Solving Corrosion Problems in Steam Reforming

A case history is a BASF steam reforming methanol/ammonia plant, in which an improvement in the design of the waste heat boilers has eliminated plant breakdowns

M. Appl and K. Feind,
BASF AG, Ludwigshafen/Rhine,
West Germany

Table 1. Operating conditions, methanol plant waste-heat boilers

	First design	Second design
Gas inlet temperature, °C	858	858
Gas outlet temperature, °C	320	340
Gas pressure inside tubes, bar	21	21
Boiling water temperature, °C	314-317	314-317
Boiling water pressure, bar	100	100
Heating surface, sq. m.	370	310
Maximum permissible pressure, bar	120	120
Test pressure, bar	144	144
Number of tubes	354	357
Tube material	13 Cr Mo 44 ASTM A213-65 T12	16 Mo 5 ASTM A161-T1
Tube diameter and thickness, mm.	35 × 4	35 × 6
Tube bundles	1	2
Tube length, mm.	9,495	3,674 & 4,175
Gas inlet & outlet tube sheet thickness, mm.	23	23
Gas inlet tube sheet material	13 Cr Mo 44 ASTM A213-65 T12	16 Mo 5 ASTM A161-T1
Gas outlet tube sheet material	15 Mo 3 ASTM A204-61A	16 Mo 5 ASTM A204-61A
Number of water circulation chambers	6	4-4
Weight empty, metric ton	48.5	40

Corrosion failure problems in the thin tube sheet waste heat boilers in a steam reforming methanol and ammonia plant led to some design alterations that resulted in an operating run of two years with no breakdown.

BASF AG at Ludwigshafen placed an 800-ton/day steam reforming methanol unit onstream in January, 1970, and a 1,400-ton/day ammonia unit onstream in October, 1970. In both, the reformed gases are cooled in fire-tube type waste heat boilers with 23-mm. thick tube sheets. Recovered heat is used for steam generation.

After an operation of 9 to 15 months, both heat exchangers showed the first signs of damage at the welds between tubes and tube sheets. Recurring damage forced BASF to install new coolers after some three years of problems. The new coolers have been performing completely satisfactorily since installation.

Experience in the methanol plant

The methanol plant cooler is located immediately behind the primary reformer. Gas flowing through the tubes contains about 70 mol-% hydrogen; the remainder is carbon monoxide, carbon dioxide, and methane. Boiling water flows by natural circulation through the cooler jacket from the boiler drum located above it, as shown in Figure 1. Operating conditions for the old and new design coolers are listed in Table 1.

The main dimensions of the old cooler can be seen in Figure 2. The tube sheet on the gas inlet side and the inlet cover are fitted with a layer of insulating and refractory concrete and an Alloy-800 protection plate and with ferrules into the tubes.

The first eight leaks in the tube-to-tube-sheet weld were

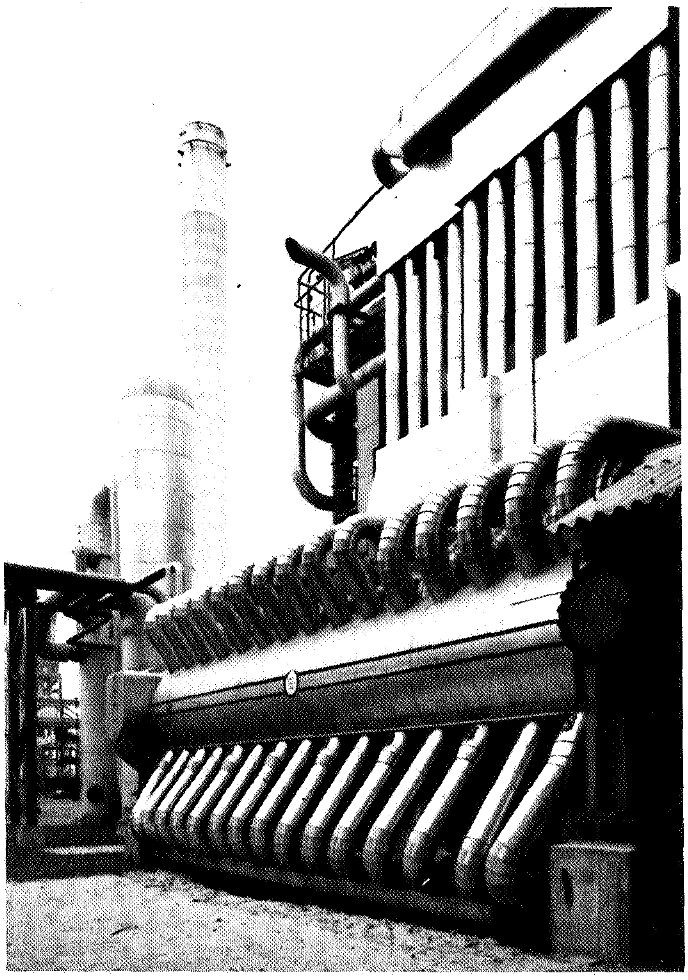


Figure 1. The methanol plant cooler at Ludwigshafen.

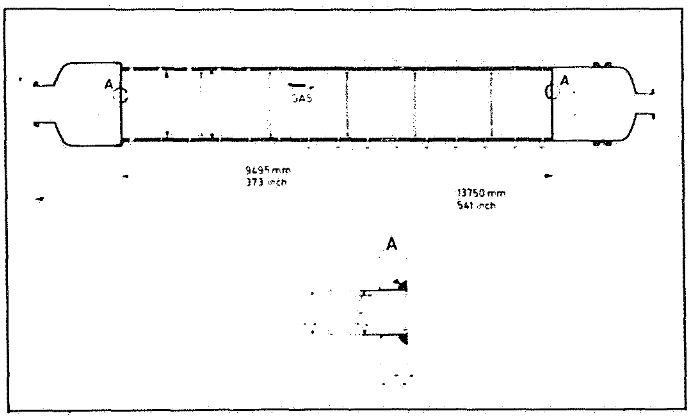


Figure 2. Methanol plant waste-heat boiler (first design).

