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Replacing a 1,000-Ton/Day Ammonia Converter

Failure found due to using non-reduced catalyst; and circumstances in specific case showed replacement a better approach than repairs of the unit

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IMC Chemical Group, Inc., formerly Commercial Solvents Corp., operates a 1000-ton/day Kellogg ammonia plant in Sterlington, La.

Put on stream in October, 1967, it was one of the six plants of this type in the world to utilize the "Slim Jim" ammonia converter. These converters are characterized by their smaller inside diameter and the higher pressure in the catalyst basket rather than the annulus.

IMC planned a 21-day turnaround for August, 1975, with the following major jobs to be performed:

1. Re-tube primary reformer.
2. Replace transfer line.
3. Re-tube auxiliary boiler.
4. Change all catalyst.
5. Change our surface condenser.
6. Replace metal skin on one reformer wall.

This was to be the first time that the secondary reformer, the methanator, and the ammonia synthesis catalyst had been changed since initial start-up of the unit.

During a normal shutdown, no attempt is made to cool the ammonia converter. However, since the plan was to change the catalyst, we were going to circulate gas longer than usual to cool the converter. During the shutdown, the synthesis gas and recycle compressor tripped out, and we were unable to cool beyond 400-500°F.

As soon as the loop was depressured and various blinds installed, a nitrogen purge was started, both to clear the converter of gases and to aid in cooling down. The cool-down and purge procedure took about four days. At this time, the top bed was about 120°F, the other three being around 100°F.

Before the shutdown, a drop-out chute had been fabricated to fit the converter bottom manhead. Hose connections were provided to wet down the catalyst as it dropped from the converter.

At shutdown, the chute was installed and the catalyst dropout nozzle opened. The alumina balls came out quite freely, but very litle catalyst. The chute was removed, and several attempts made to start the catalyst flowing. Vibration was attempted with no success. A hydroblast unit was brought in and tried with no success.

It was decided then not to make any further attempt at unloading from the bottom. Preparations were made to remove the top manhead and unload from the top, using vacuum equipment. A portable, 50-ton, air-conditioning unit was connected to the bottom manhead to provide cool air up the annulus.

Trouble started at unloading with no nitrogen recirculation

No nitrogen recirculation system was available, but we decided to try unloading anyway. A strong nitrogen purge was maintained from the bottom to the top and out the manhead. Men entered the vessel under life support to begin vacuuming the catalyst. Within five minutes, the catalyst around the suction hose had turned cherry red and the operation was terminated.

It was not possible to get a nitrogen circulation system on the job-site in time to fit the schedule. It was decided to fill the catalyst basket with water and make another attempt at vacuuming. Demineralized water was put into the bottom of the basket. After a short period of time, water was seen coming down the annulus. It was at this time that we first knew we had a basket leak. Based on the estimated time elapsed from start of filling, we felt sure that the leaks were in the third and fourth beds.

As soon as the water level reached the top of the catalyst in the top bed, it was shut off as we did not want to get any solids on the basket insulation. There was so much ammonia and hydrogen escaping from the catalyst that the water appeared to be boiling. Up until this time there had been no explosive mixture escaping. Evidently the water was to some extent forcing hydrogen from the catalyst pores, and oxidizing the iron catalyst. The basket was left full for several hours and then allowed to drain. Nitrogen was kept on the vessel at all times to prevent air from contacting the reduced catalyst.

The basket was filled and drained four times with the same result: hydrogen and ammonia concentrations were too high for personnel to safely enter the vessel. At this time it was decided to steam/air oxidize the catalyst. A steam line (250-lb./sq.in.) was run to the start-up heater line. Steaming was begun, and when all beds reached 300-350°F a small flow of air was started. The first-bed temperature went up to 500°F and then began falling.

We thought we were going to be successful. As would be expected, the second-bed temperature began to rise at the same time the first dropped. During the night, the third and fourth beds went to 1,200°F. The air was cut out, and the beds cooled to 500°F with steam. Water was added to finish the cool-down.

