Catalyst Tube Performance

Control of tube metal temperatures and cycling remain key operating variables affecting high pressure reformer tube life, but obstacles to achieving these controls are not easily overcome.

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A 1971 survey *(1)* on HK-40 tube failures in high pressure primary reformer showed that reformer tube life was most disappointing when operating pressures exceed 400 lb./sq. in. gauge. Such reformer pressures are economical only in large, single-train ammonia plants employing centrifugal compressors *(2)*. Minimizing the costs and lost production associated with retubing high pressure reformers is still a challenge to all concerned. This article will show how this challenge is being met, and hopefully, will encourage the efforts of others in all phases of the subject.

A number of technical groups have an active interest in this problem of reformer tube life *(3, 4)*, and many private investigations are currently underway. Although consistent with another recent survey *(5)* conclusions of the 1971 survey should be modified slightly in light of new advances. Perhaps most significant of all are the changes in design, materials, manufacture, operation, and inspection.

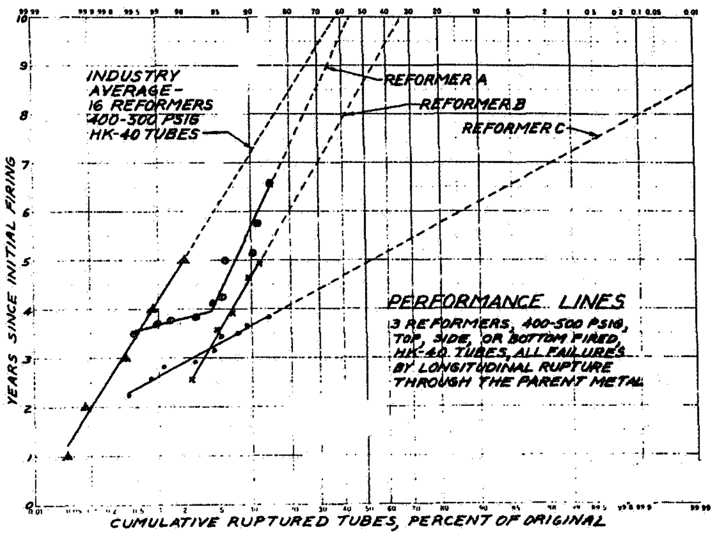

Figure 1. Reformer tube performance

Predicting Performance

Under reasonably consistent operating conditions, reformer tube failure rates follow a bell-shaped, normal probability curve, which plots as a practically straight line on arithmetic-probability coordinates. Figure 1 shows two examples of this; namely reformers B and C. Although both are high pressure reformers with HK-40 tubes, their tube performance lines are not parallel. The lower, flatter line denotes poorer performance in reformer C, which was completely retubed in less than 4 yr.

A significant change in operating conditions can drastically alter the slope of a tube performance line. In Figure 1, high pressure reformer A represents a case of operating over 3-1/2 yr. without changing catalyst in many of its HK-40 tubes. The increased temperatures that must have resulted during the latter part of this period produced a very poor tube performance line, which was abruptly improved with the first massive catalyst change and subsequent conservative operation. Based on typical stress-rupture data, average tube metal temperature must have been reduced by about 30°F between the two periods.

When interpreting Figure 1, the following points should be recognized:

1. Reformers A, B, and C represent three different commercial reformer designs. Their tube performance lines are all poor, relative to the industry average for high-pressure reformers with HK-40 tubes. No designer has a monopoly on inferior performing high pressure reformer tubes.

2. Half of the high pressure reformers with HK-40 tubes are superior to the corresponding industry average, but have not had enough failures to establish any tube performance lines. Most of them have suffered one or more tube failures in less than 6 yr., which may suggest an upper limit for the scatter band of high pressure reformer tube performance lines.

3. Although tube wall thicknesses in reformers A, B, and C were all above average, several similar reformers are approaching 4 yr. of age without any tube failures. This question of wall thickness will be considered later in this article.

4. Even though a tube performance line is straight, the percentage of the original tubes that fail in a given period varies according to the probability scale, and can reach intolerable levels in a hurry.