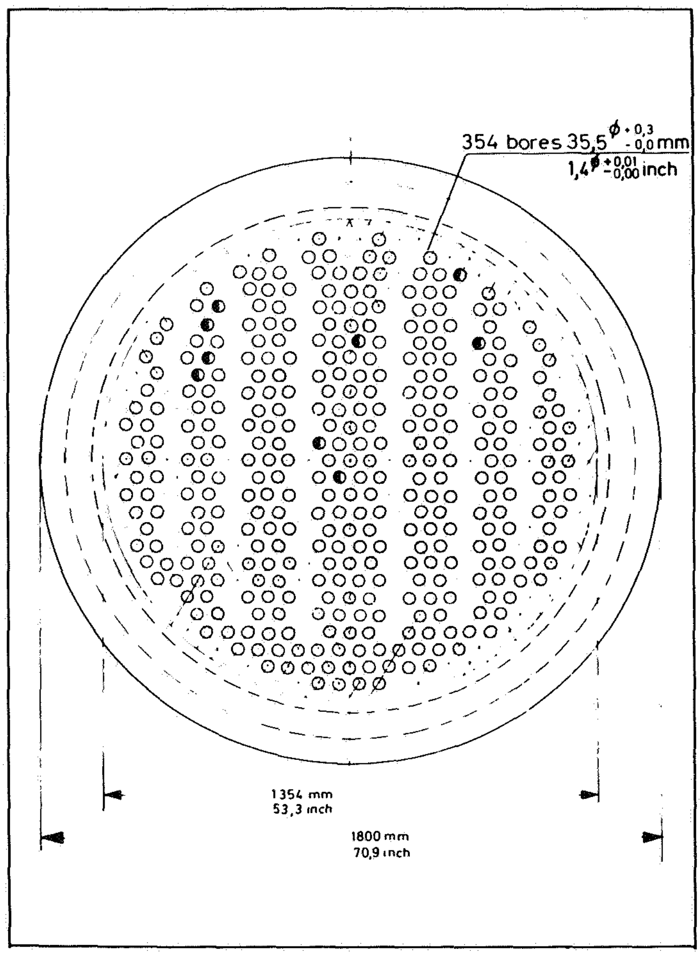


Figure 3. Position of leaky tubes in the first gas outlet tube sheet in the methanol plant waste-heat boiler (first design) in Sept., 1970.

detected on the gas outlet side tube sheet when the cooler was inspected during a shutdown in September, 1970. They are shown in Figure 3. The damaged parts of the welds were reamed out and rewelded. After repair, the cooler was pressure tested with nitrogen at 100 bar. The test revealed another leaking tube, which was then repaired. In the subsequent pressure test, no further defects were detected.

The plant then remained in operation until February 22, 1971, except for one brief shutdown. On Feruary 22, 1971, nineteen defective welds were discovered, as shown in Figure 4. After reaming out and rewelding the 19 tubes, another 13 leaking tubes were detected during a pressure test with nitrogen at 4 bar. Still another 12 were found after repairing and testing at 20 bar.

After running about 4½ months, 7 of the original 9 tubes rewelded during the first repair job in September, 1970, were leaking again. Thereupon, test pieces of tube and weld were taken for metallographic examination: One was included from a tube that had not yet leaked.

The examination revealed that all the cracks were circumferential. They commenced in the outer wall of the tube on the water side either at the root of the tube-to-plate weld or in the welding temperature influential reach. They were transcrystalline with lateral bifurcations, and some of them were filled with corroded material.

The weld and the cracks are shown in Figure 5. Even the specimen of weld from the tube that had not yet leaked displayed a crack which had already penetrated through one-third of the tube wall. In the light of all the metallographic investigations, the BASF materials testing department ascribed the cracks to corrosion fatigue, i.e., "stress induced corrosion." The possibility of sudden failure as a result of a purely static overload could be excluded. The location of the leaks detected during the first and second repair jobs, seen in Figure 4, reveals that failure mainly occurred in the upper half of the tube sheet. The analysis of the investigations and the possible causes of failure are discussed below.

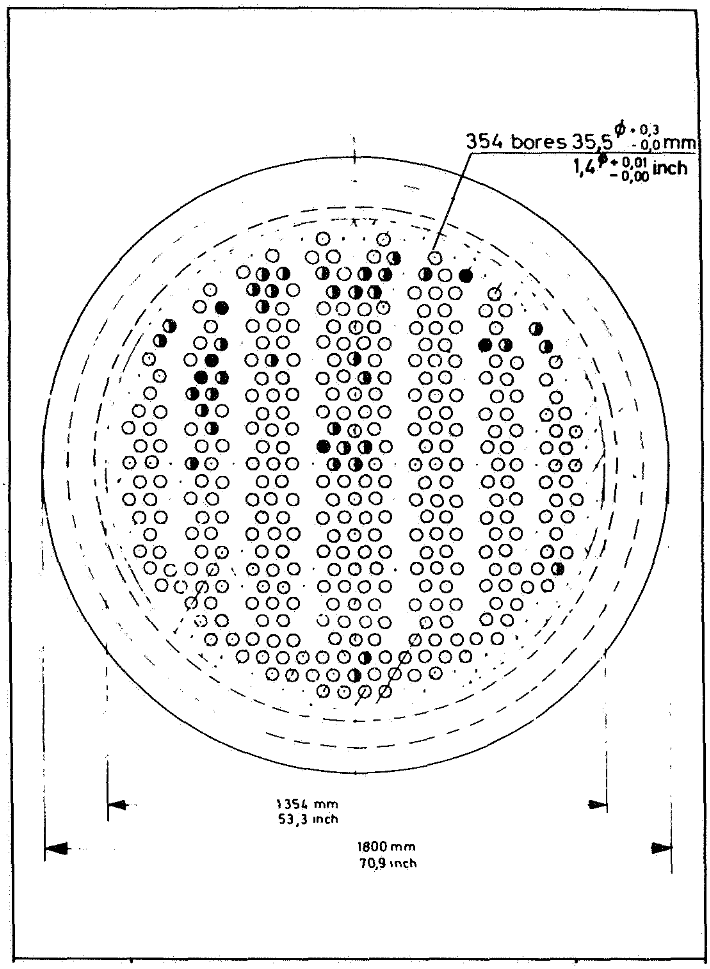


Figure 4. Position of leaky tubes in the first gas outlet tube sheet in the methanol plant waste-heat boiler (first design) in Feb., 1971.

