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AMMONIA PLANT REFORMED GAS WASTE HEAT BOILER LEAK AND ITS EFFECT ON HIGH TEMPERATURE SHIFT CONVERTER CATALYST

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RESUME

Une chaudière à chaleur résiduelle de gaz réformé dans une unité d'ammoniac de 600 t/j de capacité a connu des fuites deux fois en 1993. La première fois, la fuite a été traitée avant qu'elle ait endommagé les appareils en aval. La deuxième fois, l'unité marchait depuis environ 10 semaines avant que l'on s'occupe de la fuite. En conséquence, la chute de pression à travers le convertisseur à haute température (HTS) a augmenté jusqu'à 20 psi. Pendant l'arrêt, le convertisseur HTS a été inspecté et des échantillons de catalyseur ont été recueillis pour analyse. La couche supérieure de catalyseur a été remplacée sous atmosphère d'azote. (La performance de HTS sera examinée après démarrage et incluse dans notre exposé).

L'exposé présente l'identification de la fuite de la chaudière, la performance des catalyseurs de réaction pendant la fuite, la procédure adoptée pour rectifier le problème et l'évaluation de la performance du catalyseur de HTS après réparation de la fuite.

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INTRODUCTION

SAFCO operates a Chemico 600 metric tonnes per day ammonia plant in Dammam, Saudi Arabia. The plant was commissioned in 1969 and runs regularly at about 110% of name plate capacity.

In 1993, reformed gas waste heat boiler (RGWHB) located downstream of secondary reformer had developed leaks on two occasions. First time, plant was stopped within 10 days of appearance of leak, before it could do any damage to downstream equipment. But in the second time, performance of high temperature shift (HTS) converter deteriorated due to deposition of boiler water solids on catalyst bed surface, when the plant was run for 10 weeks with RGWHB leak.

This paper discusses identification of boiler leak, deterioration in the performance of HTS catalyst during the leak, procedure adopted to rectify the problem and performance of HTS catalyst after attending the boiler leak.

REFORMED GAS WASTE HEAT BOILER (RGWHB)

The function of RGWHB is to cool secondary reformer exit process gas from 1650°F to 760°F. The process gas is further cooled to 675°F in another heat exchanger and enters HTS converter (**Figure 1**).

The boiler was supplied by M/s. Bros Incorporated, U.S.A in 1968. Its tube bundle was replaced in 1973 and until 1993 no leakages were experienced.

General configuration of RGWHB is shown in **Figure 2**. Salient features of the boiler are as follows:

1. RGWHB is a natural circulation, fire tube type boiler producing 136,000 lb/hr of 600 psig steam (gas side pressure is 300 psig).

2. Apart from the main horizontal tubular exchanger, it has steam drum, riser and downcomer pipes, inlet and outlet reformed gas connections, internal reformed gas bypass and false tube sheet with dampers.

3. Reformed gas inlet vestibule is refractory lined CS concentric cone. Internal diameter of CS shell is 66 inch with 24 ft. as face to face distance of tube sheets. Gas outlet chamber is made of C-1/2 Mo steel with 20 inch manway and 20 inch exit nozzle.

4. Exchanger tube bundle has 366 number of 2 inch diameter CS tubes and a CS pipe of 10 inch diameter at the center. The bypass pipe is covered with a SS 310 ferrule. Gap between the pipe and the ferrule is packed with insula-tion material.

5. Close to outlet tube sheet, there is a false tube sheet with dampers. By operating these dampers, gas flow through the bypass pipe can be varied to control gas outlet temperature.

FIRST TIME LEAK IN RGWHB

After more than 20 years of replacement of tube bundle, first time leak occurred in **RGWHB** on January 26, 1993. Symptoms of the leak are listed below:

a) Consumption of boiler chemical increased steeply. Dosing pump stroke was increased from 55% to 100%. In addition, shot potting of chemical was done once in 4 hours to maintain chemical concentration within specified range.

b) High and low temperature shift converters exit CO slips decreased from 1.95% and 0.16% to 1.74% and 0.13% respectively, for the same plant load conditions.

c) Steam production in **RGWHB** decreased by 10,000 lb/hr whereas in downstream waste heat boilers increased significantly.

d) Steam supply to MEA steam reboilers in CO_2 removal section could be reduced to 80,000 lb/hr from the normal level of 86,000 lb/hr.

