Catalyst Tubes In Primary Reformer Furnaces

All the evidence indicates that centrifugally cast HK-40 is the most reliable material for fabricating catalyst tubes for present ammonia reformers.

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THE REFORMER FURNACE STANDS OUT AS THE HEART of the present day ammonia plant. From the standpoint of on-stream reliability, the design of the packed catalyst tubes is critical, and from an economic standpoint, the coil material and fabrication represent more than half the cost of the reformer furnace radiant section. In view of this, and M. W. Kellogg's considerable experience in the ammonia industry, it is now appropriate to re-evaluate the results of our practices and improvements *(1)* in regard to the "state-of-the-art" of reformer tubes. Although the article is based on our experience with reforming service, the principles considered are also common to all other designs of reformer furnace tubes.

A typical reformer tube is shown in Figure 1. Characteristically, all are vertical, have top inlets and bottom outlets, and are packed throughout their heated length with catalyst. Support of the tube may be by fixed supports or springs acting at the top or bottom, or a combination of both. The total vertical expansion of the tube must be accommodated by adequate flexibility in the inlet and outlet piping. This is accomplished by providing expansion devices; i.e., pigtails or pipe loops, or by utilizing complete flexible systems supported by springs or counterweights.

Tube dimensions, which are based on process considerations and economics, normally range from 2.5 in. to 5 in. inside diameter with wall thicknesses up to 1 in. These dimensions are adequate for most temperature and pressure conditions. Limitations are imposed on the lower range of inside diameters by centrifugal casting techniques. Tubes are centrifugally cast austenitic materials since wrought materials do not have sufficient strength at temperature for present service conditions.

Mechanical design basis

Furnace tubes are pressure parts which are subjected to heat transfer through their walls. The design of a furnace tube must consider:

