Ammonia Reformer Freeze-up

A disastrous failure of tubes in a primary reformer at a pressure of 14,000 lb. per square inch was the first such incident in 22 years of operation.

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A catastrophic failure of an ammonia reformer operating on natural gas feed in Allied Chemical's Nebraska plant resulted in an intensive investigation to determine the causes. The failure and subsequent study is the subject of this article.

Although Allied has operated 20 different natural gas ammonia reforming furnaces during the past 22 years, this failure is a type never before experienced in our operating history. The incident destroyed over half the tubes in the furnace overnight. The unit involved is a single-train, 400-ton/day NH_3 plant with a 275-lb./sq.in. Selas primary reformer followed by DMPEG CO_2 removal and a 5,500-lb./sq.in., non-refrigerated, synthesis loop. The sequence of events was as follows.

On January 2, 1974, excessive vibration was noted on the secondary reformer air blower. The plant was accordingly taken down in *routine fashion* to investigate the cause of the excessive vibration. The stage was then set for an unpredictable disaster.

Later investigation showed that at shutdown there were leaking tubes in the secondary reformer waste heat boiler. As soon as heat was taken off the train, these leaks, instead of generating steam on the process side, leaked boiler feed water into the process side of the waste heat boiler. The water flowed by gravity back into the bottom of the secondary reformer where, due to the vast heat sink in the secondary catalyst, it was vaporized sending steam back through the transfer header into the primary reformer. In the primary reformer the catalyst tubes acted as condensers converting the steam to liquid water in the catalyst tubes.

At shutdown the weather was cold, but during the shutdown the temperature dropped to minus 29°F, extremely cold even for Nebraska. An operator inspecting the primary reformer a few days later found that 72 of the 142 tubes in the furnace were destroyed. A plant engineer took the Polaroid pictures shown in Figures 2-4.

There could have been better clarity in the photographs. However, the reason they are not better is, as can be seen, some of the tubing not only split and shattered but there were pieces hanging precariously in the upper part of the reformer that could be expected to fall at any time. Thus, taking better quality pictures would have been a definite risk.

The problem our company faced was acute. It was almost spring fertilizer season, and our primary reformer was a shambles. To minimize the loss, two courses of action were taken: 1) get the unit back onstream at whatever rate it could run; and 2) minimize the time required to bring the unit back up to full rate. To accomplish these objectives, the maintenance department started removing all broken and cracked tubes, and simultaneously vendors were approached to get fastest delivery on replacement tubes.

The plant was brought back in operation under the following conditions. Fortuitously, the reformer is a two-cell unit with a dividing wall down the center and burners on the side walls. Because most of the damage was in the west cell on the windward side, the dividing wall was bricked to the ceiling and the west cell draft side was closed off. The west cell inlet process gas header was valved and blanked and the transfer line cut and capped at the connection to the east cell transfer line. The east cell was then started and operated separately, with its burners located on the east wall. Under these conditions the plant was operated at 50 to 60% of design capacity.

With the east reformer cell in operation we were in a position to work in the heavily damaged west cell while running NH_3 rates up to 60% of design. As partial shipments of tubes came into the plant they were installed during operation. And, a 4-ft. section of transfer line that had been bulged by freezing was replaced. Following replacement of the west cell tubes, a short shutdown was taken to remove the brickwork separating the draft side of the two cells and to reconnect the transfer line. Then the unit was brought up to full rate. The entire job took just a little over two months.

A major factor in the speed with which the repairs were completed was Wisconsin Centrifugal, who supplied the replacement tubes. That firm not only worked our tubing order into every available time slot in their production schedule but started up casting machinery they no longer operated just to give us maximum speed on delivery.

Steps taken to avoid a recurrence

Although this was the first time an incident like this has ever occurred in one of our plants, because of the severe losses involved we are taking the following action as a minimum to insure against its ever happening again:

1. In the past we have tried to avoid cold weather shutdowns, but in the future we will try even further to minimize the possibility of a shutdown during sub-freezing weather.

