Ammonia Plant Heat Exchanger Problems

Useful data and recommendations for avoiding future failures result from a detailed investigation of five problems encountered in a Dutch processing facility.

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Five heat exchanger problems in Exxon's 1,500-short ton/stream day ammonia plant in Rosenburg, the Netherlands, illustrate a broad spectrum of failure mechanisms. Specifically, they covered the following:

1. Carbon dioxide removal system reboiler tubes failing from improper heat treatment of stainless steel U-bends.
2. Waste heat boiler tubes failing from overheating (augmented by boiler water corrosion).
3. Syn gas compressor intercooler and syn loop water cooler tubes failing from shell-side cooling water corrosion.
4. A feedgas preheat exchanger cracking at the shell-to-tubesheet joint due to excessive differential thermal expansion.
5. Low-temperature shift feed cooler tubes failing from flow-induced tube vibration.

Improper U-bend heat treatment

The CO_2 removal system reboilers at the Rozenburg ammonia plant use shift converter effluent gas to boil promoted hot carbonate solution. Shift effluent is on the tube-side (U-bends), and there are two horizontal shells in parallel. Tube material is Type 304 stainless steel.

Within one month after initial plant startup (November, 1968) a sharp rise in the H_2 content of the CO_2 venting from the CO_2 system regenerator was noted. Investigation showed one of the reboiler bundles to be leaking, and the plant was then shut down for repairs. Leakage was eliminated by plugging off 48 U-tubes in the offending bundle. The identical parallel bundle showed no signs of leakage.

The reboilers were returned to service with no significant new leakage. After two years, the bundle which had had the initial leaking tubes was pulled and replaced. Visual inspection of the pulled bundle showed cracks in the U-bend area. A thorough investigation of the failure cause was then initiated.

One complete U-tube was sent out to a metallurgical testing laboratory for analysis. Visual inspection of the outside of the tube showed two circumferential fissures, approximately 1/2-in. in length, in the outer radius of the U-bend. Figure 1 shows the location of the fissures. Dye penetrant inspection of the entire bend and adjoining straight tube sections showed no other defects.

The U-bend and an adjoining straight tube section were cut lengthwise along a diameter to permit inspection of the

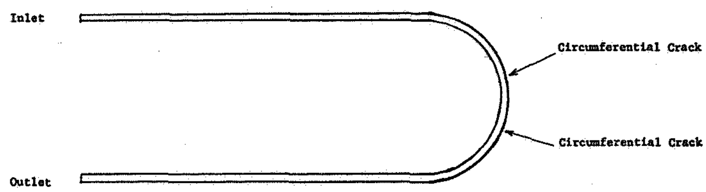


Figure 1. Location of visible fissures in leaking tube taken from Catacarb reboiler.

bore. The two U-bend cracks seen from the outside of the tube were also visible on the inside, as they had penetrated the full wall thickness. No other defects were perceptible with the naked eye, but dye penetrant inspection of the bore revealed several minute circumferential fissures, 1/4 to 1/2-in. in length. As with the two larger cracks found previously, these small cracks were located in the outer radius of the U-bend; i.e., the portion in tension. Neither visual examination nor dye penetrant check indicated any defects in the straight portions of the tube.

The tube wall thickness was measured at numerous locations, and in all cases was found to exceed the specified 0.071 in. nominal wall. No evidence of pitting attack was found. Chemical analysis confirmed the tube material as ASTM A213 Type 304.

Specimens for microstructural examination were taken at several tube cross sections. Away from the zone which had experienced cracking, the tube metal was found to have the normally expected structure; i.e., austenitic with ASTM grain size 8. However, in the U-bend region, an uninterrupted network of carbide precipitations along the austenite grain boundaries was found. In this same region, but not in the zones with normal microstructure, a slight degree of corrosion was noted along the grain boundaries at the surface of the bore.

Numerous micro-cracks, undetected during dye-penetrant inspection, were found near the two cracks which extended through the entire wall thickness. These micro-cracks originated at the surface of the bore, and followed intercrystalline paths. Figure 2 shows one such crack, and also depicts the carbide precipitations at the grain boundaries.

Based on the microstructural examination results, it was concluded that the failures were due to improper heat treatment of the U-bends. Unstabilized austenitic stainless steels,

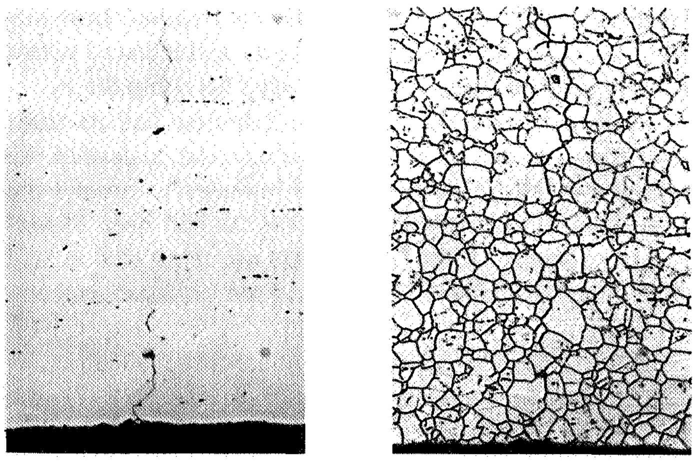


Figure 2. Photographs of microcracks originating at the bore of Catacarb reboiler tube U-bend (X200). Left, unetched; and right, 10% oxalic acid (note carbide precipitations).

such as Type 304, have a strong tendency to precipitate carbides when heated into the 800-1500°F range. These precipitations were found only in the bent portions of the tube, indicating local heating at an unfavorable temperature range either during bending or during installation of the tubes. Most probably, the local heating represented an attempt to stress-relieve the U-bend area, although no such heat treatment was specified in the exchanger mechanical design.

The actual cracking mechanism apparently was triggered by the slight corrosion noted at the carbide-precipitated grain boundaries on the bore of the tube. This hypothesis is confirmed by the fact that the observed intercrystalline cracking originated at the surface of the bore. It is unclear exactly what caused the observed grain boundary corrosion. Wet CO_2 is not generally believed to initiate such cracking. Possibly the agent was polythionic acid, formed during the startup phase when the sulfur-containing high temperature shift catalyst was reduced.

Neither the replacement bundle nor the original parallel bundle have ever shown any signs of leakage. Evidently, only one bundle was subjected to unfavorable U-bend heat treating. The failed bundle, pulled in 1970, has never succeeded in passing a hydrotest in the shop even though roughly 80 tubes have been plugged off to date (vs. 48 when the bundle was removed from service). Apparently, each successive hydrotest causes more micro-cracks to fully penetrate the tube walls, and new leakers result.

The lesson learned from the story is:

- Do not stress relieve Type 304 stainless steel U-bends, or those of any other unstabilized austenitic grade (e.g., Type 316).

Overheated waste heat boiler tubes

The secondary reformer effluent waste heat boiler at Rozenburg, shown photographically and schematically in Figures 3 and 4, has a vertical U-tube design. 1,500-lb./sq. in. gauge boiler feedwater flows through C-½Mo tubes, and hot secondary reformer effluent flows on the shellside. Hot gas entry is directly to the bottom U-bend area.