1. Allowable stress value for the specific material as a function of temperature

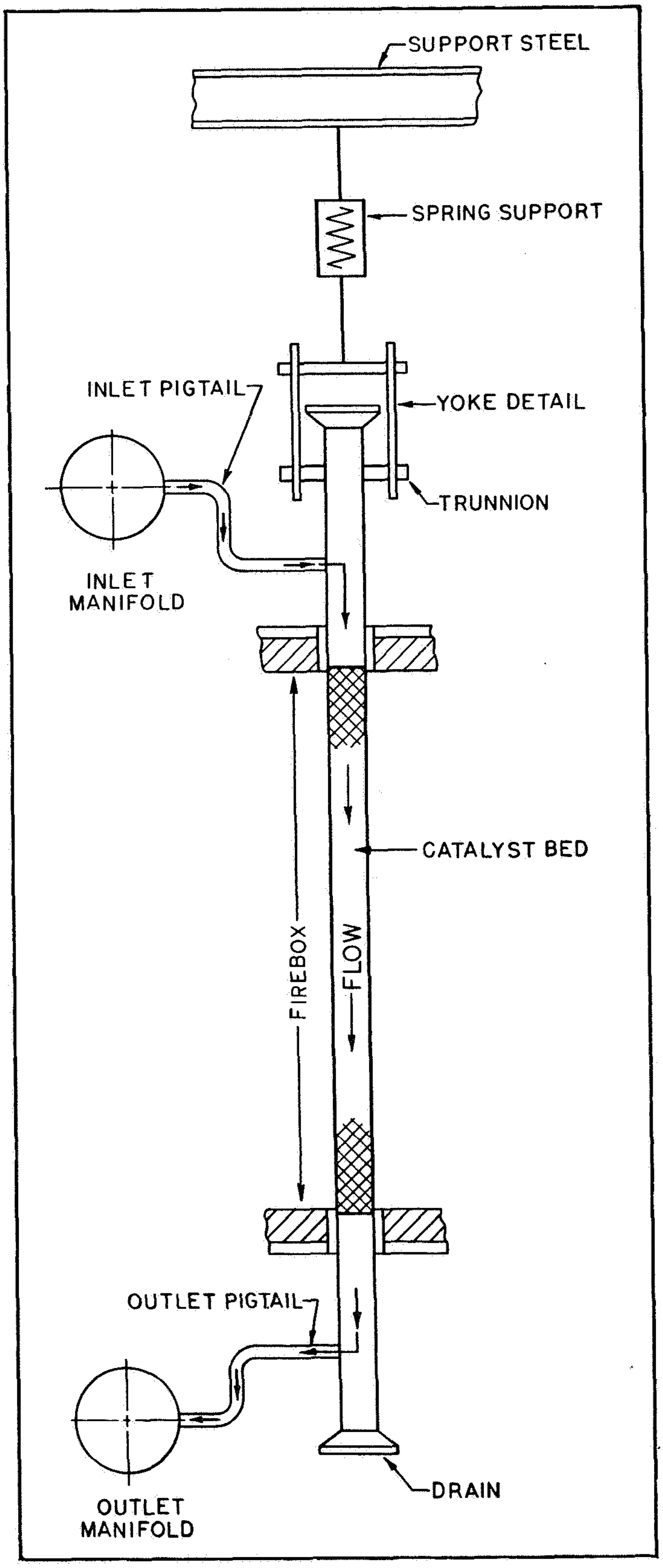

Figure 1. Schematic of typical reformer tube.

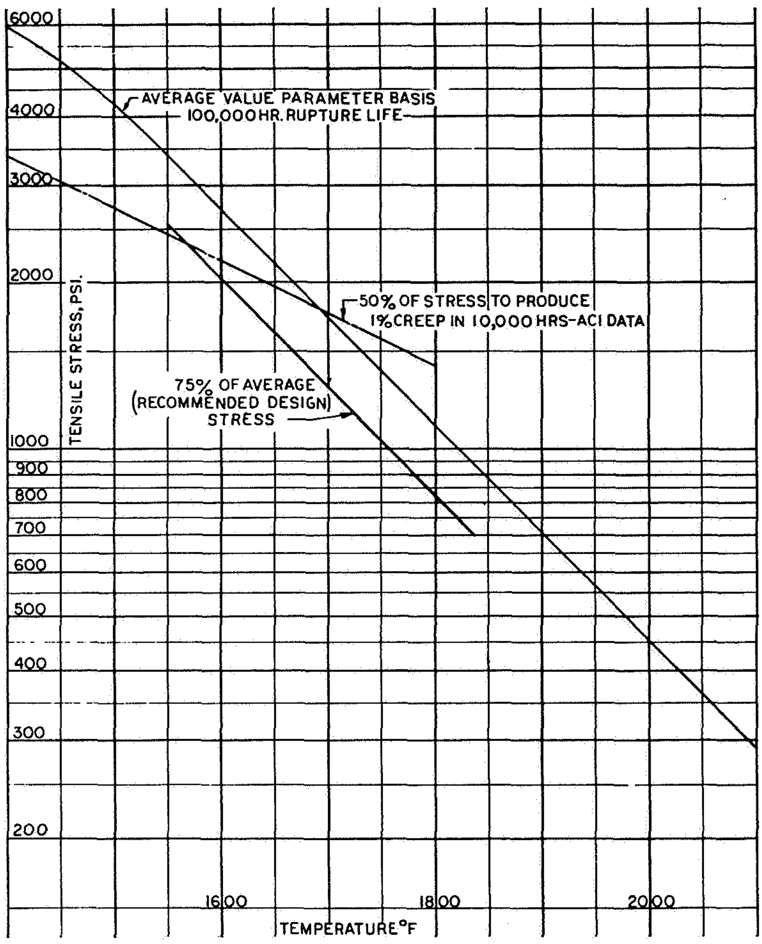

Figure 2. Allowable stresses for cast 25 Cr—20 Ni (HK-40).

2. Methods to calculate all expected stresses
3. Methods to calculate expected metal temperatures

For the design of packed catalyst tubes in reformer service, these considerations are interrelated and the adequacy of the final design is dependent on the validity of the methods for each of these calculations. The severity and nature of the service makes it imperative that conservative values be used to assure adequate and safe service.

The material selection, stress basis, stress, and temperature calculations have evolved through numerous phases to achieve their present status. A firm base of more than ten years experience with cast catalyst tubes now permits conclusions as to the validity of the methods and procedures presently being used.

The tube material selected as a generally accepted industry standard for current design temperatures is centrifugally cast 25% chromium—20% nickel (HK-40). Its selection is based on its superior resistance to both rupture and deterioration at the elevated temperatures commonly encountered in reformer service. HK-40 is specified as 0.35% to 0.45% carbon. This carbon content provides the optimum combination of strength and weldability. The same requirement is applicable to the weldments made to connect the as-cast tubes into longer tube assemblies.