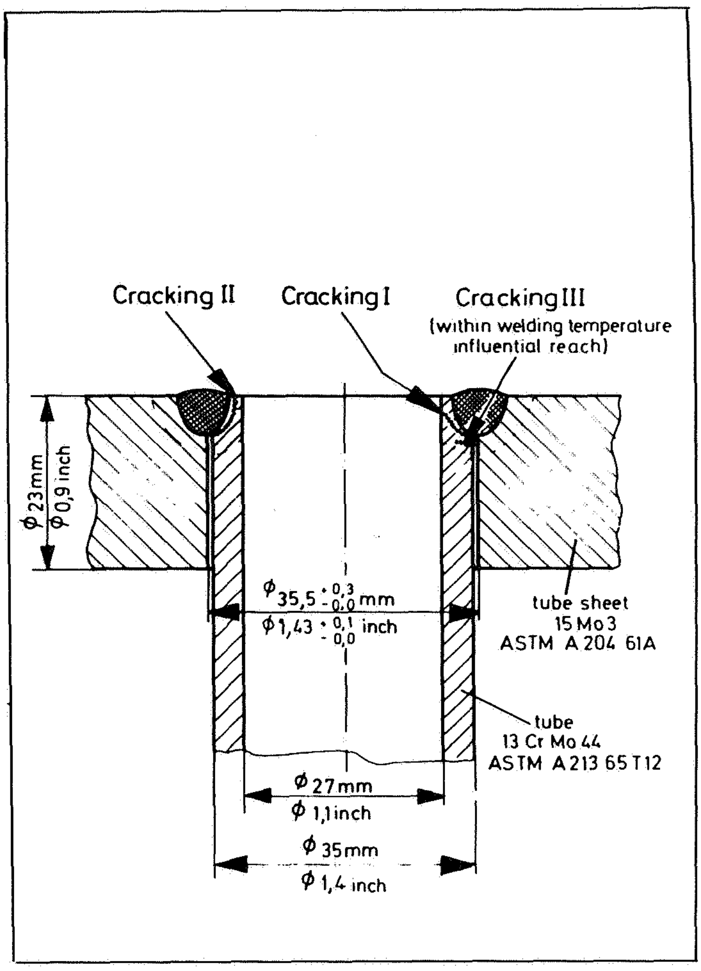


Figure 5. Schematic of tube welding on the methanol plant waste-heat boiler (first design).

Feedwater quality questioned

The boiler feedwater was demineralized. The quality, the amount of hydrazine proportioned, and the oxygen content were continuously controlled. At first, this did not offer any explanation for the source of the corrosion that, superimposed on the mechanical stress, must have accelerated cracking. Nevertheless, it can be assumed that mass transfer is impeded in the annulus between the tubes and the tube sheet, owing to the tolerances allowed and the unsatisfactory fit obtained by rolling the tubes in the tube sheets.

Poor mass transfer may greatly aggravate the otherwise mild corrosion conditions in the annulus. This would also explain the occurrence of corrosion at the tube sheet on the gas outlet side, because there is no stream cushion between the tubes and the tube sheet.

The formation of a continuous ceramic layer of magnetite is interrupted in the annulus filled with liquid on the gas outlet side. In view of the poor thermal conductivity and the lower breaking tension, it can be assumed that the layer of magnetite tends to crack in the vicinity of the root gap of the weld when the waste heat boiler temperature and load fluctuate. This is particularly the case where the welding temperature effect is felt, because the strains incurred by the reduced strength may exceed the critical value for the layer of magnetite. Then, owing to the more rapid build-up, the layers subsequently formed are more porous.

Because the two tube sheets have been designed to act as membranes, the axial forces induced by the internal pressure must be taken up by the bundle of tubes. The value calculated from the cooler design data for the mean axial stress in the tubes is 12.6 kg./sq. mm. Wire strain gauge measurements in the individual tubes at the design pressure were made by the manufacturer prior to delivery. A value of 1.7 kg./sq. mm. was obtained in the tubes at the outer extremity of the tube sheet; and 14.3 kg./sq. mm. in the center of the plate.

When the tubes were being reamed out for repair, a resilience of 0.5 to 2 mm. was determined. Thus, there were residual stresses in the tubes in the cold state.

It can be calculated that an additional tensile stress of about 0.24 kg./sq. mm./°C is induced in any tube that is at a lower temperature than the adjacent tubes or the jacket.

In view of the high static axial stress in the tubes, slight local or temporary differences in temperature could cause the stress to rise above the permissible limit. Such differences could occur as a result of variations in gas stream into the tubes, or fluctuations in the flow rate and temperature of the gas fluctuations in the flow rate of the water, or differences in the amount of steam in the six water chambers of the cooler that are separated by baffles.

The water circulation rate between the last baffle and the tube sheet on the gas outlet end was measured during operation, and a value of 40 ton/hr. was obtained. However, no fluctuations in temperature or pressure could be determined during operation on either the gas side or the water side.

Thermal stresses found not sole cause

Pressure testings and recurrent startups and shutdowns with more thermally-induced stresses in the cooler cannot be the sole cause of the breakdowns, because after the first repair in September, 1970, the plant remained on stream five months with only one shutdown. Yet, at the end of this period, seven of the nine rewelded tubes were found to be leaking again.

The possibility cannot be excluded that notch effects jeopardized the welds during starting up due to the high static stress incurred. The manufacturer's recommendations were also adhered to during start-up and shutdown. The cooler has been designed so that the tube sheet can also take up the additional stresses incurred when cold gas flows into the preheated cooler.

During operation, vibration measurements were made on the outer jacket of the heat exchanger. Only very small amplitudes were observed at frequencies of 2, 5, 25, and 48 Hz. Thus, the measurements yielded no indications that would definitely point to the existence of vibration stresses in the tubes. According to the data available for the water system, it is unlikely that vibrations are excited in the tubes by water circulation or by pulsations in evaporation in the water chamber in front of the damaged tube sheet.

Later, an opportunity arose to investigate the possibility of any vibrations of the tubes in the holes of the baffle separating the fifth and sixth water chambers. This did not reveal any visible marks that would have indicated vibrations of the tubes.

The holes in the tube sheet were drilled to a tolerance of 35.5 + 0.3 or −0 mm. The tolerance for the outer diameter of the tubes was 35 ± 0.5 mm. Thus the maximum possible clearance between the tube and the tube sheet is 1.3 mm.

The material for the tube sheet is 15Mo3. It has a somewhat lower elastic limit than that of the material for the tubes, 13CrMo44. This pairing entails that the tubes cannot be reliably rolled into the thin tube sheet. Therefore, the axial forces in the tubes must be completely taken up by the weld between the tube and the tube sheet.

In the design of the cooler, no notch effect was assumed for the root of the weld. If a stress concentration factor of at least 3.5 is taken for the notch effect, it can be demonstrated that the effective tensile stress in the vicinity of the root of the weld must be close to the elastic limit at the operating temperature.

The investigations and conclusions just discussed do not give any reliable indication as to the cause of the breakdowns. Yet, owing to the progressive damage to the cooler in the methanol plant, BASF was forced to find a remedy as quickly as possibly, even though the cause was not accurately known.

