**Background & Details of Hydrogen Reformer Incident**

The facility where this incident occurred produces hydrogen in three hydrogen reformer units. The hydrogen is produced by steam reforming of methane. Two of the reformer units were constructed in 1979. The third reformer involved in this incident was constructed in 1987 and put on line in 1988.

**Steam Reforming**

The steam methane mixture enters the catalyst filled tubes at a temperature of 572 °C and a pressure of 362 PSIG. The methane is reformed with the steam on the nickel alumina (NiAl) catalyst to produce:

\[
\text{steam} + \text{methane} \rightarrow \text{carbon monoxide} + \text{hydrogen} \\
\text{H}_2\text{O} + \text{CH}_4 \rightarrow \text{CO} + 3\text{H}_2
\]

815°C (1500°F)

The radiant section of the furnace contains eight (8) banks of reforming tubes. Each bank or row contains forty-six (46) tubes for a total of 368 tubes composed of spun cast HP-45 Niobium Modified Alloy with a design wall tube temperature of 935°C (1715°F).

The tubes are mounted vertically with the flow entering in the top and exiting at the bottom. Each tube has a 10.2cm (4") ID and is 12 meters (39’10") long containing 102 cubic decimeters (3.6 ft³) of nickel alumina (NiAl) catalyst. Figure 1 provides the general layout of a radiant tube.

The furnace also has two convection sections containing boiler feed water and mixed feed (steam/gas) preheat coils.

Heat for the reforming process is supplied by nine (9) rows of natural gas burners installed on the top of the furnace. Each row consists of twelve (12) burners. The hot gases from the burners travel downward through the radiant section and are directed to the convection section via flue gas tunnels running along the furnace floor.

**INVESTIGATION AND FINDINGS**

A formal investigation was conducted to determine the cause of the incident. A lead investigator was assigned to conduct the investigation with support from a multidisciplinary team (process, maintenance and technical). Eyewitness interviews were conducted immediately after the incident. An inspection of the incident area was conducted as soon as the area was secured for entry. The investigation team established a sequence of events and conducted a root cause analysis. Due to the extent of the damage access was not granted into the furnace for several days. Much of the initial evidence was gathered with photos and videos.
Production was loss from the damaged hydrogen reformer for 71 days. The cost of retubing the furnace was approximately $20 million, which does not include other associated shutdown costs. The cost of a new catalyst charge was approximately $1 million.

The Incident

Isolated hot spots occasionally develop on these radiant tubes during operation. Rather than shut the furnace down to replace these isolated tubes, the tubes are externally pinched at their inlet and outlet without shutting down the furnace. Since these tubes are isolated with no process gas flow to keep them cool, they tend to grow. On line insitu evaluation of 6 previously pinched tubes revealed that they had encroached onto the flue gas tunnels and other, in service, tubes as a result of severe bowing. The decision was made to shut down this unit to remove these tubes and cap the inlet and outlet headers before they damaged adjacent in service tubes or the flue gas tunnels. There was a planned shutdown scheduled, however due to the rapid bowing it was deemed necessary to remove these pinched tubes as soon as possible. A window of opportunity presented itself to do this maintenance 7 months earlier than the scheduled outage. This was also a minimum scope shutdown involving only the reformer furnace. Since this was to be winter shutdown, the decision was made to leave steam in the steam generating circuit to prevent freezing.

The plant was successfully shutdown and the reformer furnace isolated. The 6 bowed tubes were removed from the furnace and preparations for startup commenced approximately 1 week after shutdown.

The startup procedure required the furnace to be heated up to 350°C (662°F) prior to introducing 4136 kPa (600 psig) steam into the radiant tubes. Once steam flow is established the furnace temperature is increased until 500°C (932°F) is reached, at which time the methane feed is introduced and the unit is brought on line producing hydrogen. On the day of startup at 10:39 PM just after 4136 kPa (600 psig) startup steam was introduced into the reformer furnace inlet the control room alarm journal reported an extreme positive pressure spike at the same time a single loud bang was reported by the operations personnel on the furnace structure. An emergency shutdown of the furnace was initiated and the start up aborted.

