A REVIEW OF PRIMARY REFORMER CATALYSTS

A factual discussion on life of tubes plus a review of actual failures of units in operation

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WILLIAM SCHARLE, Air Products & Chemicals: Within the past year, we made the decision to purchase a complete set of reformer tubes. And I say purchase, not install. I thought it might be interesting to briefly review our history and also some of the thinking related to the economics that went into this rather major decision.

First on the history of the plant, we have a 600 ton plant, and in December of this year the plant will have been on stream five years. At this point in time we have had to shut the plant down on five occasions for a reformer tube, and on these five occasions we have also found six other tubes that had some flaw that caused us to make the decision to remove that tube. So at this point in time we've had a total of eleven tube problems.

Now of the eleven tubes, five of the failures were in the upper or middle sections, and since the plant has started we have been logging optical temperatures periodically. These five tubes have had some history of having a hot spot at some point in its history. And in these tubes we've periodically changed out the catalyst on a selective basis, and we completely changed out the reformer catalyst in June of 1969.

From a metallurgical analysis point of view on the failed tubes, we have found that the samples which have been analyzed have shown the typical stress to rupture characteristics. Examination has shown some carburization-oxidation but our metallurgical review indicates that it was not felt that this was involved in the actual mode of failure.

Of the other remaining six tubes, which were in the bottom one third of the furnace, these were tubes that had no history of having any period of operation as hot spots, and let's say, were not over 1650 degrees Fahrenheit. So we asked oursevles, why are the tubes failing? These tubes were designed at some nominal hundred thousand hour life figure. Possibly part of this can be understandable due to some of the operating temperatures, but this does not explain the whole problem. Is something happening to the metal itself, or is our total problem a combination of both? Our analysis of the operating condition shows that we certainly could not have predicted all the failures. In fact, even the temperature of the failed tubes which had some period of operating at higher temperatures, the failures could not have been predicted based on an analysis of the design curve.

So this is where we are, and though our total operation, we feel, has been excellent, we're still faced with a lot of unknowns in reformer tubes, and we feel that we must take a very conservative approach to trying to preserve our corporate profits. What will happen one, two or three years from now if the failure curve increases significantly? This could create a real problem.

We estimate that based on the couple of failures that we've had in our 600 ton/day plant, that a one tube failure costs about $50,000 including repair cost and lost production. Outage time is about three days for a tube failure. During the past year, we have gone into quite a bit of detail to see what will be involved when we want to replace all these tubes, even if they lasted a hundred thousand hours.

So having gone through this complete exercise and making a critical path schedule and doing a detailed cost estimate, we think that approximately 15-17 individual tube failures would be a break-even point on changing out the complete furnace. And actually, if part of the job can be done concurrent with a turn-around every other year, it may be even reduced under that. We estimate the complete furnace retubing to take 3-3½ weeks.

So then the next question you ask is what is the penalty for stocking these tubes? Assuming a reasonable cost of money which probably doesn't vary too much from company to company, and taking into consideration material escalation, which is a fact of life, we find out that the penalties in our mind is a pretty small number, something probably in the neighborhood of $15,000 a year.

So on this basis, even though our history has certainly not reached a point of major concern on tube failures, we have made the decision to buy a complete set of machined tubes, and these tubes of course have been purchased in accordance with the revised specifications of M. W. Kellogg which has a somewhat thicker wall and a more conservative design stress basis than the original tubes.

And we feel that one of the real key points is the flexibility to be able to make a decision whether we want to change out one of the 5 harps during a scheduled or unscheduled turnaround, or possibly more harps. The decision can only be made on the most recent history of tube failures. With lead time for material of 9-10 months required, we just want to be in a position to not get caught. We feel that the entire reformer can be changed out in three to three and a half weeks. This, of course, can vary based on the furnace design and approach on prefabrication.

In summary, with the varied experiences on reformer tube failures and the remaining unknowns, we feel a conservative position must be taken, and on that basis APCI has purchased a complete machined set of new tubes in accordance with the up-to-date Kellogg specifications which has a more conservative design stress value based on the original tubes. The furnace would be retubed when the failure history would economically dictate. We are also seeing continued improvements in reformer catalysts which is an important factor in helping to prevent hot spots and hot bands. Also, the plant operations in general does not see the frequent startups and shutdowns experienced in the early startup period. All of these factors should put us in an excellent position to predict a significantly improved tube performance after the initial retubing.