Thus, when the plant was shut down March-May, 1971, the cooler was cut open on the plant site. The bundle of tubes on the gas outlet side was shortened by 0.59 m., and a new tube sheet was welded in (material:

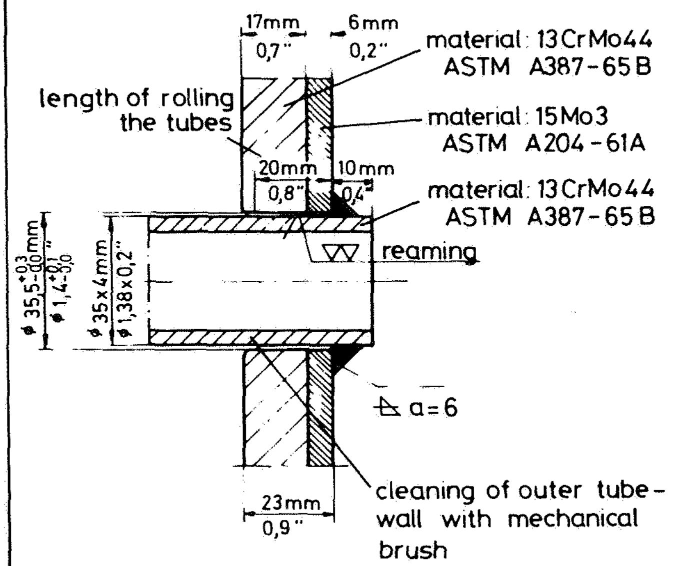


Figure 6. Tube welding in the second tube sheet on gas outlet side of the methanol plant waste-heat boiler (first design).

13CrMo44 for the tubes, but with a 6-mm. thick 15Mo3 weld overlay). Owing to this overlay, a filled weld between the tubes and the tube sheet was then projected, as shown in Figure 6. In other words, the weld differed from that in the original design seen in Figure 2.

As a result of shortening the bundle of tubes, the sixth water chamber was eliminated. The rate of circulation of water was increased by diverting the risers and downcomers on the final water chamber to the gas outlet end of the cooler.

Unfortunately, this major repair job also did not solve the problem. In March and April 1972, about 10 months after the new tube sheet had been fitted, the gas outlet temperature decreased steadily from 322 to 312°C. Simultaneously, an increase in the water vapor content of the synthesis gas was determined by dew point measurement.

Problem remained unsolved

Thereupon, the plant was shut down. On May 9, nine leaking tubes were again found on the tube sheet at the gas outlet end. The nature of the damage indicated that cracks had first appeared in five of the tubes and that the high-pressure steam had damaged the other four. In addition, the escaping steam had eroded an area measuring 110 × 145 mm. from the wall of the dome cover.

The damaged tubes had circumferential cracks of 5 to

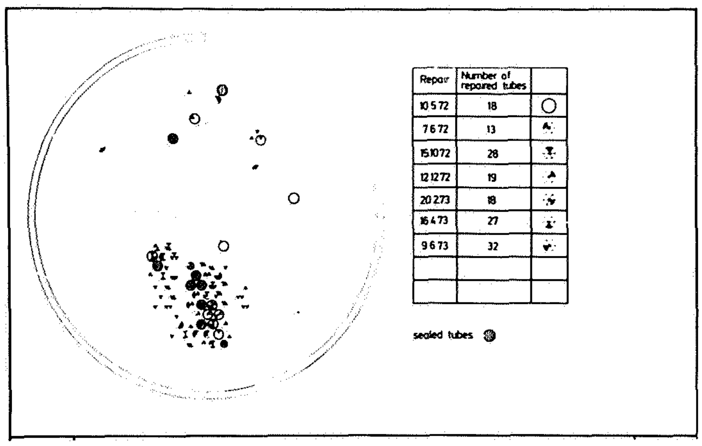


Figure 7. Position of leaky tubes in the second gas outlet tube sheet of the methanol plant waste-heat boiler (first design).

15 mm. length at distances of 8 to 13 mm. from their ends. In some cases, the sides of the cracks were strongly eroded. It was safe to say that the cause of the damage was the same as that in the previous cases. The period of time that had elapsed before the damage commenced was also roughly the same as that that had elapsed before the first repair job.

After the nine tubes had been rewelded, the pressure was increased in stages to 90 bar. By this means, nine other leaking tubes were detected. The position of the points of failure in the tube sheet, the chronological course of the damage, and the number of leaking and not reparable tubes are shown in Figure 7.

Almost all the leaking tubes in the first repair job were in the upper part of the tube sheet. In contrast, the bulk of the damage in the new tube sheet was found in the lower part.

Wire strain gauge measurements, after the new tube sheet had been installed, revealed flexural stresses of about 5 kg./sq. mm. superimposed on the axial stress in the tubes in the lower half of the bundle. This unequal stress distribution probably resulted from the temperature differences that occurred when the circumferential weld line on the jacket was being annealed during the major repairs. Differences of more than 100°C were then registered between the upper and lower parts of the cooler.

New and better design boiler acquired

After the new tube sheet had been repaired in May 1972, it was decided to acquire a new waste heat boiler of improved design as soon as possible. Inasmuch as it had to be installed in the existing plant, the only type that could be considered was a horizontal fire-tube design. In view of the high temperature of the gas at the cooler inlet, i.e., 860°C, the manufacturer advised against replacing the thin tube sheets by thick rigid tube sheets.

The design of the new cooler allowed for the following conclusions, which were drawn from the damage observed in the original cooler.

The root weld acts as a mechanical notch and is also a metallurgical source of weakness; it was probably subjected to excessive mechanical stress owing to design features and to the additional flexural stresses imposed during manufacturing. Cracking was evidently accelerated by corrosion in the annulus between the tubes and the tube sheet.

These conclusions aroused thoughts on how the tubes could be connected on the gas outlet side to the tube sheet without annulus and how they could be secured over a thicker joint weld and tube wall. Various means of weldings without annulus are shown in Figure 8. For various reasons, they were not considered for our new cooler.

Our materials testing department investigated a number of designs of welds for tubes subjected to vibration stress.

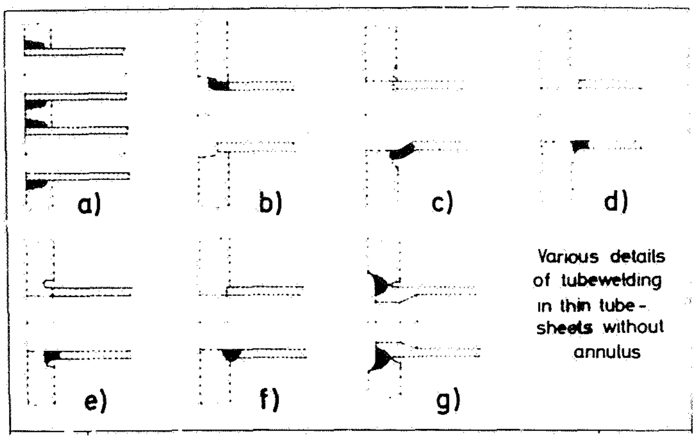


Figure 8. Various details of tube welding in thin tube sheets without annulus.

