BRITTLE FRACTURE OF CENTRIFUGALLY CAST STAINLESS STEELS

Because of what is now known about causes of stress-corrosion cracking in reformer tubes and brittle fracture in gas collecting manifolds, safety hazards in future naphtha reforming plants will be greatly reduced.

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Premature failure of the materials of construction represent one of the most serious safety hazards in an ammonia plant today. This is particularly true when they occur without warning, as is the case with a brittle type of failure. It is of fundamental importance that a thorough knowledge of possible brittle failure mechanisms are understood, and that the design of plant and the selection of materials is backed with sufficient experience to minimize the possibility of such failures.

Power-Gas Corp. utilizes the I.C.I. catalytic steam naphtha reforming process for the production of ammonia synthesis gas and has extensive experience with the process in ammonia and town's gas plant manufacture. During development of the process two metallurgical problems, happily now overcome, presented serious difficulties in the way of reliable and safe plant performance. One of these has been stress-corrosion cracking of centrifugally cast A351 HK alloy reformer tubes. The other has been brittle fracture of the A351 HU alloy commonly used for reformer gas collecting manifolds in Britain.

The primary reforming furnace is heated by down-firing burners and contains vertical reforming tubes packed with catalyst. The tubes are 25 to 40 ft. long, have a 4 to 5 in. bore, and ½ to 1 in. wall thickness. They are centrifugally cast in 25% Cr/20% Ni, alloy HK.

Stress-corrosion cracking experiences

The reforming tubes operate at pressures up to 450 lb./sq.in. gauge and at temperatures between 700 ° and 900 °C. In the earlier plants it was the rule to position the gas offtake on the side of the tubes at hearth level, and to extend the tube base some 2 to 3 ft. below the furnace. This assures that the bottom extremity was sufficiently cool to fit a flange, making catalyst extraction by gravity a simple operation.

Figure 1 shows the main components of the old type tube base. These include a carbon steel flange, an internal insulation canister, catalyst support column, and external lagging. Such a design resulted in a hand warm temperature at the flange and a steep temperature gradient up to the gas outlet position. Condensate collected in the tube base, and the liquid/gas interface occurred at the height of the tube where the tube wall temperature corresponded to the dew point. In a 400 lb./sq. in. gauge plant this was usually about 180 °C, corresponding to the height of about 16 in. above the base flange.

The first indication of trouble with this design arose in a town's gas plant, but it was equally applicable to ammonia plants where the same design of tube base was used in the primary reformer. Six months after startup of the plant it was noticed, by an extremely observant operator, that six of the tubes in a furnace load of 38 were exhibiting tiny beads of moisture on the external surface of the dead leg section. By making observations over a few

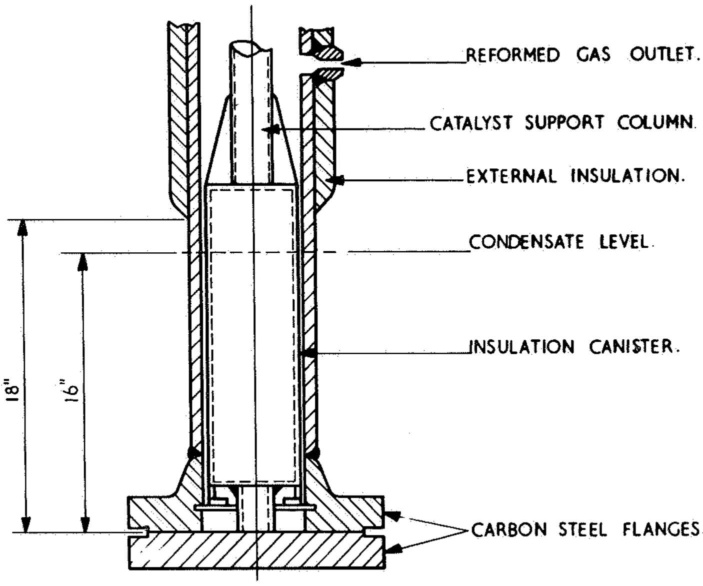

Figure 1. Principal components of reformer tube "dead leg" section.

days it became apparent that more tubes were developing moisture droplets, and that the moisture was forming at the same level above the tube base on all the tubes.

The plant was shut down and the subsequent investigation revealed that cracking had propogated through the tube wall of half the tubes in the furnace, and that the remainder were all severely cracked. The cracks had occurred circumferentially, initiating on the tube bore at the wind and water line where it was evident from the water marks that soluble salts had concentrated over a band about 2 in. wide. Fluctuations in operating temperature and pressure had caused the position of the dew point to rise and fall.

