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A PRESENTATION OF TYPICAL EQUIPMENT CORROSION PHENOMENON IN LARGE SCALE AMMONIA PLANTS *

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Since the mid seventies, some thirteen modern large scale ammonia plants have been built and come into operation successively in China. Generally speaking, most of these plants ran smoothly during the initial operation and the design daily capacity has been met. But during the last three years, shutdowns due to equipment and piping corrosion did also occur. The most typical ones are: primary steam reforming furnace tube failure; CO_2 removal reboiler corrosion; corrosion in water coolers and circulation pumps. As to the category of corrosion, there are pitting, SCC, corrosion fatigue, cavitation corrosion, erosion corrosion, crevice corrosion (sediment deposit) and electrochemical and biological corrosion due to bad control of water treatment.

For lacking experience, at the very beginning, one of the reboilers corroded and penetrated after 66 days' operation. In another plant, premature failure of the reformer tubes occurred due to frequent emergency shutdowns. However, most of the problems have been solved at present after taking measures for prevention of corrosion. Now let us present the case stories as follows.

1. TYPICAL CASE HISTORY

A. Primary Reformer Tube Failure

(1) Since modern reformers are designed with a tube life of 10^5 hours, no noticeable tube corrosion has occurred in our new plants yet with an exception of one plant in which premature failure occurred two years after commissioning. Most of the cracks located at the vicinity of the meltin line of the weld seams between different tube materials. Following the results of chemical, metallographic examination and modern electronic probe analysis, we find the main cause of fracture is corrosion fatigue. And the reason of fatigue is frequent emergency shutdown. The cracked portion of the tubes is ground and the rewelded tubes are utilised without replacement.

(2) By the way, we would like to present the history of a 300 TPD ammonia plant. This is an old plant operating since April 1966. The reformer worked under 20 kg/cm^2 pressure with natural gas as feedstock. Up to June 1979, 922915 tons of ammonia has been produced and 165 pieces of tubes were replaced, i.e. 1.785 piece of reformer tube is consumed per ton of ammonia. The inte

and number of replacement of tubes is as follows.

Date	No. of tubes replaced
1971 Feb.	30
1971 June	10
1971 Sept.	34
1972 Jan.	25
1972 March	4
1973 March	9
1974 July	29*
1975 Aug.	11
1976 March	2
1977 April	3
1977 Nov.	2
1978 Feb.	1
Total	165

Remark* 12 tubes were replaced for retire without failure.

155 of the above mentioned 165 tubes are a certain manufacturer's product, their working life is as follows.

Working hours	No. of tube
61460	1
58200	1
57440	1
52200	29
43820	1
41400	8
36400	4
34460	1
31300	18
29420	8
28300	30
26540	1
26300	10
24500	30
20160	1
9360	1
6850	6
4320	1
3960	1
Total	155

Besides, 6 more tubes are still under operation with a working time of 68040 hrs. Altogether, the average life of the tubes is 32000 hrs.

Several pieces of another manufacturer's tubes have also been used with an average life of 60000 hrs.

As can be seen from the above situation, during the first one or two years many reformer tubes failed because of frequent shutdowns of the plant due to unskillfulness. But it must be pointed out that this plant was built many years ago and the reformer tubes are designed with a ruuture time of 50000 hrs. That is why the tube life is shorter.

B. CO_2 removal system reboiler corrosion

Plant A used Benfield solution in the CO_2 removal system and commissioned on May 5. Up to Aug. 14, 1977 the two reboilers corroded and leaked 5 times, and the plant was shut down for 792 hrs. totally.

The shell of the above mentioned reboilers is made of 304 type stainless steel and the tubes are made of 304L steel. On Dec. 24. 1976, 7 months after commission, the tube bundle leaked the first time. We pluged the corroded tubes and worked once again. But during the following 130 days, there occurred three more times of leakage. On May 5, 1977 the bundle was taken out for inspection and corrosion was found in many places on the bundle. Based on 342 days operation, the maximum corrosion rate was found to be 0.94 mm/yr. According to the inspection, impingement thinning off and pitting was noticeable on the corrded spots. No Cl^- accumulation and intergranular corrosion and crevice corrosion is found after examination by electronic microscopic energy dispersive analysis.