We use an "all-organic" chemical for controlling scale and corrosion in all waste heat boilers including **RGWHB**. Boiler chemical was not present in **RGWHB** outlet gas, as it decomposed to carbon dioxide and other by products at high temperatures.

The plant was run for 9 days with the boiler leak and in this short period, no serious effects on **HTS** catalyst were seen. Pressure drop across HTS converter remained same at 4 psi. 1993 annual plant turnaround, originally planned for April, was taken in advance to attend to **RGWHB** leak.

The boiler had two leaking tubes and a circumferential crack in the center bypass pipe near the outlet tube sheet. Nine tubes were having defects like hair line crack at the inner surface, fitting and mechanical damage, erosion and fissures. Totally eleven tubes were plugged and the center bypass pipe crack was ground up to 22 mm depth (pipe thickness 25 mm) and welded. Plant was started back on February 25, 1993.

SECOND TIME LEAK IN RGWHB

After eight months of operation, **RGWHB** started leaking again on October 29, 1993. Initially the leak was minor, but after a crash shutdown due to power failure, leak increased. Estimated amount of boiler leak was 25,000 lb/hr. This is almost double the quantity experienced in the first time. Plant was kept running continuously till the year end with boiler leak to achieve production targets.

EFFECT OF BOILER LEAK

On running the plant with boiler leak, performance of HTS converter catalyst deteriorated. In HTS converter, carbon monoxide is converted to carbon di-oxide by reaction with steam, in the presence of iron oxide catalyst, according to the equation:

$$CO + H_2O \dashrightarrow CO_2 + H_2$$

This reaction, known as "water-gas shift reaction" is exothermic. HTS converter has two beds in parallel and both beds are installed one over the other in a single vessel **(Figure 3)**. HTS converter was charged with chromia (Cr_2O_3 - 9%) supported iron (Fe_2O_3 - 89%) based catalyst in May 1992. Total catalyst volume is 1650 CF. HTS inlet temperature was maintained at 675°F.

Pertinent performance factors of HTS catalyst which was affected by RGWHB leak are as follows:

A. CO SLIP:

HTS exit gas CO concentration was 2.0% before the leak occurrence. It increased gradually to a maximum of 3.05% in 10 weeks time. Inlet temperature could not be increased above 675°F due to quenching of gas by boiler water.

CO slip values analyses at different locations on different dates are given below. Bottom bed CO slip was higher.

Date of analysis	14.12.93	05.01.94
No. of days after leak appeared	50	72
HTS top bed exit	1.56%	1.48%
HTS bottom bed exit	2.78%	3.55%
HTS common exit	2.37%	3.02%

B. BED TEMPERATURE PROFILES:

Three temperature indicators are available in each bed at bed depths 16%, 66% and 95%. Inlet and outlet temperature indication points are common for both beds. Temperature profiles before and after occurrence of the leak in RGWHB are shown in **Figure 4**. After the leak, temperature profiles of both beds changed significantly. Temperature at 95% bed depth of bottom bed (close to outlet) was 10°F less than that of top bed.

C. APPROACH TO EQUILIBRIUM:

Estimated value of approach to equilibrium before the leak was 62°F and it increased to a maximum of 189°F after the leak.

D. PRESSURE DROP:

Pressure drop across HTS was 4 psi since charging of catalyst in May 1992. After the boiler leak, pressure drop gradually increased to 20 psi as shown in **Figure 5**. Earlier, maximum pressure drop experienced in this vessel was 8 psi with previous catalyst charge of same type, after 8 years of onstream life.

DISCUSSION ON HTS CATALYST PERFORMANCE

While running the plant with boiler leak, we had following opinions on the dismal performance of HTS catalyst, which were based on performance data analysis carried out regularly:

1. Gas flow to each bed was unevenly distributed as CO slip and bed temperature rise were different for both beds. Flow through the top bed gradually reduced to about one fourth of the total flow.