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W. J. SALOT, Allied Chemical Corp.; Now I have some data that covers 16 primary reformers and almost as many companies. I'm presenting it not with the idea of disputing the philosophy of Bill Scharle. I think in his situation his plans are logical and justified. However, situations in different reformers are different. Figure 1 is the basic data chart. It is really just raw data obtained from representatives of the 16 reformer operators.

There is a general trend of lines running up from the lower left corner to the upper right. They represent catalyst tube durability in the various reformers. The ordinate is the total cumulative number of leaks in catalyst tubes in each reformer. Each reformer has its own line plotted on the chart.

The abscissa is the time since the initial firing, and it goes up to five years or so. These 16 reformers are all similar in that they're all almost 500 psi inlet pressure. I've deliberately left out data on lower pressure reformers on the assumption that their performance is not directly comparable to higher pressure reformers. There are people who don't agree with that, but that's the way the data is plotted. It covers only high pressure reformers.

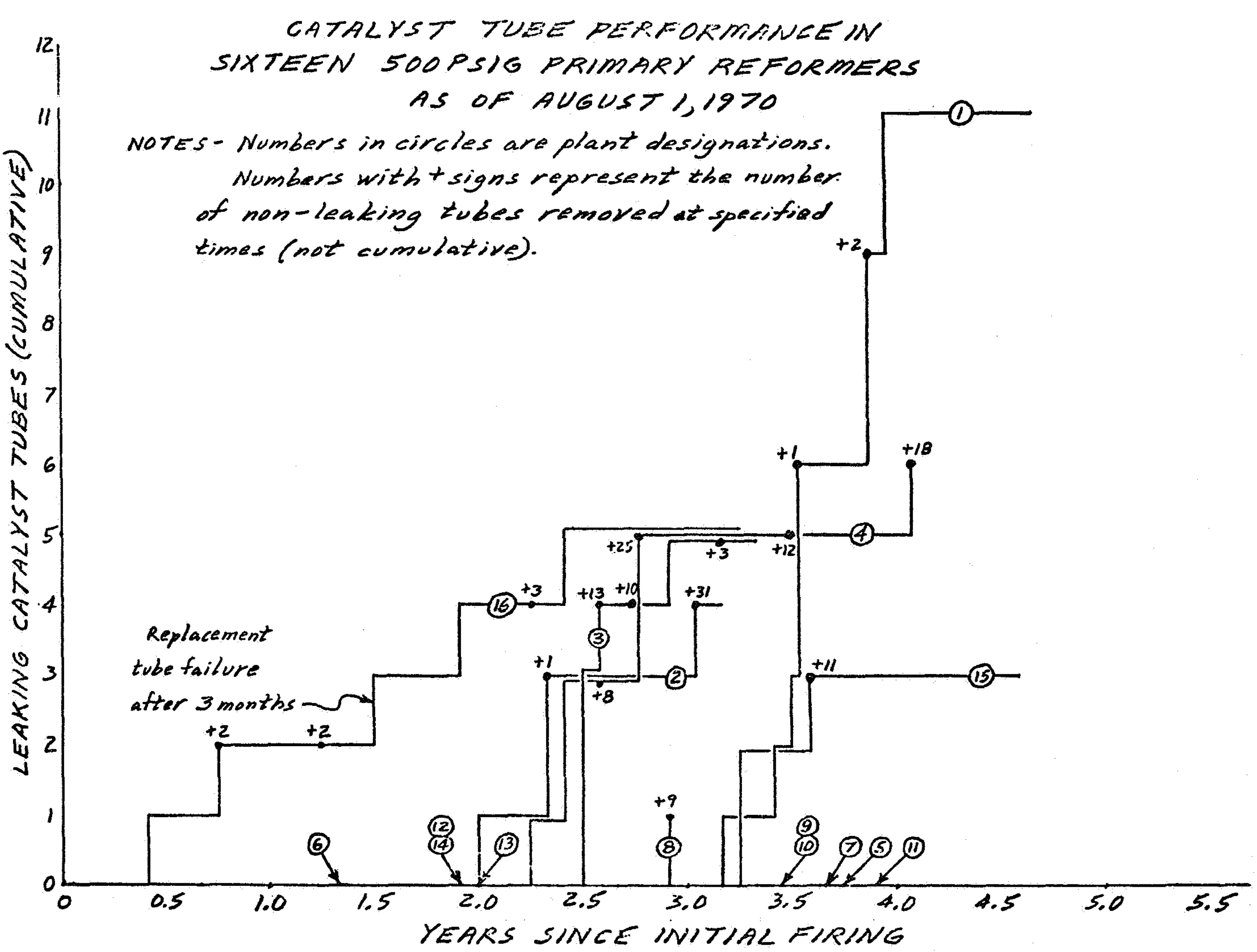

Figure 1. Catalyst tube performance in 16 primary reformers showing cumulative leaking tubes and years since firing.

The lines represent actual leakers. The tubes removed without leaking are not shown by lines but they're shown by numbers on the lines with a plus sign in front of them. If you look at the left hand line representing Reformer No. 16, you will see it had several premature tube failures. Other reformers did not have failures before they were two years old. You can draw some general conclusions from this chart, but I recommend that you don't jump to any of them yet. There are some confusion factors involved here.

It's not obvious from the chart, but each reformer doesn't have the same number of tubes in it. The number of tubes in these reformers varies from 210 to 420 so that a reformer having four leakers out of 420 tubes has only about one per cent leakage, but four leakers in a 210 tube furnace would represent about two per cent leakage. So to compare one reformer to another, we ought to be comparing percentages and not total leaks.

Another confusion factor is the definition of a leak. I thought at first that it was obvious, but there is a gray area. If you see flame coming out of the side of your tube when it's in service, that's a leak. If you shut the plant down, run an ultrasonic leak test on the tubes, and detect actual leakage of gas at an opening, that's a leak. But what do you call it if you shut down, inspect the tubes, and find a crack on the outside by visual observation or dye check? Is that a leak or not? For the purposes of this chart, I say it is a leak, on the assumption that any crack that reaches the outside will have reached the inside first, and therefore, is a crack all the way through. But this may not necessarily be so.