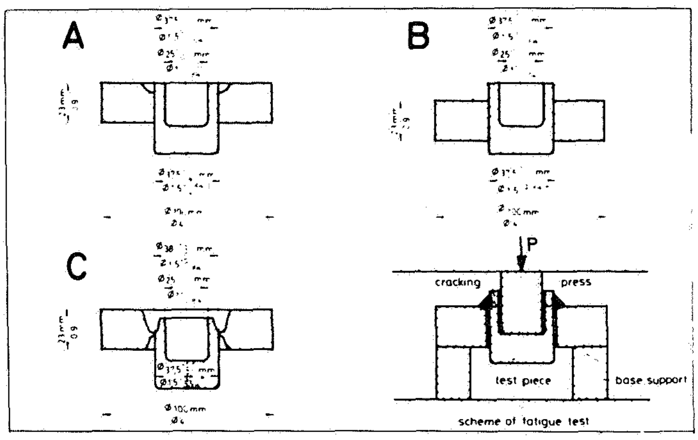


Figure 9. Test pieces for high-frequency pulsator test.

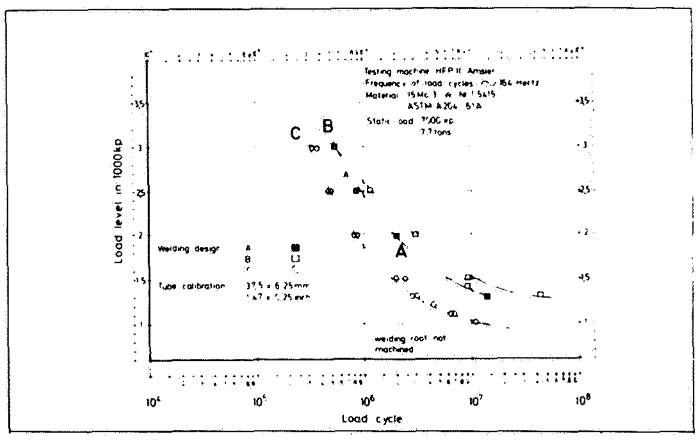


Figure 10. Fatigue test (DIN 50100).

Fatigue tests were carried out on three different designs, designated A, B and C in Figure 9. The material from which the test pieces were made was 15Mo3. Before the test, the test pieces were stress-annealed at 600°C for one hour. The tests were carried out in a high-frequency pulsator at room temperature. The frequency of loading was 164 Hz., and corrosion effects were not included. A constant load of 7,000 kg. was applied, and cyclic loads of 900 and 3,000 kg. were superimposed on it. A value of 7,000 kg. was selected as being approximately equal to the axial load on the tubes in the waste heat boiler.

Wöhler curves representing the results of the tests are reproduced in Figure 10. The cyclic load superimposed on the constant load of 7,000 kg. has been plotted against the number of load cycles to failure. Each plotted point represents a test piece that has failed.

A comparison of the three curves for the specimens A, B and C shows that design B, i.e., that with the projecting tube and the fillet weld, displays the highest fatigue strength. The lowest values were obtained with design C. Further experiments demonstrated that favorable values for the fatigue strength could also be obtained with design C if the root of the weld is rounded off by machining. Of course, this is not possible in constructing the gas cooler.

This investigation made a considerable contribution towards the design of the new gas cooler for the methanol plant, which is shown in Figure 11. The main difference from the old design is that the bundle of tubes has been split into two parts with intermediate tube sheets. This reduces the load imposed on the welds dependent on the length of the tube bundle.

In the previous, badly damaged cooler, the axial loads on the tubes were taken up completely by the welds between the tubes and the tube sheet (the effect achieved by rolling the tubes into the plate was probably negligible). It was therefore intended to reduce drastically the stresses in the vicinity of the welds in the new cooler. The sum of the lengths of the two bundles of tubes is 1 m. less than the total length in the previous item of equipment.

The sketch in Figure 11 illustrates how the tubes are welded into the tube sheet of the first bundle on the outlet side and into that for the second bundle on the inlet and outlet sides. By means of welding-neck nipples, the wall of the tube was thickened from 4 to 7 mm. at the weld.

In view of the favorable results obtained in the fatigue tests, these nipples were welded into the tube sheet with a projecting fillet weld. The material for the tubes and tube sheet was selected so that the walls of the tubes could be made to rest closely against the sides of the holes in the tube sheet by post weld expansion, or as closely as these thin plates would permit.

In summer, 1973, during a shutdown lasting one month, the almost unrepairable cooler was replaced. After the new one had been installed, the additional measure was adopted by maintaining the pH value of the boiler feed water at 9.8 by injecting caustic soda into demineralized water in the boiler drum.

Breakdown also occurs in the ammonia plant

In the ammonia plant, the waste heat boiler is in the gas stream between the high-temperature shift conversion and a water-tube type cooler in series with the primary

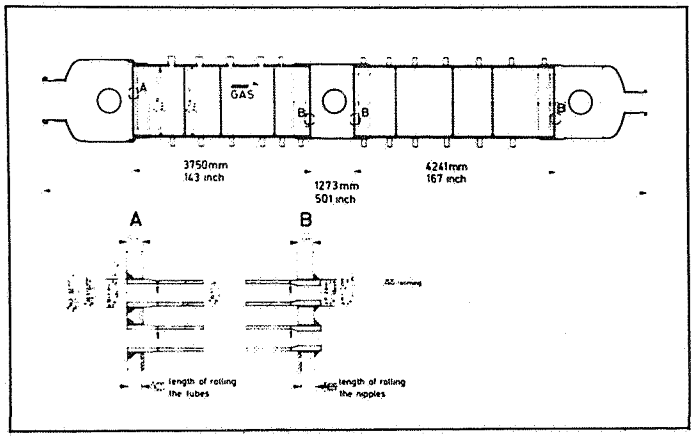


Figure 11. Methanol plant waste-heat boiler (second design).