2. Following shutdown, purge steam and water from the

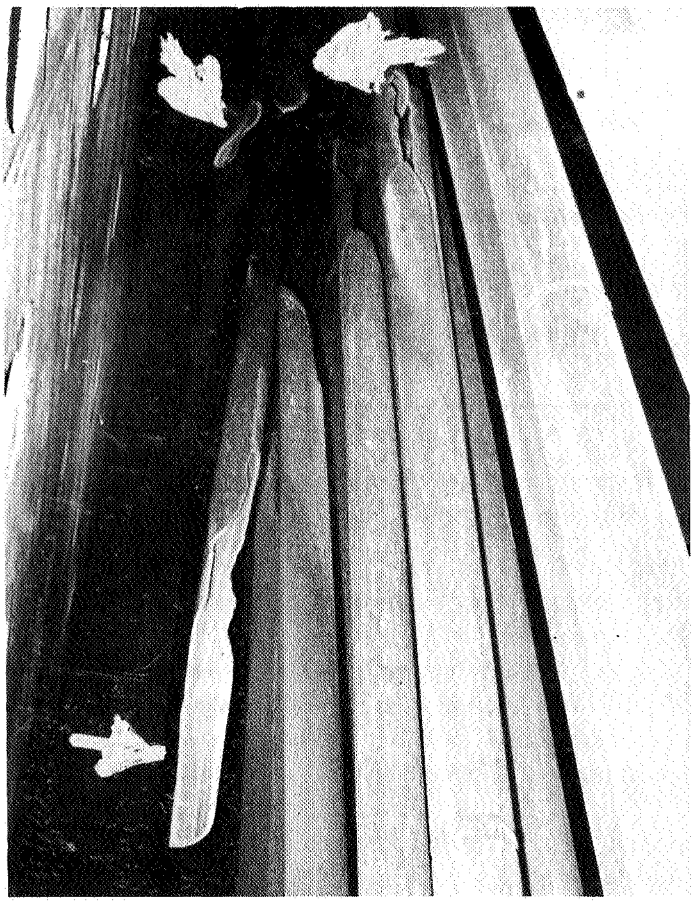

Figure 1 and 2. Two views of the hanging remains of severed tubes, with the fractured ends indicated by the arrows.

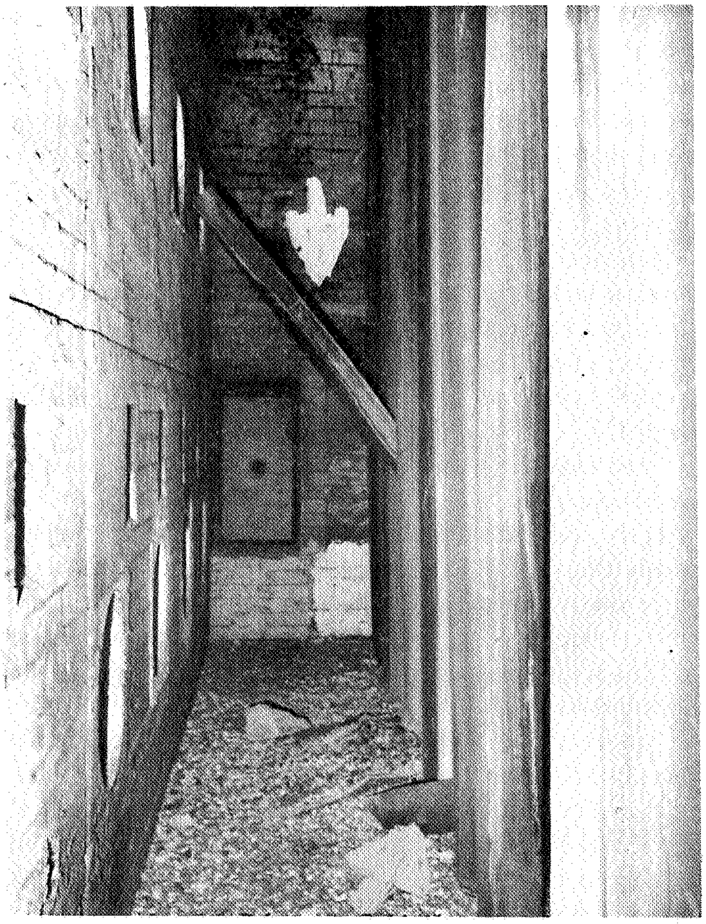

Figure 3 and 4. Two views of fallen pieces of shattered HK-40 tubes lying in catalyst and rubble on the floor of the reformer.

reformer with an inert gas, such as nitrogen or CO_2.

