

Catalyst Fusion

In an effort to prevent future catalyst deterioration, care is taken that the top and bottom manyways of the secondary reformer are not open at the same time.

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The design of the secondary reformer in a 1,000 ton/day ammonia plant operated by Hill Chemicals is typical of such units. The hot reformed gas enters from a water jacket transfer line, passes down through an annular space around the air line, and then flows past the air nozzle where it mixes with the incoming air stream. The combined stream passes through the catalyst bed and it's support to waste heat boilers located adjacent to the secondary reformer. The vessel has a top flanged head that contains the inlet air line and mixer nozzle, and a bottom insulated flanged head. Both heads are located on the vertical center line. The reformer catalyst volume was 75% filled with 3/4 in. x 3/4 in. nickel catalyst rings, with the remaining 25% being 1 in. x 0.6 in. chromia catalyst rings on top.

This reactor was started up in October 1968, and has been down six times since. It has been entered twice; once after three months operation following oxidation with steam and air, and once after cooling with nitrogen without oxidation. The pressure drop on this vessel increased as time went on, reaching about 35 lb./sq. in. at the end of the run with rates at 115% of design. As the normal pressure drop is about 7- to 10 lb./sq. in., this was disturbing. The activity of the catalyst was within limits even while operating at above normal rates.

Examination of the catalyst

In October 1970, the plant was shut down, the secondary reformer oxidized with steam and air, and then cooled. Upon entering the vessel we found the catalyst level had dropped about 20 in. in 1 yr. of operation. The high temperature chromia catalyst was removed without difficulty and found in good condition. The upper third of the nickel catalyst was found to be slightly fused with the rings cemented together wherever they touched as seen in Figure 1. This bond could easily be broken, but the noticeable condition was the size reduction. As best we can measure, the 3/4 in. x 3/4 in. x 3/8 in. rings had shrunk to 5/8 in. x 5/16 in. rings, a linear reduction of 17% and a volume reduction of 40%. For the most part, these rings were regular in shape and dark gray in color. About 10% of them were deformed. The size contrast can be noticed by



Figure 1. Slightly fused, shrunken catalyst taken from the upper one-third of the bed.

comparing them with the unused catalyst ring, Figure 1, and with a number of new catalyst rings, Figure 2.

After about one-third of the catalyst had been removed, we noticed that the catalyst rings were about 10% larger than the rings at the top, and about 50% deformed. These rings were stuck or fused more solidly than the top ones. This material, Figure 3, had a light coating of a fine, reddish material which was identified as an aluminum compound.

By the time we reached the bottom fourth of the nickel catalyst bed, the rings had become severely deformed, and were fused into a continuous mass as, shown in Figure 4. Although deformed as if in a plastic state, the rings were about the original size with little or no shrinkage. This material was much softer than the top rings. Although the rings were pretty well collapsed, there are some voids visible through which the gas passed.

Figure 5 shows that the bottom 2 ft. of catalyst was in deplorable condition. Although the rings were full sized, they were completely collapsed, with no visible free areas or voids through which the gas could have passed. As can be seen, this solid mass adhered to the 1 in. dia. alumina balls that made up the catalyst support. The rings appeared to

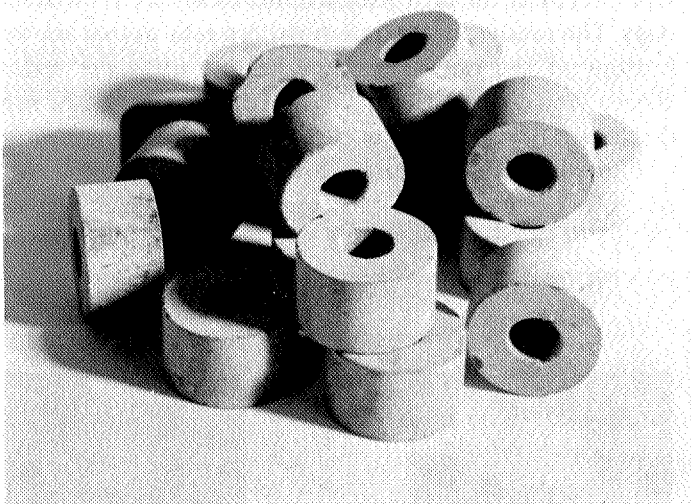


Figure 2. New, unused catalyst.

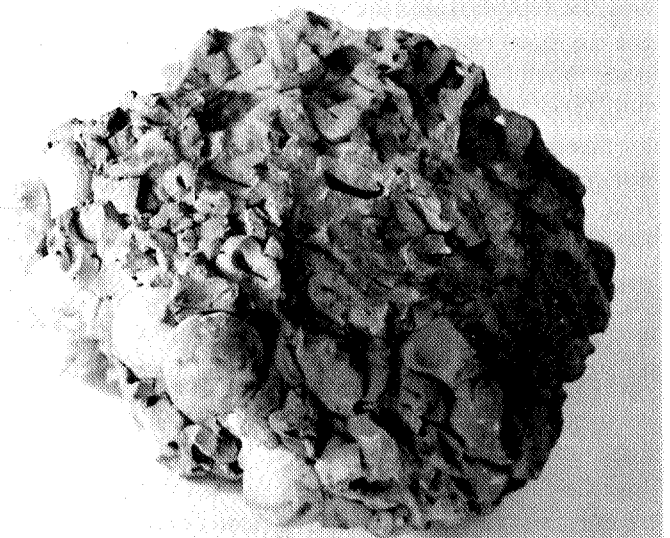


Figure 5. Fused, collapsed catalyst taken from the bottom 2 ft. of the bed.