At the time of the incident there were 7 people on the furnace. Four were operations staff plus three maintenance personnel. One serious injury was sustained to an operator by flying shrapnel.

The investigation revealed that as the steam flow was increased it picked up some remnant water and carried it into the furnace. Under the conditions present, the water underwent an instantaneous phase change and the energy release was sufficient to rupture the tubes (see Figure 2). The entire event was calculated to have taken only a few milliseconds but involved extremely high-energy release rates. The power generated by a small amount of water entering a single tube at 10 lbm/sec would be 25,500 HP – 28,300...
Subsequent shock calculations indicate that the dynamic pressure to fail the reformer tubes would be 41.3 mPa (6000 psi) and the yield strength for this material would be no greater than 21.4 mPa (3100 psi). The volume of water to create this pressure would be approximately 0.4 kg (0.9 lb.). This was sufficient energy to catastrophically fail 5 tubes.

**Extent of Damage**

A total of 46 reformer tubes were destroyed in the incident. The inlet portions of 5 tube assemblies were ejected from the furnace with sufficient force to severely injure one worker and launch debris beyond the furnace structure. The other 41 tubes were subsequently destroyed either by shrapnel strikes or by the impulse released into the firebox after the initial tube ruptures. Five of the flue gas tunnels were destroyed and the firebox walls were penetrated in several locations by tube shrapnel.

Broken light fixtures, insulation and walkway gratings damaged by shrapnel impacts were found above the furnace and on a west-side furnace platform.

The investigation team condemned the entire reformer radiant tube section as there was no method to prove the integrity of the surviving tubes and there was too much damage to simply conduct repairs. The furnace was subsequently retubed.

Photos 1 through 6 detail some of the damage to the reformer furnace.

The steam flow enters the hot catalyst filled tube through the inlet pigtail and would be normally passed down through the catalyst and exit via the outlet header. Entrained water impinges on hot catalyst and possibly on the pipe wall and “instantly” flashes. This produced an extreme local pressure excursion and shock wave. The shock wave reached the pipe wall and initiated longitudinal cracking due to a hoop stress shock. It then progressed upward at sonic speed (~24,000 in/sec in 320°C steam at 75 psia) and downward (although impeded by random reflection at catalyst surfaces). Longitudinal cracking further extended due to the advancing hoop stress shock.

The shock wave reached the flange about one millisecond after water flashed at the catalyst and imparted an axial shock load on the tube. This resulted in sudden lateral brittle fractures progressing from the inside out and the upper and lower tube sections separate.

The now unconstrained upper tube end is launched out of the furnace by the extreme internal pressure. This also causes radial displacement of the free tube end segments. In areas of normally brittle material (hot areas within the furnace), high bending loads result in horizontal brittle fractures and the generation of shrapnel. Ductile material near the flange is able to yield without fracturing and produces a “banana peel” effect immediately below the flange assembly. Photos 7 and 8 detail one of the 5 tube failures

**Radiant Tubes**
Two distinct modes of failure were noted on the radiant tubes. The categories were arbitrarily picked as a means of distinction.

Category A Tubes

The five tubes noted above as having had their upper ends grossly lifted exhibited unique fracture features.

All of these tubes showed complete mechanically brittle circumferential separation on multiple planes of the tube material between ~14 cm to 45 cm (~0.5 ft to ~1.5 ft) below the flange. The different planes of circumferential cracking were bounded by mechanically brittle (no local distortion) longitudinal cracks running toward the flange. This indicates that longitudinal cracking preceded circumferential cracking. In many cases, the remaining material between the longitudinal cracks was highly deformed radially. Longitudinal cracking generally arrested in or near the flange hub and was sometimes accompanied by circumferential tearing at this point. Some large pieces of shrapnel found on the furnace roof, believed to have come from this region of these tube assemblies, also exhibited significant distortion in some areas and very little in others. Whether this distortion occurred before or after separating from the tube is unknown. Hence, the extent of distortion and longitudinal cracking below the separation is unknown. Although these sections would have been subjected to similar loads, the same extent of gross radial distortion (yielding) as described above is not likely due to the anticipated brittleness of tube sections exposed to radiant heating within the firebox.

