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Safety in ammonia plants

REMOVAL AND REPLACEMENT OF CATALYST IN AN AMMONIA CONVERTER

Internal damage to an ammonia converter required that the ammonia synthesis catalyst be removed and replaced. Here's how it was done, without incident, in 30 working hours.

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The following is a description of the essential steps taken in removing the catalyst. A continuous nitrogen purge of the ammonia converter was established to prevent air from contacting the catalyst when the vessel was opened. The bottom pressure vessel closure was removed and a catalyst removal hopper, Figure 3, was attached to the bottom flange. The purpose of the hopper was to provide a gate to control the rate of catalyst discharge, and to provide a means to deluge the catalyst with water before it contacted air.

A gasoline engine driven belt conveyor was installed under the hopper to remove the discharged catalyst to waiting dump trucks. A fire hose was arranged to play over the catalyst on the conveyor belt as it moved to the truck. A water supply was also attached to the catalyst removal hopper to assure that only wet catalyst contacted the air. Once all the catalyst removal apparatus was in place, the catalyst dumping commenced. After about six hours of dumping, 90% of the catalyst had been removed. The remaining 10% (about 250 cu. ft.) could not be induced to fall out of the converter without entering the vessel.

Several steps were taken to make the vessel safe for entry. All lines entering the vessel were either blinded or had spool pieces removed. The vessel was filled with demineralized water to absorb excess ammonia, and then the water was sewered. The vessel was again filled with demineralized water to a level just below the manway, to displace noxious vapors in the catalyst basket. The manways above the top catalyst bed were then opened and a breathable air mixture was blown into the space above the water in the basket. Telephone and radio apparatus was set up for communication between people inside and outside the vessel.

Once all the safety preparation was completed and the air mixture in the vessel was found breathable and free from explosive mixtures, the water level was then lowered to a point just below the top catalyst bed. As quickly as possible after lowering the water level, four men with shovels entered the top bed to scrape the catalyst into the drop-out chutes. This catalyst fell into the second bed. It was essential to scrape this catalyst off the beds while it was still wet, since it is pyrophoric when dry. A fire hose was kept in the vessel with the men so that the catalyst could be wet down with demineralized water as necessary. Since the catalyst support trays in the top three beds were covered with wire screen, the fire hose was not useful for moving the catalyst to the chutes. The catalyst would not slide on the screen.

When the top bed was free of catalyst, the manway into the second bed was opened. The water level was lowered below the second bed, and the catalyst was scraped out as was done in the top bed. This procedure was repeated for the third bed.

When the bottom bed was exposed, about 250 cu. ft. of catalyst, including that scraped from the upper beds, was found. Since the bottom of the basket is lined with cast refractory, it was possible to wash the catalyst out of the vessel using the fire hose and demineralized water. This catalyst was conveyed onto trucks for dumping as before.

On one occasion the fire water playing on the conveyor belt was turned off. Gases evolved from catalyst in the dump truck ignited shortly thereafter. Once the quench water flow to the belt was re-established, the fire went out.

The catalyst was hauled to a field, about 2 min. drive from the converter and spread in a layer about 6 in. deep. Spreading was accomplished from the tailgate of trucks, so that other spreading equipment was not needed. After spreading, the catalyst ignited and remained hot for several hours.

Description of damage

After the catalyst was removed, internal inspection revealed that the central riser pipe had been pushed upward 5 in. The upward movement of the pipe caused a symmetrical distortion of the bottom channel of the heat exchanger.

When the catalyst basket is empty and at ambient temperature, the central riser pipe is supposed to extend 3 in. into the socket of the gas collection manifold. There was a 2-in. gap between the socket and the end of the pipe, after the pipe moved up. The screen, which prevents small catalyst particles from passing between the riser and the socket, had broken and was pushed into the socket in one area. With the pipe out of the socket and a breach in the screen, the riser pipe and the collection manifold filled with catalyst and alumina balls. Catalyst particles were jammed into the ends of the heat exchanger tubes.

