Corrosion in a Naphtha Reformer

A satisfactory solution reported in this case history of an approach to some unusual failures in an ammonia plant in India, now returned to operation

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Some unusual corrosion problems in a side-fired naphtha reformer furnace included large-scale failures on the catalyst tube top stub-end weld and the inlet pigtail stub-end weld. And, the outlet pigtails had developed high creep in three years of operation. Two isolated cracks were also detected in the HK-40 collector system.

The reformer is in a 750-ton/day ammonia plant operated by Madras Fertilizers Ltd., in Madras, India. It is of Haldor Topsoe design, and was built by Chemical Construction Co., with completion in May, 1971. During the July, 1974, turnaround the series of failures were found.

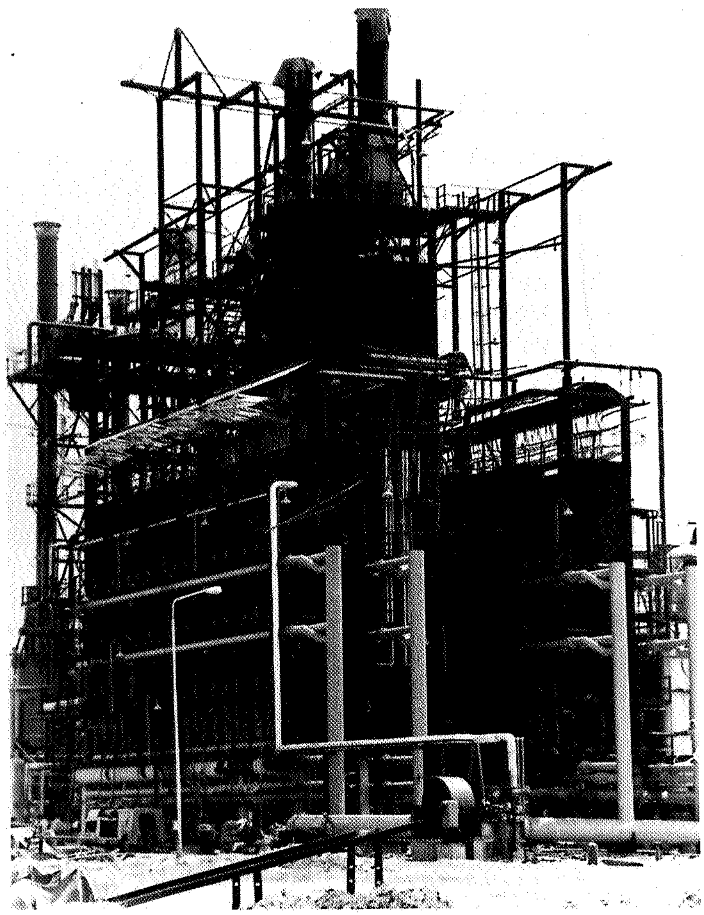


Figure 1. Rear view of the primary reformer, showing inlet pigtails at top and partially insulated outlet pigtails at bottom. One of the two forced-draft fans is in foreground. Induced-draft fans are at the top.