The temperature of the reformer effluent impinging on the U-bends is around 1,655°F. The tubeside design temperature is 650°F, although the C-½ Mo tubes have the same allowable stress up to about 750°F, and the temperature must exceed 850°F before their strength falls significantly. Because the incoming gas temperature is well above what the tube metal can tolerate, successful operation of this exchanger depends on the cooling effect of the boiling water flowing through the U-bends. Since the design water

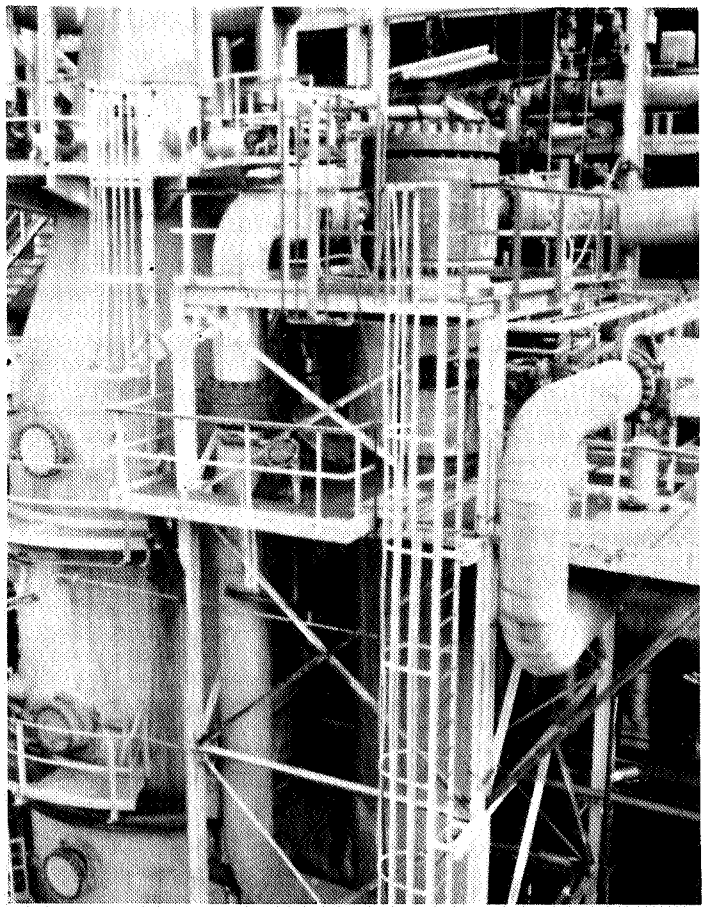


Figure 3. Photo of reformer effluent waste heat boiler shown in service next to secondary reformer.

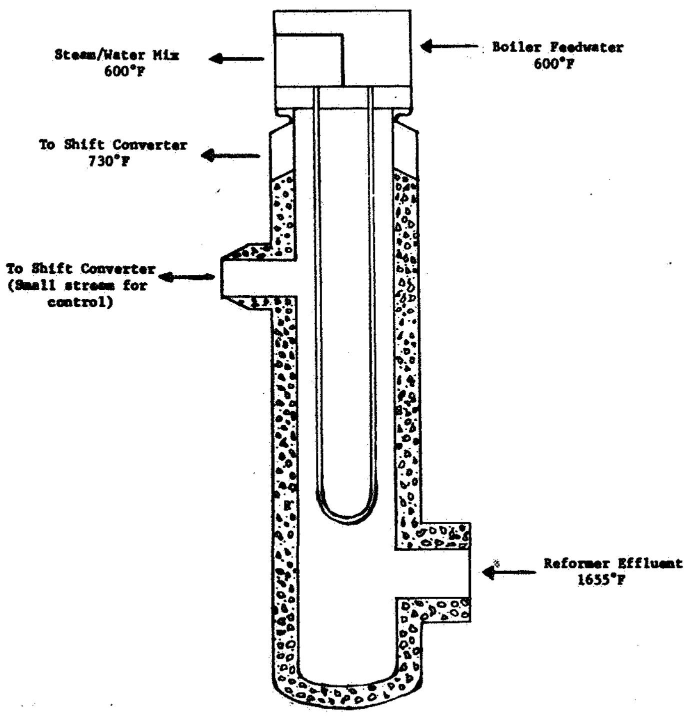


Figure 4. Schematic of reformer effluent waste heat boiler.

Table 1. Brief history of waste heat boiler bundles

Date	Events
November, 1968	Startup (No. 1 bundle).
Jan-Feb., 1969	16 tubes plugged due overheating. Citric acid cleaned.
July-Aug., 1969	Three tubes plugged. No. 1 removed from service + citric acid cleaned. No. 2 citric acid cleaned + installed.
February, 1970	No. 2 citric acid cleaned.
November, 1970	No. 2 citric acid cleaned.
Sept.-Oct., 1971	27 tubes plugged due pitting on bore. Citric acid cleaned.
December, 1971	Observed leak in No. 2.
February, 1972	Found one failed tube and four leaking plugs in No. 2. No. 2 removed from service. No. 1 returned to service (two outer tube rows retubed in same material).
May, 1973	No. 1 removed from service. No. 2 sulfamic acid cleaned + returned to service (three outer rows retubed in 5 Cr-½ Mo).
August, 1973	Found one failed tube in No. 2 outer row. Failure due to tube roller left behind after retubing. No. 1 reinstalled (pressure test showed no leakers) after sulfamic acid cleaning.
September, 1973	No. 1 bundle had many leakers due accidental injection of HCl to BFW. Removed from service and sent for complete retubing (all tubes C-½ Mo). No. 2 sulfamic acid cleaned + reinstalled.
March, 1973........	No. 2 removed from service (no leakers). No. 1 HCl-cleaned and installed.

temperature is 600°F, a fairly close approach of the metal temperature to the water temperature is necessary.

Unfortunately, there have been several tube failures in this boiler. Tube plugging has been required on six separate occasions, several times forcing the plant down for immediate repairs. Purchase of a spare bundle was also necessary, as were two partial and one complete bundle retubing. Table 1 presents an abbreviated summary of the history of the various waste heat boiler bundles.

The first tube failures occurred in January, 1969, only a few months after startup. The event that triggered the failures was gross overheating due to a large secondary reformer effluent temperature excursion. All of the failures were located in the outer three rows of U-bends.

In August, 1969, after three more leakers were found, the original bundle (No. 1) was replaced with a new one (No. 2). In September, 1971, 27 leakers were found and plugged in the No. 2 bundle. Failures again were confined to the outer tube rows and were in the U-bend area. In February, 1972, the No. 2 bundle was removed from service (one more failed tube was found), and replaced with a partially retubed (two outer rows only) No. 1 bundle.

While out of service, the No. 2 bundle had its three outer rows retubed in a 5 Cr-½ Mo material, instead of the original C-½ Mo. This change was intended to protect the outer rows against gross overheating, as had been experienced in January, 1969. This bundle was reinstalled in May 1973, although the No. 1 bundle had not yet developed any leakers.

The last two occasions where boiler tubes failed cannot be attributed to the exchanger design. In August, 1973, the No. 2 bundle was removed from service due to a leak caused by a tube roller apparently left behind after retubing (water flow to tube was blocked off and the tube metal overheated). In September, 1973, the No. 1 bundle was destroyed due to an inadvertent injection of hydrochloric acid into the boiler feed water.

To pin down the root cause of these frequent waste heat boiler tube failures, various failed tube samples have been sent out for metallurgical testing laboratory analysis. The results have consistently indicated significant fouling and corrosion on the bore of the U-bends attributable to impurities in the boiler feedwater. Even in the case of the first failure, where a gas temperature excursion actually precipitated the tube ruptures, subsequent investigation found deposits and corrosion in and adjacent to the U-bend areas. Figure 5 shows the deposits found in a tube taken from the bundle (No. 1) removed from service in May, 1973. Tube samples taken from earlier bundles showed even more evidence of fouling. Figure 6 shows serious pitting corrosion found on a tube taken from the No. 2 bundle pulled in February, 1972.

Because waterside deposits act to insulate the tube metal from the necessary cooling effects of the boiling water, the tube metal temperature will be considerably elevated if fouling occurs. The estimated U-bend metal temperature with design inside and outside fouling factors is 743°F, but if there is significant deposition of boiler water solids, the inside fouling factor will exceed design, and the metal temperature may rise well above this level.