2. Increase in pressure drop might have been due to either or both of the following factors:

   a. Disintegration of top layer catalyst particles due to droplets of liquid water entering from **RGWHB** leak and vaporizing on catalyst surface.

   b. Accumulation of boiler water solids, due to vapourization of liquid droplets on catalyst surface.

3. More amount of water droplets could enter the top bed because of the configuration of gas inlet line to both beds. The vertical gas inlet pipe runs up to the top bed with a tee-off connection to supply gas for bottom bed. Due to inertia, most of the liquid droplets would travel straight to the top bed. This could be the reason for more restriction in gas flow through the top bed.

4. High steam gas ratio and less flow resulted in more conversion and less CO slip in the top bed.

5. With **RGWHB** leak, concentration of chloride in **HTS** inlet process gas condensate was about 0.19 ppm. Normally chloride content is less than 0.01 ppm at this location. The effect of chloride on **HTS** catalyst activity is insignificant at this concentration level.

<u>SHUTDOWN ACTIVITIES</u>

Plant was shut down on January 7, 1994 for annual turnaround to attend to **RGWHB** leak. While shutting down the plant, several precautions were taken to prevent further damaging of **HTS** catalyst by **RGWHB** leak. **HTS** converter was isolated before cutting natural gas feed to primary reformer. This was done to avoid water entry from **RGWHB** leak while bed was under cooling. Catalyst beds were cooled initially by low pressure steam and later on by circulating nitrogen. Temperature of top portion of the bed was reduced from 675°F to 100°F.

Observations made and activities carried out under nitrogen atmosphere in **HTS** vessel are as follows:

1. Top bed loading manway was opened. Light grey colour dust was noticed **(Photograph 1)**.

2. A technician with breath air apparatus went into the converter and removed all alumina lumps. (The lumps are too big to evacuate).

3. After removing the lumps, about one inch thick layer of dust was seen above catalyst surface **(Photograph 2)**. The dust material was found to be penetrated up to two feet depth.

4. Therefore two feet layer of catalyst (114 CF) was evacuated and later on, bed was found to be free of dust **(Photograph 3)**.

5. Fresh catalyst of same type was charged for 10 inch height (48 CF) followed by reloading of 4-6 inch layer of alumina lumps.

6. Loading manway of top bed was closed.

7. Bottom bed loading manway was opened and all the above steps were repeated. Amount of dust accumulated in the bottom bed is about one fourth the amount noticed in the top bed.

Total time taken for carrying out the above activities was 11 hours. As **HTS** catalyst charge volume was on the conservative side and volume of same type of catalyst available in stock was insufficient, we did not load 2 feet layer of catalyst. Samples of catalyst and dust were taken at different locations and sent to the laboratory of catalyst vendor for analysis.

Leak test carried out in **RGWHB** indicated the center bypass pipe was leaking badly at the previously repaired place and no tubes were leaking. The cracked weld joint of the bypass pipe was ground to 25 mm depth around and welded. It was decided to replace the boiler in the next available opportunity due to repeated leaks caused by thermal fatigue.

BACK TO NORMAL RUN

During start up, normal **HTS** reduction and desulphurization procedures were followed because of loading of small amount of fresh catalyst. After the plant start up, performance of **HTS** catalyst was satisfactory. Its CO slip and pressure drop values returned to 2% and 4 psi as experienced before occurrence of boiler leak. Estimated approach to equilibrium value reduced to 54°F at an inlet temperature of 688°F. Following are the high lights of dust and catalyst analysis report received from catalyst vendor:

1. X-ray fluorescence analysis of the dust indicated a high sodium content of 49% and iron content of 14%.

2. Average crush strength of catalyst was 15 lb and was as expected for a used catalyst. Crush strength of new catalyst is 30 lb.

Presence of high amount of sodium in the dust indicates accumulation of boiler water solids on **HTS** catalyst surface was the main contribution of **RGWHB** leak. The catalyst did not suffer from any permanent deactivation. Removal of top layer catalyst along with the dust restored normal performance of HTS catalyst.