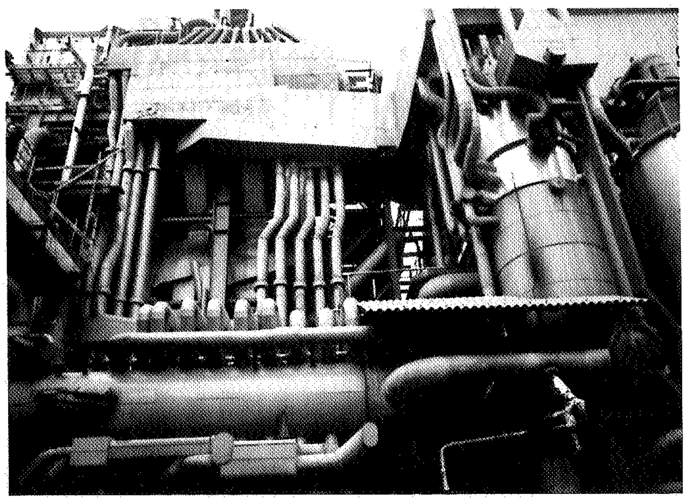


Figure 12. Waste heat boiler in the BASF ammonia plant.

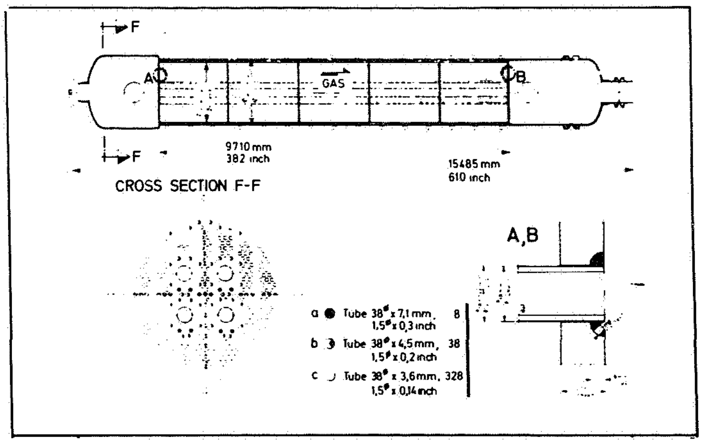


Figure 13. Ammonia plant waste-heat boiler (first design).

reformer, as seen in Figure 12.

The composition of the gas flowing through the tubes is about 57 mol % of hydrogen and 22 mol % of nitrogen, and the remainder is carbon monoxide, carbon dioxide, methane and argon. There is natural circulation of boiling water through the cooler jacket from the overlying boiler drum.

The operating data are presented in Table 2. The main dimensions of the former cooler and the design of the

Table 2. Operating conditions, ammonia plant waste-heat boilers

	First design	Second design
Gas inlet temperature, °C	460	460
Gas outlet temperature, °C	360	370
Gas pressure inside tubes, bar	31	31
Boiling water temperature, °C	322	322
Boiling water pressure, bar	119	119
Heating surface, sq. m.	454	260
Maximum permissible pressure, bar	120	120
Test pressure, bar	156	156
Number of tubes, and tube diam. & thickness, mm.	328 38 × 3.6 38 38 × 4.5 8 38 × 7.1 4 168.3 × 16	407 38 × 5
Tube material	13 Cr Mo 44 ASTM A213-65 T12	16 Mo 5 ASTM A161-T1
Tube bundles	1	1
Tube length, mm.	9,710	5,431
Gas inlet and outlet tube sheet thickness, mm.	23	23
Gas inlet tube sheet material	13 Cr Mo 44 ASTM A387-65B	16 Mo 5 ASTM A204-61A
Gas outlet tube sheet material	15 Mo 3 ASTM A204-61A	16 Mo 5 ASTM A204-61A
Number of water circulation chambers	5	4
Weight empty, metric ton	75	39

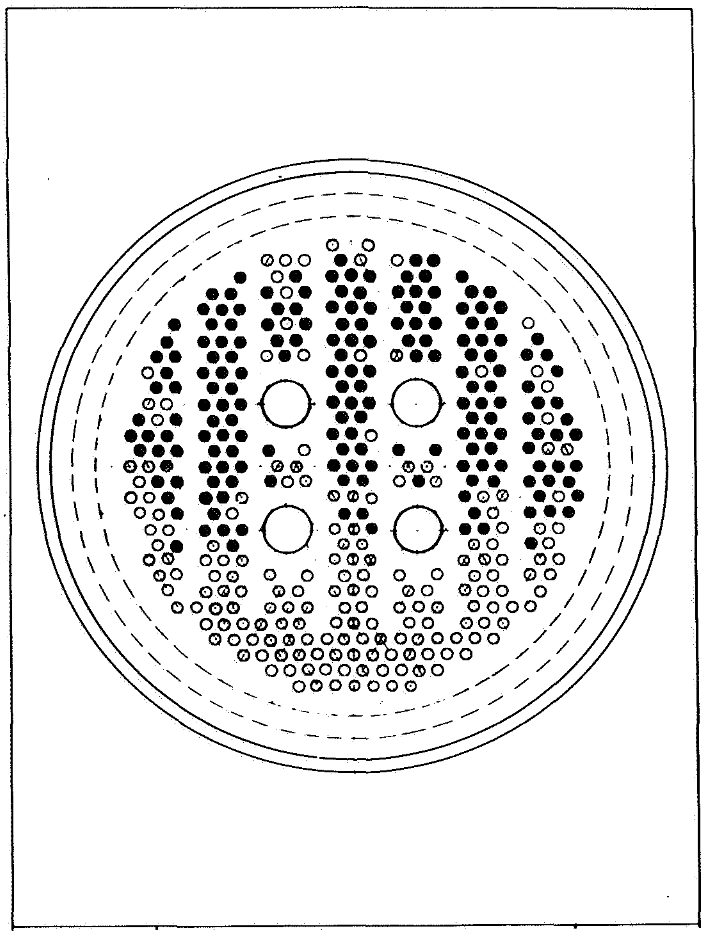


Figure 14. Position of leaky tubes in the gas outlet tube sheet of the ammonia plant waste-heat boiler (first design).

tube sheet and the tube-to-plate weld can be derived from Figure 13.

A feature in common with the gas cooler in the methanol plant is that the gas inlet cover and the tube sheet on the gas inlet side are coated with a thermal insulation. Over the insulation is an Alloy 800 protective plate with ferrules in the tube ends. In contrast to the cooler in the methanol plant, this item of equipment has four large-diameter tubes with a throttle-clack valve at the gas outlet side as an internal gas bypass.

Damage to the tube sheet at the gas outlet end of the cooler first occurred on February 1, 1972, after the plant had been on stream 15 months. A total of 17 tubes had to be carried out at about two-month intervals until February, 1973.