Considering the facts available, one can put together a pretty good picture of the failure mechanism. The following factors all work together to cause tube failures at the outer row U-bends:

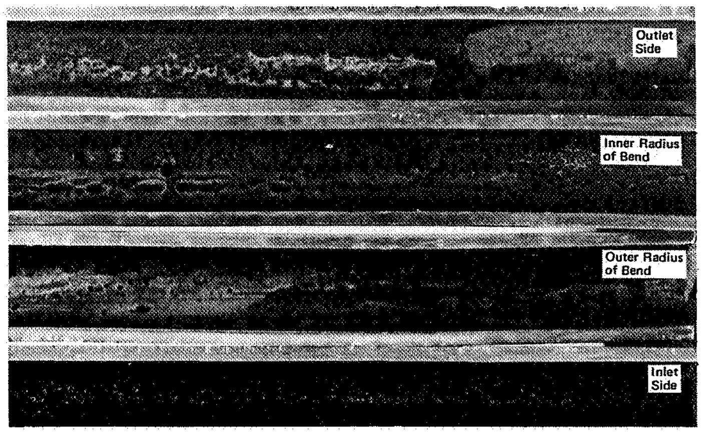


Figure 5. Deposits on bore of tube taken from No. 1 bundle after May, 1973, removal.

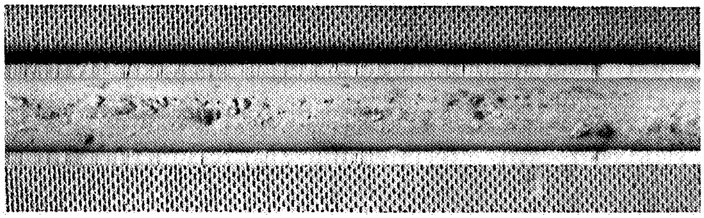


Figure 6. Pitting corrosion found on tube taken from No. 2 bundle after February, 1972, removal.

- A vertical U-tube watertube boiler is extremely sensitive to feedwater solids content. Any solids or corrosive material in the water tend to collect and concentrate in the U-bends, which represent a low point in the system. No blowdown is possible.
- U-bend fouling raises the metal temperature by insulating it from the water.
- The U-bends are the first area that the incoming hot gas hits, and therefore see the highest heat flux.
- The U-bends are the thinnest tube sections to start with due to the bending elongation.

Thus one can conclude that, when corrosion and bending have reduced the wall thickness, and when waterside fouling and high heat flux have raised the metal temperature, tube failure at the U-bends results.

The obvious questions are: "What produces the boiler feed water impurities?" and "What can we do about it?"

At Rozenburg, the first answer is primarily cooling water leakage into the vacuum condensate, although less than ideal control over water treating chemicals has probably been a contributor. Since early 1970 (and perhaps even before that), the plant has had considerable trouble with surface condenser tube failures, due to a combination of tube vibration and cooling water corrosion. This has led to a more or less continuous input of cooling water into the boiler feedwater (no condensate polisher is employed).

As for the second question, several things have been done, and more are planned. We have:

- Employed frequent waterside chemical cleanings, initially with citric acid, later with sulfamic acid, and most recently with hydrochloric acid (HCl cannot be used with the No. 2 bundle because of austenitic stainless steel tube/tubesheet welds on the 5 Cr-½ Mo tubes).
- Instituted a policy of recycling as much contaminated vacuum condensate as possible (roughly 2/3) back to the makeup water tank for demineralization, whenever surface condenser leakage is high.
- Tightened up the high pressure boiler feedwater and boiler water quality targets to those shown in Table 2.

To achieve these tight water quality standards we plan to:

- Revise the boiler feedwater piping so that vacuum condensates will go only to the 600-lb./sq.in. gauge offsite boilers, where poorer water quality can be tolerated, and not to the supersensitive 1500-lb./sq.in. gauge U-tube waste heat boilers.
- Replace the present leaking surface condenser with a new one designed to eliminate tube vibration, and which will have a split cooling water flow arrangement to permit onstream plugging of leaking tubes.

Table 2. Current boiler feed water and boiler water quality standards at the Rozenburg ammonia plant

	Target
Boiler feed water:	
Conductivity(1), mmhos	0.3
Iron, ppm. as Fe	0.01
Oxygen, ppm. as O_2	0.02
Boiler water:	
Silica, ppm. as SiO_2	0.5
Hardness, ppm. as $CaCO_3$	0
M alkalinity, ppm. as $CaCO_3$	5-10
Phosphate, ppm. as PO_4	2-4
Conductivity, mmhos	15-30
Ammonia, ppm. as NH_3	0.5
pH	9-10

(1) Measured after a cation bed to remove NH_3

- Go eventually to an all volatile, zero solids type water treatment if the vacuum condensate rerouting completely eliminates hardness from the 1,500-lb./sq.in. gauge boiler feedwater.

In addition to combatting fouling and corrosion on the bore of the waste heat boiler tubes, we have looked for other ways to reduce the tube metal temperature in the critical U-bend area. One potential method, currently being tested, is to insulate the outside surface of each U-bend (not the straight tube sections) with "Fiberfrax" paper. "Fiberfrax" is a product of Carborundum Co. It is a silica/alumina mixture with a maximum continuous operating temperature of 2,300°F. "Fiberfrax" paper is a thin sheet of "Fiberfrax" that can be cut and cemented in place as an insulating layer.

A 0.04-in. layer of "Fiberfrax" paper coated on the waste heat boiler would greatly reduce the differential between metal operating temperature and boiling water temperature, without significantly adding to the pressure drop. This would protect the U-bends from overheating even if fouling from boiler water solids deposition occurs. Also, such an insulating layer would reduce the susceptibility of the boiler to a secondary reformer temperature excursion.

However, this would represent a prototype application of "Fiberfrax" paper, and there is a danger of plugging up the exchanger and/or downstream equipment if the paper falls off the U-bends. Because of this, we installed the paper (with calcium aluminate cement and nichrome wire) on *one* U-bend of the bundle installed in March, 1974. If, after six months or a year in service, the paper on the test U-bend is still in place, all U-bends of future bundles will be wrapped with "Fiberfrax."

Summing up the Rozenburg experience, we can say that a vertical U-tube watertube waste heat boiler design has an inherent supersensitivity to impurities in the boiler water. If these exceed certain very tight specifications, tube failure from overheating and corrosion in the U-bend area will result. "Fiberfrax" paper insulation has the potential to significantly reduce the sensitivity of the design to inside fouling or process gas temperature excursions, but test work on its adherency must be completed before it can be safely applied.

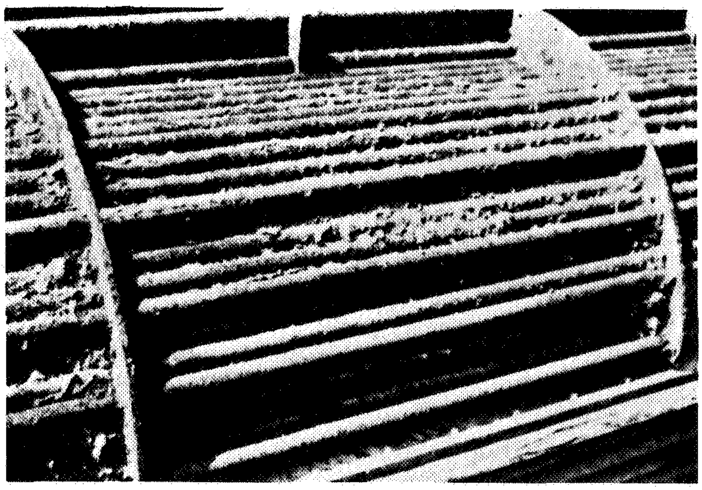


Figure 7. Photo of syn gas intercooler bundle pulled in February, 1973.