If you used the other definition, the overall results would not be much different.

Another confusion factor is the wide scatter in the performance of these reformers. There is some scatter in the lines that you see plotted on the graph, but that's only part of it. If you look along the lower horizontal line representing zero tube failures, you'll see that 9 of the 16 reformers have yet to have a tube failure. Four of them represent the four youngest reformers, all under two years old. That's not surprising, but it is surprising to find five other reformers bunched together in the age group from 3 years to 4 years with no failures at all. Just think what would have happened if I had sampled on the nine reformers that hadn't had any leaks. How optimistic we could be about the future of our reformers! And on the other hand, if I had sampled on the seven reformers that have had leaks, the average performance would have appeared worse than it is. It seems to me the way to look at it is to lump all the factors together, average the good reformers and the bad reformers, and plot them on a log-log chart to minimize the scatter.

The left half of Figure 2 represents the early life of the reformers. Although plotted differently, it comes from the same data as Figure 1. There are only 2 lines on this chart, instead of a separate line for every reformer. I have combined all the leaks in all the reformers to make the upper line. The lower line represents all of the tubes I removed, whether they're leakers or not.

Again, the two lines are going upward from left to right. The figures I used required me to have four log cycles in one direction and two in the other, and I ended up having to change the time direction from abscissa to ordinate. In other words, on this chart, time marches on from the bottom upward, instead of left to right. The bottommost line is a tenth of a year, the midway point up the ordinate is one year, and the top is ten years from initial firing.

The abscissa represents percent of total. In other words, I have plotted percentages instead of total leaks or total tubes removed. We can now better compare reformers with varying numbers of tubes. There is not too much sense that can be made out of the lower left hand end of the plot. It is erratic because of those premature failures and replacements that occurred in one reformer, as pointed out on the other chart.

Let's ignore those premature failures because they are rare and unlikely to happen again. The other points do line up better as you can see. These lines are really segments of lines because not all of the reformers have reached a sufficient age to provide complete data for the curves. So the first points at the far left are totals for 16 reformers, but after one and a quarter years, the age of the youngest reformer, the data drops to 15 reformers. Then gradually, as the ages increase, the number of reformers represented by the data decreases. Hence, the reliability factor becomes increasingly important at longer operating times where data is based on relatively few reformers.