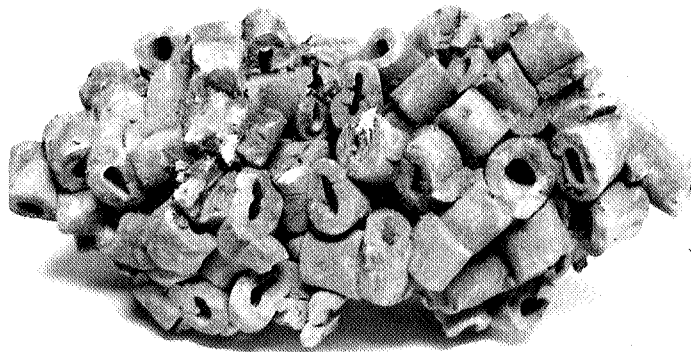


Figure 3. Fused catalyst with a fine, reddish coating.



Figure 4. Deformed catalyst taken from the lower one-fourth of the bed.

have been deformed while in a plastic state. The reason for the pressure drop was easily understood. As was the case with the previous material, this bottom catalyst was very soft and was removed by cutting up rather than breaking up. Although the catalyst was snug against the refractory lined wall of the reactor, it was easily removed, and no damage of the wall was observed. The alumina ball bed support was also in good condition.

Cause of the problem

The evidence easily displays the difficulty, but the cause is not so easy to determine. The fused, hard, shrunken catalyst in the upper part of the bed is the usually expected condition. The full size, soft, collapsed catalyst at the bottom, that had obviously been in a plastic state, is not often seen in this service. Due to the full size of the catalyst, this condition would be the result of a, single event. The catalyst manufacturer predicts that this material would need to reach 2600°F to become plastic unless there is an emaciating material present, forming an eutectic. No unusual material was found. Normally the bottom of the secondary reformer would be expected to be the coolest part of this reactor, which would rule out high temperature under normal conditions. The feed gas for this unit is about 10% nitrogen, which would reduce the air requirement, yielding a lower top temperature, but possibly a higher bottom temperature due to less reforming. If the conditions were not uniform over the reactor area, channelling could be suspected. Another factor is the gradual change from the top to bottom; the rings steadily increase in size along with the amount of deformation, and the relative hardness decreases as does the open area.

Two theories have been proposed as to the cause. The first one is that while down and the top and bottom heads were off, a slight updraft of air set up a localized oxidation of the unreduced portions of catalyst at the bottom. Due to the low flow, the heat was not removed from the catalyst,

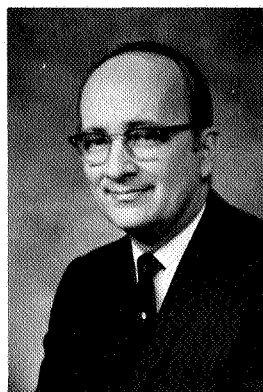
and the temperature reached levels in excess of 2,000°F. If the air flow had been higher, the temperature level would have been reduced and the increase in temperature indicated on the thermocouples in the wall. Due to this localized reaction, it would not have been detected or noticed. The other theory is that some time the natural gas flow to the reformer would have been shut off or greatly reduced while the air flow continued at a high rate consuming the combustibles and starting a high temperature oxidation of the catalyst.

While these theories in some ways answer the question, each only answers it partly. The pattern profile of the catalyst favors the second theory, but operational data disputes this theory on several points. First, the trip sequence of the unit automatically shuts the air flow off before the methane reaches a low level. In all of our shutdowns, the air was tripped first. Second, there are recorder-mounted thermocouples located in the piping leaving this reactor, and the highest temperature ever recorded in any circumstance has been 1,900°F.

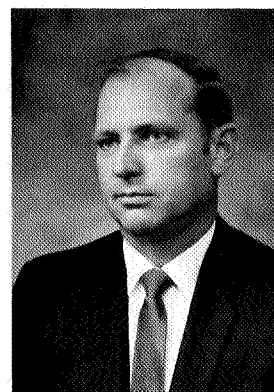
The updraft theory has the circumstance of the shutdown activities to support its point. The top and bottom head have been off simultaneously while down; once following oxidation with steam and air, and once

while reduced. In each instance, the heads were off several days. The catalyst deformation pattern tells us that the very bottom of the reactor was the hottest while the updraft theory would predict that the hottest zone would be some distance above the bottom.

Our preventive measures have been to thoroughly check our trip mechanism at each opportunity, which we have always done, and to establish a procedure that the top and bottom manways will not be open at the same time. #



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