5. If many tubes are removed before they fail, the percentage of them that would have failed, had they been

left in service, should be considered when plotting a performance line. Replacement tube failures should be plotted separately.

6. The same approach can be used for other reformers, but the results will probably vary with pressure and tube material.

Optimizing Design

Material abnormalities, manufacturing deficiencies, and maloperation are not peculiar to high pressure reformers. Why then is average tube performance inferior in such reformers? By the process of elimination, design may be the overriding factor. Much effort is being devoted to it.

The usual design assumption is that tube life in the creep range is essentially governed by pressure stresses in the hoop direction. For low pressure, this has been found acceptable, but, for high pressures, it is questionable on two counts:

1. For high pressures, it requires a thick tube wall to meet the pressure stress limit, but it neglects the residual and thermal stresses which increase with wall thickness. These neglected stresses are normally tensile in the inner half of the wall thickness.
2. For high pressures, combined triaxial pressure stresses in the inner half of the wall thickness are significantly higher than pressure stresses in the hoop direction.

On both counts, the inner half of the wall thickness is critical. Creep rupture usually initiates beneath the surface in the same region *(6)*, as shown in Figure 2.

How do the neglected factors contribute to subsurface fissuring? Obviously, the stress and temperature profiles through the wall thickness must interact in a way that produces the most severe stress/temperature condition at the fissure origin. The idealized stress profile diagrams in Figure 3 roughly characterize the mechanisms involved.

Consider both a thick wall tube and a thin wall tube with the same inside metal temperature and heat flux. In

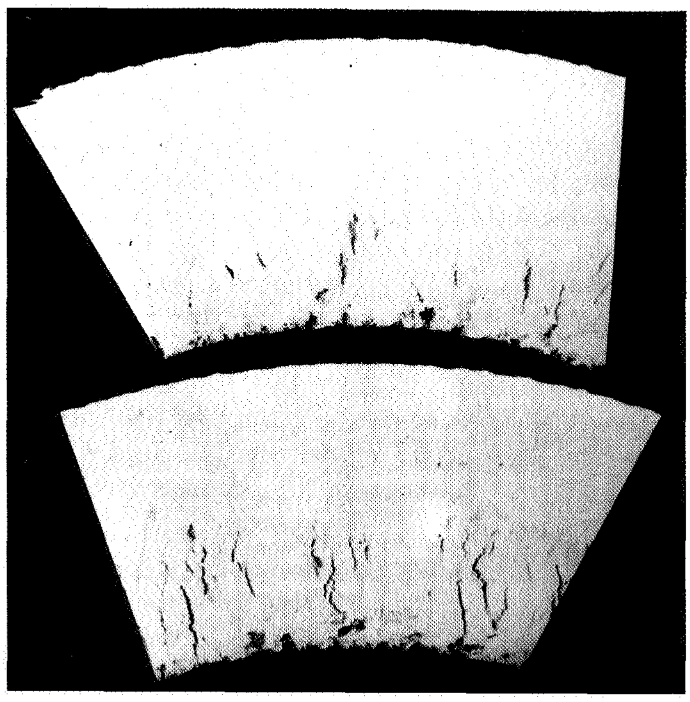

Figure 2. Subsurface fissures of HK-40 parent metal.