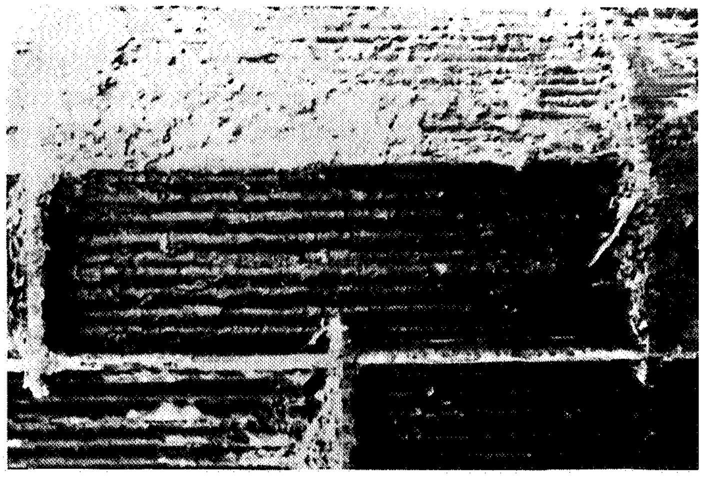


Figure 8. Photo of syn loop water cooler bundle pulled in May, 1973.

Cooling water corrosion reduces exchanger life

Cooling water corrosion of carbon steel heat exchanger tubes has always been a problem at the Rozenburg ammonia plant. The exchangers with the worst experience are those which, due to their high process-side pressure level, operate with cooling water on the shellside. These exchangers are the syn gas compressor intercoolers (two shells) and the syn loop water coolers (four shells). A brief history of the experience with these exchangers is in Table 3.

Thus, after less than six years of operation, the syn gas compressor intercooler bundles have each required replacement twice, and the newest set of bundles have already started to leak. Over the same time period, one syn loop water cooler has been replaced, another has been completely plugged off, and the remaining two original bundles are leaking. Figures 7 and 8 are photographs showing the conditions of a syn gas intercooler bundle pulled in February, 1973, and of a syn loop cooler bundle pulled in May, 1973.

Carbon steel heat exchangers with cooling water flowing on the shellside have proven troublesome in many plants. This is because it is essentially impossible to avoid localized stagnant areas where fouling and associated pitting corrosion are favored. When, as in the Netherlands, the effective chromate-based inhibitors are prohibited, the situation becomes especially difficult to cope with. Because of this, a broad three pronged approach to the goal of improving bundle life was followed:

1. Improving the quality of the cooling water itself.
2. Adjusting heat exchanger operating conditions to minimize fouling and corrosion.
3. Improving the intrinsic resistance of the coolers to fouling and corrosion via better bundle designs and better materials.

Table 3. Brief failure history of water-on-shellside exchangers

Date	Event
November, 1968	Plant startup.
November, 1970	First syn gas intercooler leaks found (27 tubes).
September, 1971	Both intercooler bundles replaced.
June, 1972	First syn loop cooler leak detected. Large amounts of ammonia begin entering cooling water.
February, 1973	Both intercooler bundles replaced for second time.
June, 1973	One syn loop cooler bundle replaced.
January, 1974	Intercoolers leaking again.
March, 1974	One syn loop cooler bundle completely plugged off awaiting opportunity to install spare.

Looking at the cooling water quality, bacterial control was not found to be up to the tight standards needed for shellside cooling water exchangers. Bacteria counts of up to 500,000 colonies/ml. (vs. a target of 50,000) were measured, a smelly sludge was noted in the cooling tower basin, and sulfate-reducing bacteria, notorious for their corrosivity, were found in heat exchanger fouling deposits.

The poor bacterial control was traced to high ammonia and nitrite concentrations, originating primarily from the leaking syn loop coolers and some leaking nitric acid plant exchangers. Table 4 gives typical compositions of the make-up and circulating cooling water at the Rozenburg plant. Note the 50 ppm. ammonia and 10 ppm. nitrite in the circulating water. Chlorine (via "shock" treatments) has been used as the primary biocidal agent (with a supplemental quaternary ammonium biocide), and experience indicates that, under normal conditions, a *free* residual of 1 ppm. is sufficient to achieve excellent bacterial control. However, the ammonia and nitrite present in the water consume chlorine by the following reactions:

$$Cl_2 + NH_3 \rightarrow \underset{\text{(Monochloramine)}}{NH_2Cl} + HCl \quad \left[4.2\,\frac{\text{ppm } Cl_2}{\text{ppm } NH_3}\right] \tag{1}$$

$$Cl_2 + NH_2Cl \rightarrow \underset{\text{(dichloramine)}}{NHCl_2} + HCl \quad \left[4.2\,\frac{\text{ppm } Cl_2}{\text{ppm } NH_3}\right] \tag{2}$$

$$Cl_2 + NO_2^- + H_2O \rightarrow NO_3^- + 2HCl \quad \left[1.9\,\frac{\text{ppm } Cl_2}{\text{ppm } N_2O_3}\right] \tag{3}$$

The quantity of chlorine added (35 ppm.) was not nearly enough to react to all of the ammonia and nitrite present; therefore, no free residual was achieved. The resulting

Table 4. Typical current compositions of RFC makeup and circulating cooling water

Component	Expressed as	Makeup	Circulating water return
Calcium hardness	ppm. $CaCO_3$	270	420
Magnesium hardness	ppm. $CaCO_3$	100	150
Total hardness	ppm. $CaCO_3$	370	570
pH	pH	7.9	8.1
P alkalinity	ppm. $CaCO_3$	0	0
M alkalinity	ppm. $CaCO_3$	180	200
Chlorides	ppm. NaCl	490	750
Conductivity	mmhos	1400	2300
Iron	ppm. Fe	0.3	0.5
Suspended solids	ppm.	6	20
Ammonia	ppm. NH_3	1	50
Nitrate	ppm. NO_3	10	50
Nitrite	ppm. N_2O_3	0.2	10
Corrosion inhibitor	ppm.	–	40
Zinc	ppm. Zn	–	4
Bacteria count	colonies/ml.	4000	30,000
Cycles of concentration		–	1.5

chloramines, although they also have a biocidal action, are only about one fiftieth as effective as free chlorine, and evidently were not sufficient to keep the bacteria in check.

It was not practical to add enough chlorine to achieve a free residual despite reactions 1, 2, and 3 (stoichiometry would require more than 400 ppm.). Other biocides were tested, but all were either not effective enough, prohibitively expensive, or potential pollution problems. Finally, it was reasoned that, if chloramines were one fiftieth as good as free chlorine, and 1 ppm. chlorine residual was good enough, then a 50-ppm. (measured as Cl_2) chloramine residual might do the trick. Therefore, the chlorine shock dose level was increased to about 80 ppm., the shock period was extended from two to three hr. and, at the same time the dose of supplementary biocide was boosted as well. This triple-barrelled approach proved quite successful, and continues in use today. Initial bacteria kills are complete, and post-treatment bacterial growth rates are so low that it is unusual for microbe levels to reach even 50,000 colonies/ml.

After bacterial control was achieved, emphasis shifted toward reducing the corrosivity and fouling tendency of the water. A proprietary mixture of organic phosphonate, zinc sulphate and cationic polyamine dispersant has been used for corrosion and fouling control. As with chlorine, it was found that dosage levels of these compounds were insufficient to achieve the desired results. Phosphonate and polyamine dosages were doubled, and the addition point of these compounds was changed from the cooling tower basin to directly upstream of the critical shellside cooling water exchangers to maximize the local concentration. Zinc concentrations were raised as well; from 2-3 ppm. to 3-4 ppm.

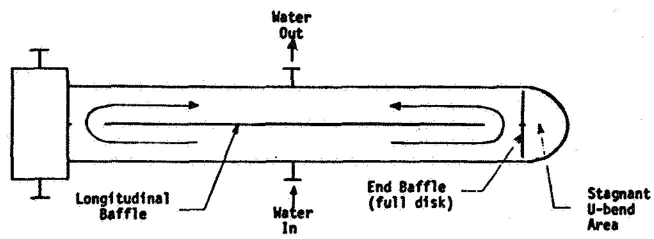
The pH value also plays an important role in determining the water corrosivity and fouling tendency. Higher pH's reduce corrosivity, but increase the tendency for hardness scale to form. By experimentation, we found we could safely increase our pH operating range from 7.0-7.5 to 7.6-8.2. However, above 8.2, excessive scaling resulted.