In order to repair the converter, it was first necessary to remove the catalyst from the center riser pipe and the collection header, and unplug the exchanger on top of the converter. The bulk of the catalyst in the riser pipe was washed out by playing a stream of high-pressure, demineralized water into the 2-in. gap between the riser and the socket.

After cutting off the top exchanger channel, it was found that the tube pluggage was all at the bottom ends of the tubes. The plugged tubes were easily cleared by dropping a small diameter rod through each tube.

In order to clean the collection header the screens on the vertical cylindrical members of the header were removed for access. With the aid of an industrial vacuum cleaner and a 2-in. hose, all catalyst particles of significant size were pulled out of the header.

Since it was impossible to obtain a new bottom exchanger channel in the time available, it was decided to reinforce the existing channel with gussets. By repairing the channel in this fashion, the riser pipe was left 5 in. short. This condition was corrected by adding a 5-in. spool piece just below the exchanger channel.

The screen covering the joint between the center pipe and the socket in the collection manifold was replaced with a larger, two-layer screen. The inner screen is four-mesh, of coarse wire, and is intended to provide structural support for the ten-mesh, outer screen. By virtue of its greater height, the new screen should be exposed to less internal stress, due to movement of the pipe, (relative to the socket) than was the case with the shorter, original screen.

There was also screen failure at the joints where the central riser pipe passed through each of the top three trays. This repair is similar to that made at the riser to socket joint in the collection manifold.

Before re-assembly of the converter, the expansion joint above the exchanger was also replaced. This joint had been dented, apparently through stretching. At the conclusion of these repairs preparations were made to replace the catalyst.

Catalyst replacement

Contract catalyst removal service was available to dump the old catalyst into nitrogen filled trucks so that the catalyst could be reused. There were three reasons why no attempt was made to salvage the catalyst.

1. In order to preserve the efficiency of the catalyst it would have been necessary to restore the catalyst to the same relative position in the same bed from which it was removed. The probability of accomplishing this goal was considered remote.

2. Since the catalyst was completely reduced, it could not be recharged in an oxygen containing atmosphere. The risk to workmen with breathing apparatus working in an inert atmosphere inside the converter was considered too high to warrant attempting to reload the catalyst.

3. Although it is theoretically possible to oxidize the catalyst before removal, the limited experience available indicates a high probability of converter and catalyst damage.

Since we were able to obtain only 25% of the replacement charge in the unreduced state on short notice, the balance was pre-reduced catalyst.

The following safety precautions were taken for charging the catalyst:

1. A compressed breathing air supply by hose was provided to the catalyst bed being loaded.

2. Each of the two men inside the converter were provided with a self-contained breathing apparatus for escape purposes.

3. A blower was installed at the top of the exchanger to assure that the flow of air was down through the catalyst. This precaution was taken to control dust and to remove the ammonia vapors present in the prereduced catalyst.

4. Sound powered telephones were provided for communication between the inside and outside of the vessel.

5. Thermocouples in all catalyst beds were monitored continuously to detect temperature rise.

6. The man-ways into the top catalyst vessel were constricted by air hoses, the catalyst hose, and rope ladder ties. As a result, it was necessary to provide a quick disconnect just inside the man-way for the 4-in. catalyst loading hose. Once the 4-in. hose was removed, exit from the vessel was easily accomplished.

7. By means of a quick connect coupling the catalyst could be deluged with nitrogen, if necessary, after the workmen had escaped.

8. Based on previous experience, it was elected not to use vibrating screens or other vibrating equipment on the pre-reduced catalyst. In one case, pre-reduced catalyst has burned as a result of excessive vibration.

Basically, the procedure for recharging the catalyst was to drop the catalyst to the bed in question through a 4-in. polyvinylchloride hose. To accomplish this a funnel was mounted about 3 ft. above the man-way into the vessel. The 4-in. hose was attached to the funnel and draped through the vessel to slow the fall of the catalyst.

The catalyst was poured from the drums, across a screen, into a concrete bucket. The concrete bucket was raised by crane and discharged, at controlled rate, into the funnel described above. Two clean concrete buckets were used to conserve time. At the bottom of the hose a workman distributed the catalyst by moving the end of the hose as necessary. Periodically, it was necessary to shorten the hose by cutting off the end.

