# FAILURE OF PRIMARY REFORMER OUTLET PIPING

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The Shell Chemical Co., Ventura, Calif. Ammonia Unit has been in operation since the latter part of 1953. On May 20, 1963, when at regular operating conditions, one section of the Type 304 stainless steel primary reformer 12-in. outlet piping suddenly ruptured in its longitudinal weld seam. Gaseous flames shot horizontally a distance of at least 50 ft. Fortunately, no one was injured, and the fire was extinguished quickly by shutting off the primary reformer feeds. Subsequent inspection revealed cracks in longitudinal weld seams of virtually all welded piping. No cracks were observed in the thicker circumferential field weld seams nor in the parent metal.

A mixture of natural gas and steam enters the radiant section of the primary reformer furnace tubes at the present conditions of 1,000 ° F at 110 lb./sq. in. gauge in contrast to the original conditions of 1,000°F at 95 lb./sq. in. gauge. The mixture is reacted in the tubes and about two-thirds of the natural gas is converted to hydrogen and carbon oxides. The gas mixture exits the furnace tubes at 1,350°F and 85 lb./sq. in. gauge, originally 1,400°F and 70 lb./sq. in. gauge.

## Type 304 stainless steel piping

The primary reformer furnace outlet line originally installed was composed of seamless and welded Type 304 stainless steel piping. Samples of the failed piping and some of the seamless piping were shipped immediately to Shell Development Co., a Division of Shell Oil Co., Emeryville, Calif., for their examination. A basic summation of their findings is as follows:

1. It appears that the main longitudinal weld seam failures were a result of high temperature stress rupture.
2. Heavy carburization had developed at the inner walls. As expected, this carburized layer was brittle.
3. The base material of all Type 304 stainless steel pipe samples submitted for examination showed a marked reduction in ductility as compared to normal Type 304 stainless steel. Brittleness, as revealed by flattening tests, was present at both ambient temperatures and approximately 1,450°F.
4. In view of the severe embrittlement, they recommended replacement of the remaining original seamless Type 304 stainless steel piping still in service.

## Incoloy alloy 800

In contrast to the outlet piping, the Incoloy alloy 800 furnace tubes have given excellent service. The maximum recommended surface temperature for these tubes is 1,775°F. Pyrometer readings have indicated hot spot temperatures as high as 1,700°F. A 75,000-hr. metallurgical examination of one tube by the International Nickel Co. showed that there is still considerable service life remaining in these tubes. The results of their examination are as follows:

1. The tube resembles unused material. There was no visible external evidence of any deterioration, cracking or bulging.
2. The grain structure was coarse and mixed with grains 0.0035 in. to 0.15 in. in diameter.
3. The exterior surface was nitrided to a depth of 0.060 in. Chemical analysis showed 0.16% nitrogen in this area. Another tube removed for examination after 50,000 hr. service showed a nitrided layer 0.046 in. deep containing 0.18% nitrogen.
4. The slight nitrogen absorption from furnace atmospheres produced only a slight reduction in room temperature ductility but high temperature ductility was unimpaired.
5. The exterior surface has an irregular thin film of oxide. Below the oxide film there is a narrow layer of intergranular oxidation.
6. No carburization was noted on either the inner or outer surfaces. A slight decarburization, however, was noted on the inner surface.
7. X-ray analysis shows no evidence of sigma phase.

## Phases causing embrittlement

There are a number of phases that can cause embrittlement of the 300 series austenitic stainless steels. High temperature embrittlement has been recognized for some time as having been caused by long-time exposure above 1,200°F. It is possible that the cause for embrittlement of the subject piping could be the well known Sigma formation but the exact cause would definitely be a subject for further investigation. The Type 304 stainless steel welds could have been more affected by the embrittlement because of possible iron precipitation (called Delta iron) during the welding operation. In addition, the stress rupture failure of the main outlet piping longitudinal weld seams could also have been due to exposure to higher-than-normal operating temperatures and could be remedied by using heavier wall or seamless piping.

Because of favorable experience with Incoloy alloy 800 tubes, replacement of all outlet piping with this material is being considered.

## Similar service conditions

Based on experience at the Ventura Plant, type 304 stainless steel is considered unsuitable for reformer outlet piping for Ventura service conditions. It is recommended that, before a 300 series austenitic stainless steel is used in similar service conditions, a thorough investigation be made to determine the suitability of the chosen material for the service.

