A LOOK AT HIGH TEMPERATURE REFORM PIPING

This view is from the standpoint of the engineer who has to coordinate design of a high temperature piping system or make one operate after a failure.

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Problems in reformer piping are not new: They have been with us since reforming began. They have been getting more attention lately, however, because they have been magnified by process and equipment changes.

In addition to these changes, recent emphasis on large, onetrain units places all the eggs in one high temperature basket. Thus a sensitive piping area, which some time ago would have had an alternate or partial alternate in parallel units, now has to be higher pressure, higher temperature in a larger size and without any alternate.

This situation came about as ammonia process efficiency went up, and so did plant size. Table 1 shows what happened to pressures and temperatures between 1956 and 1967. An explanation for this change in temperature due to process efficiency increase can be taken from a curve of secondary outlet temperature vs. pressure, steam to gas ratio, and primary heat duty, as given in Figure 1.

While pressure increased from about 8 to 30 atmos., steam to carbon ratios have dropped from 5 to 3. At constant steam to carbon of 5, a pressure rise of from 8 to 30 atm. means an increase in secondary outlet temperature of from 1,500 to 1,700°F for fixed methane content of 0.3%. The drop in steam/carbon ratio from 5 to 3 then requires a further rise in temperature from 1,700 to 1,800°F. All three changes—preheat, pressure and steam to carbon ratio—mean more stress on hot piping.

Table 1. How reforming pressures and temperatures have changed in the past 10 years.

Transfer line problems

The increase in pressure and decrease in steam/carbon ratio have changed the situation at the exit to the secondary reformer. Secondary exit problems generally are not as severe from a piping standpoint as that between the primary and secondary transfer line. This is because the distance is generally short from outlet of the secondary reformer catalyst to the inlet of the first cooling step.

This places the transfer line in a more difficult situation. It has to absorb expansion of itself and, in some cases, those of reform tubes too. This might be a matter of 1 in. or 6 in., depending upon the type and arrangement selected. It may also have abrupt size changes, and at some point change from an externally insulated pipe to a refractory lined duct.

The transfer line operates at temperatures where both carburization, decarburization and sigma phase are possible. In addition, temperature variations can cause thermal fatigue.

For purposes of design problem discussion, two typical arrangements will be discussed here. Arrangement 1, where the reformer tubes are fixed at top with growth down, except for differential expansion, is shown in Figure 2. Arrangement 2, reformer tubes fixed at the bottom with growth upward, is shown in Figure 3.

The first generally requires a moving bottom header and an unlined riser to the secondary inlet level. Expansion of the tubes is partially cancelled by the expansion of the riser to the secondary. However, the unlined header and riser must be designed to accommodate horizontal expansion and differential vertical expansion.

In large, high temperature piping even with sophisticated stress analysis, this is difficult to accomplish in such a complex system. If there are points of stress concentration, the system will be particularly subject to stress at those points during periods of upset operation. If there is any deterioration of the welds or main piping material, such high stresses may lead to failure.

A large modern reform furnace may have 400 catalyst tubes. They are connected at both ends. Each connection is a possible

Figure 2. Arrangement 1: Tubes are fixed at top with growth down except for differential expansion.

Figure 3. Arrangement 2: Tubes fixed at bottom with growth upward. :

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source of trouble. Designers of furnaces using Arrangement 1 have minimized this problem *at* the hot end by direct connection of tube ends to a cast or Incoloy alloy 800 header. Reformers of this type have been successful but subject to difficulty in some areas as follows:

- 1. Where arrangement was made to remove catalysts through connections which remain inside the furnace during operation.
- 2. Where inadequate flexibility was allowed to absorb stresses from piping and reform tube expansion.
- 3. Where materials selected had difficulties, due largely to carbide precipitation.

Use of direct connection with no provision for catalyst removal, except by vacuum from the top, has been quite successful.