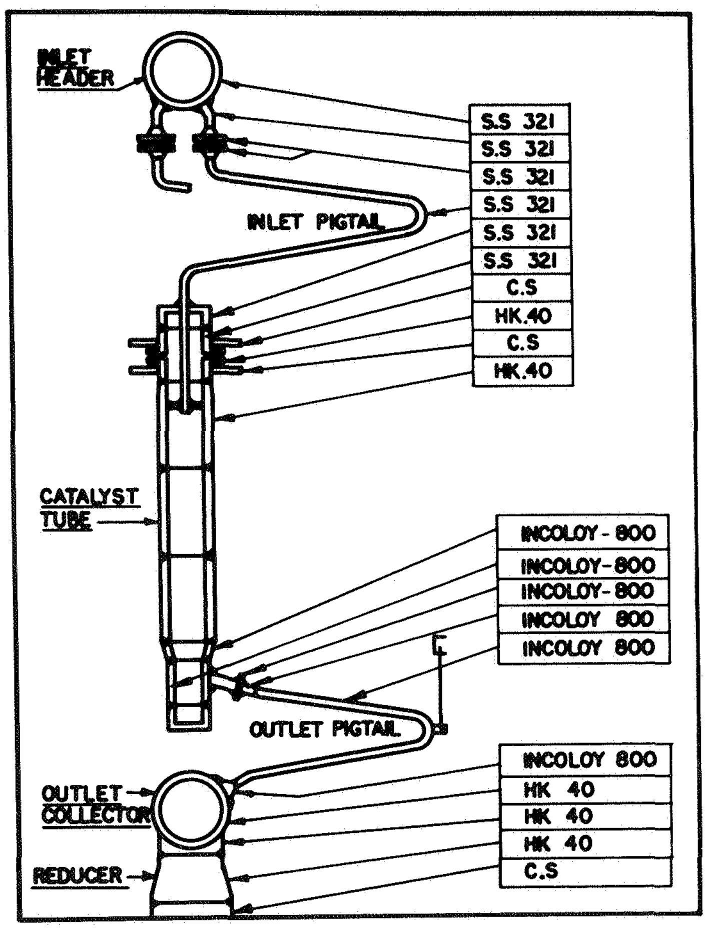


Figure 2. Primary reformer materials of construction chart.

They were widespread and necessitated major repairs to catalyst tubes, pigtails, and the collector.

The reformer has been operating satisfactorily at 92 to 94% load since the repair work was finished.

The primary reformer has two radiant furnaces connected to a convection section in the middle. Each furnace has 120 tubes arranged in two staggered rows. The furnaces are side-fired with liquid naphtha at several levels, with 15 burners at each level permitting close modulation of the heat input. A photograph is shown in Figure 1.

The catalyst tube arrangement and materials of construction are shown in Figure 2. The top of the tube is welded to a schedule 80 HK-40 stub end with a loose carbon steel flange which is bolted to a carbon steel loose flange of the inlet pigtail. The bottom of the catalyst tube is welded to an Incoloy assembly to which is welded the Incoloy-outlet pigtail. The other leg of the outlet pigtail terminates at the HK-40 collector. The collector tee is welded to the refractory-lined transfer header through a centrifugally-cast HK-40 reducer.

The reformer has been operated consistently at less than design conditions. The normal load is less than 92% and the tube skin temperature is held at less than 880°C (design 920°C). Much attention is paid to temperature measurement. Readings are taken every day, and necessary burner adjustments are made. Optical pyrometers used for the measurements are calibrated every three months.

The quality of steam is good. A typical analysis is: silica as SiO_2, 0.02 ppm.; chloride as Cl, 0.2 ppm.; and sodium as Na, 0.1 ppm.

Feed naphtha contains less than 0.1 ppm. sulfur. Operation of the reformer has been fairly steady except for a few stops and starts during initial start up. First charge of catalyst was changed in July, 1972, and the second in August, 1974, when the material failures were detected.

Besides tube temperature measurement, on-stream inspection of the reformer consists of checking the freedom of movement of all sliding supports and hangers of the inlet and outlet headers and collectors. During catalyst changes the bottom welds of all the tubes suspected to have run hot before the turnaround are radiographed. The weld between the HK-40 reducer and the carbon steel transfer header, which was particularly difficult to make during construction, is ultrasonically examined every shutdown.

Outlet pigtail sagged within first year

The Incoloy 800 outlet pigtails are welded to the socket at the bottom of the reformer tube and to the Incoloy stub on the collector at the other side, as seen in Figure 3. Design conditions are 465 lb./sq. in. gauge and 816°C. The pigtails are supported by a "J" clamp at the "U" bend.

Slight sagging of pigtails was noticed within one year of operation, but the amount of sag was not considered abnormal for horizontal pigtails. Sagging became pronounced in early 1974. During a shutdown in July, 1974, creep and sag measurements were taken on one sample pigtail. This tube had a creep of 7% close to the weld with the catalyst tube. Ultrasonic examination at this region showed higher attenuation than the rest of the tube. The problem of such an abnormally high creep in three years of operation was referred to Haldor Topsoe and Amoco International Oil Co. (AIOC) for their comments.

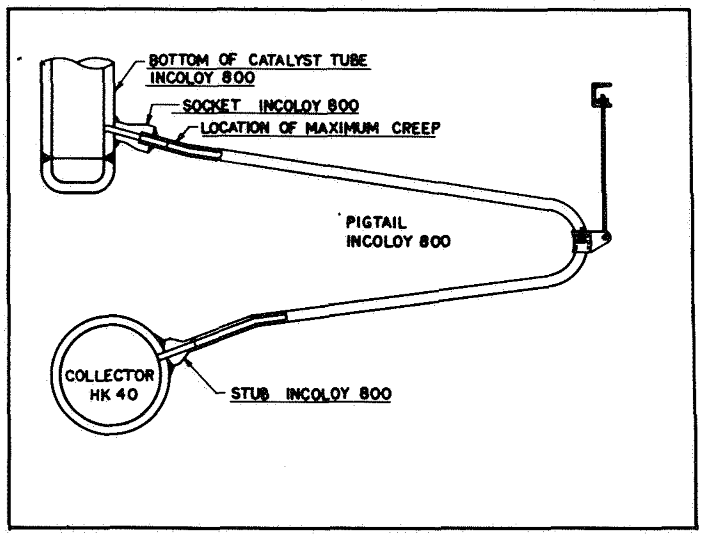


Figure 3. Outlet pigtail.