After the seventh repair, the record showed that 189 of the 378 tubes in the cooler had to be rewelded. Of these, 31 tubes had to be rewelded for the third time; 46 for the second time; and 80 for the first time. A total of 32 had to be sealed. The positions on the tube-sheet of the tubes repaired is shown in Figure 14.

The nature of the damage and its analysis corresponded exactly to that previously determined in the cooler of the methanol plant. All damaged tubes were in the upper part of the tube sheet, as was the case in the first repair on the methanol plant gas cooler.

Here, too, it was decided in 1972 to construct a new cooler. This equipment was installed in summer, 1973, during a one-month shutdown of the ammonia plant. Since then, it has been running without trouble. The main dimensions of the new cooler and the design of the tube sheet and the tube-to-tube sheet weld are shown in Figure 15.

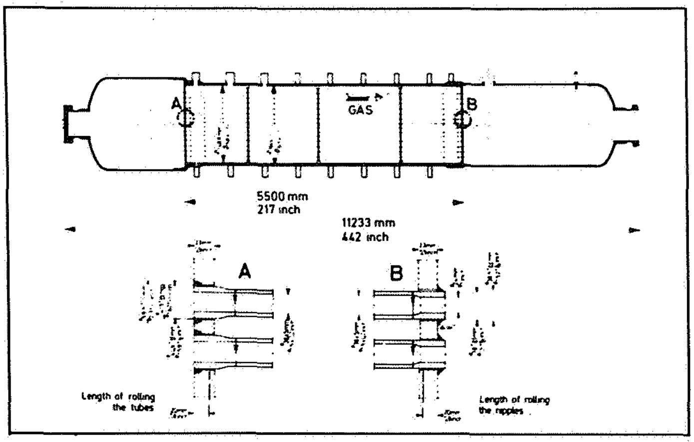


Figure 15. Ammonia plant waste-heat boiler (second design).

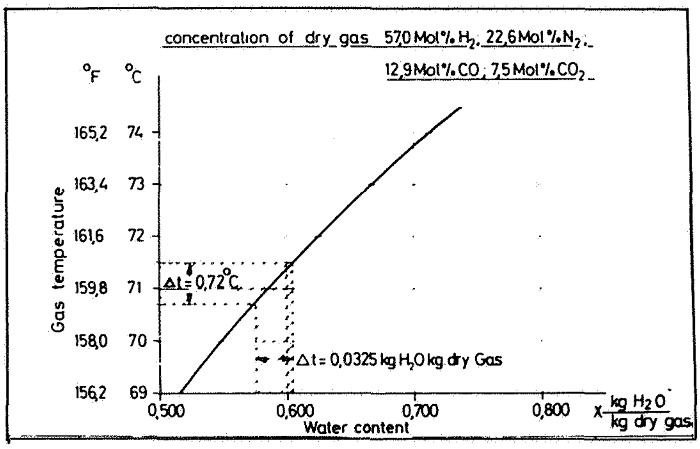


Figure 17. Saturation characteristic of ammonia plant gas at atmospheric pressure.

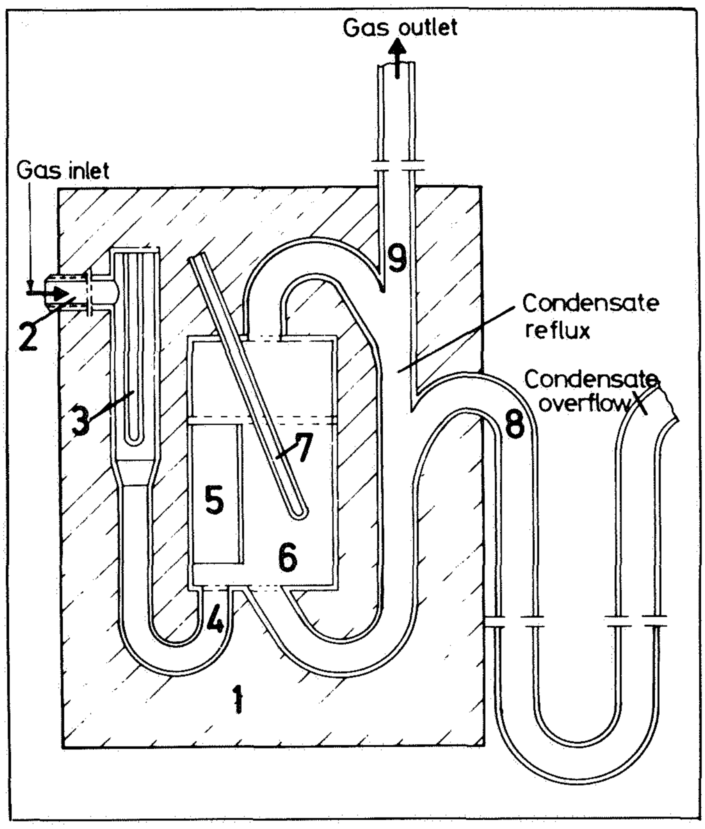


Figure 16. Measuring saturation temperature of steam/gas mixtures.

Again, the main difference between the old and the new gas cooler is that the bundle of tubes has been shortened, in this case by 4 m. to a length of 5.5 m. The wall thickness of the tubes was increased from 4.5 to 5 mm., and nipples were used for welding the tubes into the two tube sheets. The wall thickness of the nipples on the tube sheets at the gas inlet end is 7 mm. The same material has been used for the tubes, nipples and tube sheets: 16Mo5. Another significant modification is the elimination of the bypass tubes in the bundle.

As a result, there are now 407 tubes of the same diameter in place of the previous 378 tubes of various diameters and wall thicknesses. Instead, an external gas bypass tube was installed with a throttle-clack valve in the cooler outlet as before. Again, the welding-neck nipple on the tube sheet at the gas outlet end was fillet welded. This strengthened the tube-to-plate weld and assumed the shape that the fatigue tests had proved to be the most favorable.

Reliable measurement method needed

The large number of leakages detected in the two former coolers in the methanol and ammonia plants forced BASF to adopt some reliable measuring technique that would help detect damage at an early stage. Timely recognition is essential to prevent severe subsequent damage by water-jet erosion and to allow shut downs and repairs in the two large single-line plants to be prepared in advance.

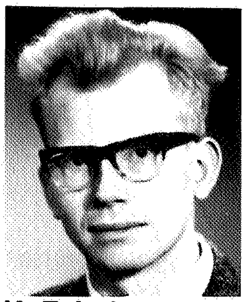
A method BASF considers reliable for the early detection of leakages in waste heat boilers is the measurement of the moisture content of the gas in front of and behind the cooler concerned. For this reason, the saturation temperature of the gas was monitored in front of and behind the two coolers. The gas flowed continuously through the sampling points. The instrument used was a type for which BASF had been granted a patent in 1957 (German Patent No. 1002963). A sketch is shown in Figure 16.