Figure 2, at a magnification of X120, shows the very fine type of cracking which occurred. The transgranular nature of the cracks is very similar to stress-corrosion cracking in wrought stainless steels. Perhaps the only difference of note between the cracks is that the branching characteristics in the cast steel are not quite as marked as in a wrought stainless steel. This is perhaps a reflection of the coarser grain size of the cast material.

The classical conditions for stress-corrosion to occur in stainless steels are: A stress concentration, a temperature in excess of about 80 ° C, and the presence of a chloride containing electrolyte or a strong alkali. In the case in point, the stress concentration was provided by a very steep local, thermal gradient across the wind and water line, a temperature of about 180 ° C and a chloride concentration of 0.3% in the water line deposit. The

Figure 2. Stress-corrosion cracks in A351 HK alloy.

chloride had gradually accumulated during the previous six months operation from small quantities carried over in the process steam and from the catalyst.

It was shortly after this experience that stress-corrosion cracking was confirmed on another plant. This time it was associated with tube support pads, which had been fillet welded on to the external surface of the dead legs to support the tube from the base. Cracking was confined to the tube directly beneath the fillet weld, and was clearly associated with the highly stressed weld region. In this instance also, a high chloride concentration was apparent on the tube bore where the cracks had initiated.

Applying proper remedies

To remedy the situation in the shortest possible time there appeared to be two alternatives. One was to replace the dead leg sections with a material not subject to stress-corrosion cracking in chloride environments. The other was to remove the dead leg altogether and make the tube outlet the bottom extremity of the tube so that the presence of condensate was eliminated, thereby stopping stress-corrosion.

The first alternative was chosen, largely because it retained the base flange which still allowed the principle of catalyst extraction by gravity to be applied. The second alternative would have required catalyst extraction from the top of the tube by a suction technique, because flanges could not be designed to operate continuously with safety at the maximum gas temperature of 900 °C.

The tube base in these circumstances had to be permanently sealed by a welded on tube base closure.

The 1% Cr ½% Mo ferritic steel was chosen as the dead leg material to resist stress-corrosion cracking. The weld between the dead leg and the HK alloy tube was positioned carefully in relation to the external lagging. This was to ensure that the weld operated with a safety factor of 100 ° C above dew point but below a nominal 450 ° C. Thus on one hand there was no possibility of condensate coinciding with the austenitic steel and on the other hand the ferritic steel was not being extended to the limits of its high temperature properties.

When tubes with ferritic dead legs were put into service the weld temperatures were monitored continuously, to ensure the specified temperature range was being achieved and maintained. It came as a great surprise therefore, when it was found that cracking had again occurred in the HK alloy section of tubes above the ferritic dead leg. The cracking occurred in both the austenitic tube material and the austenitic weld. The ferritic tube was neither corroded nor cracked, Figure 3.

There was no doubt from the temperature records of the monitored welds that they had been permanently above dew point during operation. This fact was confirmed by spot radiographic checks of the condensate level taken while the plant was working, which showed the condensate to be 2 to 4 in. below the weld. The

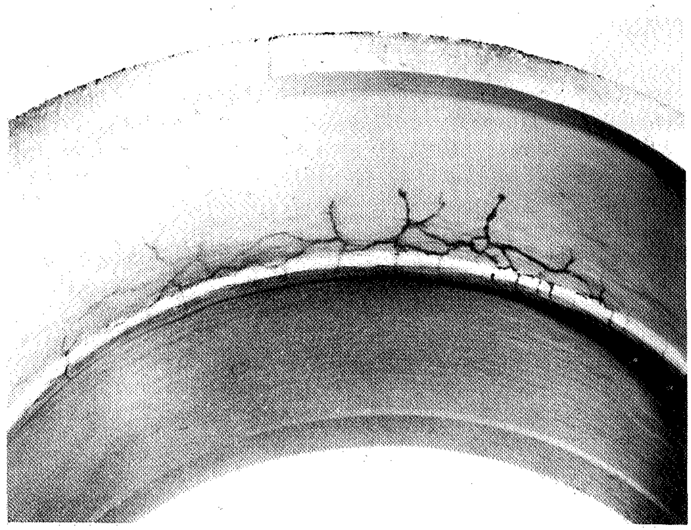

Figure 3. Stress-corrosion cracks at ferritic dead leg in a dissimilar metal weld.

cracking was again of the branching type, transgranular, and in appearance identical to the cracks in Figure 2. They were again identified as stress-corrosion cracks, which by definition require the presence of an aggressive electrolyte to form.

It was known that the primary reforming catalyst contained potassium combined in the form of alumino-silicates and that in certain circumstances this could be hydrolized to release potash. It was postulated, therefore, that the potash thus released could be transported in the gas stream and deposited on parts of the plant which were cool enough for the potash to condense upon. Such a part was the dead leg section.