The higher dosages of corrosion inhibitor and dispersant compounds, coupled with the lower intrinsic water corrosivity associated with the high pH operation, proved very effective. Hot return water corrosion rates (as indicated by "Corrator" probes and corrosion coupons) are now below 1 mil./yr. with local corrosion rates in water exiting the critical water on the shellside coolers in the 2-3 mil./yr. range. This compares with readings of up to 10 mil./yr. prior to water treatment improvements.

Concurrently with the program aimed toward improving cooling water quality, the other operating variables were explored. Based on observations of various fouled coolers which had been operated with different cooling water velocities, it was concluded that a minimum of 5 ft./sec. was required to avoid excessive corrosion promoting deposits. Unfortunately, although sufficient cooling water supply and pressure were available, it was not possible to increase the water flow through the critical shellside cooling water exchangers, due to mechanical limitations in the bundle designs.

The syn loop cooler bundles, as shown schematically in Figure 9 at A, have a "G" shell design, with a horizontal longitudinal baffle. The strength of this baffle, and the strength of its longitudinal sealing strips, limit the shellside pressure drop, and hence limit the cooling water velocity. Moreover, there are several local low velocity areas in the design. During the May, 1973, plant turnaround, inspection of the areas where the transverse baffles cross the longitudinal baffle revealed very heavy fouling deposits. Also, the design flow pattern bypasses the U-bend area (full disk end baffle), leaving it stagnant and subject to highwater temperatures.

A. Original "G" Shell Design



B. Modified "Split E" Shell Design

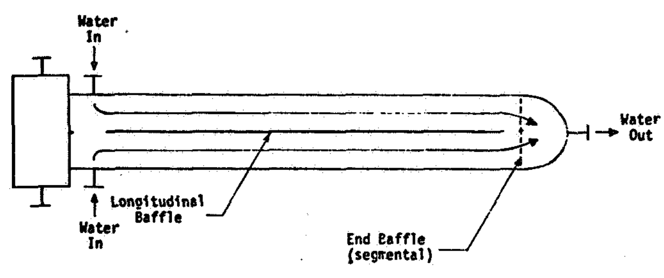


Figure 9. Modifications to converter effluent cooler. Original "G" shell design is shown at A, and modified "Split E" shell design is shown at B.

To eliminate the localized "dead" areas, and to permit an increase in cooling water flowrate and velocity (limited by allowable pressure drop across the longitudinal baffle seals in the original design), the following design improvements have been incorporated in replacement bundles now in stock or on order:

- The U-tube row closest to the longitudinal baffle has been omitted, but the corresponding tube holes in the transverse baffles have been left in.
- The shellside flow pattern has been changed to a "split E" shell design as shown in Figure 9 at B.

Omitting the inner row of U-bends will eliminate the "dead spots" at transverse/longitudinal baffle crossings where heavy deposits had been found, by allowing water to flow through the vacant tube holes in the transverse baffles. It was realized that this extra "bypassing" introduced into the flow pattern will hurt the effective temperature driving force somewhat, but it was estimated that the reduction in fouling level would more than make up for this factor. Also, since there will be improved access to the center of the bundle, turnaround cleaning (with a high pressure water jet) will be simpler and more effective.

The rearrangement of the shellside layout to what can be called a "split E" shell design (for lack of a better name), has a number of advantages as follows:

1. It eliminates the stagnant area around the U-bends.
2. It removes any limitation on the shellside pressure drop because pressure levels above and below the longitudinal baffle are essentially the same. This permits use of maximum available cooling water header pressure drop to maintain high water velocity.
3. It eliminates any concern over the quality of sealing between the longitudinal baffle and the shell, because there is little driving force for leakage, and almost no effect on heat transfer if leakage should occur.

The syn gas compressor intercooler, as shown schematically in Figure 10, are "F" shells (two shellside passes), again having longitudinal baffles. As designed, cooling water velocities were less than 3 ft./sec., and the water flow could not be increased, because the longitudinal baffle strength limited allowable shellside pressure drop to only 7-8 lb./sq.in. To eliminate this restriction the following bundle design changes—details shown in Table 5—were made, to allow the full pressure drop available in the cooling water headers (40 lb./sq.in.) to be taken across the longitudinal baffle:

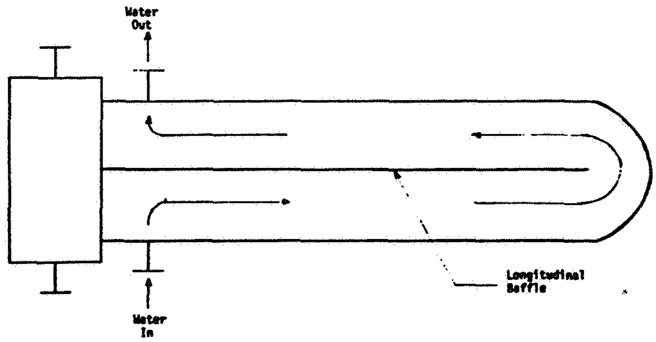


Figure 10. Cooling water flow pattern through "F" shell syn gas compressor intercoolers.

- The longitudinal baffle thicknesses were increased.
- The number of sealing strips was increased.
- The baffle spans were reduced by increasing the number of transverse baffles.
- The longitudinal baffle to shell clearance was reduced on one bundle.

The modifications should easily permit future operation at 5^+ ft./sec., even with considerable bundle fouling.

Finally, the possibility of replacing the carbon steel exchanger tubes with a more corrosion resistant material was explored. About 20 ammonia plants (mostly in the United States) were contacted to exchange experiences with cooling water on the shellside heat exchangers. Several were found that had had good experience with 304 stainless steel in this service, and one indicated favorable cupronickel experience. However, the cooling water chloride level, shown in Table 4, at Rozenburg is about 750 ppm. (as NaCl), and as previously noted, ammonia concentration runs about 50 ppm. Because of this, it was felt that use of an austenitic stainless steel, or a copper alloy, would be very risky.

Deciding to continue with carbon steel as the base tube material, consideration was given to phenolic epoxy type tube coatings. Industry experience with these coatings has been generally favorable, and it was found that experience of other plants in the Rozenburg area was also quite good. Based on these proven commercial successes, plastic coating was ordered for the replacement syn gas intercooler and syn loop water cooler bundles. These bundles are scheduled for installation this year.

Summing up the actions taken to improve the life of the shellside cooling water exchangers at the Rozenburg am-

Table 5. Revised designs for syn gas compressor intercoolers

	First stage		Second stage	
	Original	Revised	Original	Revised
Longitudinal baffle thickness, mm	13	18	15	19
Number of longitudinal baffle seal strips	8	10	8	10
Clearance longitudinal baffle/shell, mm	5	5	6	5
Number of transverse baffles	12	14	11	14
Maximum unsupported longitudinal baffle span, mm.	467	425	618.5	481
Maximum allowable pressure drop across longitudinal baffle, lb./sq.in.	9	44	7	41

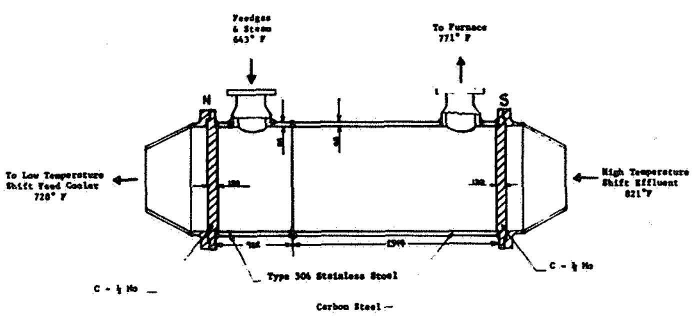


Figure 11. Mechanical design and operating conditions of original feedgas preheat exchanger (dimensions are in mm.).

monia plant, we can say that:

1. Excellent biological control has been achieved by shock dosing with chlorine to a 50-ppm. chloramine residual.
2. Water corrosivity has been greatly reduced by increasing inhibitor and antifoulant concentrations, and by raising the pH level.
3. Bundle designs have been modified to permit at least 5 ft./sec. cooling water velocity, and to eliminate local stagnant areas.
4. Protective plastic coating has been provided for the carbon steel tubes.