# DISCUSSION

WALTON—Sun Olin: Our primary reformer transfer line started out as being 347. We had six different occasions where we had to shut down due to cracks in the 347 piping. The cracks were always in the heat affected zone of a longitudinal weld.

When we revamped this unit and added the secondary reformer about a year and a half ago, we replaced most of the 347 with 316. This 316 so far has looked good. On the shut down in July we had a crack in a section of the 347 which was left—which had not been replaced—and found on further investigation and X-ray that there were two more locations in the 347 which had cracks developing. So we have replaced an additional section of the 347 with 316. We still, however, have all of the pigtails and both the bottom headers of 347. It appears that the 300 series lines have a limited life. In the case of the shell 304 line it was ten years and in the case of the Southern Nitrogen 310 line it was near six years.

With the low pressure units (the earlier reformers were at much lower pressure), you don't have quite so much worry—a certain amount of cracks can be tolerated—but with 100 lb. to 300 lb. reformers, this is more of a problem, and a great safety hazard. The thing that concerns me now is, what will be the life of a 316 transfer line? I think it would be very helpful if others would remove sections from their 300 series and Incoloy transfer lines, obtain physical tests, and report to this group the results along with their experiences. This might prevent some catastrophic failures.

STOCKBRIDGE—Southern Nitrogen: We had an incident involving a rupture on the pipe of a primary reformer which was reported last year and can be found in Volume 5 of "Safety in Air and Ammonia Plants." Our line was 310 stainless steel and we also found the trouble to be definitely associated with the weld. We replaced with Incoloy. We were convinced by International Nickel Co. that Incoloy was the only thing to use. Not being a metallurgist, it was difficult to assess these things. Ours was a 10-in. line from the primary to the secondary reformer. We replaced it in its entirety with Incoloy. This was pipe fabricated from plate and welded with Inconel 182 rod. In our repairs we use Incoweld A rod as well as Inconel 182.

LAWRENCE—Central Nitrogen: Mr. Stockbridge and Mr. Walton, I would like to ask both of you gentlemen a question. How do you recommend testing the connecting pipe from the primary reformer with regard to X-ray and retest and so forth? Are there any developed procedures or do you feel that one should be specified?

WALTON: We examined the piping with dye check and the welds by X-ray; the X-rays showed the poor condition of these two welds that I mentioned in the 347.

STOCKBRIDGE: The question was asked about the analysis of the weld. It was analyzed for us by International Nickel and it was 310 stainless steel. They informed us that 310 stainless at certain concentrations of carbon is subject to fissure and that this was the case in our welds. All of the materials involved—the 310 stainless steel plate and the welding rods used—were within the allowable tolerances for 310. But that even though they were within the allowable tolerances, a range of carbon concentration in the weld can be brought about that will cause fissuring. This, as I understand it, is definitely an age phenomena.

HOUSER—Navy Bureau of Ships: I hesitate to come into this discussion since I'm completely ignorant of reformers. However, in the Navy we are extremely concerned about the properties of stainless steel called carbide precipitation. In many of our stainless steels we use an extremely low carbon content, so that during the welding process there will be no appreciable carbide precipitation.

As I understand it, carbon tends to precipitate during the welding process. It precipitates extensively if there's a lot of carbon; it precipitates less extensively if there's less carbon or to a lesser degree if there's less carbon. This causes me to ask the question: were the stainless steels that were used in these instances low carbon stainless steels? That's question number one. Question number two: the gas quite obviously has some carbon in it; is there a tendency for this gas to give up its carbon to the metal and form carbides in the stainless steel?

JONES—Canadian Industries Ltd.: I'm hesitant to comment, since we are not presently operating reformers and have no direct experience. However, there are a number of things which one might say, in a general way, about abrupt ruptures in hot transfer lines. First of all, the use of low carbon grade stainless steels would not be appropriate for service at temperatures above 800°F. Their mechanical properties and creep strength are much inferior to the regular carbon content or stabilized grades in the 1,000°F to 1,400°F range in which reformer transfer lines probably operate. Some carbide precipitation would also occur, even with the low carbon grades, after prolonged heating in this temperature range. The development of an embrittled condition, or loss of ductility at operating temperature, would be most likely due to the formation of complex carbides in the metal structure; these carbides being given the general name sigma phase. The use of low carbon grades, if otherwise feasible at 1,300°F, would not assure freedom from sigma phase formation.