Although HK-40 has the high carbon content required of a high strength material, it develops low ambient temperature ductility upon aging. However, service experience has shown that low ductility is tolerable in a system designed to minimize stresses at these critical conditions.

More highly alloyed iron-chromium-nickel base materials are sometimes used when warranted by the temperature and pressure conditions. Their aged ductility can be even less than that of HK-40. For heat absorbing tubes, addition of tube wall thickness does not proportionately increase resistance to pressure at temperature due to increase in temperature gradient across the wall. Therefore, stronger materials to withstand higher pressures are an industry requirement if reforming conditions continue in their normal upward trend.

Most of these stronger materials are proprietary alloys which have had limited reformer service experience. In many of these alloys being considered, ductility at temperatures below operating metal temperatures is low, and careful consideration of thermal and mechanical stresses is required. There are unknown or unpredictable factors such as, gas-metal reactions, phase changes, mechanical properties, and fabrication problems, which will be determined only after tests in operating furnaces. Manufacturers' data is helpful in preliminary screening, but the most reliable judgment of new materials is derived from actual service tests.

The majority of tubes in service today have been welded assemblies of standard as-cast tubes. Currently, there is some consideration of tubes which are machined or honed on the inside surface to remove all, or the bulk, of the inside as-cast porosity. The advantages expected with a smooth defect free inside tube surface are:

1. Freedom from mechanical notches and casting defects
2. Lesser chance of deterioration because of lesser

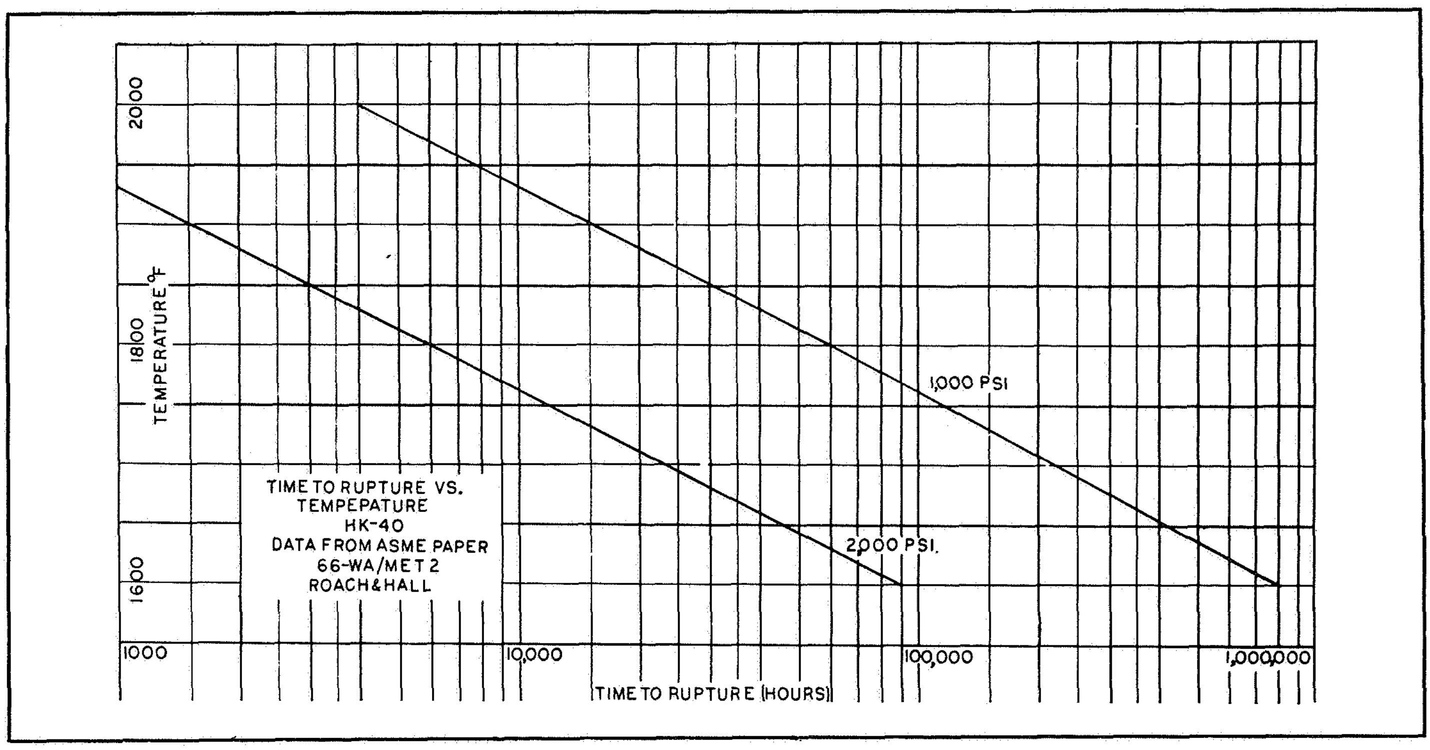

Figure 3. Time to rupture vs. temperature in HK-40 tubing.

surface area, and fewer theoretically stagnant areas

3. Control of dimensions, diameter and wall thickness

In reformer services none of these expected advantages are considered necessary for ensuring satisfactory service. Based on our experience with bored tubes, the additional expense of machined or bored tubes is not justified. Approximately 10% of the tube in service, and of the reported failures described below, have been internally machined tubes. To our knowledge, there have been no reported tube failures attributable to inside porosity or inside surface roughness. The rate of deterioration, although theoretically affected by surface area and roughness is much more dependent on temperature, gas ratios, and impurities. Roughness appears to be a factor only in marginal conditions. The expected advantages of machined or honed tubes should be balanced against an approximate additional cost of $12/ft. for honing or machining in the U.S.

Allowable design stresses

For HK tubes in reformer service the stress to produce rupture in a specified time period is now considered as a more accurate long time design stress criterion than a stress to produce a specified creep in a specified time period at these imposed temperatures. The generally accepted stress criterion appears to be 100% of the average stress to produce rupture in 100,000 hours. This criterion has been recommended and judged as a conservative method by some designers *(2)*. However, we feel 75% of this stress represents a conservative method.

M. W. Kellogg has established allowable stresses for cast 25 Cr-20 Ni (HK-40) based on Estruch's *(3)* published values for stress to produce rupture in 100,000 hours. The stresses used are taken at the minimum of the scatter band of Estruch's values, which is considered as 75% of the average values, Figure 2. This means that, based on present knowledge, it is expected that all tubes in a furnace will last a minimum of 100,000 hours in service if the design temperatures are maintained. This conservative approach is warranted in spite of the resulting increase in tube wall and substantial additional cost.

Under operating conditions the tube is subjected to pressure, weight, and thermal stresses. The wall thickness of the pressure part is based on the pressure stress acting in the circumferential direction, usually referred to as "hoop" stress. The pressure stress acting in the axial direction is approximately one half of the hoop stress. The designer can choose from the following methods to determine the pressure stress acting on the tube wall:

1. Bailey's Method
2. Lame's Method
3. Barlow's Formula
4. ASME Section I Method
5. ASA Method
6. API Method
7. Mean Diameter Formula

The Mean Diameter Formula has had experimental verification in that the calculated unaxial rupture data correlates with tube rupture life *(4)*. The formula reasonably estimates the rupture life of tubes over a wide range of material, tube size, thickness, and temperatures. For a typical reformer application, all of the above mentioned stress formulas will result in a calculated wall thickness within a ± 5% range. The Mean Diameter Formula, therefore, is judged as the most convenient and the best suited for present reformer tube design.

Weight stresses imposed on the coil are almost exclusively oriented in the axial direction. These stresses result either from axial loads or from bending moments acting perpendicular to the axis of the coil components. The weight stresses may be evaluated by conventional beam and column formula. The weight and pressure stresses, properly combined, must be less than the allowable design stress.

Thermal stresses are induced as the system temperature changes. Differential expansion of the sys-

Figure 4. Longitudinal rupture in a HK-40 tube.

tem elements occur due to temperature differences or different coefficients of expansions of the coil elements. The intent of the design is to recognize where these differences develop and make provisions to keep stresses to a minimum. Since thermal stresses are transitory, they are not combined with the weight and pressure stresses. In addition, radial thermal stresses are developed due to the temperature gradient through the wall and are a function of the thermal gradient, tube dimensions, and the tube physical and mechanical properties. Permissible thermal stress is governed by a combination of cold allowable stress, hot allowable stress, number of cycles anticipated, and an experience factor.