When the plant was shut down for a turnaround in August, 1974, for catalyst change, all the pigtails were inspected for creep. The summary report of the inspection showed: tubes with creep above 8%, 9; tubes with creep between 6 and 8%, 37; and below 6%, 194.

The high creep could not be accounted for by operating temperatures, which had always been conservative and well below design. Individual hot catalyst tubes could not account for the general widespread increase in creep of the outlet pigtails.

Samples from high-creep locations were metallographically examined. The grain size of the tubes was found to be ASTM 6 to 7 corresponding to mill annealed material (1,800°F). The original specification required the tubes to be "solution annealed" (2,100°F) with a grain size of 6 or larger.

The test certificates mentioned the tubes "as annealed" with a grain size of 6 to 7. This slight, but significant, variation in heat treatment condition had unfortunately been overlooked by the fabricator and the surveyors. Mill annealed Incoloy 800 has only about 25% of the creep rupture life of the "solution annealed" material at design conditions.

Replacement delivery time was 12 months

A complete set of Incoloy 800, solution annealed replacement pigtails was ordered immediately, with delivery promised in 12 months. Meanwhile, pigtails with high creep were replaced selectively from the 26 spares available. The spares were solution annealed in India and the grain size checked metallographically before use.

Nine pigtails with over 8% creep were replaced completely. The top legs of 37 pigtails with 6 to 8% creep were replaced. Additional sling supports were provided on the top legs of pigtails with excessive sag.

These measures, along with the favorable low operating temperatures due to fresh charge of catalyst, were expected to ensure safe operation of the pigtails till new tubes became available by end of 1975.

The catalyst tubes are made of centrifugally-cast HK-40, 6-in. OD × 15/16-in. thickness. The top of the tube terminates in a 5-in., Sch. 80, HK-40 stub-end with a carbon steel loose flange, seen in Figure 4.

When the catalyst tubes were being air-blown after new charge of catalyst loading in August, 1974, leaks were found in 57 tubes by soap test at the weld between the tube and the stub-end. Dye-check from inside at this location on all the tubes showed cracks in 232 out of 240 tubes. The cracks were both circumferential and transverse in the heat-affected zone (HAZ) of the butt weld. Transverse cracks had propagated up to 1½ in. on either side of the root of the weld.

Metallographic analysis of the cracked stub-ends was done at the Indian Institute of Technology, Madras, Haldor Topsoe, and AIOC. Almost similar conclusions were