Vacuum unloading was again started. The catalyst in the first bed was stuck together but easy to break up. There was quite a bit of fusion in the second bed. The third and fourth beds were fairly easy to unload. The first cracks were noted in the third bed.

Ultrasonic inspection of the cracked areas in the fourth bed was begun. The bottom (5-ft.) level in the fourth bed showed 95% cracks on the circumference, with penetration varying to about 50% of wall thickness and originating from the outer wall. In the fourth bed at the 12-ft. level the cracks were about 85% of the circumference.

Cracks were apparent at regular intervals through the first bed, where penetration was about 1/16-in. from the outer wall. Crack elevations appeared to coincide with insulation shroud supports welded at 4-ft. intervals on the outside basket wall. At least one vertical scan was run on each bed, but no other cracks were found.

To repair by only patching cracks would not give continued structural integrity. The chloride stress corrosion cracking would continue. An entire basket lining similar to one made earlier in Iran should be structurally sound if other internals were not damaged. The rebuilding of the basket outside the pressure shell would be very difficult to maintain critical alignment and elevations to permit reinsertion.

At this time there were four possible choices open to us. 1) repair the basket in place; 2) remove basket and repair in shop; 3) remove the top of converter and replace basket with a new one, if available; and 4) replace entire converter, if available. Pullman Kellogg were involved in all discussions and inspections, and they indicated that Nos. 1 and/or 4 were their preferences. We tended to agree.

Complete replacement found elsewhere

Enough 304 stainless steel, ⅜-in. plate was found to line the entire converter basker. This was to be sheared into 18-in. strips for insertion through the top and bottom manheads. At this time, we learned of a 1,500-ton/day, 3,000-lb./sq.in. converter which was in New Orleans that could possibly be purchased. Pullman Kellogg was asked to see if this converter could be adapted to our loop. This was confirmed, and negotiations began toward the purchase. Work was stopped and preparations for the removal of the damaged converter were begun.

The only crane that could lift the nwew 535-ton converter in New Orleans was damaged during a test lift. The only other crane nearby was at CBIN in Memphis, Tenn. Arrangements were made to have a tugboat move the hopper barge from New Orleans to Memphis where the converter would be loaded onto two special flatcars for rail transportation to Sterlington.

The converter arrived on site, and erection and piping work was started. The interchanger for the new converter was not completed, so the old interchanger had to be modified to fit. Loading of the converter was begun about 20 days after delivery to the site.

During the loading of most of the bottom bed with pre-reduced catalyst, only canister-type breathing protection was employed by the workmen. It soon became evident that this would not be sufficient because there was too much ammonia in the vessel. The remainder of the system was loaded using a life-support system.

The next time we have to load an ammonia converter, we will definitely use pre-reduced catalyst and load using a life-support system for the entire vessel. It was necessary to keep the catalyst drums out of direct sunlight and to keep them dry.

We have arrived at three possible sources of chloride contamination in our vessel: hydrostatic test water, basket insulation, or catalyst. The first two sources have received the most attention in the past. We found that the test water used in our vessel contained 9 ppm. chlorides.

At that time, we decided to take a look at the catalyst itself. Two different methods by two different laboratories were used to determine the chloride concentration of the catalyst. One method used water to leach the chlorides, and the other was an X-ray fluorescent technique. Both indicated chlorides present in the 80-100 ppm. range. The data are not conclusive, but do confirm that chlorides are present in an undesirable quantity. Also, the result does not mean that the trouble arises during the reduction step. However, water and chlorides are present at elevated temperatures during this period.

A "mini-survey" of five other converters of the "Slim-Jim" type and one C. F. Braun unit was made. Of the six, four failed and two did not. The four that failed were all started up using non-reduced catalyst; the two that survived both used pre-reduced catalyst.