Types of materials used in headers

Materials used in the header are both cast and wrought. Cast material has been used particularly, when the header was inside the furnace and subject to higher temperatures, similar to those in the catalyst tubes themselves. Materials used for unlined collecting headers and transfer piping are:

1. Centrifugally cast piping - HF, HK, HT & HU

2. Wrought Incoloy piping.

 $HF(21-9)$, as used in several installations, appears to be one of the better materials from a price and strength standpoint. It has been subject to some failures, due largely to carbide precipitation in and adjacent to welds and in static castings. Failures in HF occurred particularly at points of stress when units were going up or down. There are, however, installations where HF is

giving satisfactory service. Alloy balance is particularly important in HF: One analysis might be satisfactory and another not.

HK (25-20), has been used with considerable success. There have been some problems at welds, apparently due to carbide precipitation. Also the material is somewhat subject to failure from severe thermal shock. HK, although more expensive, appears better than HF particularly from a sigma and carbide precipitation standpoint. There are many installations where HK is performing well. Strength of this alloy and others varies considerably with carbon content.

HT (14-33), is currently specified by some manufacturers as the preferred material. The alloy has improved shock resistance; sigma is practically eliminated. Carbide precipitation and consequent cracking at cool down or start-up are also minimized.

HU (18-37), is similar to HT but of higher alloy content. It is particularly good for oxidation resistance.

Incoloy alloy 800 (20-32, wrought) is generally free from problems encountered with cast alloys, although there have been some problems with welding. However, it is not as strong and is more expensive. Selective use of Incoloy has been made by many manufacturers where more conservative design indicated use of Incoloy alloy 800. When pigtails are used at the bottom of the reformer tube, they are normally made of this alloy (Arrangement 2).

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__ Centrifugally cast fittings

Fittings are something of a problem with centrifugal piping since they have normally been made as static castings. It is difficult to make large static castings as sound as centrifugally cast pipe. Large section cooling may lead to imperfections in the fittings which then can lead to stress concentration and failure. Careful fabrication of statically cast fittings has resulted in many satisfactory jobs.

Fittings can be made up with sections of centrifugally cast pipe. Care must be exercised in this type of fitting to avoid imperfections in welds. Most recently, fittings joining centrifugal cast: ings have been made Centrifugally and machined inside and outside to assure soundness. Arrangement 2, shown in Figure 3, generally requires an unlined collecting header connected to a lined horizontal run and riser to the secondary inlet.

Pigtail connections from tube outlet to an unlined header are generally of solution annealed Incoloy alloy 800. Since they are small and subject to movement, centrifugally cast material is generally .not suitable for this service. The unlined header itself could be of any material mentioned above, provided proper care is taken to avoid stress concentration in piping and fittings.

Where flexible connections are made by small diameter tubing from tube ends to header, added operating flexibility is achieved in several areas. For example:

- 1. It is easier to provide for catalyst removal at tube bottom.
- 2. Since the tube ends are not directly connected to the header, tube bottoms do not have to move in a horizontal plane. The flexible connection takes care of this.
- 3. Tubes and piping can be relatively independent of each other from an expansion standpoint.

Problems with this type installation, perhaps more expensive than Arrangement 1, are due to the large number of welds, which can cause difficulty if not adequately made, and to increased heat loss. Space requirements are also higher with the independent suspension.

The connection between unlined and lined piping as used in Arrangement 2, and shown in Figure 4, has had its share of difficulties. One of the main problems again is stress concentration, particularly if welds are made at thé base or apex of a conical expansion section. Add to piping stress the temperature differential between ends of an expansion section (perhaps 1,100°F) and it is obvious that extreme care must be exercised in the design.

Figure 4. How connection between unlined and lined piping is made.

Successful uses of lined pipe

Continuing with arrangement 2: A lined pipe is used for the horizontal run and riser to the secondary reformer inlet. This type of line has been used for years in high temperature service. When pressure started to rise and internal temperatures rose as well, there was a tendency toward unlined cast and wrought piping. This has more recently been reversed as temperatures climbed even higher because of the current increase in reforming pressure.