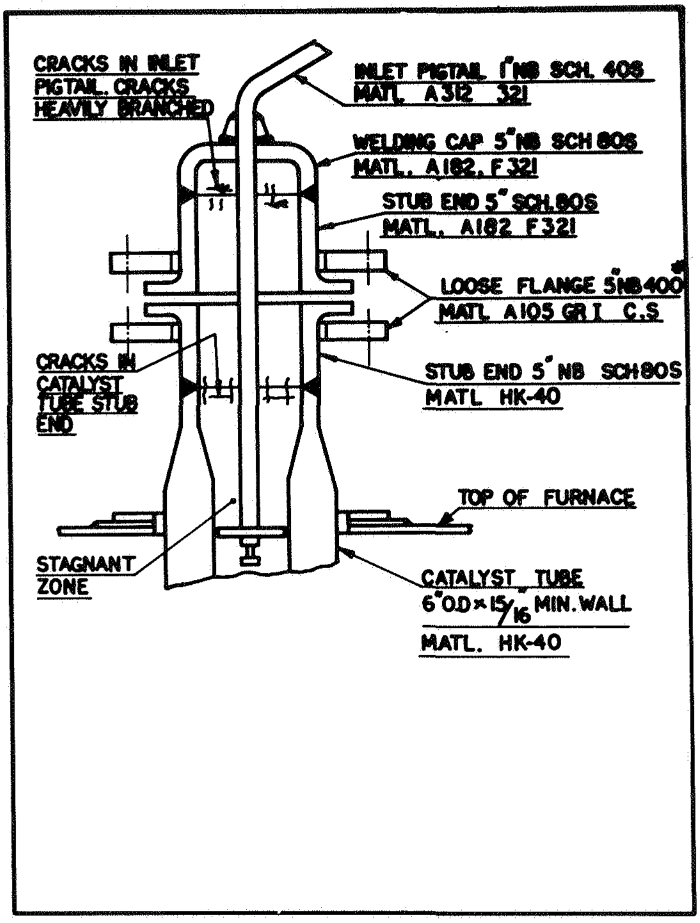


Figure 4. Catalyst tube and inlet pigtail.

reached in these independent investigations. The cracks were found to be predominantly transgranular in the weld metal and the HAZ, while they were intergranular in the parent metal. This is typical of chloride-induced stress corrosion cracking. Metalographic structure of the tube was found normal and in agreement with the low operating temperature. Attempts to locate the contaminant by electron microprobe analysis were unsuccessful. Elaborate swab tests by MFL on the stub-end and the inlet pigtail yielded negligible chlorides.

Unusually large scale repair project

Repair work of the cracked reformer tubes was probably unprecedented in its magnitude. All 240 tubes were physically removed from the furnace to the maintenance workshop. The tubes were air-tested at 100 lb./sq. in. gauge in a demineralized water tub. No cracks except those at the stub-end weld were found. All tube butt welds were dye-checked and found satisfactory. Many welds and specifically known hot areas on the tubes were sample radiographed. No cracks were detected. The stub-ends were cut off and the tube ends machined down to remove all cracks and dye-checked.

A world-wide search for replacement stub-ends was made. Only Incoloy 600 material was readily available for fabrication of stub-ends at five weeks delivery. HK-40 stub-ends were quoted at 10 to 12 weeks delivery. In view of the high resistance to chloride stress corrosion cracking of Incoloy 600 stub-ends and its favorable delivery, purchase was immediately approved in favor of Incoloy-600 from the U.S.A.

The new stub-ends were welded to the catalyst tube using TIG root run with Inconel 82 filler wire and MMA filler runs with Inconel 182 electrodes. All the root welds were dye-checked and the finished welds were 100% radiographed and dye-checked. No post-weld heat treatment was used. Completed tubes were hydrotested to 1,100 lb./sq. in. gauge using demineralized water. Welding is shown in Figure 5.

Although the corrodents responsible for the stress corrosion cracking have not been conclusively established, the evidence is strongly in favor of cracking induced by precipitation of corrodents.

We investigated the possibility of steam condensing at the uninsulated portion of the catalyst tube. During operation, about 18 in. of the bare catalyst tube is exposed to atmosphere outside the furnace ceiling due to expansion. Thermocouples were welded to measure the tube skin temperatures of the pigtail cap and tube stub-end.

The measured temperatures were below the dew point of the process feeds, even during normal operation. Continuous condensation and reevaporation of steam at these portions are strong possibilities. The exposed portion on one tube was insulated, and the skin temperature measured indicated an increase of 270°F.

When the situation was referred to International Nickel (India) Ltd., they also gave the opinion that the cracking could have been due to steam condensation in the dead-space at the top of the catalyst tube. The following information received from them is worth noting:

"In the mid-sixties there was quite a spate of stress corrosion cracking problems in steam naphtha reformers in the U.K. and a number on the continent. The tube-top failures were, with an occasional exception, all ascribable to the presence of chlorides in the steam concentrating and condensing in the relatively cold dead-space above the pigtail entry. Since at that time, side entry and exit pigtails were standard practice of many design-firms holding ICI reforming licenses."

Madras Fertilizers, therefore, decided to insulate all the exposed portion of the catalyst tube system except the carbon steel loose flanges, at the next available opportunity. Though the inlet system has axial entry, the extension