Results of lab tests

Laboratory experiments simulating conditions in the dead leg had by this time shown that concentrated potassium hydroxide could condense on the tube bore at temperatures up to about 400 °C. The position of the cracking, above the weld, was in fact at a temperature of about 400 °C. This, coupled with the large stresses associated with the weld, indicated that cracking had been caused by caustic potash which had accumulated on the tube bore.

At the time of the failure, no laboratory test results were available to substantiate that HK alloy would crack in potash at 400 °C. But recently this evidence has been obtained and it is confirmed that KOH will cause HK alloy to stress-corrosion crack.

The next stage in our design was to dispense with the dead leg arrangement altogether, and adopt a hot base by sealing the base of the tube at gas outlet level with an HK alloy closure casting. This ensures tube base metal temperatures are the same as the outlet gas temperature. Thus caustic potash can not condense and the possibility of stress-corrosion cracking is removed. The change in design has meant changing to tube top catalyst extraction, but this is a very small price to pay for the assurance that stress-corrosion will not occur again at the tube bases.

Brittle failure of gas collecting manifolds

Reformed gas collecting manifolds are subject to expansion and contraction stresses whose occurrence cannot be completely eliminated by design. The choice of materials for manifolds is not numerous since their duty requires manifolds to operate continuously at 700—800 °C and 450 lb./sq.in. gauge in reformed gas atmospheres. There is a sufficiently wide selection of materials, however, to enable the choice to be made between strong but usually brittle alloys, whose yield strength exceeds the calculated expansion and contraction stresses, and a relatively weak but ductile type of alloy which will yield without fracture when the yield point is exceeded.

On early plants my own company favored the thought that if the manifold material were to be made from a strong, but brittle alloy the expansion and contraction stresses could be designed below the alloy's yield point so that it could not fail. Consequently the A351 HU cast alloy was selected. This alloy has a nominal composition of 0.4%C, 18% Cr and 37% Ni. It is fully austenitic, with an "as cast" structure of austenite grains supersaturated with carbon surrounded by a carbide and austenite eutectic. In this condition the material is ductile, having a room temperature tensile elongation of over 15%.

When the alloy is aged at temperatures above about 450 °C, however, the carbon of supersaturation in the austenite is precipitated throughout the matrix, at first as very fine carbide particles, which grow in size as aging proceeds. The effect of aging on low and intermediate temperature ductility is quite dramatic. The 15% elongation of the as cast alloy falls to less than 4%. In practical terms this means that at temperatures below about 600wC the aged alloy will fracture in a brittle manner when the applied stress exceeds the yield point.

Precautions taken to minimize stress rasiers when designing a manifold in HU alloy included:

1. Fully machining the cast tube inside and outside to remove surface roughness.
2. Ensuring no sudden changes of section: Transition sections were made gradually tapering.
3. Minimizing the number of external welded-on attachments.
4. Ensuring that the manifold was not flexed but instead allowed to expand freely along its axis.

Despite these precautions, brittle failures of manifolds in town s gas reforming plants have occurred. In all of these cases the cause was a sudden plant upset involving a rapid change in make gas temperature, resulting in rapid chilling of the manifold and in brittle failure.

Figure 4 shows the fractured ends of a manifold tube which had been subjected to such a drastic thermal quench. It is clear that the fractured surfaces are brittle and there is no evidence at all of plastic deformation in the fracture region. The material has obviously been completely unable to relax the sudden high stress buildup by yielding.

It is only fair to say that there are a large number of manifolds in HU alloy which have not failed. But because the alloy has proved so sensitive to upsets involving sudden temperature changes, it is now my company's practice to utilize the considerably tougher wrought 20% Cr/35% Ni, alloy 800 for manifold construction. This is done despite the fact it is weaker and considerably more expensive than the cast HU alloy.

Figure 4. Brittle failure of A351 HU alloy manifold.

Alloy 800 owes its improved ductility to a lower carbon content (0.10% maximum) and also, to a lesser extent, to its finer grain size. It is an alloy which does not significantly age at service temperatures, so that its high ductility is retained over the full working temperature range from ambient to 850 °C. Since it has been used there have been no cases of failure. It is confidently expected that should an alloy 800 manifold be subject to thermal shock treatment that it would deform rather than crack. In this respect the safety of personnel and plant is upheld.

The two types of brittle failure which have been described have both been very costly experiences and either one could have resulted in serious plant accidents. The important outcome has been that lessons have been learned and included in current design practice so that on future plants safety hazards are reduced by a large factor.