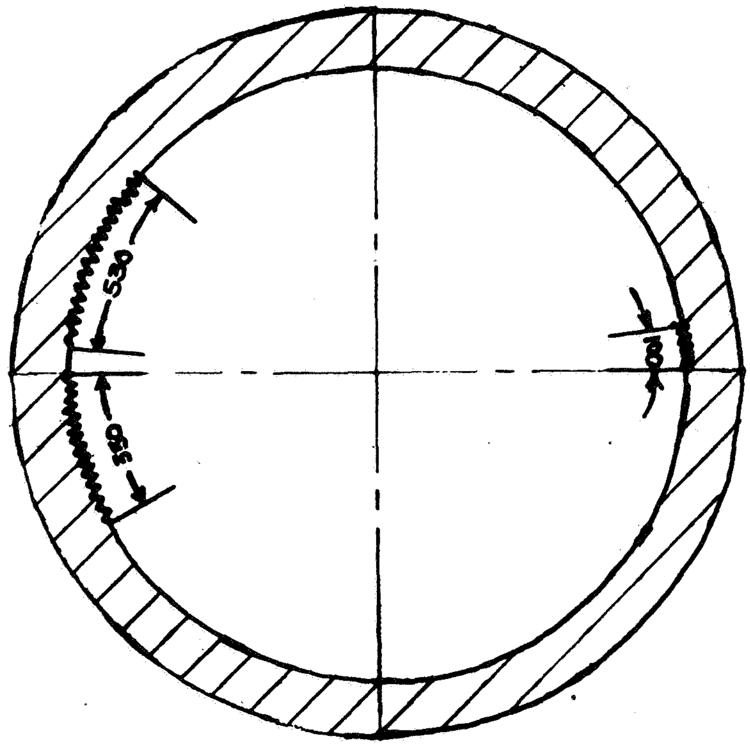
Thermal expansion stress in feedgas preheat exchanger

The Rozenburg ammonia plant preheats a feedgas/steam mixture with high temperature shift converter outlet gas in a single-pass, fixed tubesheet exchanger. Shift converter effluent flows through the tubes and the feedgas/steam mixture flows on the shellside. Tubes are C-½ Mo, whereas the shell is part carbon steel and part Type 304 stainless steel. The bimetallic shell is intended to balance the axial thermal expansion of the shell vs. that of the somewhat hotter tubes, because Type 304 stainless steel has a higher thermal expansion coefficient than carbon steel or C-½ Mo. Figure 11 is a sketch of this exchanger, showing the mechanical design and the operating conditions.

In May, 1973, after 4-1/2 yr. in service, an inspection of this exchanger revealed three circumferential cracks at the junction of the stainless steel shell section and the C-½ Mo tubesheet. No gas leakage had been noted, however. Cracks were in the vicinity of the weld. Crack lengths were 21, 13 and 4 in. Figure 12 shows the orientation of the cracks.

The cracks were ground out as far as practicable, but appeared to penetrate deep into the shell wall. The ground-out crack area was welded with Inconel 182 filler wire, and final dye penetrant checks revealed no indications of new cracks. The shellside was successfully hydrotested, and the exchanger returned to service. Visual inspection in August, 1973, and March, 1974, indicated that the new weld is still in good condition.

An investigation of the failure revealed that the cause was excessive *radial* differential thermal expansion at the joint between the C-½ Mo tubesheet and the stainless steel shell section. Note that the codes normally used for exchanger mechanical design do not cover such radial thermal expansion stresses. Detailed theoretical calculations, based



View Looking North

Figure 12. Orientation of cracks found at north shell/tubesheet junction of feedgas preheat exchanger (dimensions are in mm.).

on ASME Section VIII Division 2 (more sophisticated analysis than Division 1) code criteria, showed that the maximum stress intensity at the outer surface of the joint is 105,000 lb./sq.in. vs. a maximum code allowable of only 54,300 lb./sq.in. This, of course, explains the observed cracking. A contributing factor may have been the poor type of shell to tubesheet joint shown in Figure 11, which in fact is no longer permitted under the Dutch pressure vessel code.

A complete new replacement exchanger is currently on order. The new design, in Figure 13, eliminates the need for a stainless steel shell section by going to a much thicker tubesheet, and to C-½ Mo for the shell material. C-½ Mo is

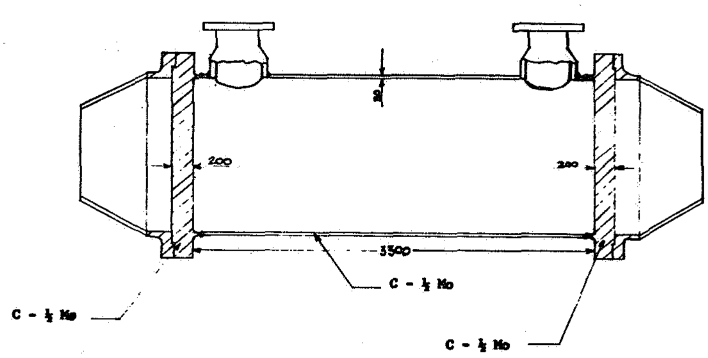


Figure 13. New mechanical design of feedgas preheat exchanger eliminating bimetallic shell construction (dimensions are in mm.).

much stronger than the original carbon steel at the design metal temperature (820°F) and therefore the shell design was able to employ a thinner and more flexible shell to reduce the tubesheet loading from axial thermal expansion differences. With tubesheet and shell made from the same material, the radial thermal expansion problem at the joint is eliminated. In addition, shell to tubesheet joint construction has been improved to conform to the latest Dutch code requirements.

There is a lesson in this story also:

- Standard mechanical design procedures and codes cover standard designs. Non-standard designs (such as a bimetallic shell construction) require more comprehensive analysis to check for possible "side effects."

Rapid tube vibration failures

The low-temperature shift feed cooler at the Rozenburg ammonia plant uses boiler feedwater flowing on the tubeside (U-tubes) as the cooling medium. These are six tubeside passes with crossflow in the shellside.

Performance of this exchanger had always been poor, with heat transfer coefficients typically running at around 65-70% of design. A check of the design coefficient indicated that it was reasonable, assuming ideal crossflow on the shellside. However, a check of the exchanger internals, seen in Figure 14, showed that the original design relied only on a highly perforated (approximately 20% open area) impingement plate, located directly underneath the inlet nozzle, plus the bundle pressure drop, to provide axial distribution of shellside flow. Both the inlet and outlet nozzles are in the center of the bundle, and full disk tube support baffles (total of four) effectively isolate the center of the bundle from the ends. Examining the layout, it was considered that the shellside flow distribution was probably very poor, and that this would account for the observed low heat transfer coefficient.

To correct this deficiency, a new inlet distributor was designed, as shown in Figure 15, and installed in March, 1974. The new distributor consists of a perforated plate, located in the same place as the old impingement plate, but extending over the full length of the bundle. Directly under the inlet nozzle an unperforated section has been left in, to protect the tubes from direct gas impingement. Extra holes have been added to the area adjacent to the solid portion to compensate for the unperforated area in the center section of the bundle.

The inlet distributor change proved quite successful in improving the heat transfer performance of the exchanger. The heat transfer coefficient rose 56% above what had been experienced with the old distributor, and in fact slightly exceeded the design value. Unfortunately, however, there was also an unlooked for "side effect." Within three months after the distributor change, the plant had to be shut down for repair of heavily leaking exchanger tubes.

Shutdown inspection revealed that several tubes had failed by cutting at the baffles. The location of the failed tubes is shown in Figure 16. Note that the failures were directly underneath the section of distributor which had extra holes added adjacent to the inlet nozzle projection. Tube pulling in the area surrounding the failed tubes revealed evidence of baffle cutting in the top three rows of tubes, but none below that.