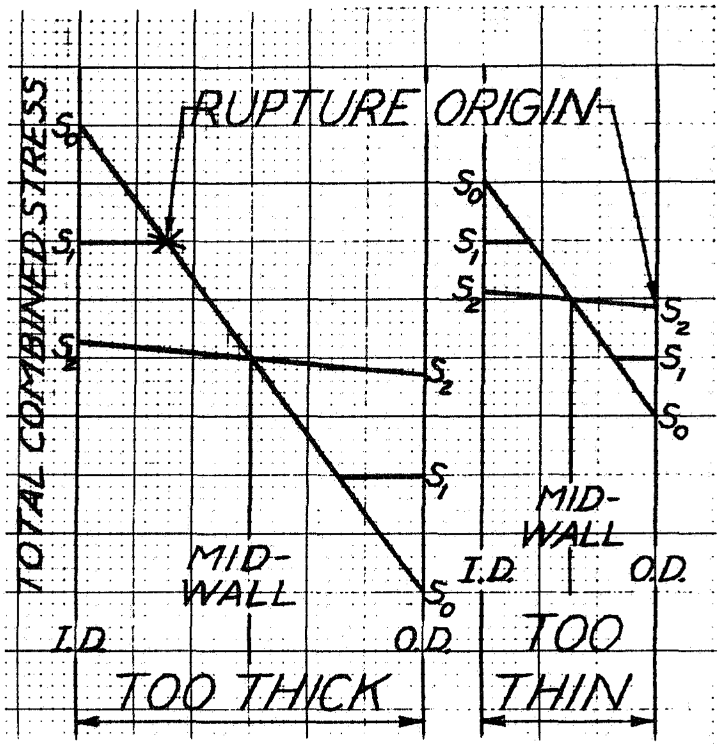

Figure 3. Idealized stresses.

each case, the initial combined stress profile S_0 - S_0 starts out with high tension at the inside and high compression at the outside. Inside and outside surface stress relax rapidly, governed primarily by the cooler metal temperature at the inside surface. Since these temperatures are the same for both tubes, the intermediate stress profiles S_1 - S_1 are each reached at about the same time. During this time, the stresses near the middle of the wall thickness have not yet begun to relax. Metal temperatures in this region are higher in the thick wall tube than in the thin wall tube. Stress rupture may therefore initiate at subsurface point X in the thick wall tube, and not at the corresponding point in the thin wall tube, even though both points were at the same stress S_1 for the same time. In such a case, the thick wall tube was too thick because fissuring started before residual and thermal stresses had fully relaxed.

Conversely, fissuring may not start in the thin wall tube until after residual and thermal stresses have fully relaxed and only the pressure stress profile S_2 - S_2 remains. In such a case, the thin wall tube is too thin. A thicker tube would lower the pressure stress profile S_2 - S_2, thus permitting more stress relaxation and longer life. Theoretically, a tube that is much too thin would first fissure at the hotter outside surface.

These examples suggest maximizing tube life by optimizing wall thicknesses along the length of the tube. The optimum wall thickness at a given elevation is the one in which stress relaxation ceases and fissuring starts at the same time. It will be thinner at the top than at the bottom.

If reasonable estimates of localized pressure, inside metal temperature, and unit heat flux could be made, a near optimum tube wall thickness for replacement tubes in an existing reformer could be calculated using the above approach. Conversely, the effects of modified firing on the life of existing tubes could be better estimated. Either