The principle underlying this method is that the water vapor content can be determined by measurements of the superheat and saturation temperatures of the gas mixture. The instrument is located in a block (1) of thermal insulation material. The gas flows through the inlet (2) to the measuring system into the section (3) in which the pressure and temperature of the superheated gas is measured. It then flows through the inlet (4) into the water-filled chamber (6). The length of pipe (5) maintains circulation and thus ensures thorough mixing of the water in the chamber (6). The temperature of the water at the point measured (7) is taken as the saturation temperature. The overflow (8) ensures a constant water level in the chamber. When the gas flows through the water, its water vapor content is increased by the conversion of sensible heat into latent heat of evaporation. It leaves the measuring vessel through the pipe (9). Part of the water vapor condenses in the gas outlet, where there is no longer any thermal insulation. The water thus formed flows back into the measuring chamber, so that an adequate supply is always available there.

The saturation curve at atmospheric pressure for the gas in the ammonia plant after the secondary reformer is shown in Figure 17. If the temperature of the gas at the outlet drops by 20°C as a result of the influx of boiling water, the moisture content of the gas will increase by

$\Delta x = 0.0325$ kg. H_2O/kg. of dry gas.

According to the curve in Figure 17, this increase in moisture content will raise the saturation temperature from 70.7°C to 71.4°C, i.e., by 0.72°C. Therefore, if a reliable indication is to be obtained on any leakages, the saturation temperature must be measured as accurately as possible. That is why two identical measuring instruments were installed—one in front of and one behind the cracked gas cooler. Thermocouples are fitted for measuring the temperature in the water chambers of these instruments. If they are connected to give a direct reading of the difference between the saturation temperatures at the two points of measurement, this value will be a reliable indication of any leakage. #


K. Feind


M. Appl

DISCUSSION

JOHN LANCASTER, Kellogg International, London: We had a parallel experience with a thin tube sheet exchanger. The cracking that occurred in the welds was associated with pre-existing cracks that were present due to the use of a defective welding technique. An alloy steel tube sheet and alloy steel weld rods were used; the preheat was inadequate and it was demonstrated by metallurgical analysis that cracks were present in the weld. We put the failures down to the co-existence of fairly high stress in the tubes with the sharp notch effect of the cracks.

FEIND: I would say such a type of waste heat boiler with thin tube sheets, is necessary when you have high inlet temperatures but for inlet temperatures usual in ammonia plants after the first waste heat boiler, it would be the best to have a cooler with thick rigid tube sheets, not with such thin tube sheets.

Q. Could I ask two questions. One is I think all the failures occurred on the outlet tube sheets. This I would think rathervsurprising unless perhaps you believe the insulation of the inlet tube sheets was such that the operating temperature there was in fact lower than the outlet tube sheets. Second point, I'm not quite clear—after welding the tubes into the tube sheets were the welds stress relieved or tempered?

FEIND: Yes, in many cases the inlet tube sheet is the first point of failure with such waste heat boilers, but in our case it wasn't so. In our case the colder outlet tube sheet was the only damaged sheet and the cracks were there.

In the inlet tube sheets was nothing. The ferrules into the tubes make a good safety against overheating the inlet side of the tubes. And your second question; The welds were stress releaved by tempering.

APPL, BASF, Germany: I would like to add a little to the question. In the ammonia cooler, one could argue that at least theoretically inlet temperature could be lower than outlet temperature, because we are coming to the boiler with a gastemperature of only 450 or 480 degrees centigrade, and we have an insulation on the inlet side.

The outlet gas temperature with 370 degrees centigrade is not so far from inlet temperature. But that situation is really not the case in the methanol plant cooler, where we are going in with a gas temperature of 860 degrees and out with 350 degrees. In that case even with our insulation we have a temperature which is fairly above outlet temperature.

And another thing, I probably should say, is with respect to that method for estimation of the steam content of the gas. It is a very useful tool because normally in waste heat boilers you often deal with the phenomenon that suddenly your outlet gas temperature is dropping down by some 10 or 20 or 30 degrees, very suddenly. After having rised continuously over a month or two or three due to some fouling of the cooler then suddenly a layer of that material which caused the fouling is going off, and now you are always arguing whether it's splitting or falling off of such a layer, or could it be a leakage.

And by that estimation of due point you exactly can determine what had happened.

BERNIE BRODWIN, M.W. Kellogg Co.: I'm not absolutely sure—you mentioned tube rolling, was this done prior to the welding or after or both, at both times?

FEIND: The rolling was done after the welding, but in such a thin tube sheet it's impossible to have a good rolling because for a length of 23 mm you wouldn't obtain good rolling. It's impossible.

BRODWIN: Did you use rolling to help align the tubes for the welding at all? Was a light rolling used at all at that point, prior to welding. Or did they just align the tubes and support them before welding without any rolling? The reason I ask is this is not uncommon to do a light rolling to hold the tube in place while you are welding, and then a subsequent rolling afterwards.

FEIND: The rolling was not done for align the tubes. Here was it done after the welding.

BILL SALOT, Allied Chemical: I'm not sure that the question was answered as to why the outlet tube sheet failed rather than the inlet. I noticed in the paper, one factor that might explain it is that the outlet tube sheet material was different than the inlet tube sheet material in both of your examples.

APPL: I would say that this was the case only in the beginning, but when we repaired the methanol cooler we took for the outlet tube sheet instead of 15 Mo 3 also CrMo 44 which is the same material as for the tubes.

The difficulties therefore could no longer arise from difference in elastic properties of material. After that repair we got again cracks.

Q. In the picture that I saw you showed a change, but you changed from carbon molytube sheet to 13 chrome tube sheet with a carbon molycladding it looked like.

FEIND: We changed the material for the first tube sheet repair of the methanol plant cooler because the rolling would be better with that design, and for better welding we had a 15Mo3 weld overlay.

Q. But the front tube sheet which apparently never failed was a 13 chrome tube sheet welded to the 13 chrome tube. The back tube sheet which did fail—why did you feel it necessary to weld it to the carbon half moly?

APPL: The reason was also that we feared to reweld again, and in that case it would have been easier to weld carbon moly than 13 chromo 44, in which latter case you have to make a proper heat treatment. It is always better if you have a 13 chromo 44 tube sheet, to make a layer with 15 Mo 3. In this case you can, if you have a repair, easily weld without elaborate heat treatment, which you would have to do in the other case in order to avoid cracks.