As each bed was filled it was leveled and inspected before closing. The entire operation was completed without incident in thirty (30) working hours.

Probable cause of damage

Of the possible causes of the ammonia converter damage, three are considered more probable than others.

Differential thermal expansion — When the compressor tripped and the check valve allowed back-flow through the converter, cooled syn-gas was drawn back into the converter. It is possible that this gas cooled the central riser pipe so that it withdrew from the socket by thermal expansion. If, due to misalignment, the riser could not slide back into the socket on cooling, the riser would have been pushed upward to collapse the exchanger channel. If the screen around the riser to socket joint collapsed during the subsequent start-up, or had already failed, the riser then filled with catalyst.

Ratchet effect — The screens around the riser at each catalyst support tray and at the riser to socket joint were found to be damaged. A piece of the screen at the riser to socket joint was found in such a position that it would have been between the pipe and the socket had the pipe been in the socket. If this piece of screen and catalyst particles became wedged between the pipe and the socket or between the pipe and the catalyst trays, a ratchet effect may have resulted. During start-up or shutdown, temperature changes occur which would produce differential growth and movement of the riser pipe and the catalyst basket. On each shutdown or start-up the riser pipe could have been withdrawn slightly from the socket. Due to the presence of foreign material in the slip joints around the riser, it may have been impossible for the riser and catalyst basket to return to their original relative positions.

Once the riser was completely withdrawn from the socket, misalignment of the pipe and socket may have caused final deformation of the exchanger channel. On the subsequent start-up the screen over the riser to socket joint may have collapsed and allowed catalyst to fill the riser.

A combination of the thermal expansion mechanism and the rachet mechanism is also probable.

Jammed riser — It is possible that the riser was jammed during the original assembly so that the exchanger channel was already dented. Successive start-up and shutdown operations could then have caused weakening of the screen by flexing, due to differential growth between the riser and the basket. The back flow resulting from the above mentioned compressor trip could then have dislodged the weakened or broken screen. On the subsequent start-up the riser and gas collection manifold could have filled with catalyst.

There was no evidence available from operating records or from observation of the damage to support any particular mechanism of failure to the exclusion of others.

Preventive action taken

Several steps have been taken to prevent recurrence of this incident, regardless of mechanism.

1. The piping around the syn-gas compressor has been up-graded, in accordance with the latest Kellogg design, so that back-flow cannot occur unless the check valves at both the suction and discharge of the high pressure case should fail simultaneously.

2. As mentioned above, the design of the screen at slip joints around the riser was changed in an attempt to reduce stress of the screen wire due to differential growth of the basket and riser.

3. The start-up procedure has been modified to reduce the rate of temperature change in the ammonia converter during start-up. It is felt that, if the temperature change is gradual, more even heating and less differential growth will result.

CF Industries, Inc. has two 1,000 ton/day M.W. Kellogg anhydrous ammonia plants at Donaldsonville, La. The older of these two units was put on-stream in December, 1966, and the newer plant in March, 1969. In May, 1970, after about 3½ years of operation, it was found that internal damage had occurred in the ammonia converter of the older plant. In order to repair this damage, it was necessary to remove and replace the ammonia synthesis catalyst.

Analysis of operating data observation of the damaged equipment did not reveal the exact mechanism by which the ammonia converter damage occurred. Since manifestation of the damage occurred following a trip of the syn-gas compressor, accompanied by back-flow in the syn-loop, it is believed that part of the damage is related to the unusual upset conditions. Measures have been taken in the repair and in the operation of the converter to counter recurrence of this damage by all the probable failure mechanisms, except damage during fabrication or construction.

Note that the following comments on the events preceeding failure are made with reference to Figure 1.

Events preceding failure

During the first week of May, 1970, the topping turbine driver for the syn-gas compressor was replaced with a new turbine of shortened shaft design. When the plant was started again compressor operation was smooth, except for a relatively high vibration (0.74 mils) on the syn-gas compressor governor. Since this vibration amplitude was not high enough to indicate serious damage to governor parts, the machine was not shut down again to replace the governor bearings.