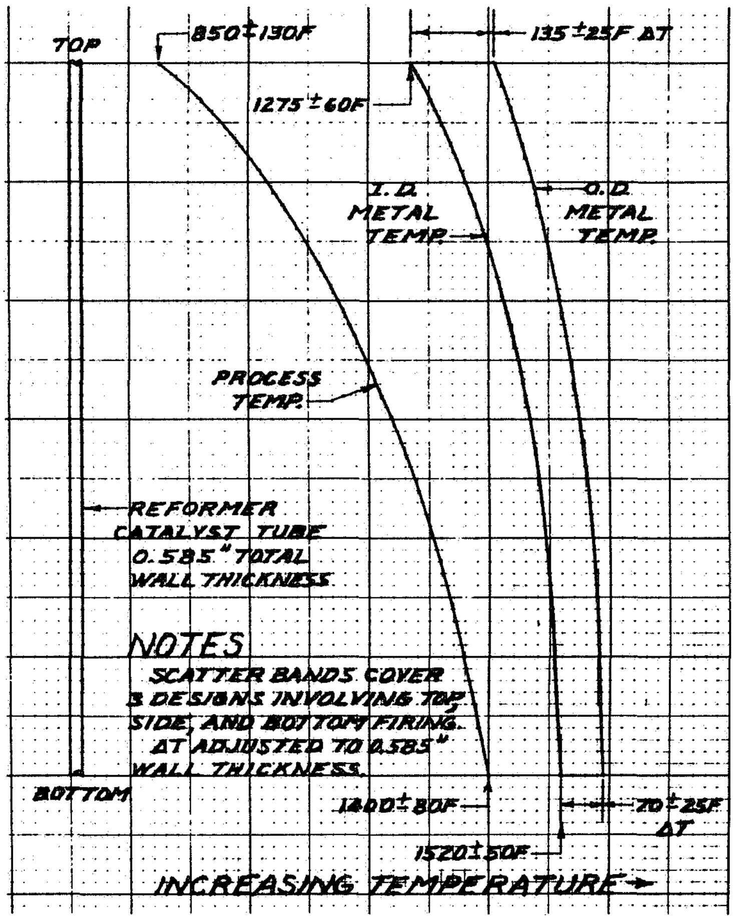

Figure 4. Typical 400- to 500 lb./sq. in gauge reformer catalyst tube performance.

calculation is tedious, but would be facilitated by the preparation of standard design charts.

The same applies for a reformer in the design stage, except then the values of key factors are not yet fixed. Figure 4 shows a range of typical design conditions for catalyst tubes covering three different commercial high pressure reformer designs adjusted to a common tube wall thickness. Despite the similar temperature profiles, the broad temperature ranges show there is much room for design manipulation of inside metal temperatures and through-wall temperature gradients without leaving the bounds of commercial experience. The potential benefits of optimizing tube walls for longer life are thereby greater in the design stage.

Other design considerations, not covered above, have been suggested as affecting tube life, but the only one that is known to be significant is thermal cycling. While much remains to be learned, it is known that thermal cycling generally reduced creep rupture strength while increasing creep rates. In other words, it has the same effect as an increase in temperature, and could be incorporated in any design procedure on an equivalent temperature basis.

Materials and Manufacture

Tube replacement programs in several, large, high pressure reformers with HK-40 tubes have been completed or are scheduled for the near future. Replacement tube material commitments are generally for HK-40 with minor refinements, but a variety of other alloys, mostly proprietary, have been adopted by some.

Most of the other alloys are not really new, and have been previously used in lower pressure, higher temperature, hydrogen and methanol reformers where emphasis has been placed on the need for high temperature creep rupture strength. At the usual lower temperatures in ammonia plant reformers, the creep rupture strength superiority of these alloys is not as great, and presents a problem in cost justification. Furthermore, some of these alloys may have lower creep rates and lower rupture ductilities, each of which tends to reduce the time required for subsurface fissuring.

The optimum alloy for high pressure reformers should have the best combination of creep rupture strength, creep rate, rupture ductility, and cost. Most alloys have not been analyzed in this light.

The catastrophic oxidation problem has not spread, and seems to have isolated itself as avoidable via controlled alloy composition.

Centrifugal casting is being challenged in some applications by either weldforming or extruding, but it is still the predominant method of manufacture for high pressure reformer tubes. It does cause high as-cast residual stresses, which are somewhat detrimental in that they steepen S_O - S_O in Figure 3. Reversing or reducign residual stresses by cooling techniques or autofrettage may not be practical, and thermal stress relief causes straightening problems which may not be economically justified, but the goal of reducing residual stresses seems to justify some pursuit. For instance, if cooling the solidified casting from the inside by some simple means, such as blowing air through it from the pouring end, would improve the residual stress pattern, it could be verified simply by evaluating etch rings taken from each end.

One already commercial innovation consists of centrifugally cast tubes with reduced shrinkage voids at the inside surface, now being offered as an alternate to bored or honed tubes. Although massive tube replacements have been *(7)* or will soon be made using bored tubes, some of the drive behind this trend has been lost because fracture origins in high pressure tubes consistently appear to be well outside of the shrinkage region.

Ideally, the welds that join castings into reformer tube assemblies should have the same creep characteristics as the parent metal. If they did, circumferential fissures in the center of a weld, as shown in Figure 5, would be virtually impossible. Note their similarity with the longitudinal parent metal fissures in Figure 2. The failure mechanisms are similar. In most cases, the worst weld cracks are through the middle, rather than at the edge, of the weld. The evidence of weld deterioration in high pressure reformer tube service has increased during the past year with:

1. Weld leaks in two different reformers
2. Over 20% of the welds checked in another reformer were found cracked
3. Rechecks of weld cracks in two reformers after 1 yr. showed many cracks had opened up noticeably.