Successful installations of lined pipe now consist of: Waterjacketed carbon steel, or plain carbon steel for the pressure containing part and, a refractory liner to insulate the carbon steel. Most installations also include vapor stops to keep hot gases from flowing between refractory and carbon steel, and finally an internal stainless steel sleeve to avoid erosion of or collapse of the refractory liner.

There have been many successful installations of this type. Perhaps the most foolproof is that with the water jacket. The complaint against the jacket is that a small failure cannot be detected except by a rise in water temperature. Then, it is difficult to locate.

No jacket is required if the refractory, sleeve liner, and vapor stops do their job. If they don't, the pressure containing carbon steel will overheat. As it overheats and expands, the steel shell expands away from refractory, the opening for hot gas passage increases, and so does the temperature of the pressure containing steel. Figure 5 shows the result. Temperatures of 1,200°F are not uncommon on carbon steel, pressure containing pipes where the lining has failed.

How sleeves can help

Wrought austenitic stainless steel sleeves have been used inside refractory to separate flowing gases from refractory. These liners have generally been successful. However, there is a tendency for thin sections of stainless to distort if held at high temperature for extended periods. This is particularly true if the section is under stress, either imposed during manufacture or from a service condition. In service, stresses can be minimized by designs which provide adequate clearances between ceramic and stainless and between stainless sleeve section.

Vapor stops, too, are subject to question. Without proper expansion allowance, they will crack refractory and provide ready access for hot gases to reach the carbon steel shell. Some installa-

Figure 5. Result of overheating is to cause the steel shell to expand away from the refractory.

tions have been made with neither vapor stops nor sleeve liners. These installations use two types of castable liner. One is an insulating type against the steel to keep it cool. The other is a hard, dense, castable refractory to resist erosion from the flowing gas stream.

Both layers of refractory are firmly fixed to the carbon steel with suitable anchors. There are, however, no vapor stops as such. Careful installation of material with experienced personnel has brought good results in this type of installation. Some installations have painted the outside of lined piping and equipment with temperature sensitive paint. Overheated areas are then apparent from the color of the section.

Cost considerations

Cost of various types of piping are worth discussing, if only to show that the best solution should be selected without worrying about the cost. Shutdown of a 600 or 1,000 ton/day ammonia plant is more expensive than considerable care in the transfer line.

Cost of a system to connect the primary and secondary reformer is impossible to decide without selecting a particular arrangement. Some relative estimating figures can be established for a given size of pipe on a per foot basis. Assuming 500 Ib./sq.in. and 1,500°F as design conditions, 12-in. O.D. cast piping installed might cost approximately:

Refractory lined piping might cost \$75 to \$125/ft., depending on the design used. If we assume that the total length of the transfer line is as much as 100 ft., it is obvious that the cost differential between one type of piping and another is not a major factor.

Unlined pipe will probably have additional length since additional expansion must be taken care of when it is used. One type or another will depend mainly on the arrangement used. For example: in this discussion, Arrangement 1 will probably use a transfer line with more unlined pipe and Arrangement 2 a transfer line with more lined pipe.

Comments above on header material also apply generally to the transfer line itself. Fitting and welds to fittings can be a major problem where the material selected is one of the centrifugally cast types. Operation in the 1,400-1,600°F range requires that the alloy hold carbon in the proper range, be essentially free from sigma, and resist thermal fatigue.

Figure 6. Where failure occurred in statically cast fitting welded to centrifugally cast pipe.

Examples of applications

Several hypothetical transfer line examples can illustrate the problems in operating modern high temperature reform units. To cite a few:

Case A. Failures occurred repeatedly at points where pipe thickness changed. The action taken was:

- 1. Thickness of pipe sections were made the same.
- 2. Welds were remade with a 0.35 to 0.40 carbon rod of type 309 or 310.
- 3. Stresses were decreased by:
	- A. Improved insulation.
	- B. Installation of windbreaks.
	- C. More uniform heating.
	- D. Reducing the number of rate changes and shutdowns.
	- E. Carefully introducing process gas into the reformer on startup, thus decreasing rapid change in temperature or uneven heating during loading of the furnaces.