Now let's look at the right half of this chart. Again, we see two lines representing leaks and tubes removed. I've extrapolated these lines to the right hand edge of the chart. The right hand edge represents one hundred percent of the tubes. So when the lower extrapolated line reaches it, all of the original tubes in the average of these 16 reformers will have been removed. The chart shows that if tube removals continue at the same rate, the average reformer will have all its tubes removed in seven years.

Similarly, the upper extrapolated line shows that only 15 to 20 percent of the tubes removed are leakers. This is by coincidence almost the same figure that Bill Scharle used.

I would like to stop here because this is the end of the data and what I consider to be facts. From here on out it is opinion, theory and philosophy.

Supplement from author:

• At the Denver Ammonia Safety Symposium in September, 1970, I presented a log-log plot indicating that, if tube removal rates do not change, the average of sixteen (16) high pressure primary reformers will have all of its original tubes removed in about seven (7) years.

This was a straight-line extrapolation on log-log coordinates, and assumes that tube removals increase parabolically with time.

I now believe it is more accurate to make a straight-line extrapolation on probability coordinates. This assumes that tube removals have a normal distribution with time. An approximation to it is to extrapolate the available log-log plot to only 50 percent tube removal, and then double the corresponding time variable. The resulting estimate is twelve (12) years before all original tubes are removed from the average reformer.

If I update this data in 1971, it will reflect the above change in thinking.