During the early morning hours of May 11, the syn-gas compressor overspeed trip came unlatched, and shut the compressor down. Since the machine did not overspeed, it was reasoned that vibration due to the bad ball bearing in the governor had caused the trip latch to disengage.

After the machine tripped, the relief valve at the suction of the high pressure case of the syn-gas compressor lifted and vented for an unusually long time. Subsequent investigation revealed that the check valve in the syn-gas compressor discharge was broken and had failed to close. With the syn-gas compressor down and the discharge check open, the contents of the synthesis loop was vented through the relief valve at the second case suction until the discharge valve was closed.

After the bad governor bearings and discharge check valve were repaired, an attempt to re-start the plant was made. While attempting to put the syn-gas compressor online, it was discovered that the 1,500 lb./sq. in. gauge steam gimbel valve by-passing the topping turbine could not be closed completely. It was necessary to shutdown again to repair the by-pass valve. After the steam by-pass valve was repaired, the plant was started again. To all outward appearances, the start-up appeared normal through the lighting of the ammonia converter, using the start-up heater. When it was attempted to increase the flow to the ammonia converter, the converter pressure drop increased to about 160 lb./sq. in. gauge.

At this point it was suspected that serious damage had occurred inside the ammonia converter. It was also possible that the unusual flow conditions during the compressor trip had caused collapse of the expansion joint in the in-out exchanger atop the ammonia converter, or had caused the tube pluggage in the exchanger. Inspection revealed that the exchanger tubes were plugged from the bottom.

After rodding out the exchanger tubes, it was decided to try re-starting the plant without further investigation. Since this procedure had been successful under similar circumstances for another Kellogg plant, and because further investigation entailed removal of the synthesis catalyst, it was hoped that unplugging the tubes would permit operation of the plant, at least at part rate.

As it turned out, this procedure was unsuccessful. Upon re-starting the plant, the pressure drop in the ammonia converter was about 120 lb./sq. in. gauge with only about 30% of normal flow. While the flow was held constant, the pressure drop in the converter continued to increase. There was no alternative but to remove the catalyst for internal inspection of the synthesis converter.

In order to cool the catalyst and converter as quickly as possible, for catalyst removal, several unusual steps were taken. The pressure in the synthesis loop was lowered to 500 lb./sq. in. gauge and the hydrogen to nitrogen ratio was increased to kill the ammonia synthesis reaction. Maximum quench was applied to the catalyst beds to reduce feed temperature. By continuing to circulate through the converter, the catalyst beds were cooled from 900° F to about 250° F in about four hours. Further cooling to about 100° F was accomplished using a nitrogen purge. Quench gas could not be cooled below 250° F, due to process limitations.

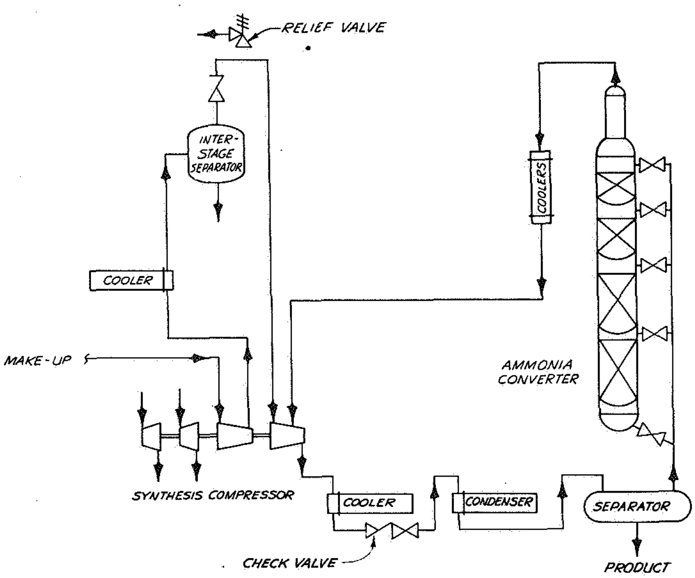


Figure 1. Simplified flow diagram of synthesis loop.