CONCLUSION

Repeated leaks were experienced in reformed gas waste heat boiler. Running the plant with boiler leak affected the performance of **HTS** catalyst. After the removal of top layer catalyst containing boiler water solids, **HTS** catalyst performance became normal. Boiler leak was attended and purchase action was initiated to replace the boiler.

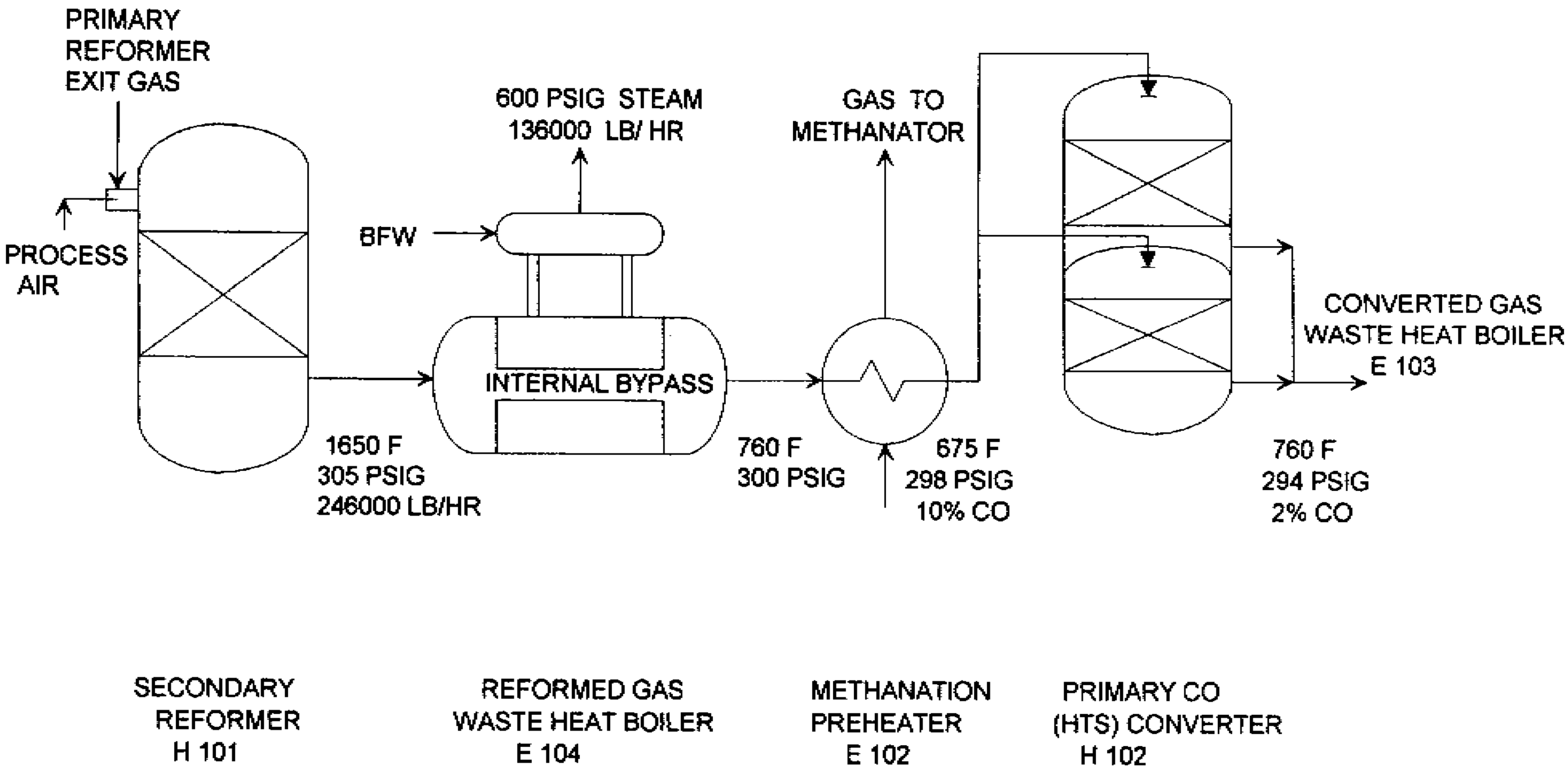

FIGURE 1. SIMPLIFIED FLOW DIAGRAM (TYPICAL OPERATING VALUES)