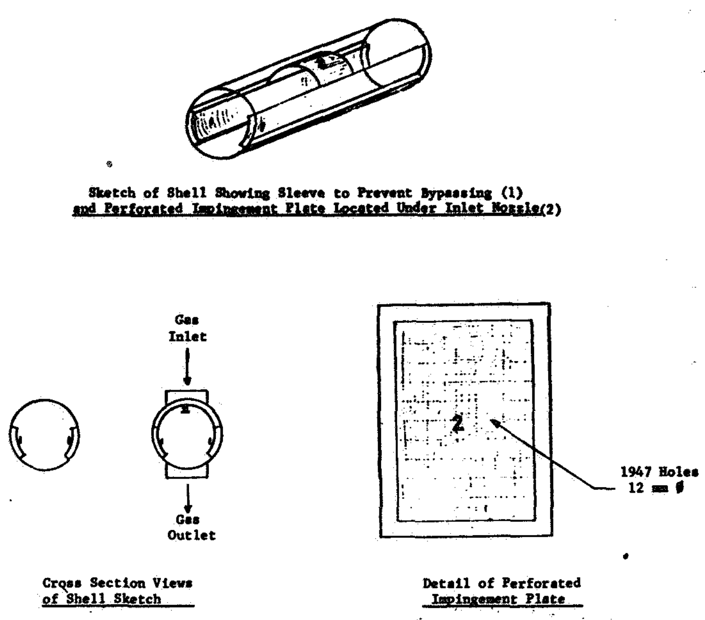


Figure 14. Original layout of low-temperature shift feed cooler.

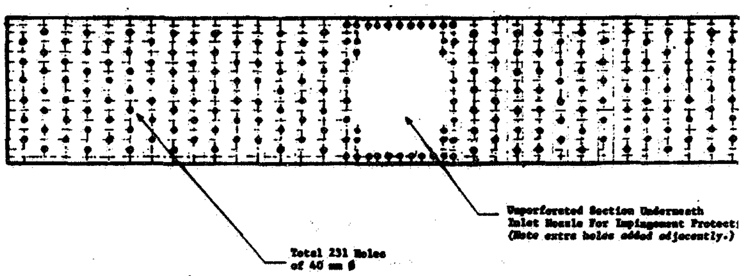


Figure 15. Layout of improved shellside inlet distributor for low-temperature shift feed cooler.

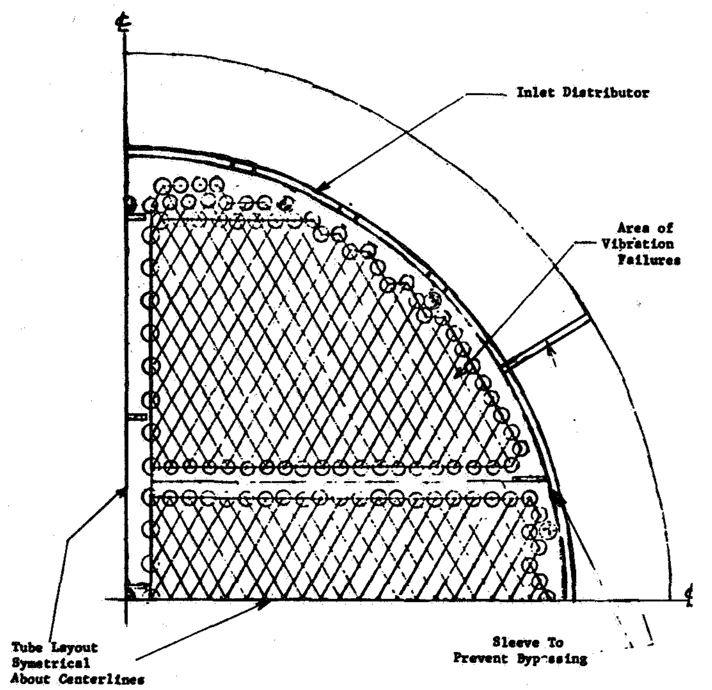


Figure 16. Location of tube vibration failures in low-temperature shift feed cooler.

From the appearance and location of the failures, a tube vibration problem was indicated. To confirm this, theoretical calculations were made to check for flow induced tube vibration. Calculations were based on a method outlined in a paper by J. S. Fitz-Hugh of Oxford University. (*1*) The critical flow velocities which cause flow-induced tube vibration are given by:

$$V_c = \frac{Dd_o}{16SL^2}\sqrt{\frac{Eg_o\,(d_o^4 - d_i^4)}{\pi\,(M_t + M_i + M_o)}} \qquad (4)$$

where: V_c = the critical vibration velocity, ft./sec. or m/s.
d_o = the tube outside diameter, ft. or m.
d_i = the tube inside diameter, ft. or m.
E = Young's elastic modulus for the tube material, ft.lb./sq.ft., or N/sq.m.
g_o = the Newton's Law constant, 32.174 lb_m – $ft/lbf - s^2$ or 1.0 $kg\text{-}N\text{-}s^2$
M_t = the mass/length of the tube metal, lb_m/ft. or kg/m.
M_i = the mass/length of tubeside fluid contained, lb_m/ft. or kg/m.
M_o = the mass/length of shellside fluid displaced, lb_m/ft. or kg/m.
L = the unsupported tube span, ft. or m.
S = the Strouhal number, dimensionless.
D = a constant, dimensionless.

Values of S and D are given by Fitz-Hugh.(*1*) S, the Strouhal number, is a function of tube geometry. D depends on the tube end support conditions (i.e. clamped, hinged, or somewhere in between) and takes a different value for each vibration mode. A tube support between two baffles can be considered as having end conditions somewhere between clamped-hinged and clamped-clamped, provided that the tube to baffle clearance is 1/32 in. or less. (*2*) A tubesheet can be considered as a clamped support, so that a tubesheet to baffle span is closer to a clamped-clamped condition than is a baffle to baffle span.

For the geometry and fluid conditions present in the low-temperature shift feed cooler, the following values of V_c were calculated (all in ft./sec.): clamped-clamped; first mode 7.0, second mode 19.2, third mode 37.7; and clamped-hinged; first mode 4.8, second mode 15.4, third mode 32.1.

Based on actual plant operating data taken during the period with the new distributor in service, the crossflow velocity of the shellside fluid ranged from 14.2 ft./sec. at the inlet gas temperature to 10.6 ft./sec. at the outlet temperature.

A comparison of the actual velocity range with the tabulated critical vibration velocities indicates that the exchanger inlet velocity is quite close to the second mode vibration critical. Considering that the tube failures were located under a section of the distributor which had a higher than average hole density, the local inlet velocity must have been somewhat higher than 14.2 ft./sec., and would therefore be right in the range calculated to produce tube vibration. Moreover, Fitz-Hugh (*1*) suggests a safety margin of at least ±20% around the calculated critical velocity to avoid vibration problems.

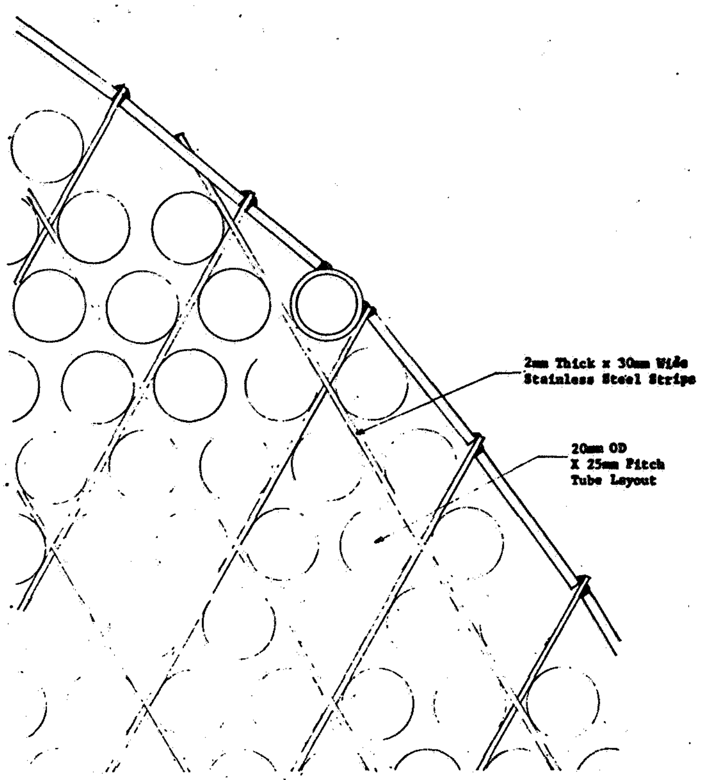


Figure 17. Detail showing field fabrication of temporary "baffles" for low-temperature shift feed cooler.