3. Keep the reformer warm, either with a few burners on lazy flame or, if maintenance is required on the reformer, close it in around the bottom and maintain an auxiliary source of heat inside, even if it means building wood fires on the floor.

4. Provide double-block-and-bleed on the reformer at any point where water or steam could be admitted to the unit.

5. Provide auxiliary heat on the bleed between each double block. This showed up as a serious factor in our case because even where double blocks with bleed between were installed, the bleed would have soon frozen and sealed itself off in the temperatures encountered during our incident.

6. Give special attention to draining any tube bundle carrying liquid which could be turned loose in the system in event of a leak.

In reviewing the overall incident we attempted to assay the temperature and pressure at which the tubes had failed. Pressure determination was simple. From the strength data for aged, HK-40 alloy tubes at low temperature we readily calculated that the 4-in. tubes would have ruptured at 14,300 lb./sq.in. However, from the strength of ice data (*1*) we could calculate that it would be impossible to fracture our tubes.

This led to the question of whether the explosive-like destruction of the tubes might be attributed to some mechanism other than the freezing of water. Our reformer specialist pointed out that when reformer tubes have been operated for long periods of time, some develop cracks; and the presence of such cracks would of course reduce the effective wall thickness and accordingly reduce the force required to rupture a tube. However, in view of the number of tubes involved in our incident–and because some of the tubes were relatively young–the presence of cracks was not regarded as the probable explanation for many tube fractures.

The next step was search further in the literature. The physical properties of water are very well defined in the liquid and vapor phases. But, there is a paucity of data on physical properties of water in the solid phase. Since the original theory of Chadwell hypothesizing water I and water II in 1927 (*2*), there have been 15 additional theories (*3*), and with the recent discovery of ice IX, there are now nine forms of ice known.

Based on data in the International Critical Tables, mainly that of P.W. Bridgman (*4*), the following solid-liquid phase diagram, Figure 5 has been constructed showing the pressure-temperature equilibrium points for liquid water and the seven known forms of stable ice which could exist at temperatures involved in our specific incident.

The metastable ice IV which can exist in the area of ice V, and ice IX which is fully stable only below –100°C (*5*), are not shown. Although the data show ice forms stable at 100°C and 350,000 lb./sq.in., the ice form of importance in freezing damage is ice I. This displays the anomalous behavior of expanding when going from liquid water to ice I, unlike the contraction that takes place upon formation of all the other forms of ice, and, in fact almost all other known chemical compounds and elements. The locus of

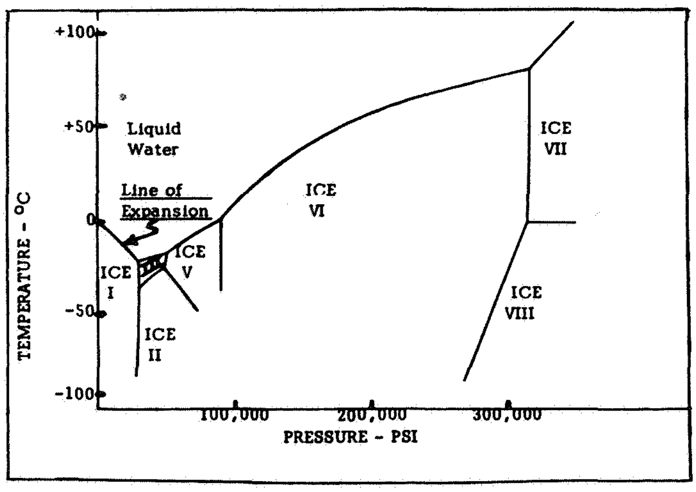

Figure 5. Phase diagram for water and the ices.

temperatures and pressures which could have burst our tubes is therefore the boundary of water and ice I, marked "line of expansion" on Figure 5.