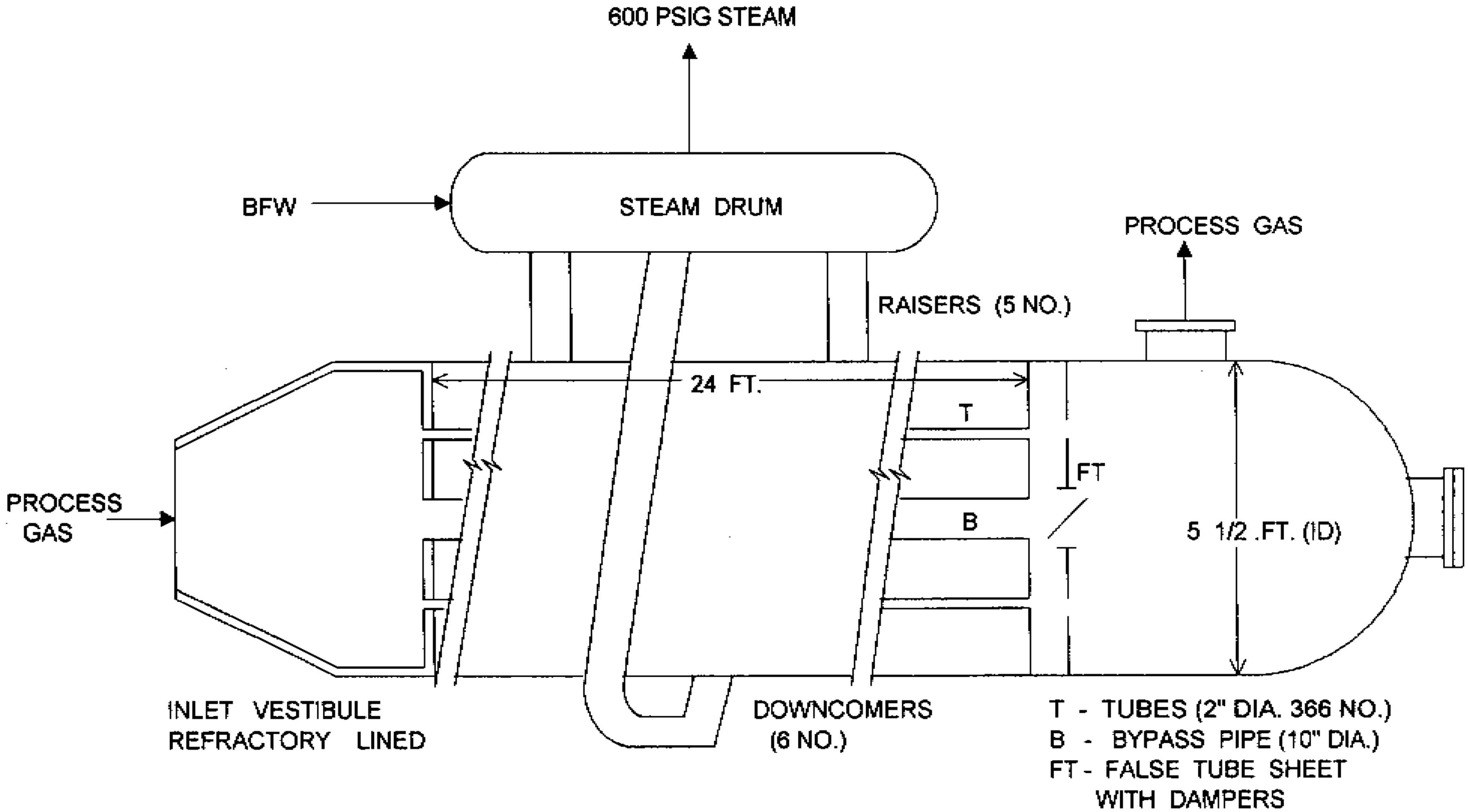

FIGURE 2. REFORMED GAS WASTE HEAT BOILER

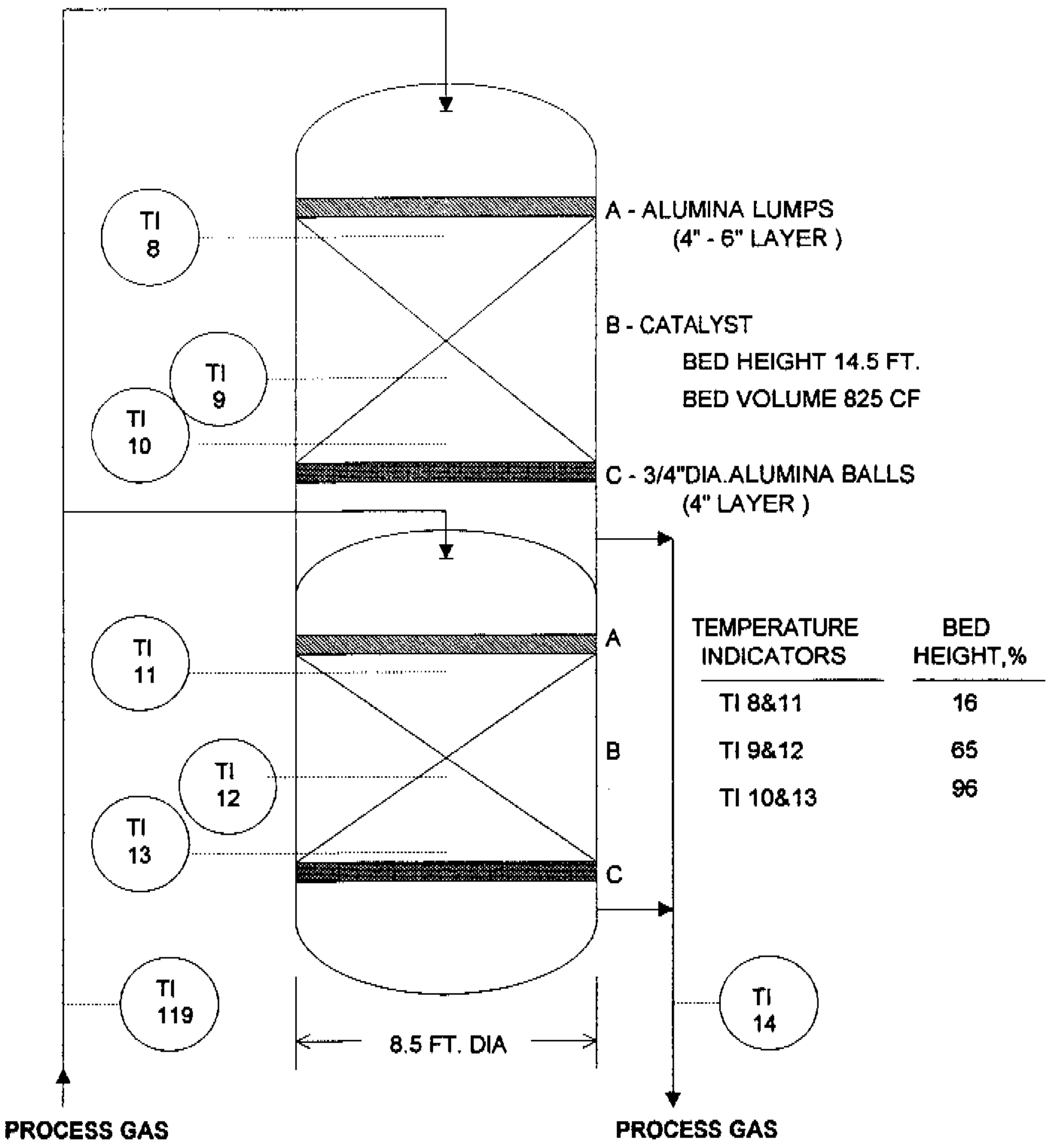