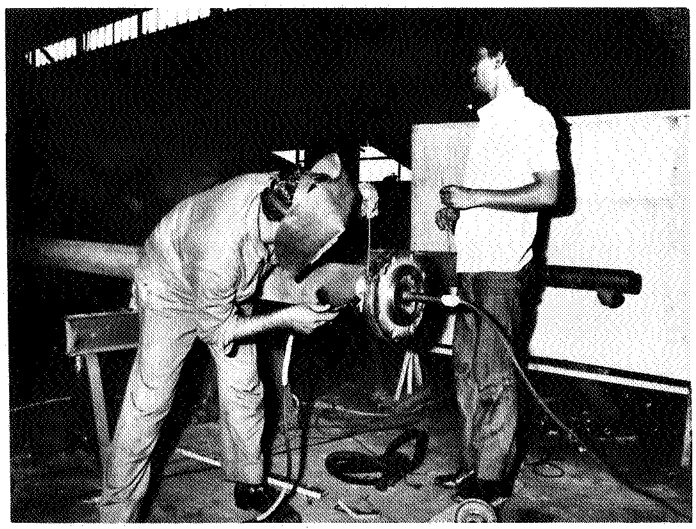


Figure 5. Welding Inconel-600 stub ends to the HK-40 catalyst tubes. Root run is being welded by the "tig" process with argon purge.

of about 16 in. of the pigtail nozzle inside the catalyst tube provides for the possibility of a dead pocket at the top near the flange.

Of the various proposals examined for relieving the stagnant condition in this zone, the most promising one appears to be the drilling of a few small holes in the inlet pigtail near the flange which would provide enough flow to maintain the inside wall above the condensation temperature.

Inlet pigtails tested thoroughly

Subsequent to finding cracks in the catalyst tube stub-ends, all 240 inlet pigtails were dye-checked. Cracks were found in 181 out of 240 pigtails at the weld between the weld-cap and the stub-end. All the inlet pigtail materials are type 321 stainless steel. The cracks were again both circumferential and transverse in the HAZ of the weld. The cracks were heavily branched, the first strong visual evidence of stress corrosion cracking.

Repairs to the cracked inlet pigtails consisted of machining off the cracked area and re-welding. The welds were sample radiographed, dye-checked, and hydrotested.

Following detection of stress corrosion cracking in the inlet pigtails, the inlet header which is also made of Type 321 S.S. was radiographed and dye-checked at the bottom where condensate could collect during shut downs. No evidence of cracking was found.

The outlet pigtails from the catalyst tubes are welded to HK-40 collector manifolds. There are 10 collectors in the reformer with 24 pigtails terminating in each collector. The downward branch from the collector is welded to the refractory lined transfer manifold through a HK-40 reducer, seen in Figure 6. Dye-check of the collector tee welds showed two cracks in collector No. 1.

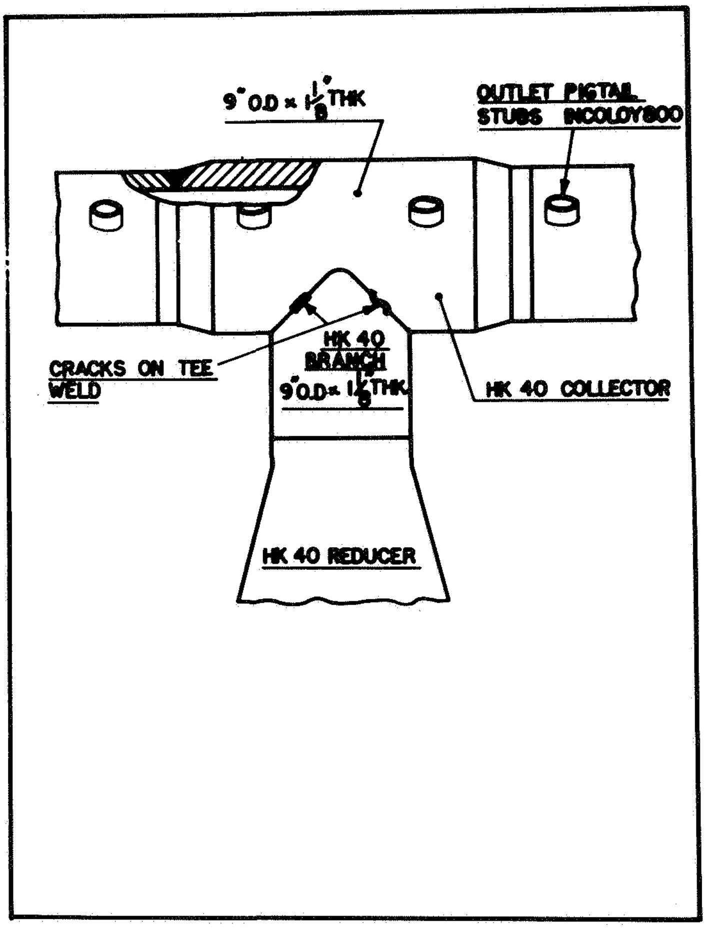


Figure 6. Outlet collector cracks.