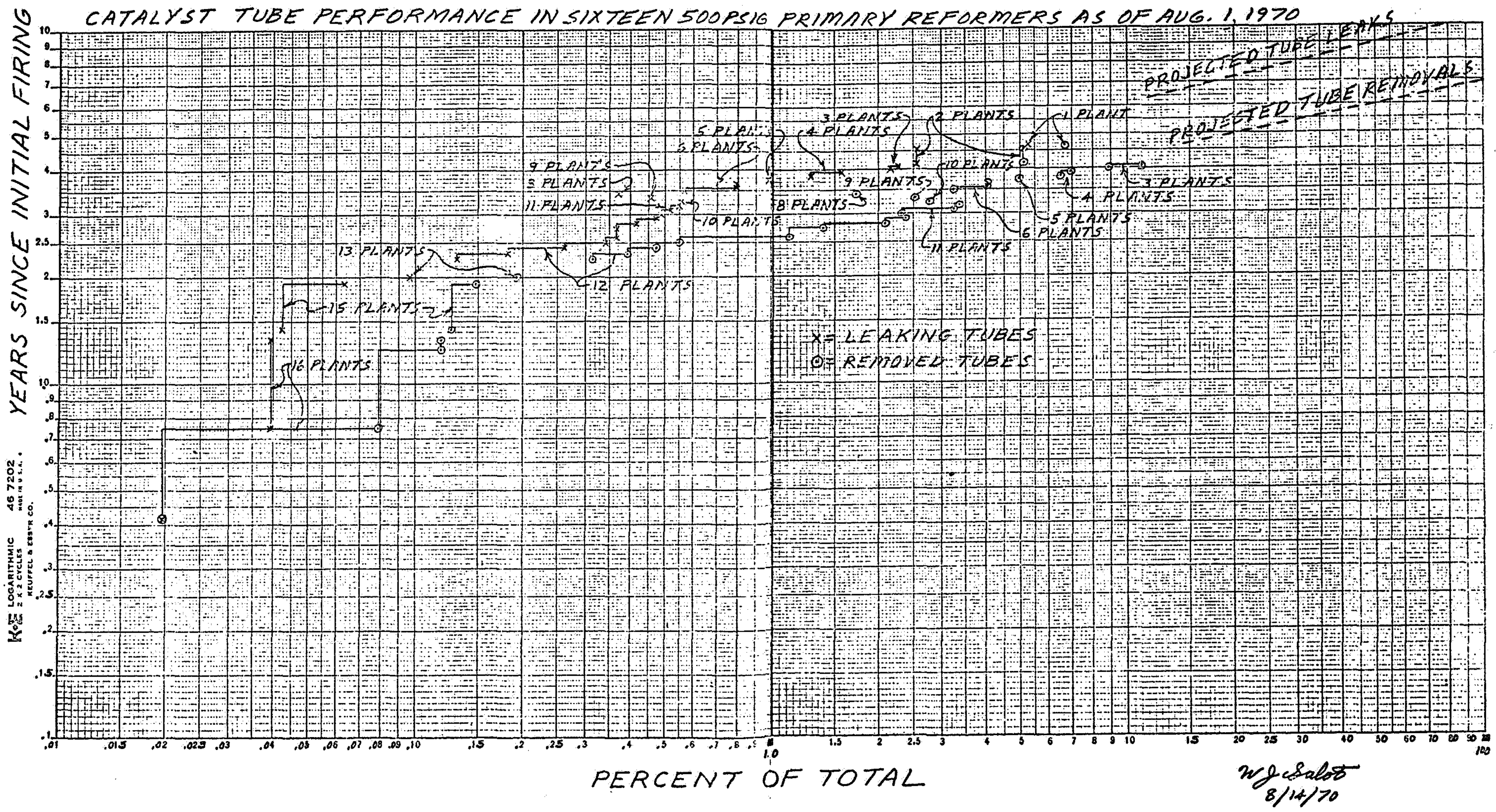

Figure 2. Catalysts tube performance in 16 primary reformers showing projected tube leaks and removals.

HAYS C. MAYO, Cooperative Farm Chemicals Assn.: I would like to ask a few specific questions just to clarify the basic data. Let's get down to two reformers because 16 is too many. Let's take your own two reformers; - how many tubes have you actually had fail in these two reformers?

SALOT: From memory, I think it's four in one and five in the other.

MAYO: All right, how many times has a unit been forced down because of these failures?

SALOT: In our plants? None.

MAYO: In other words, all your failures have been found on a shutdown?

SALOT: No.

MAYO: All right, how many times have you been forced down, then?

SALOT: None.

MAYO: Okay, I don't understand.

SALOT: You know what it means, don't you?

MAYO: No.

SALOT: It means that we run for a while with leaks.

MAYO: All right. Right now I am having trouble, though. Those units have been going how long?

SALOT: Both of them are over three years old now.

MAYO: Then if I were to take this and do my own extrapolation, I wouldn't come up with 100 percent failures in seven years.

SALOT: No. 100 percent removal; only 15 to 20 percent failures. I haven't plotted individual reformers to compare with this average. I suspect that ours would be worse than the average because we have had failures while five older reformers mysteriously have not had any. ●

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O.F. HARDY, Agricultural Division, Olin: Olin operates a Foster Wheeler terraced wall reformer at it's Lakes Charles, La. ammonia plant. The unit contains 432 A-297 HK modified tubes 3-in. ID X 0.570-in. wall as cast and 0.477-in. minimum sound wall.

The tubes are equally divided between two separately fired cells and are numbered 1 through 218 from the west.

To date this furnace has suffered 47 cycles since its startup on November 1, 1965. On one of these cycles, precisely that of January 1, 1966, malfunction of a solenoid in the shut-down system allowed fuel gas to continue to flow into the south cell without process flow through the tubes.

Extensive heat damage was sustained as evidenced by rupture of tubes Nos. 30-S and 31-S. It was estimated that metal temperatures as high as 2350° F may have been reached.

Since January 1, 1966, we have lost 9 tubes as follows:

Date	Tube No.	Time Between Failures	Time Since Start-Up
11/1/65	———	———	Start-up date
1/1/66	30-S & 31-S	———	61 days Shut down system malfunction
1/4/69	18-S	1098 days	1159 days
1/26/69	59-S	22 days	1181 days Outlet pigtail pull out
12/6/69	24-S	314 days	1495 days
4/26/70	34-S	141 days	1636 days
8/10/70	22-S	106 days	1742 days
8/15/70	19-S 108-S & 111-S	5 days	1747 days No. 111 weld No. 108 impingement
8/24/70	20-S	9 days	1756 days

Almost all of the failures have occurred at the same elevation in the furnace ie. slightly above or below the weld joining the second and third cast sections. Only four failures have deviated from this pattern. Tubes No. 19-S, 20-S and 22-S failed in the center of the section approximately 26 feet from the bottom flange. Tube No. 111-S failed in the weld between the first and second sections. Tube No. 108-S was deactivated due to flame impingement and probable damage from the weld crack in tube No. 111-S.