The ASA Piping Code formula for the permissible thermal stress is 1.25 times the cold allowable design stress plus 0.25 times the hot allowable design stress. These permissible thermal stresses refer to the stresses due to thermal effects only, and are independent of pressure and weight stresses. The ASA rules were formulated primarily for ductile material, therefore, their use in less ductile cast materials requires modification based upon experience and consideration of the operating conditions, combination of stress, location in the furnace, and susceptibility to upset or abnormal conditions.

Temperature determination

The most critical aspect of catalyst tube design is the determination of the design tube metal temperature. At design temperatures the allowable stresses are very sensitive to temperature changes. As an example, a 50°F increase at 1,600°F could decrease the allowable stress 20%.

The temperature profile of the catalyst tube is predicted by a mathematical model *(5)* which has been proven capable of describing the performance of reacting systems, and of exploring a wide range of potential operating conditions. It can take into account such factors as steam reforming reactions, reaction kinetics, heat transfer, concentrations, pressure, temperature, and burner patterns. For the design operating conditions and an assumed tube wall thickness, the model predicts inside and outside tube wall temperature at increments along the length of the tube. For use in the Mean Diameter Formula, the design temperature is considered the maximum arithmetic mean wall temperature plus an allowance for abnormal conditions.

Abnormal conditions, in which flow is restricted or uneven through the catalyst, or non-uniform catalyst activity results in localized overheating, must be considered. The tubes are able to withstand localized temperatures above design for short periods, but extended operation under over-temperature conditions will result in reduced service life. Precautions for the operation of furnaces with "hot spots" on the tubes are contained in operating instructions. The service life of the tubes is directly related to the activity and characteristics of the catalyst. Unfortunately, a discussion of this subject is beyond the scope of this article.

Cast tube fabrication

The critical points of tube fabrication are:

1. Control of tube tolerances
2. Removal of inner porosity at the weld
3. Tests and inspection to assure that specified mechanical properties and chemical composition are obtained
4. Procedures for the welding of the as-cast tube segments into long tube assemblies

While detailed specifications are essential, most of the compliance with the critical requirements in points 1 through 3 are based on the cast tube vendors proprietary know-how and experience. For this reason, the sources of cast tube are limited to a relatively few foundries who have adequately demonstrated their ability. Deviations from the specified quality have been detected in isolated cases after tubes have been accepted and put into service, but these deviations are rare, and in only two cases known to us has a foundry tube defect been the primary cause of failure.

The welding of the as-cast tube segments poses no particular problem providing the procedure is adequately defined and properly qualified. The accepted procedure normally used is the manual electric arc process with the inert gas arc process used for the root pass. Automatic welding has also been qualified for weld-out. Details of weld bevels should include removal of inner porosity which would interfere with welding. Final weldments should be free of notches and excessive ripples, and should have a controlled inner protrusion and exterior reinforcement. Attention to these points prevents the possibility of "notch effects" and possible "stress raisers". Examination of the interior surfaces of welds is by optical methods and liquid penetrant testing of the root pass. Finished welds are random radiographed. Initially, welds joining cast lengths were completely radiographed, however, results of this complete radiography, and service experience, indicate that complete radiography is not necessary. None of the tube failures described below were attributable to weld defects or weld quality. The inlet connections to the reformer tube are made outside of the firebox; and fabrication of the assembly in the unfired areas is done in accordance with normal piping practice. Cast tubes are preferably not extended outside of the furnace heated zone due to the low ductility of the material at ambient temperatures and the possibility of stress corrosion due to condensate accumulations.

Deterioration

In addition to the required strength at elevated temperatures, reformer tubes must have resistance to deterioration both from products of combustion (externally) and process gases (internally). Gas-metal and corrosion reactions considered as possible deterioration mechanisms at temperatures between ambient and 1,800°F are: carburization, decarburization, oxidation, sulfidation, salt attack, stress corrosion, nitriding, and intergranular attack.

These reactions will all be considered with reference to the standard HK-40 tube in steam-methane reformer service. Reactions of other alloys and other processes can be anticipated based on their particular components.