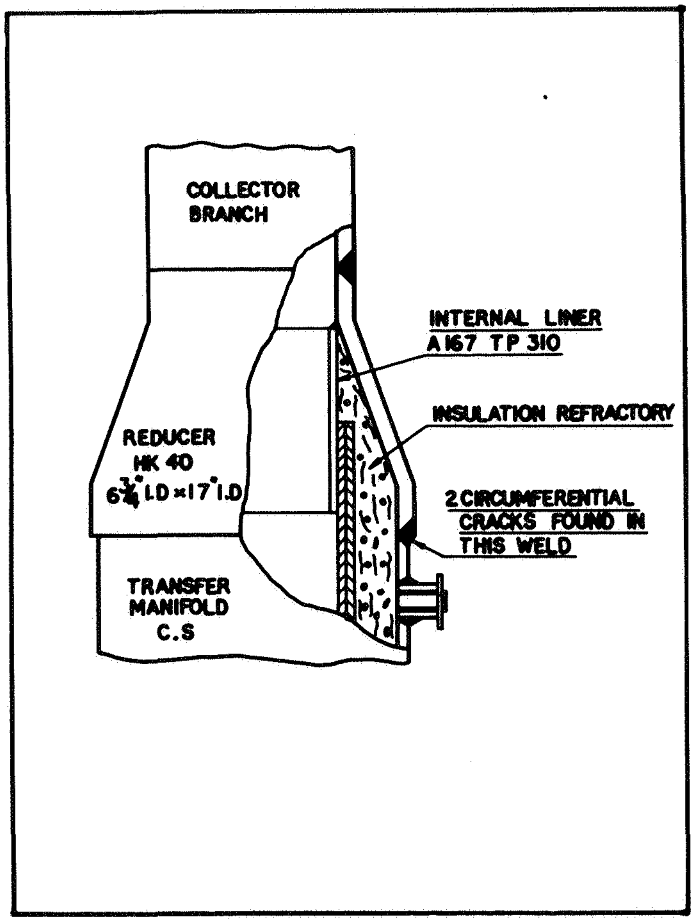


Figure 7. Reducer weld cracks.

Field repair welding of used HK-40 material is considered to have a chance of success. The collector tee was therefore solution annealed at 2,100°F for 5 hr. Solution annealing was successful only in the third attempt; the first two attempts had to be abandoned when the heating elements failed on reaching 2,100°F.

After solution annealing, the cracks were ground to a depth of ¾ in. As the cracks tended to propagate with the heat from large grinding wheels, material had to be removed with small cutters. The cracks were not chased to the root, for fear of further propagation during material removal and welding. The grooves were welded with Inconel 182 electrodes. A few surface cracks which developed during welding could be ground out and welded. No post-weld heat-treatment was employed.

The large end of the HK-40 reducer is welded to the carbon steel transfer header which is internally lined with refractory, as shown in Figure 7. Making and inspecting this weld presented quite a few problems during project construction. The completed welds had to be ultrasonically examined as internal refractory made radiography impossible.

Because of the initial problems, the welds are ultrasonically examined on every shut down. During the air test of the reformer in August, 1974, one weld was found to have a leak about 2 in. long. Subsequent ultrasonic examination showed another crack, about 180° from the first, which had propagated ½ in. from the root.

The cracks were ground out up to the root and welded by MMA with Inconel 182 electrodes. This welding presented no problem, as the HK-40 material had not been subjected to the high operating temperatures. The completed repair weld was ultrasonically examined.

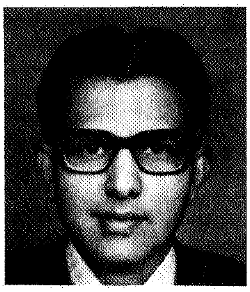
Conclusions

The information gathered from various organizations and our own investigations lead to the following conclusions:

The sagging and excessive creep of the outlet pigtails are the result of using mill annealed Incoloy 800 material instead of solution annealed material.

The reformer inlet system design could favor continuous steam, condensation and evaporation even during normal operation, which could lead to stress corrosion cracking.

The weld cracks on HK-40 outlet collector Tee-weld and HK-40 reducer to carbon steel header weld are isolated instances. We believe that these are due to propagation of weld defects left during initial fabrication. #



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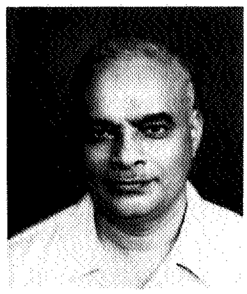

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