Once the mechanism for the tube vibration failures had been theoretically confirmed, the question of course became "What do we do about it?" For a short-term fix, two rows of tubes surrounding the failures were plugged off, and the extra distributor holes adjacent to the inlet nozzle projection were eliminated. To raise the critical vibration velocity safely above the actual inlet velocity, the unsupported span length (appears squared in the denominator of the V_c equation) was reduced by creating temporary extra "baffles" in the top portion of the bundle. These "baffles" were created by forcing 0.079 in. thick stainless steel strips in between every other tube row, as shown in Figure 17. Since the tube-to-tube clearance is normally only 0.065 in., the force fit strips created a rigid assembly that effectively clamped the tubes in place. The long-term fix will employ a complete new bundle which will have nine tube support baffles vs. the original four, but which will continue to use an improved inlet distributor to provide a good heat transfer coefficient.

An interesting question remains as to why there were no vibration problems before the improved inlet distributor was installed. The best theory available is that, with the very poor flow distribution, the center sections of the bundle had inlet velocities above the critical, and the outer sections had inlet velocities below the critical. Two old and as yet unexplained failures, located about 2/3 of the way into the bundle, may have occurred at the point where the shellside flow velocity in the center section dropped down far enough (from gas cooling) to match up with the critical vibration velocity.

From this experience with the low-temperature shift feed cooler, and from the previously mentioned vibration related surface condenser tube failures, we have learned to:

- Watch out for flow-induced tube vibration, especially in large exchangers with long unsupported tube spans.

Broad range of heat exchanger problems

Summing up the Rozenburg heat exchanger failure experience discussed here, trouble has resulted because:

- An apparent attempt to stress relieve Type 304 stainless steel U-bends led to carbide precipitation at the grain boundaries, and hence to tube failures from intercrystalline cracking.
- Deposition of boiler feed water impurities in the U-bends of the vertical watertube waste heat boiler led to tube failures from overheating and corrosion.
- Cooling water, flowing on the shellside of carbon steel cooler tubes, and having relatively poor water treatment, caused rapid tube corrosion failures, forcing frequent bundle replacements.
- A bimetallic shell design in a fixed tubesheet exchanger, intended to minimize *axial* thermal expansion differences, led to cracking at the shell to tubeshell junction due to the *radial* thermal expansion difference.
- An inlet distributor change in a crossflow exchanger led to rapid tube failures from flow-induced vibration.

Acknowledgement

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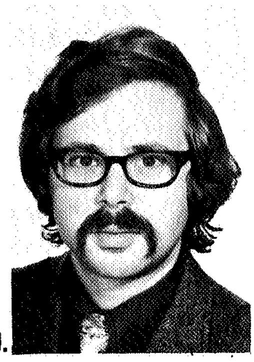

OSMAN, R. M.

DISCUSSION

BOB PRESCOTT, C F Braun Co.: It seems possibly an oversimplification to attribute the failure in the preheater exchanger simply to thermal stresses since the thermal stresses at the stainless shell to ferritic shell weld are actually higher than they are at the tubesheet to stainless shell weld. And this is true because the stainless shell to ferritic shell weld is at uniform temperature whereas the stainless shell to tubesheet stresses are diminished by the fact that the tubesheet temperature is much higher than the stainless shell.

I would suggest possibly that there may be a less than perfect weld at that juncture. It's a very difficult weld to make, so difficult in fact that most of us do not use that particular detail any more. We weld a stub to the tubesheet or we build up a nubbin with weld metal so that a butt weld can be made.

So there may have been notches, Bob, or some pretty serious stress raisers that contributed to the shell to tubesheet weld failure. I have one other question on the waste heat boiler and the possibility of insulating the outer row of tubes. It seems to me that if insulation were applied, this would move the hot spot upward into the bundle to the first uninsulated row of tubes. I would like you to comment on that, if you would.

The other thing that disturbed me a little is attributing the failures in the reboiler tubes to sensitization. As with Exxon, we do not know how these reboiler tubes became sensitized. There was no heat treatment ever specified or intended on these U bundles. However, if sensitization is the culprit, it's somewhat disturbing to note that there is a considerable amount of ordinary 304 stainless steel in this plant in the as-welded condition with sensitized heat affected zones. So there must be some other factor that got to these tubes, and hopefully this other factor will not get to your heat affected zones.

OSMAN: Well, I'll answer your questions in order. As far as the possibility of a poor weld at the shell to tubesheet joint, of course this is a very real one. However, there were three cracks found, and one of the cracks was about ten inches long. So it would have meant that there were quite a number of weld defects, and quite extensive weld defects.

Now I am not a mechanical engineer, so I haven't personally made stress calculations on the exchanger, but the indication I had from our mechanical engineering people was that the stress at the shell to shell bimetallic joint was less because of the much more flexible situation there.

As far as insulating the U-bends moving the hot spot up further into the bundle, this is a potential problem, but the insulation layer would be very thin so that we will still get a fair amount of heat transfer in the outer rows, and what we hope is that it will tend to average things out and really will cut down the peak heat flux.

On the sensitization of the 304 stainless steel, if I'm not mistaken we had evidence of a failure of this type in a hydrogen plant, with polythionic acid causing the cracking itself. Perhaps Paul Krystow has some more details on that.

PAUL KRYSTOW, Exxon Chemical Co.: Unfortunately you have me up a barrel. I really do not have much background on the particular problem which you have cited regarding the failure of type 304 in the hydrogen plant, but I'd like to talk further about the U-bend failure. The microstructure of the U-bend definitely indicated that sensitization had taken place and although there might be other portions of the tube that were not sensitized, the U-bend region experienced substantial carbide precipitation indicating sensitization. This could indicate that the bending operation may not have been carried out properly or, as your paper suggests, the U-bend may have been stress relieved after bending.

OSMAN: The one other comment I had on that, is that if, as we suspect, it's a sulfur compound from the high temperature shift reduction that actually triggered the cracking, in this reboiler you would have the highest concentrations of these compounds present in conjunction with a liquid phase, because downstream of this reboiler, we discard the condensate. Therefore, possibly this represents a more severe condition than seen by the rest of the stainless steel equipment in the system.

ED LEWISON, M.W. Kellogg Co.: I just want to say one word in defense of that tube sheet to shell shoulder joint. It's used frequently. It's shown in the code, but at six or seven hundred degrees, then you have to use a little bit more—well, I guess conservatism. I think I wouldn't use it at that temperature.

OSMAN: It was perhaps especially bad because we had this thermal expansion differential right at the relatively inflexible joint. But the fact is, that although, as you indicate, the U.S. codes permit this, the Dutch codes stopped permitting this type of joint, presumably because others experienced this type of problem. I know that we were not allowed to use that type of joint in the new design, and I don't know if we would have wanted to anyway, but we weren't allowed to.

Q. I think this type of joint is not suitable for this service, but what's more I doubt that a thicker tube sheet is a good solution. I don't know why you went to that.

OSMAN: Well, actually Exxon practice would not have required the increase in the tube sheet thickness. This was again a requirement of the latest Dutch codes. In order to meet their code requirements, we had to increase it to 200 millimeters.