Although not listed as deterioration, the most significant change in properties of HK-40 is the lowering of ductility due to carbide precipitation which takes place as a result of exposure to furnace temperatures. As a measure of the change which takes place, tensile test elongation drops from over 10% in the as-cast condition to 1% or 2% after a short time in service.

The following conditions have been found in tube exposed to normal reforming conditions: carburization, decarburization, oxidation, and nitriding (of the outside surface). Under expected conditions of metal temperature, furnace firing, and gas composition, the rate at which these reactions occur in HK-40 tubes is such that there is no significant change in tube life or serviceability. Under upset conditions, high temperatures or contaminants in the process stream or fuel, the normally innocuous reaction rates may be accelerated to allow early failures of tubes.

Carburization is an increase of carbon content of the tube material by diffusion of carbon into the tube. The source of this contaminent can be solid carbon (from soot laydown) or carbon diffusing directly from the methane feed. Carburization can lower ductility, especially at room temperature, as well as lower oxidation and corrosion resistance.

Decarburization is the removal of carbon from the tube material by reaction with the steam and products of gas decomposition. For each set of conditions (temperature and gas ratios) through the length of the tube, there is an equilibrium carbon content at the tube surface. With sufficiently long time and without mechanical interference, the theoretical equilibrium surface carbon content will be reached by means of carburization or decarburization. Decarburization can result in a surface layer with lower carbon content compared to the matrix carbon content. Although the low carbon surface layer is theoretically weaker than the base material with normal carbon content, decarburized layers normally found in reformer tubes are only a few thousandths of an inch thick and have no measurable effects on tube strength.

Table 1. Known failures in cast 25 Cr - 20 Ni tube (HK-40) in high pressure reforming service.

Tube Life at Failure (months)	Number of Failures	Type of Failures	Cause
7	1	Creep-Rupture	Overheating
8	1	Fracture	Cast Defect
11	1	Creep-Rupture	Overheating
12	1	Creep-Rupture	Unknown
18	7	Creep-Rupture	Unknown
25	1	Creep-Rupture	Unknown
30	1	Creep-Rupture	Unknown
30	4	Corrosion	
39	2	Creep-Rupture	Overheating
40	3	Creep-Rupture	Overheating
44	2	Creep-Rupture	Overheating
Total	24		

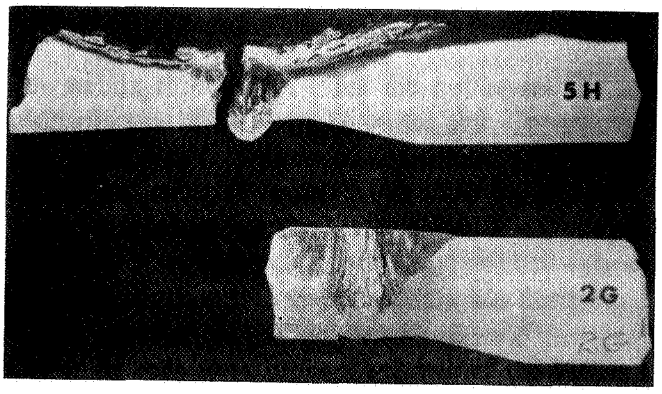

Figure 5. Salt attack at Inconel weld in Incoloy 800. (below: original condition, above: after attack)

Oxidation (or scaling) occurs when the oxidizing potential from CO_2 or H_2O (internally), or CO_2, H_2O, and O_2 (externally) is greater than that which produces decarburization. The normal protective oxide coating on tube surfaces, primarily chromium oxides, limits oxidation of underlying base metal. If the coating is broken, or if fresh metal surfaces are exposed, oxidation of chromium carbides at grain boundaries, and of iron rich matrix material, can take place. Depending on physical form and composition, oxides may or may not be protective. In some cases, intergranular oxidation is self limiting in that the oxides formed prevent further oxidation. In other cases, stresses and strains can fracture the oxide build up and thus allow further oxidation. It is this latter type of progressive intergranular attack which accompanies stress-rupture failures.

Nitriding is the formation of metal nitrides on external tube surfaces by reaction with the nitrogen in the furnace atmosphere. Nitrides at low temperatures are hard and brittle and are sometimes used for wear resistant surfaces on mechanical equipment. In reformer tube service, the nitriding reaction with HK-40 is slow and the presence of nitrides is usually an indication of overheating. No failures of reformer tubes due to nitriding are known.