The final resting place of these five tubes, the reported single bang, the full thickness of the fracture faces especially in regions of gross radial deformation and the distortion direction conclusively indicated that failure was due to “simultaneous”, sudden, high internal pressure loads applied near the upper end of each assembly.

Category B Tubes

The remaining 41 damaged tubes had fractured at various lower elevations and exhibited quite different macro features than were shown by the Category A tubes. The only macro feature these tubes had in common with those described above was the unquestionably mechanically brittle nature of the fracture faces (no local distortion). Nothing suggested that failure was primarily due to internal pressure excursions. Rather, evidence such as tube flattening with associated longitudinal cracks as well as angled cracks is indicative of externally applied bending loads. Several of these tubes exhibited varying degrees of impingement damage, due to impacting shrapnel or falling tube sections.

Process Evidence of a Wet System
The startup procedure did take into consideration the need to have the reformer furnace feed system water free and steps are included to ensure that any water would be either drained form the system or evaporated as steam during heat up. Shortly after gas burner lighting commenced, the reformer mixed-feed temperatures began a rapid ascent before settling at ~143°C (290°F). At the same time, but at a slower rate, the reformer outlet header temperature began to increase and eventually settled at approximately the same temp as the reformer inlet. However, no flow was going through the feed line and reformer radiant tubes. The process piping system had been purged with nitrogen and the process down stream of the reformer furnace was still isolated. The system pressure also began to increase to ~40 psig. (Saturation temperature of 40-psig steam is 141°C.)

The temperature of the reformer inlet and outlet remained constant at ~143-146°C, even though the portions of the radiant tubes in firebox were approximately 350°C. A constant temperature profile indicated that water was still present since steam generation occurs in equilibrium with water at a constant temperature, until all water is vaporized.

The investigation team calculated that after the Induced and forced draft fans were restarted, the mixed feed and superheater coils gave up approximately 56 MBtu of heat from 0900 to 1630 hrs, as evidenced by the temperature rise. This corresponds with the production of approximately 30,000 lbs of condensate over the 7-hr period. Further, from 19:00 to 22:00 hrs, the mixed feed preheat coil absorbed approximately 14.6 MBtu of heat. This would be equivalent to producing approximately 18,000 lbs of steam over this 3-hour period.

The Figure 3 depicts these key process conditions prior to the incident.

**Sources of water**

The entire furnace feed system was analyzed. Piping configurations and witness testimony identified several ways water could enter the feed system and get trapped. During the shutdown sequence, the steam system will become wet as pressure is reduced and temperature falls. This is normal and expected so the design of steam and feed systems incorporate vents and drains to facilitate water removal.

Steam was left in the steam generating system and throttled to keep approximately 344kPa (50 psig) in the system to prevent freezing.

There is an argument that there is always an opportunity for water to accumulate in the steam system upstream of the reformer furnace as, at some point, the steam is commissioned to a “cold“ system so the fact that steam was left on should not be a factor. However, this change is a contributor to the overall accumulation of water since the steam was commissioned for days rather than hours as per the startup procedure. This
would have provided an extended time frame for water to accumulate in areas that would not drain.

The most likely source of water accumulation would be in the mixed feed preheat coil (see Figure 4) for two reasons. The inlet header to this coil will not fully self-drain and the tubes had become slightly bowed over time.

Since there was no accurate means to positively identify the source of trapped water for this incident, the investigation team recommendations were focused on addressing the most likely water sources and points of accumulation and procedural changes to deal with ensuring a dry feed system exists prior to adding the startup steam.

**Comparison to Previous Start-ups (2000 & 1995)**

The process data from the previous two shutdowns was reviewed in order to verify the conclusions regarding the source of the water. In previous startups, the reformer inlet temperature response was much slower to the heat input through the convection section and did not plateau during the startup sequence. Hence, there was no indication of boiling in the mixed feed preheat coil. While the temperatures did increase, this is attributed to conduction and general elevated temperatures in the “penthouse” region at the top of the furnace.

The reformer outlet temperature instruments hardly responded at all, and remained below 50°C (122°F) until steam flow was introduced to the tubes. No pressure increase was observed on the system.