Case B. A unit operating successfully had a shutdown due to a failure further downstream. On startup, a failure developed adjacent to the weld between a centrifugal casting and a statically cast elbow. On inspection, the statically cast fitting was found to have many small surface cracks, as shown in Figure 6. Other fittings were inspected and found to have similar cracks.

Attempts at repair of the major crack were made by grinding and welding. Grinding aggravated the problem by spreading the cracking.

A sample of the adjacent pipe was cut and polished in a plane perpendicular to the axis of the pipe. Touching the side of the outside diameter of the polished surface with a grinding wheel produced a crack some % in. into the apparently sound metal, as depicted in Figure 7. This example illustrates quite forcibly the brittle nature of the alloy after being in service for some time under conditions conducive to embrittlement.

Repair of this failure required replacement of the fitting and part of the adjacent piping. High temperature heat treatment of

Figure 7. Example showing how grinding produced crack in apparently sound metal.

the pipe and fitting before repair was attempted might have so'ved the problem and saved the fitting. Temperatures of about 2,200 °F would probably have been required to restore durability to the metal. Such heat treatment is difficult or impossible in an operating plant.

Case C. An inlet connection to the primary reform furnace failed. The failure affected nearby connections and before shutdown could be effected, two more connections failed. Process gas was shut out of the primary. The decrease in gas to the secondary had in the meantime caused temperature to soar in the burner above the catalyst.

When the process gas was removed, the high temperature gas from the secondary backed through some of the piping causing temperatures of approximately 1,700°F in wrought flexible piping. Welds connecting the piping failed increasing damage to the system.

Action taken to prevent future failures:

- 1. Flexible inlet connectors were replaced with more rugged equipment.
- 2. Secondary lining was repaired.
- 3. Secondary catalyst was largely replaced.
- 4. Secondary burner repairs were made.
- 5. Primary catalyst was inspected and topped where necessary.
- 6. Piping repairs were made.
- 7. Instrumentation was reviewed and revised so that future failures of this type would immediately cause shutoff of air to the unit.

Case D. An expansion piece connecting a refractory lined duct and an unlined pipe failed at the small end of the expansion piece. Repairs were attempted, but welds would not hold on the HK statically cast material which had been operating at 1,500°F on the hot end and approximately 400 °F on the cold end.

Repair was made by casting a higher nickel piece with rounded contours at both ends to ease stress concentration. The alloy change also decreased the possibility of brittle failure.

Case *E.* A refractory lined duct showed blisters at an elbow. Temperature stick indication of the bulged piece showed 1,200 °F before low pressure steam spargers were rigged.

The plant was operated for two months in this fashion until a convenient shutdown time arrived. Repairs were made by removing the bulged section, replacing insulation through the hole which was then rewelded.

Case *F.* A system using Arrangement 1 had been operating satisfactorily for some time. The weld connecting a centrifugally cast riser to an internally lined section failed.

Failure was attributed to improper support of the reform tubes themselves. Because of inadequate support, unusually high stress developed at the failed connection. Corrective action taken involved review of the tube support system to insure adequate, uniform support of the tubes.

Design discussion

From the aforegoing, certain conclusions or guides can be made relative to design and operation of high temperature pipe in reforming. Among these are:

1. *Unlined piping.*

A. Inlet piping requires: (1) Adequate flexibility, (2) overdesign to allow for deterioration of piping with time—depending upon the type of material used, (3) extreme caution with designs using flexible hoses, and (4) adequate inspection procedures to locate trouble spots before failure.

B. Connections to inlet and outlet reformer tubes require: (1) Welding procedures during fabrication and erection to be strictly controlled, (2) designs to limit sharp changes in thickness or direction, and (3) flexibility to minimize possible stress concentration.

C. Outlet piping requires: (1) Material least affected by carbide precipitation, sigma phase, and thermal fatigue, (2) operating procedures which minimize upsets and stress or shocks to the piping system, and (3) minimum field welds and proven procedures for welding.