Description of converter

The ammonia converter, Figure 2, is a four-bed, quench-cooled type reactor, designed by M. W. Kellog. The catalyst basket cannot be removed from the converter without cutting the pressure shell. The top three catalyst beds are supported by perforated trays at intermediate levels in the basket. The bottom catalyst bed rests on a bed of alumina balls, which, in turn, is supported by the bottom of the basket.

A gas collection manifold is covered by the alumina balls, which support the bottom bed of catalyst. The collection manifold is designed so that gas is collected through screened openings near the wall of the basket, and then is transmitted to a centrally located socket by three pipes.

A central riser pipe slides inside the socket in the collection manifold and is attached to the heat exchanger at the top of the converter. At the locations where the central riser enters the socket and where it passes through the catalyst support trays, stainless steel screen barriers prevent the catalyst from entering the socket or passing from bed to bed.

Manholes in the pressure shell and in the basket permit entry to the top catalyst bed. Manholes in the catalyst support trays for each of the top three beds permit entry into

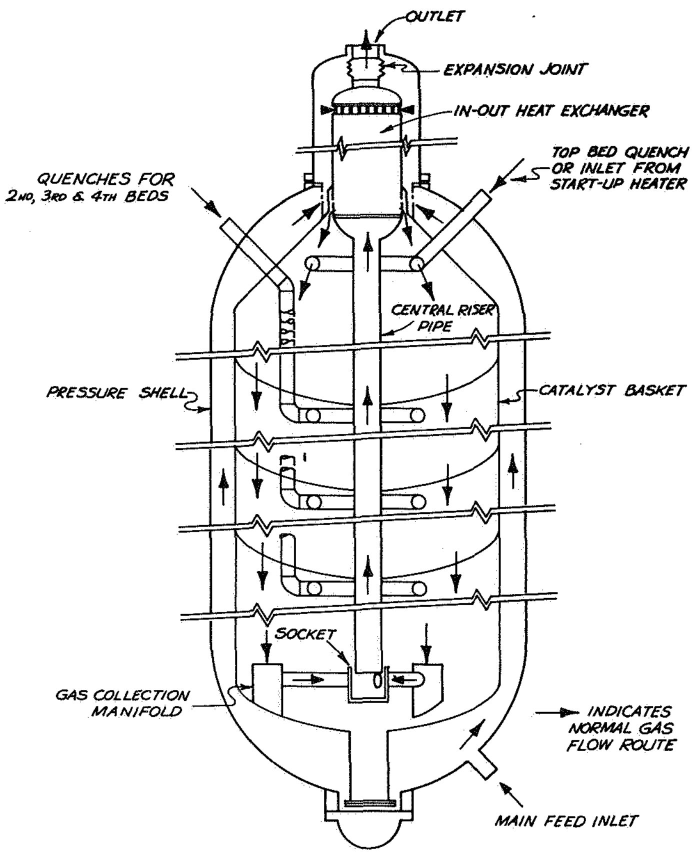


Figure 2. Schematic diagram of ammonia converter.

the beds below. Not shown in Figure 2 are the catalyst drop-out tubes. Each of the top three beds has several tubes which extend from the catalyst support tray into the catalyst bed on the tray below. With this arrangement, the catalyst in one bed can fall to the bed below when the ends of the drop-out tubes are exposed.