The equilibrium temperatures and pressures for water and ice I have been plotted more precisely in Figure 6. It can be seen that at –9°C the freezing pressure of water was in equilibrium with the strength of our tubes. Therefore, at –9°C and 14,300 lb./sq.in., our tubes with sound wall ruptured. In an attempt to explain the extreme destruction of our tubes, rather than mere splitting, we calculated delta V for tube and ice at the failure point. The calculations show that while the tubes could increase internal volume by only 8% at the rupture pressure, the water freezing at –9°C would expand by 12% in going from liquid to ice I.

As a matter of interest we plotted the strength of a used HK-40 tube of 0.61-in. wall (a modern high-pressure reformer tube). (*6*) Applying the same method as above, it appears that the 0.61-in. wall tube should rupture at about –18°C and 26,000 lb./sq.in. Since the maximum pressure at which ice I can exist is about 30,100 lb./sq.in., a tube which could stand such a pressure without exceeding the elastic limit could not be damaged by freezing water.

It should be of interest to mention a few extraneous facts of interest the investigation turned up:

After our freeze-up we took an unruptured section of tube containing catalyst and ice to the shop, cut off a section, and forced out the circular block of ice containing catalyst. After thawing, the catalyst was tested and found

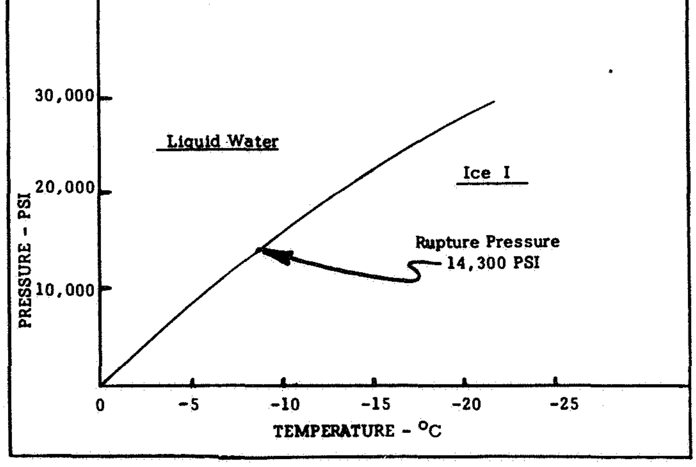

Figure 6. Freezing pressure of water.

in good condition.

In a standard Kellogg unit of vintage 1965, the secondary waste heat boiler on shutdown will contain residual water.

Finally, the following illustrates another means by which the higher ices can do damage while in the solid phase. If ice III, shown on Figure 2, is gradually depressurized to form ice I, the phase-change expansion from ice III to I can take place with explosive velocity. As an example, the Arctic explorer Barents' log states that on "the 20th hour of the 10th day of August in the year 1596" he anchored his vessel to a block of ice which was aground on the coast of Novaya Zemlya. Suddenly, and without any perceptible cause, the rock of ice burst asunder into hundreds of smaller pieces with a tremendous noise, and to the great terror of all the men on board.

We still have a great deal to learn about the behavior of the most common chemical compound on the earth's surface. #

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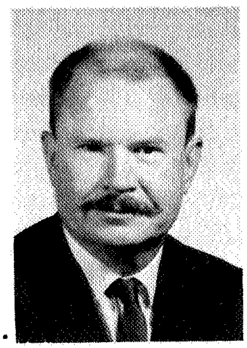

JOHNSON, E. R.

DISCUSSION

PAUL KRYSTOW, Exxon Corp.: I was just wondering since the tubes had microfissures that some of the water entered into the fissures and then froze and this in turn caused the failures?

JOHNSON: Since some of the tubes showed a different configuration in the fracturing, no doubt as Mr. Salot had pointed out, there were cracks present and these probably resulted in some of the failures being so different. Yes, this was probably the case. I hadn't thought of that but it probably explains the variation in how the tubes split when they ruptured.

Q. The primary reformer catalyst wasn't in bad shape. What about the secondary reformer catalyst after being hit by the water from the waste heat boiler?

JOHNSON: It appeared that the water in leaking through, as it came into the secondary reformer, got up to just about the bottom of the catalyst and the rate of flow of water was such that it generated steam rather than actually immersing the secondary catalyst. So in this respect we lucked out. Our luck wasn't all bad.