I have a good deal of respect for International Nickel Co's. recommendations, and believe they will rarely recommend a high nickel alloy unless they believe it to be essential, or representing the most satisfactory all-round choice from the customer's viewpoint. I would support their recommendation that Incoloy be preferred for this service rather than the contractors recommendation of Type 316 stainless steel. Incoloy should have the necessary ease of fabrication, creep strength, freedom from sigma phase formation, and inert behavior versus the hot reformed gas stream. It also has a somewhat lower coefficient of thermal expansion than the 300 series stainless steels, and this should reduce the thermal shocks and strains which transfer lines may suffer.

On the other hand, Type 316 stainless steel is quite prone to sigma phase formation, and is just as likely to become embrittled as the other 300 series stainless steels. It is less resistant than Incoloy to stress corrosion cracking, although this is probably not a factor here.

While on the matter of safety, I suppose that the 25 Cr-20 Ni centrifugally cast furnace tubes also become embrittled but rarely seem to fail in an abrupt or dangerous manner. The furnace will, within reasonable limits, contain the combustion of the additional gas until a crash shut down can be made. On the other hand, the furnace tubes are subject to a minimum of restraint and thermal strain along their length, and are rarely subject to thermal shock.

The trend towards higher reformer temperatures and pressures, and larger single stream units, will probably result in larger energy releases in future transfer line ruptures. The thermal radiation from massive incandescent fireballs of flaming gas can be lethal for surprising distances.

SHERMAN—Du Pont: I have a question regarding what happens when a reformer tube ruptures. Would you care to comment on that?

JONES: I believe that the general mode of reformer tube rupture will be that of creep cracking. This is a long term process in which, as a consequence of sustaining loads at high temperatures for long periods of time, there is continuing nonelastic deformation of the material, or creep, which eventually results in fissures and rupture.

Initial porosity, inclusions, or local thin wall areas in the furnace tubing can be responsible for local failure. The creep strength is also dependent upon the composition of the alloy chosen, and such things as the grain size and macrostructure of the tubing walls. Local overheating of the tube walls, due to the design or adjustment of the furnace and its burners, or hot tubes, due to reduced process gas flow in individual tubes, perhaps because of catalyst caking or collapse, are all factors which reduce tube life because they reduce creep strength, which is an inverse function of temperature.

Creep, as the term suggests, is accompanied by a change in dimension. Thus, there will always be a small bulge, or measurable increase in diameter, in a tube which has failed this way. Usually too, the adjacent metal is found to be quite noticeably responsive to magnetism, although the original alloy is usually nonmagnetic.

Creep cracks develop slowly, and with all the variables I have mentioned which influence their rate of formation, the designer will generally be satisfied with 4,000-hr. or 5-yr. life to first tube failure. Generally this will mean that the majority of the tubes in the furnace will last more than ten years.

Creep cracks will usually result in a slow escape of process gas initially. This might be seen as a bright area or hot spot on the tube or adjacent tubes, or picked up by gas analysis of the furnace flue gas. Perhaps it will become more important to detect these leaks quickly as reformer pressures increase.

SHERMAN: I really was interested in knowing what was the outward phenomena. Do you have an unsafe situation outside the reformer when this happens?

JONES: I have no experience in this area. There is little doubt that a small gas leak inside the furnace is less serious than an extensive external rupture. Perhaps other people present who have had internal furnace failures would comment.

SIMMS—Phillips Petroleum: To answer your question partially, we have experienced actual failure in the furnace, that is, complete separation of the tube into two pieces when under normal operation. This does give you quite a fire, as you might expect, in the furnace itself. Other than that, I don't know of any particular problem, assuming you immediately proceed with a crash shutdown. Perhaps the greater risk is small cracks that may occur in circumferential welds, usually near the bottom of the tube. These cracks are not easily observed, but they cause an essentially invisible flame impingement on an adjacent tube. This can set up a localized condition that far exceeds the allowable skin temperature for the tube metal. I don't know that this can be proven but we have observed that if a crack appears in one tube, and operation is continued, a crack soon appears in the adjacent tube.

STOCKBRIDGE: What material would you use?

SIMMS: We would use 25 Cr-20 Ni centrifugally cast tubes. We have these tubes operating at between 100 and 150 lb. pressure. We also have 347 tubes operating at a much lower pressure in one of our older plants.