The operation condition of plant B is similer to plant A, but the construction design of the reboiler is better. From Oct. 27, 1976 (commission) to Aug. 1, 1978, the plant ran 11450 hours. During this period, leakage occurred only two times on April 13, 1978 and July 11, 1978, 85 tubes (i.e. 6.2% of the total reboiler tubes) were pluged. Since Aug. 1 after the maintenance, no problem has been found. This means that the inspection and maintenance is successful.

During the inspection we found the protective film in the vanadium activity area to be faultless. But in the corroded area of the bundle, the tube surface is somewhat rough and longitudinal white gullies exist, the protective film lost. Metallographic structure is dual-crystal austenitic, grain size 4-5 grade, without intergranular corrosion. The chemical analysis matches the composition of SA-249 and TP 304L steel.

In plant C, GV solution is used in the CO_2 removal system. The plant began to operate on Oct. 20, 1978 and corrosion leakage occurred on Jan. 9, 1979. After mending, the reboiler was put to work on Jan. 12 the same year. On Jan. 13 leak was detected again and the plant was started up on Feb. 23 after repairing

On Mar. 3 once again the reboiler leaked. After that, the equipment worked until now without leakage. Through macroscopic examination noticeable thinning of tube wall can be detected at the corroded portion. There are also deep valleys, pitting, and impingement penetration. Since the construction design of the reboiler is incorrect, local gas velocity is too high.

Hence, incorrect design may increase the corrosion rate of an equipment as shown. After modification of the construction, corrosion is controlled.

C. Corrosion in water coolers

The quality of the cooling water differs from each other in the ammonia plants and the factors inducing corrosion are different also. But water cooler corrosion is very popular. Take plant A as an example, scaling, fouling, biological and other types of corrosion occurred because of unstability of water quality. In this plant biological corrosion is quite serious. Before 1977, experience in controlling of the cooling water quality was lacking and Fe^{++} content in the scale was as high as 50-60%. Since 1978 management has been improved and the Fe^{++} content was lowered to 20% with heat transfer coefficient K-value increased evidently.

The circuling water in this plant contained not only sulphate reducing bacteria, sulphur bacteria but also nitrite, nitride and de-nitride bacteria.

Condition of water quality	Bacteria units / ml	NO_2^- ppm.	NH_3 ppm.	NO_3^- ppm.	Turbidity ppm.	Cl^- ppm.	Residue Cl_2 ppm.	COD
NORMAL	270	0.452	137.5	14.2	11	65.5	0.37	3.6
deteriorating	2400	23.2			14.7	89	0.03	15.44
deteriorated	44×10^4	108	147		37.4	99.5	0	22.72

As shown in the table, deterioration of the water is characterized by rapid increase of NO_2^- content.

One year after commission, the lubricant cooler of the BFW pump of this plant was corroded and penetrated. Nine coolers were repaired or replaced during the maintenance after 2 years' operation. The other coolers, though not repaired, were scale-corroded to different extent.

Coolers repaired or replaced during 1977 are as follows.

Item	pcs. of tubes corroded
(1) Methanation cooler	3
(2) Feed gas compressor 1st. cylinder cooler	1
(3) Ammonia condenser	1
(4) BFW pump lubricant cooler A	10-15
(5) ditto B	8
(6) NH_3 condenser	2
(7) Crank case lubricant cooler A	4
(8) ditto B	1
(9) Reducer lubricant cooler	1

9 more coolers were repaired or replaced during the maintenance in Aug. 1978, they are :

(1) Air compr. 1 st. cyl. intercooler.
(2) Feed gas compr. bypass water cooler
(3) Air compr. 1 st. cyl. water cooler. (74 tubes leak)
(4) Air compr. 2 nd. cyl. water cooler. (10 tubes leak)
(5) Feed gas compr. 1 st. cyl.after cooler.
(6) Ditto 2 nd. cyl.after cooler.
(7) 170-C cooler (8tubes leak).
(8) BFW pump A cooler (5 tubes leak).
(9) Urea plant cooling water pump turbine lub. water cooler. (23 tubes leak)

According to the inspection, most of the corrosion is pitting with a depth of 0.2-0.3 mm, individual pitting is as deep as 1.0 mm and penetrates at last. The maximum pitting area on the dish heads is 4-10 cm^2 with a depth of 6-8 mm. Fouling is quite serious.

Afterwards, better chlorination and biocide control together with other measures taken improved the water quality effectively.