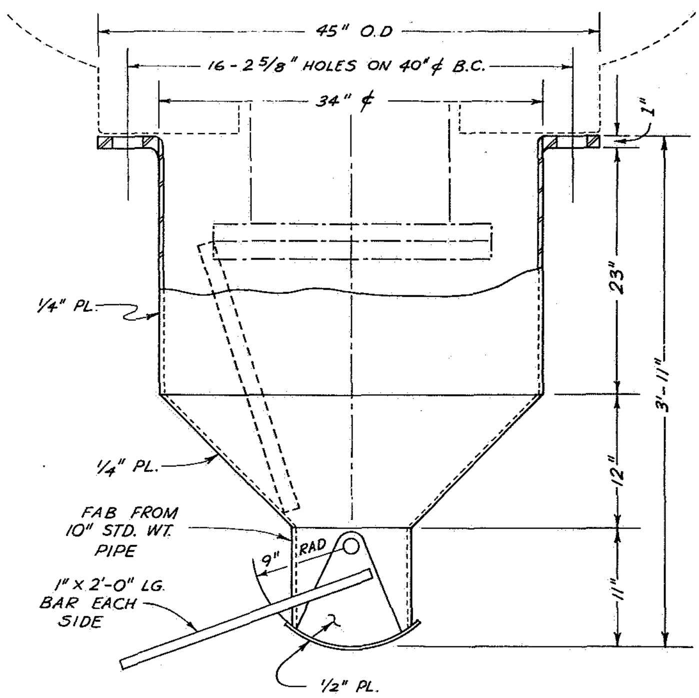


Figure 3. Catalyst removal hopper.

Catalyst removal

Plans to remove the catalyst were quickly developed with the help of Gulf Chemical Co., which was planning to remove catalyst during their turnaround. The motion pictures of synthesis catalyst removal shown by I.C.I. during the 1969 Ammonia Safety Symposium were of great benefit in making plans for catalyst removal.

DISCUSSION

SAMUEL STRELZOFF, Consultant: You say that a recently designed ammonia synthesis converter has a pressure drop of 60 pounds through the converter. Is this through the converter alone or plus the piping of the synthesis loop?

DELONG: I believe it is through the converter.

STRELZOFF: Let me rephrase the question. If the pressure drop has been increased to 120 pounds, should I understand that this increase has taken place gradually? Or is that suddenly?

DELONG: As soon as we started to increase the flow through the converter after we got the temperature up, the pressure drop came right on up. Before, when you're going through the startup heater, your flow is at such a low rate that you don't see this pressure drop. So it wasn't something that had come on over a period of time; it's something that happened quickly and the next time we tried to come up, it was there.

STRELZOFF: Now after you have removed the catalyst, have you reanalyzed its screening analysis? Did you see any - let's say destruction or mechanical destruction of catalyst that might have led to the increasing pressure drop?

DELONG: No; the catalyst was all in excellent shape, and if we could've felt that we could've re-used it any way, we could've saved ourselves considerable money, but we felt the risks of re-using it were too great.

Q. How long did it take you to remove the catalyst from the vessel?

DELONG: The pipe extends down into that bottom collection header, or is supposed to can extend down in about 3 inches.

MCFARLAND: Yes but does it have an outer tube around it?

DELONG: No.

MCFARLAND: It isn't within a sheath tube?

DELONG: No. It just sits down in there.

MCFARLAND: I see.

DELONG: Screens are wrapped around it to keep the catalyst out. This is the expansion joint from the heat exchanger down. Of course you have a regular expansion joint up top, going out the top.

DELONG: The flooding of the vessel and the removal of the rest of the catalyst took about four hours.

Q. In what condition was the metallic material within the converter. Did you find the stainless steel catalyst support grids in good general condition, Were they still ductile, weldable, etc.?

DELONG: Everything looked good inside with the exception, of course, of the screens and where it dented the head of the exchanger.

IAN MCFARLAND, ICI America: If this cube running up the center is uncased, it's lying in the catalyst. Am I correct? We had a pilot-operated safety valve on the high pressure loop and the bushing where the pilot was attached to the body of the valve blew out, and caused the loop to depressure very suddenly. This caused an expansion bellows between the two passes of the heat exchanger to rupture due to the high differential pressure caused by unequal depressurization. This experience would lend some credibility to the case for having a pressure differential due to the sudden high flow.

Q. How long was it from diagnosing some of the trouble was it before you came back on stream again after the repair?

MCFARLAND: Then can I suggest a possible fourth solution? This historically goes back some years, and I think it was our friends in African Explosives and Chemical Industries who had a problem which was seemingly inexplicable. Theirs was a completely different type of converter. It was a tube cooled or TVA type converter, in which we had tubes within the catalyst bed, and support tubes in between the top and the bottom. They had trouble for a period, which I don't think was ever really cured, evidenced by the support tubes pushing clean out of the bottom tube sheet. Now the only reasonable answer we could find for this at the time was a possibility of catalyst arching within the beds. The catalyst arches across holding the tube, and when things try to move, it will not allow it and the tube just pulls out. This was sufficiently strong in the case of these converters as I recollect, where they had tubes probably an inch and a half diameter, which I believe were bolted at the bottom and welded, and they were just pushed clean out.