Although weld leakage is still an infrequent mode of failure, superior welds could practically eliminate it. Some

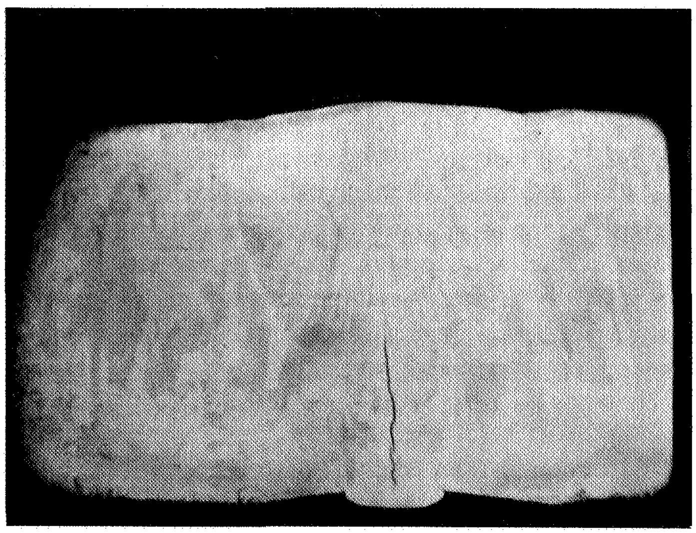

Figure 5. Subsurface fissures of HK-40 weld metal.

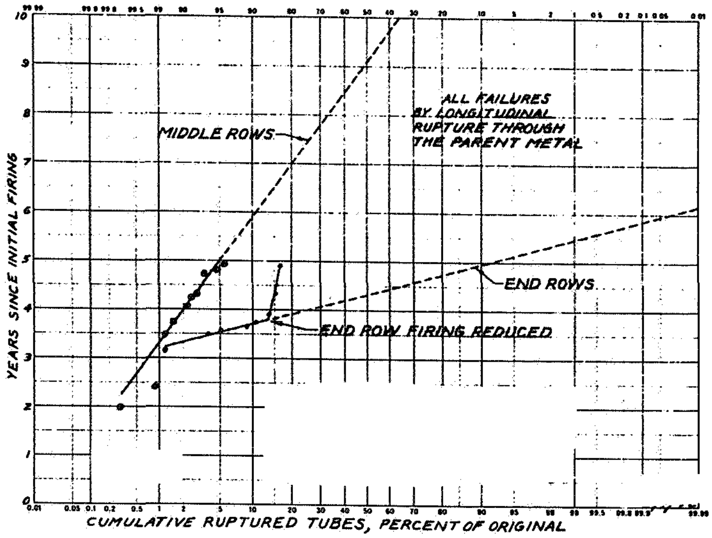

Figure 6. Radiant wall effect on tube performance in one high pressure reformer.

improvement has been claimed for welds made by an automatic TIG process *(8)*.

Controlling Operation

One benefit of improved temperature control was demonstrated in reformer A of Figure 1. Inadequate control of temperatures in tube rows adjacent to radiant walls caused non-uniform tube performance in one high pressure reformer, as shown in Figure 6. Based on typical stress rupture data, average tube metal temperatures must have run about 40°F hotter in the end rows than in the middle rows. When the difference in tube performance was noted over a year ago, the end row firing was significantly reduced, and resulted in the pronounced improvement shown. All failures were by longitudinal rupture through the parent metal.

This sensitivity of tube life to temperature has led to extensive efforts at temperature monitoring, and has pointed up the difficulties of doing so, such as:

1. Lack of an instrumented dummy tube in the firebox for purposes of pyrometer calibration,
2. Lack of sufficient peepholes for proper inspection coverage,
3. Lack of a pyrometer that is both accurate over a sufficient range of temperature and will measure temperature at large numbers of points in a reasonable time without physically overwhelming the operator,
4. Lack of a convenient system for cumulative recording and retrieval of many individual tube temperature histories.

Each of these difficulties has been attacked to varying degrees by many reformer operators.