The turbidity of the fresh water is extremely high during the flooding season in one of the plants and alkinity is too high in another plant. The type of corrosion and preventive measure is of course different.

D. Erosion corrosion of circulating water pumps

The impeller of the circulating water pump in plant C was corroded and penetrated at the inlet after 3405 hours operation. Maybe this is due to the improper selection of material.

These are only some typical examples in aspects of importance.

2. ANALYSIS TO CORROSION CAUSES

A. Reformer tubes

(1) Creeping

Most reformer tube failures are caused by creeping. And creeping is in turn induced by local or abrupt overheating. The metallographic structure of a new 25 Cr-20 Ni tube is supersaturated austenitic with Cr_7C_3 framework carbides distributed on the basic metal. After long term high temperature operation, $Cr_{23}C_6$ and σ phase will precipitate out. The $Cr_{23}C_6$ crystal grains grow coarse. The strength of such austenitic basic metal with carbon depletion lowers and the reformer tube will creep under inner pressure. Generally, the tube diameter enlarges locally, with strength of material decreasing continuously and the tube fails at last. A lot of creeping failure is originated from process factors, such as carbon or salt deposit on catalyst with a result of overheating; heating up too quickly during start-up, low steam rate could also cause overheating; improper emergency shutdowns sometimes causes overheating.

(2) Thermofatigue

This is caused by non-uniform expansion and contraction due to temperature gradient among different parts of the reformer tube. The low temperature part of the tube restrains the high temperature expansion and thermo-stress arises. After operation under high temperature, carbide or σ phase would precipitate in the basic metal of the reformer tube. The strength decreases and the material is embritted. Under repeated cyclic thermostressing fatigue will occur and cracks will propagate until leaking.

(3) High temperature corrosion.

(4) Stress corrosion

Therefore, to prevent premature failure of the reformer tubes, the unit should be operated in strict accordance with the operating manual.

B. Reboiler

Solution boiling is a very complicated phenomenon, the heat transfer process is also quite complicated, Vapor phase and bubbles are formed in the solution as heat is being transferred to the liquid through the tube wall. Experiments show that bubbles will increase violently as the temperature difference ΔT is increased to a certain extent.

Since the temperature difference between the gas and liquid phase in the reboiler is as high as 55°C and the maximum temperature exists at the inlet near the top of the bundle, so the process solution will boil violently near the upper tube sheet. Vanadium film is hard to form at this area under such condition. In addition, the first solution outlet nozzle is apart from the tube sheet, so the gas and solution flow with a velocity as high as 70 ft/sec. this increases metal corrosion. Moreover, the construction design is incorrect, the volume over the boiling surface is too small and the cross-sectional area for the vapor flow is not large enough, this tends to accelerate the corrosion rate.

After modification of the reboiler contruction, it has been working over 7676 hours and no leakage has occurred.

C. Water cooler

The reason of fast propagation of bacteria in the cooling water is:

(1) The position of the chlorination pipe outlet is too high, the chlorine evaporises and the concentration is lowered.

(2) The blowdown outlet is located near the circulating water return piping, part of the inhibitor is blown off through this pipe lowering the effective concentration.

(3) The cooling pond is quite large in area, since there is no cover, the sun light helps the bacteria to propagate and during night time a lot of insects fall in the water, increasing equipment fouling.

After taking measure to solve the above problems, the water quality is improved and corrosion decreases evidently.

D. Circulating water pump

The reson of erosion is due to low Av NPSH and coating has no effect, so we think it is better to choose erosion resistant steel such as 2Cr13 etc. to fabricate the impeller.

3. SUMMARY

To prevent or inhibit equipment and piping corrosion in ammonia plant, we think the following is important.

(1) Correct corrosion resistant material should be specified during the engineering phase. Since shutdown of a large scale ammonia plant costs a lot, utilizing corrosion inhibitor and coating to save expensive alloy steel must be evaluated with the service life of the equipment and shutdown costs.

(2) The construction design of the process equipment should be correct so as to reduce corrosion problems.

(3) Strict inspection and test must be conducted during the fabrication, welding and erection process. Be careful not to injure the equipment or induce inner stress.

(4) Prevent atmospheric corrosion during transportation and storage of the equipment.

(5) The operation should be stable and the plant should be managed scientifically in accordance with the operating manual.

(6) The designer, fabricator, operator, maintenace personnel should learn to raise their level to combate corrosion.

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