FIGURE 3. DETAILS OF HIGH TEMPERATURE SHIFT CONVERTER

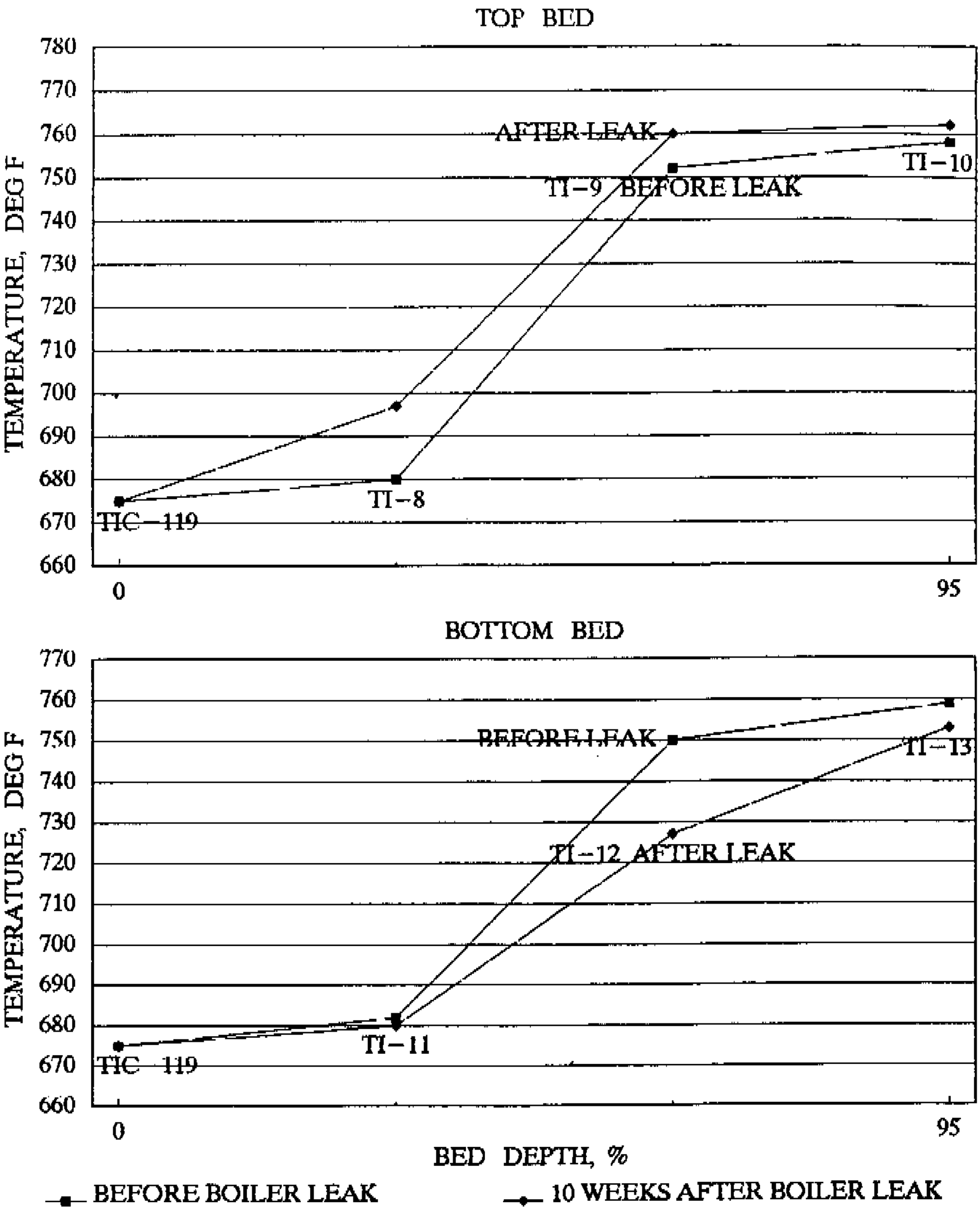

FIGURE-4. HTS BED TEMPERATURE PROFILES