Other elevated temperature reactions which, by comparison with the gas-metal reactions described above, are not expected and cannot be tolerated, are sulfidation, salt attack, and metallic contamination. These types of attack are similar in that the contaminant can react with or dissolve normally protective constituents of the tubes. The attack then proceeds either by allowing accelerated carburization and oxidation, or by a self renewing continuation of the corroding reaction where the corrosion product decomposes allowing a continuing penetration. These types of attack, depending on a foreign material, usually a solid agent, are normally spotty in occurrence, and by comparison with adjacent unaffected material, are sometimes referred to as "catastrophic".

Stress corrosion cracking by aqueous contaminants is theoretically possible and has been reported in wrought components and cast tubes where condensate collected. This has not been a problem where the design is such that condensate cannot collect.

Although there is an imposing list of mechanisms which can be described as deterioration of reformer tubes, they fall into two simple classifications:

1. Those which occur in normal operation and are not harmful—carburization, decarburization, oxidation, and nitriding (outside surface).
2. Those which occur only when contaminants are introduced—sulfidation, salt attack, liquid metal attack, stress corrosion.

Those in the first class can be serious if temperature or process is out of control, but in normal operation they are not a problem. Those in the second class are serious but can be prevented by maintaining the cleanliness of the furnace, equipment, and process streams. This cleanliness is vital during construction, start up, operation, shut down and especially during maintenance and turnaround operations.

There have been research results which indicate that variations in tube chemical analysis, grain structure, and surface conditions can affect carburization and oxidation. If process (temperature or gas composition) changes require greater carburization resistance, these controls can be applied.

Experience

The following shows our own experience with nearly 9,000 tube assemblies in 32 ammonia reformer furnaces operating over 450 lbs./sq. in. gauge pressure.

Years Service	Number of Tube Assemblies	Number of Reported Failures
0-1	1,922*	0
1-2	964*	0
2-3	4,454	12
3-4	1,416	12
4-5	210	0
	8,966	24

*Thicker tubes with 75% of average stress to rupture in 100,000 hours.

Of this total of 8,966 tubes, the failures are less than 0.3%, Table 1. Earlier experience with tubes operating at lower pressures and of other materials has not been included in the preceding summary. This experience has been adequately covered elsewhere *(6)*.

It has been estimated by one cast tube manufacturer that the failure rate has been ½ of 1% on a production of 45,000 tube assemblies over a 12 year period. Service experience should definitely improve with the refinement of operating techniques. The adoption of conservative stress values, previously mentioned, is another important factor in improving the experience record.

Known tube failures fall into several classes. Most of those reported are stress rupture failures associated with overheating. As experience and test data accumulate it has become possible to predict the behavior of HK-40 tubes. Knowing two of the three variables of stress, temperature, and time enables prediction of the third, Figure 3. Overheating is generalized due to catalyst deterioration or restricted gas flow. Failure initiates at grain boundaries and proceeds through the wall. As fresh metal surfaces are exposed, oxidation proceeds along the fracture path. As overheating continues, the primary fracture penetrates through the wall, while numerous parallel secondary grain boundary fissures are evident. Fracture surfaces are filled with magnetic oxides and there is very little evidence of ductility in the failure. In tubes, these failures are nearly always longitudinal in direction because the maximum primary stress is the pressure stress, Figure 4.

Failure of tubes due primarily to an unexpected gas-metal or corrosion mechanism are rare. Many of the conditions listed under *Deterioration* are accelerated by overheating and are frequently found in tubes which have failed by stress rupture. In most of these cases the deterioration is an interesting side phenomenon which has not contributed to the failure.

Notable exceptions were tube failures concluded to have been caused by carry over of sulfur containing compounds *(7)*. Similar attack has taken place in and on Incoloy 800 due to water treating salts, Figure 5. Elevated temperature accelerated the combined carburization, decarburization and, molten salt attack.

In summary

We have shown the design, fabrication and material selection considerations applied to centrifugally cast HK-40 reformer furnace tubes. Service experience has shown that they are reliable engineering components whose behavior is predictable. This successful experience, (less than 0.3% failures from all causes), verifies that a conservative design approach has been applied to minimize failures. Based on our analysis of the isolated failures, we conclude that properly utilized HK-40 centrifugally casting continues to be the most reliable choice for present ammonia reformer conditions. #

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