DELONG: Well, you're suggesting that maybe just the action of the catalyst against this center tube may have restricted it and then when you changed temperature it punched itself up. I think this might be true with a combination of a lot of these things. It could be.

Q. It would seem that the first thing that you looked at here to explain the cause would be the fact that the thin gas compressor tripped. And you had to reverse flow, and then you had a period of venting. Did you eliminate the possibility that the change in reversal of pressure, and forces due to gas pressure, deformed this tube sheath?

DELONG: The checkvalve failed. As many of you know sometimes they're not too reliable. We hope that what we've done in working on this checkvalve will keep this from happening. The thing that we are now doing is upgrading the innerstage piping so that we won't have this venting. If it does, we won't have backflow.

Q. Is it possible that the pressure itself did the damage you're striving to explain?

BRUCE BERKLOW, CF Industries: We looked at the possibility of pressure collapsing this head or imploding this head, and it looks remote, because we're backflowing through the system, I've forgotten exactly what the diameter of the relief valve was, but I believe it's a 6 inch relief valve, and the pipe is about 14 ID pipe. So the volume of the system downstream from the point where the head collapsed is very small in relationship to the volume of the other parts, so I think it's unfeasible that we could've got enough flow through a 6 inch vent to cause a big pressure differential through this 14 inch pipe. So I don't believe that happened.

Q. You made a specific point that you used demineralized water for spraying upon the catalyst and also filling the converter. Was this a matter that that's the water that was available? Or did you have a particular reason for using demineralized water?

DELONG: Only demineralized water when we were filling the catalyst to keep any chloride contaminates or anything else from getting into the vessel. The firehoses that you put on to quench the catalyst was just regular firewater or cooling tower water.

PETER AMBROSE, Imperial Oil: We had a case which is somewhat similar in our Methanol Plant, a 100 ton/day Unit with an external heat exchanger in the reactor loop.

DELONG: Well actually we went ahead and took a shutdown and replaced all the internals in the transfer line at the same time, which ended up being the job that kept us down longest. so basically, though, even with all the ups and downs and fooling around, we had got the catalyst in and out and done everything, and were ready on that phase in about 3 weeks. But other things kept us down a little longer.

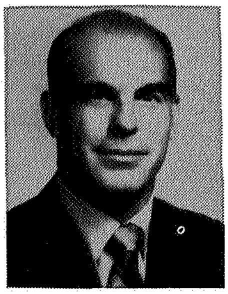
Q. Can you give us any more details on the checkvalve which failed?

DELONG: I don't have all the fine points regarding the valve. As I remember, it's a spring-actuated or spring-started valve. The spring was supposed to start the valve shut, and then the flow coming back is to slam the valve back into its seat. The spring was completely gone. The only change we made is to check the metallurgy and try to improve the material. Of course, we'll inspect this valve a little more carefully, probably, than we have in the past and inspect it at every shutdown.

Q. You mentioned that you took the shutdown as an opportunity to replace the transfer line. Why?

DELONG: About 2 years ago we had a failure in our transfer line where this is a refractory line, and this is the old refractory, and we had decided some time ago that we were going to go ahead and put in a new liner which is the latest design. So we just took the opportunity - we were going to do it when we shut down - oh, about a month. We thought we were going to stay on til about July, until after the season was over, so we just ended up doing it the same time, since we were going to have to be down for 2 to 3 weeks. We thought we'd jam everything in at once.

There was no problem with the line at that time, although when we inspected the line, we did find quite a bit of voiding of insulation in there, and we think that we replaced it at a good opportune time. I think most people that have had this old style line have replaced it with the style insulation, and as far as I know, nobody's had any trouble with the new style.



DeLong