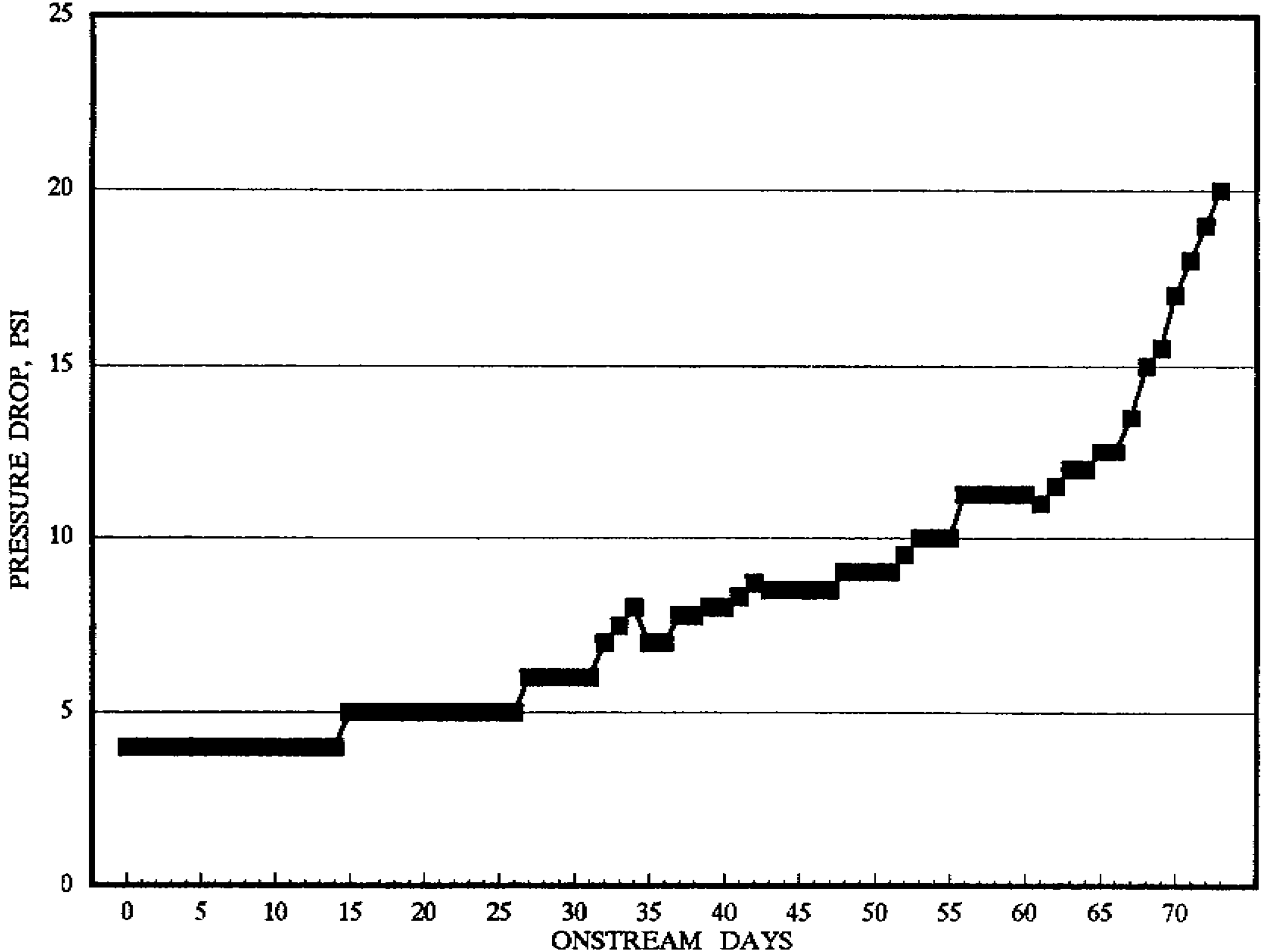

FIGURE 5. INCREASE IN PRESSURE DROP ACROSS HTS CONVERTER DUE TO BOILER LEAK

PHOTOGRAPH - 1

HTS TOP BED TOP SURFACE.
ALUMINA LUMPS / DUST.

PHOTOGRAPH - 2

AFTER LUMPS REMOVAL
CATALYST / DUST

PHOTOGRAPH - 3

AFTER REMOVAL OF
2 FT. LAYER CATALYST.