The "hot band" problem, experienced in some high pressure converters, has been reduced by means of improved catalyst *(9)*.

Operators are continually striving to reduce the frequency and severity of reformer cool downs, but conditions while in service should not be overlooked. In several instances, pressure upsets have caused sufficient back flow to blow quantities of catalyst back into inlet headers, resulting in flow restrictions to inlet pigtails.

No reliable non-destructive field testing methods have yet been developed for predicting remaining life in reformer tubes. Preplanned radiographic inspection has been adopted by several companies as the best method of detecting severe creep damage *(10)*, while in-place metallography has been tried by another *(11)*. Results of "strapping" to detect slight bulges have not correlated well with creep damage or failures, but they do help pinpoint areas requiring further investigation. Although there are methods to repair-weld used reformer tubes *(12)*, the risks of time consuming welding problems and potentially short remaining life and adjacent unrepaired areas have limited their application.

Conclusions

Tube performance is roughly predictable and can be seriously impaired by poor temperature control, as demonstrated in Figures 1 and 6.

Explanation of subsurface rupture origins, depicted in Figures 2 and 5, has led to the design approach in Figure 3, which is potentially suitable for calculating optimum tube wall thickness. It could also be used for comparing different reformer tube materials and manufacturing procedures, and for encouraging innovations in them.

While the catastrophic oxidation problem is under control, the weld cracking problem is receiving increasing attention.

Control of tube metal temperatures and cycling remain key operating variables affecting high pressure reformer tube life. Obstacles to achieving these controls are not easily overcome.

Inspection and repair methods continue to bring much frustration, but some success. #

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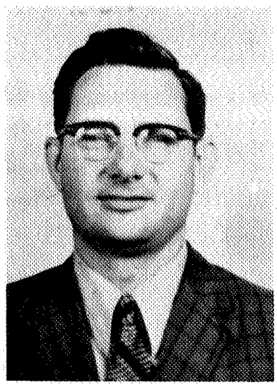

SALOT, W. J.

DISCUSSION

ZEIS, M.W. Kellogg, Inc.: Your paper pointed out quite a few areas where there's not much known about reformer tube life, but compared to where were were a few years ago, you have pointed out very many areas where we all know more about reformer tube life, and I'd say a lot of it's due to your efforts, and I'd sure like to compliment you again on your work. I have one question. Your Figure 1 showed curves A, B and C for three different designs of reformers, and it also showed the average tube life. I was wondering, assuming that C was the worst — and you showed the average — what's the best? In other words, what's the longest period of time you could expect to go without tube failures?

SALOT: Ask me that question in a few years. The half of the reformer tube network which is having better performance than the industry average have had relatively few failures. Most of them have had failures, but not enough to plot a line on the graph. I'd say, in the network itself, the best performance so far without a tube failure is about five and a half years, and still going strong. Last year, three of the older reformers had their first tube failures, so I would guess that probably the better reformers are going to be seeing their first tube failures within a few years. Maybe the top end of the scatter band will start around seven years for high-pressure units. Who knows? That's a guess.

I know of a reformer that is not in the reformer information network and, therefore, was not included in that graph, but it has gone six and a half years without a failure. It is a high-pressure reformer, but it is notable by the fact that it has a lower than average tube wall heat flux in the design, and this could explain superior performance in it.

ANON: You mentioned that you didn't have enough time to get into the maintenance procedures, and so forth. I suppose this is covered in your paper. But what have you found to be, say, the universal practical approach for inspection of catalyst tubes?

SALOT: My paper suggests that most people are putting more faith in radiography than in any other inspection technique. People have been using the strapping technique or other means of measuring bulging in the tubes, but this is not strictly correlatable with tube performance. Frequently a tube will fail with less bulging than the bulges in adjacent tubes that have not failed. I think the strapping technique will help isolate areas for further inspection by radiography. Similarly, the eddy current type of inspection does not correlate well with tube performance unless carburization and oxidation is a major problem, but it may pick up areas for further investigation. However, the ultimate seems to be radiography. I have referenced a paper presented during the past year which goes into this quite deeply, and I would refer you to it.

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