Discussion

Q. Was this location totally insulated and did no temperature gradient exist during steady state operation?

HARNBY: You are referring to the manifold. The manifold was surrounded by an insulated box arrangement. The manifold itself was not lagged. During steady state conditions the entire manifold within the box was maintained at constant temperature.

AL SACKER. Collier Carbon & Chemical: If you had a choice in transfer lines between a line that was refractory lines vs a refractory pipe containing a shroud, which would be preferable. I've heard a number of stories of failures in shrouded lines. As a company we have only experience at the moment with unshrouded lines. I would like to get some comments on this. Going along with this, what is the advisability of inserting an inspection opening, one or several, so that you can crawl into these lines for inspection and repair purposes?

Q. Are you talking about water-jacketed or non-water-jacketed lines?

SACKER: No, I'm restricting my question to those lines either refractory-lined or with a shroud.

F.W.S. JONES, Canadian Industries Ltd.: We have a line transfer system with shrouds. We've had occasion to look and are relatively satisfied with the line in the condition we know it to be. This is in a 1,000 ton plant in Canada. Our opinion is that the shrouded lining seems to be a satisfactory device to us at the moment.

G.P. ESCHENBRENNER, M.W. Kellogg Co.: You have to look at two things. One is the basic design and the other is the quality of fabrication and installation. Based on my experience I think that either one is acceptable as design. Either design can fail because of poor maintenance or fabrication. The major emphasis should not be on which design is preferred but on how to control fabrication and assure compliance with design and specifications. There are a number of methods available to do this.

W.D. CLARK, Imperial Chemical Industries, Ltd. We have two secondary reformers where the gas comes in from a side branch and instead of having the air inlet through the top of the reformer it comes in through a simple plain nozzle into the side branch. The side branch is refractory-lined and it receives the entire flame from the burning of the air and that part does not have an internal shroud. We did not know what shroud would stand the local temperatures. We did, however, put a shroud in just around the corner between branch and main shell because we weren't quite sure what would happen to the refractory where there is a sharp jutting corner. But from the experience there it does appear that a refractory without an internal shroud can be entirely satisfactory. At the present time we have some new plants with shrouds in the transfer lines and after a month or two running have looked inside and found the shroud in satisfactory condition.

Q. Mr. Harnby of Power Gas reported a failure due to alkaline cracking of austentic stainless steel. I've heard of cases where alkalinity has come over with boiler feed water in the top and has caused plugging. I've not heard of it before down at the bottom. Was this an isolated case, or is this particular to the Power Gas situation?

HARNBY: The tube base cracking has, in fact occurred on five gas plants. We believe the caustic potash which caused the cracking was transferred from the reforming catalyst, which contains potassium combined as alumino-silicates.

During operation steam in the process gas hydrolyzes these salts and the potash thus released is transported to cooler parts of the plant such as the reformer tube dead legs where it can condense.

Q. Do you think there is any difference between town gas and ammonia synthesis gas production which might have made a difference?

HARNBY: No I don't. The tube design and the catalyst in the primary reforming furnace of both town gas and ammonia plants are exactly the same. We have had failures on ammonia plants for exactly the reasons described.

Q. We had trouble joining cast HK material to wrought 800 materials. One of the problems here is what type of rod you use?

ANON: Avery and Valentine pointed out it had a lot to do with design. They showed if you used a stub-in connection you had much greater problems. It's a case of where the thermal fatigue will occur and trying to keep the weld away from there. As far as welding electrodes go, I don't think it makes much difference. The data I have seen show that most of these electrodes have very low elongation. The only saving grace in using wrought material is that the material around it has a large elongation. It's mainly a case of putting the weld away from a highly stressed area.

Q. In building a new plant you try to assure that you won't have trouble with high alloy welds. If you insist on X-raying all of the welds, how much assurance do you have that you won't have future problems if the X-rays show no cracks in the welds?

ANON: Basically you should get a good supplier for your materials. You can X-ray all you want. You're fully dependent on the supplier of the reformer tubes or reformer transfer lines.

Q. Going back to the Harnby paper, I gathered that it turned out that after you had failures it turned out the design was at fault. Is this so?

HARNBY: In the case of the reformer tube failures by stress-corrosion, the original design of tube bases was at fault.

The manifold failures were due to a combination of high induced stresses due to sudden temperature changes and the extreme brittleness of aged HU alloy.

Q. There was quite a bit of discussion on cast and Incoloy 800 manifolds. There seems to a certain amount of good and otherwise in both types of manifolds. Am I correct in assuming that most of the people in the field would like some happy medium between the two? Something that would combine the good features of the cast material with the good ductility of the wrought material?

HARNBY: This is quite so but at the present time the possible materials are either very strong and very brittle or relatively weak and ductile.