2. *Lined piping requires:*

A. Low silica content: Generally, minimum silica in refracto-

ry and catalyst particularly after the air addition in the secondary reformer.

B. Low iron contents: Important because of the ability of iron to react with CO under high pressure reforming conditions.

C. Vapor stops: Installed to avoid stress in metal and pronounced cracks in refractory.

D. Sleeve liners: With adequate expansion room *and* material selected and designed so that it will not deform under operating conditions.

E. Connections: To minimize stress and allow for heat dissipation through material of adequate strength at operating conditions.

3. *Outlet piping:* Generally requires minimizing points of stress. Reform tube support and maintenance of uniform tube support during operation is particularly important in minimizing piping stress.

4. *Inlet piping:* Generally requires material which is low in carbon and ductile. Dead ends where alternate condensation and evaporation can occur should be avoided to keep solids from depositing which might contain caustic or chloride. Service life of 5 to 10 years may be expected with 304 L. Higher Ni alloy may also be used in this service.

Materia! characteristics and degradation

Material characteristics may best be shown with curves for rupture and creep strength versus time and temperature, as shown in Figure 8 (for creep) and Figure 9 (for rupture. Data on which these curves are based are given in Table 2. Note that figures for HF are low because carbon for these tests was kept low (0.2%). Certain "super-alloys" have been used for reformer tubes and transfer line piping on occasion.

Figure 8. Comparison of creep strength of various materials.

Figure 9. How various materials compare in resistance to rupture.

The mainstay for tubes, however, has been HK as centrifugally cast. Super alloys have not appeared economical because of the good service afforded by HK. Under certain conditions, they do appear to be economical. Our concern, however, is with piping.

Piping in all the areas discussed, if unlined, and the liners themselves, are subject to deterioration from various mechanisms. A short discussion of each is given here:

1. *Sigma phase -* A hard, brittle non-metallic compound of chromium and iron that may form in normally austenitic stainless steels between 1,000 °F and 1,650 °F.

Sigma phase is particularly brittle at low temperature. If an alloy is not properly balanced in composition, sigma may form in service. During periods of upset, or during shutdowns or startups, piping where sigma has formed to any extent are subject to failure.

Much has been written about sigma phase and manufacturers and designers are generally aware of problems due to its formation. Chemical elements that promote sigma formation are: chromium, silicon, and molybdenum. Elements that inhibit the formation of sigma are nickel, carbon, manganese, and nitrogen.

2. *Carbide precipitation -* To a certain extent, carbon precipitation in fine dispersion throughout the alloy is desirable. Carbon is added to alloys for strength and other reasons. Higher carbon content is a major reason for the high strength of castings. In some alloys, however, in the range of 1,000°F to 1,600°F, excess carbides chain together at austenite grain boundaries. The result is loss of ductility and eventually loss of strength and cracking.

Provided cracking and serious deterioration has not occurred, carbides may be dissolved by proper heat treatment. Similar effects to carbide precipitation may be observed from cracking of methane at grain boundaries to form carbon (carburization).

3. *Decarburization -* or loss of carbides, can take place from the action of hydrogen, CO 2, steam, or air to deplete carbon from

the metal and cause loss of strength and cracking by a loss of carbon from the alloy.

- 4. *Thermal fatigue -* Deterioration of alloys due to temperature cycles in which stresses from expansion or contraction and from differential expansion of various phases eventually leading to cracking. Embrittlement for any other reason may increase the seriousness of thermal fatigue.
- 5. *Hydrogen embrittlement -* High pressure hydrogen at temperatures above 400 °F permeates carbon steel, reacting with impurities to cause corrosion and embrittlement. It is normally not considered to be important in the high temperature alloys used. At lower temperature, alloys sometimes must be selected to avoid attack because of high hydrogen partial pressure.

One of the major problems with reformer piping is that many operating temperatures are in the range of 900°F to 1,600"F, exactly

the range where deteriorating effects discussed are most active. The effects generally are embrittling. Piping stresses and thermal shock or fatigue accent the effects. It is interesting to note that reformer tubes which are subject to many of these effects are seldom subject to brittle failures. Perhaps this is because of the position in which they are placed in furnaces, relatively free of stress concentration as opposed to piping.