Here again, these data would probably not be considered conclusive by a true statistician. However, IMC will never load another converter with anything except pre-reduced catalyst. #

DISCUSSION

JAN BLANKEN, UKF-Holland: We operate two converters on Slim Jim, one Big Bertha, both with a higher pressure inside the basket than outside the basket. After we heard from your experience, we checked the temperature rise of the gas over the annular space and found it to be normal.

Did you check your temperature over the annualar space?

PATTERSON: We did a lot of after-the-fact checking and we noticed that since almost the initial startup of the plant, the returned gas, or recycled gas, through the annulus had been running anywhere from 20 to 50 degrees higher than design.

BLANKEN: Do I rightly remember that a normal temperature rise is 6-7°C.

PATTERSON: Right. It should have been running 107°F at the outlet, and it was running over the past years anywhere from 120-160. Now this was all after-the-fact. It had been noted before that it was higher, but we didn't put the emphasis on it at that time.

BLANKEN: It could indicate that with 7°C rise we can go on as usual, if I am an optimist.

PATTERSON: If you only got the 7 degree temperature rise, I'd be very optimistic.

BILL STAMPE, N-Ren Corp., St. Paul Ammonia Product Div.: I'd like to ask a question possibly of the heater manufacturer. You had something in your talk about replacing a wall on a reformer. We have a Lummus reformer that's about 12 years old, and we notice on surfaces that are not adjacent to any of the burners, that we're getting extensive cracking in and near the weld areas on the plates. I think we might face a massive rebuilding lest we have a whole wall fall down on us. Is this a common occurrence that we've never talked about before in these meetings?

PATTERSON: I don't know how common it is. We noticed our reformer wall several years ago with small cracks appearing and we assumed that it was the startup and shutdown and we got a carbon black plant fairly close to ours that sometimes makes some burns in. We felt like it was just a fatigue crack, and when we did do this repair work we sent off the samples for metallurgical analysis. I'm not exactly sure, but I think what they found was that it was a poor grade of metal for this service to start with. As far as I know ours is the only one in which this has occurred.

STAMPE: I might add that our furnace is a side-fired furnace, and in all the areas where we have the burners, we have no cracking whatsoever, but on the ends of the furnace and the convection section up above, the cracking is quite extensive. We've had to put braces on the outside to weld it, to hold everything together lest we lose part of the angle irons which in turn hold the brickwork up. And we use a non-desulfurized fuel gas supply, and I've speculated that it's either some type of a sulfur attack in the weld zone area, or maybe the furnace is over-insulated, and we have condensation of flue gas behind the brickwork.

In either event, if a wall were to fall off the furnace while you are running, it's not a desirable thing. We would have to rebrick it during the turnaround and it is not a very short time job.

PATTERSON: Well none of our cracks were in a structurally critical place really. They were all in the plate. The only thing they were holding really was the clips at the brick.

The never looked like they would fail as such.

DICK DAZE, Heat Research: As far as brick falling off, I think our total experience has been very good. There have been some problems in the auxiliary boiler due to overfiring and pushing the capacity of the plant beyond normal limits resulting in possible acoustical vibrations (pulsing flames) which might tend to loosen some of the insulation relative to the tieback clips. But in general I think the performance has been very good.

And of course, new refractories, of the ceramic fiber type are being installed on the arch in newer units. This insulating system eliminates the use of brick.

PHIL RUZISKA, Exxon Chemical USA: I notice you mentioned four of the ammonia converters which experienced failures were of so-called Slim Jim design. Is there anything about that design which would lead you to conclude that it would be more susceptible to problems, either intrinsically, or in the presence of a catalyst containing chlorides?

PATTERSON: Yes, the pressure basket and the gas in the normal flow pattern has got to flow from the basket out through the annulus, so during the reduction step when you are forming water, you are bringing it right out into the outside of the basket and cooling it off. And this would be where we would think you would start picking it up as evidenced by the corrosion from the outside in.

JAN BLANKEN, UKF-Holland: Just for your information, both converters we operate were filled with not prereduced catalyst except the top layer which was prereduced which means that we have had water during reduction, but we do not seem to have a problem.