standard "unsound metal" allowance of is frequently insufficient to provide the sound wall thickness specified in design.

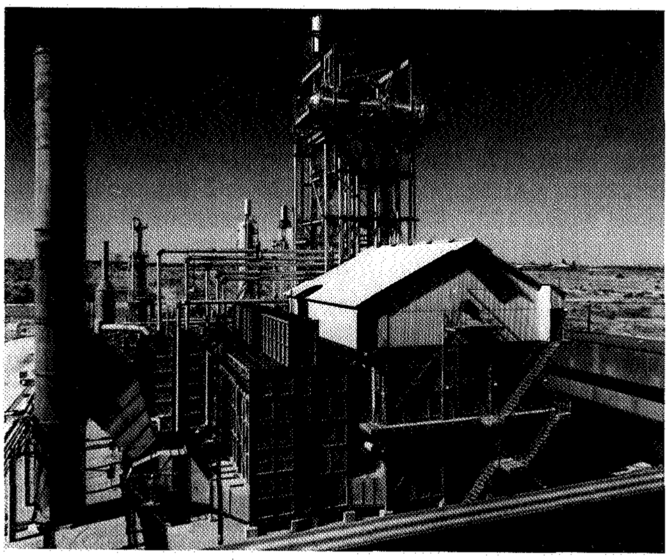

Figure 2. Reformer in a 1,000 ton/day ammonia plant; M.W. Kellogg photos.

In relatively thick wall tubes, providing surplus metal mask bore unsoundness is also of questionable merit, in relation to the thermally induced stress gradient in the tube wall. Any metal present contributing to wall thickness should be sound and able to accept working stress.

Gross bore roughness tends to make homogeneous catalyst loading more difficult, and increase the probability of bridging of catalyst, and of generating voids. Bore weld cutbacks to sound metal, necessary in "as cast" tubing for the assembly butt welds, also provide internal features favoring bridging as the catalyst shrinks in service. Catalyst voids or channels are a frequent source of local overheating of tube walls.

HK 40 specifications

Thus, the specifications of replacement HK 40 tubing should be:

1. Thickness governed by a design stress which is 60% of the mean 100,000 hr. creep to rupture stress for HK 40 at the design temperature. (A.C.I. - Battelle data).

2. Design temperature (1,700°F) providing 100°F margin over normal tube surface temperature (1,600°F) with catalyst in good condition.

3. A.C.I. HK 40 chemistry with minor modifications:

Carbon	0.38% - 0.48%
Lead	0.005% maximum
Molybdenum	0.25% maximum
Tin	0.005% maximum

4. Tubes bored to sound metal, determined against 100% dye penetrant examination (no bleedingindications.

5. Bore diameter specified with tolerance of ± 0.010 in.

6. Pull boring required. Bore finish specified as better than 32 micro in.

7. Wall thickness minimum specified. O.D. left open.

8. No weld cut backs permitted.

9. Individual tube cast lengths to be chosen to require ½ tube lengths to make assembly. E.G. 3½ tubes for 31 ft. total length. This automatically subjects a proportion of tube center sections to full examination.

10. Butt weld bore protrusions machined flush and smooth to tube bores. A proving ball or slipper 1% less in diameter than the minimum bore diameter must pass freely (water flush or gravity) through the finished tube.

The specification will otherwise be standard in its requirements.

The premium indicated by bids received from proven and preputable suppliers is less than 10% of the price of standard, "as cast" tubing, designed to the usual 75% to 80% of 100,000 hr. creep to rupture stress criterion. I should mention that tubing supplied to the recommended specification will be fully inspectable and fully inspected. The intangible "know-how" aspects of supplying allegedly sound but uninspectable tubes would seem to be unimportant under these conditions.

Management expects the second set of tubing to do better than the original one, particularly after absorbing the immense cost and significant total "off line" time associated with complete furnace tubing change-out. It could be argued that the plant should be settled down to routine, steady state operation, and this would favor better tubing life. The state-of-the-art in the design, manufacture, and fabrication of tubing should have advanced, and should be helped by better catalyst performance and refined operating practices.

Bored tubing of HK 40 is believed to represent the best available practice for 450 psig reforming in ammonia plants in this context. An improvement in average life expectancy to the 6 to 8 yr. range seems likely, given careful use. A 10% premium maximum seems to offer good value for the added assurance and more conservative design stress used. It does not seem likely that a 100% premium or more for higher alloyed tubes can be justified. It would also seem that reforming at pressures much higher than 450 psig may require better alloys, and any process gains would have to be assessed against a substantial increment in reformer capital cost.