A further point of interest is the difficulty in deciding which of the above effects is the culprit. Even the experts sometimes cannot pinpoint the cause. Preparation for one of these failures may be a prime consideration in ammonia plant safety and operating continuity.

Normal practice with original work is to use a type of weld which will result in a similar weld in strength and analysis to that of the materials being joined.

A weld is essentially a casting. Weld metal is subject to the various effects discussed above as well as to particular problems because of melting and solidifying as they occur during welding procedures.

Materials being joined are strong but, castings particularly, are not very ductile. Total creep of typical cast alloys before failure might be 0.5 to 25/c. Wrought alloys on the other hand will creep 50 to 100% before failure.

Obviously, then, care must be taken when welding cast material's. During the welding process, weld deposits and adjacent metal are melted, solidified and stretched as they cool. If either the weld or adjacent metal is stretched too much, it will fail. Some problems associated with welding are:

- 1. *Solidification cracking.* Weld metal solidifies from the outside toward the center of the weld. As solidification takes place, liquid metal must fill in the center to provide for contraction. Cracking will take place if there is not enough liquid to fill in the center voids or if the center metal, once solidified, is not strong enough to withstand stresses from contraction of the weld and surrounding metal. High temperature inputs, during welding, may lead to solidification cracking.
- 2. *Microcracking.* Remelting and solidification of isolated sections of piping during welding may lead to small cracks which are difficult to detect. Similar cracking may occur from loss

of ductility as previous weld runs are heated and cooled through the temperature range of 1,550 - 2,100°F. High silicon leads to this type of cracking due to isolation of silicate between metal crystals.

3. *Hot tearing.* As cast austenitic materials are welded, material between grains becomes liquid for some distance beyond the weld fusion. If thermal stress opens up these liquid regions, they must be filled with weld metal. If the solidification temperature of the weld metal is too high, it will not flow. The result is hot tearing or cracks in the metal adjacent to the welds.

All of the above may occur during original welding or during repair of failures. If metal has deteriorated during operation, chances of cracking during repair welding will be accentuated.

Precautions in weld repairs

Examination of metal adjacent to proposed repair may disclose possibility of failure. Grinding and chipping of surface hairline cracks in metal that has been in service, however, may extend the area of failure and render a repairable section useless. Thus, it is important to decide the seriousness of cracks and whether surface repair or chipping followed by penetration welding are required.

Where a section is questionable, it may be possible to remove it and heat-treat at approximately 2,200°F to restore ductility before welding is attempted.

Examination of high temperature piping at periods of shutdown may indicate areas of possible difficulty. Establishing regular examination procedure will allow repairs to be made before failures occur.

Repairs to HF and HK have been made with 0.35 to 0.4 carbon 309 or 310 rod. Incoweld A rod has also been used. In some cases, where material adjacent to failed welds had obviously deteriorated, new sections have been added so that welds can be made between pieces of good metal.

For welding of dissimilar materials, the following have been used:

Stainless steel to carbon steel: Stainless steel rod similar to the stainless steel section or higher

nickel rods. Inconel 82 Rod similar to the higher type alloy generally used; Incoweld A also used. Incoloy to stainless steel: Stainless steel to stainless:

Precautionary steps needed

Preventative maintenance and preparation for possible fail-

ure requires:

- 1. Analysis of entire piping systems and selection of points of possible failure.
- 2. Establishing procedures of repair for those points where failures are possible.
- 3. Maintenance of procedures to find and repair possible points of failure without destructive testing.
- 4. Maintaining adequate spares to repair piping after a failure.

This examination and discussion has shown many problems and areas of uncertainty with high temperature reform piping. Problems and uncertainties are exactly what engineers were made to solve. It should be remembered, however, that not much, has been heard from the successful piping installations. Designers and contractors have presented operators with various systems which can be safely operated if care is taken. Additional expense during initial design and during operation will provide safety and continuity of operation.

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