A STUDY ON THE PERFORMANCE OF HIGH TEMPERATURE SHIFT (HTS) CONVERTER USING PAST DATA AND NOVEL IDEAS

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Abstract

Industrial catalytic converters are provided with minimum measuring devices such as thermocouples, pressure gauges/transducers etc. and sampling points or on-line analyzers etc. to evaluate the performance of the catalyst beds. Inlet/outlet temperatures, pressures and compositions are usually monitored. In some cases, the axial temperatures along the beds are monitored to ascertain the active bed zone. If the temperature probes do not function, it is difficult to determine the performance of the bed especially when deciding whether the activity of the bed is exhausted and replacement of the catalyst is due.
This paper deals with the evaluation of the performance of high temperature shift (HTS) converter of a large ammonia plant using the historical past plant data and novel ideas like measuring converter skin temperatures etc. when operating data appeared to be confusing.

The 1000 tpd ammonia plant of Chittagong Urea Fertilizer Ltd. (CUFL) during a severe cyclone in 1991 had to make an emergency shutdown. It was reported that the HTS converter catalyst bed had suffered a thermal shock during the shutdown. When the plant was restarted, the HTS converter after four weeks of operation showed increased pressure drop across the bed, higher CO concentration at the outlet and the axial temperature profile progressively flatter. After about eight months the plant operators finding the available information and data confusing decided to replace the catalyst concluding that the activity of the bed had been exhausted. This work was undertaken prior to implementation of the decision to find what had happened with the catalyst bed.

On the basis of the plant data since its commissioning in 1987, it was found that the temperature rise across the bed was reasonable while the concentration of CO was above the design value (4 mole % against 3.12 mole %) and axial thermocouples along the bed were reading about the same temperature indicating possible channeling around the single thermowell well containing all the thermocouples. Since the changing of the thermocouples or replacing of the thermowell well was not possible by keeping the plant operational, skin temperatures of the converter at different heights and those at the nozzle flange ends and roots on the converter at three axial positions were measured to guess the temperature profile of the bed. Measurements revealed that there was a temperature gradient along the bed suggesting that the bed was active and not exhausted. By studying the Low Temperature Shift (LTS) converter performance and material-energy balances for HTS and LTS taken together, it was found that LTS had the capacity to handle the extra CO coming from HTS including increased temperature rise therefore; and the units being over designed would perform within design limits if the shift converters were closely monitored. The plant continued to produce in excess of 96% design capacity for the next ten months up to the time of scheduled overhaul when the catalyst was replaced. If the plant was shut down when this study was undertaken, the country would have to import about 50,000 t urea to meet the demand of peak season to make up for the lost production due to unscheduled shutdown for replacing the catalyst.

Introduction

The Chittagong Urea Fertilizer Ltd. (CUFL) is the fourth grass-roots complex producing urea commercially since 1987. It's 1,000 tpd ammonia plant is based on Kellogg's ammonia process utilizing natural gas as feedstock and fuel. The 1,700 tpd urea plant utilizes TEC-MTC urea D-process and is fed with ammonia and carbon dioxide from the ammonia plant as raw materials for urea production.

CUFL had an emergency shutdown on the night of April 29, 1991 during a severe cyclone. The plant was restarted on May 15, 1991; and after about four weeks of operation trouble arose with high temperature shift (HTS) converter. The pressure drop across the converter increased suddenly, the concentration of CO at the converter outlet began to increase and the axial temperature gradient of the bed as indicated by the four thermocouples in the bed, became progressively flatter. The plant operators continued the operation by monitoring the disturbing changes of **HTS** process parameters for another eight months. The concentration of CO at the HTS outlet showed about 4 mole % against the design value of 3.12 mole %, and the axial temperature gradient in the bed virtually disappeared in next few months, Fig. 2. Finding these information and data confusing as well as alarming the plant personnel concluded that the bottom portion of the catalyst bed had been active [1].

HTS catalysts would be expected to have an operating life anywhere from 2 to 5 years under normal operating condition. This batch of catalyst was charged in August 1990 by replacing the first batch after about three and half years. In reality the newly charged catalyst bed had been in operation for only nine months at the time of April 29 cyclone.

This paper deals with the evaluation of the performance of HTS converter using the historical past plant data and novel ideas like measuring converter skin temperatures etc. when operating data appeared confusing and anomalous[1].

HTS Converter

Gases from the secondary reformer are cooled to about 375°C (by generating steam), the usual temperature for the shift conversion reaction:

$$CO + H_2O \Leftrightarrow H_2 + CO_2, \Delta H = -41 \text{ kJ/mole}$$

the reaction is exothermic and is carried out in two stages with heat removal in between. The first shift conversion step is high temperature shift (HTS) conversion. The usual temperature regime for this reaction is 350-430°C while inlet and outlet content of CO in the gas being about 12 and 3 mole per cent respectively [2, 3].

The HTS converter of CUFL is shown schematically in Fig. 1. The catalyst bed volume is 55.1 m^3 (4,200 mm dia X 3,988 mm height). The inlet and outlet gas pressures are to be 31 and 30.9 kg/cm^2g respectively. The bed is provided with four axial thermocouples placed inside a single thermowell plus two separate thermocouples located at the inlet and outlet nozzles of the converter. There are three spare nozzles with end flanges on the converter at three axial positions to be used if and when necessity arises. The gas-steam stream at about 370°C enters into HTS converter from the top and passes through the catalyst bed where part of the CO is converted to CO_2 with an equivalent molal hydrogen formation by reacting with steam. The effluent stream leaves through the nozzle positioned at the bottom of the converter beneath the catalyst bed. The design value of CO in the exit gas is about 3.12 mole % when the inlet CO is equivalent to 12.8 mole %. The overall temperature rise across two shift converters (HTS and LTS) is 82°C due to conversion of CO to CO_2[1].

Operating History of HTS Converter on the Night of Emergency Shutdown

The plant had been operating at full load when the cyclone hit the area. It was planned to continue operation during the cyclone. When the cyclone was crossing over the area, the plant lost boiler feed water pumps and cooling water (the water from the cooling towers and basins was swept by the cyclonic wind). The reformer could not be supplied with steam at the specified rate. The plant then went for emergency shutdown. The system was purged at a low rate of 20 t/h of steam when the usual steam flow to the reformer is 80 t/h at the design rate. The HTS converter outlet temperature first fell to 354°C from 423°C and then rose to 510°C in less than 60 minutes[1].

The normal operating temperature for C-12 catalyst [manufactured by Catalysts and Chemicals Inc (CCI)] is 343–510°C while the maximum permissible heating rate is 83°C per hour. During the shutdown the rise in outlet temperature was 156°C in less than 60 minutes indicating that the inlet of the bed and the whole bed itself were subjected to a thermal shock. The plant operating personnel were, however, certain that no condensation took place in the catalyst bed or converter itself.

The plant was restarted on May 15, 1991 and after about four weeks of operation, the following operational deviations were observed:

(a) sudden increase in the pressure drop across the HTS converter

(b) concentration of CO at the converter outlet began to increase

(c) the axial temperature gradient of the bed as indicated by the four thermocouples A1, A2, A3 and A4 in the bed became progressively closer with no significant temperature differences amongst the bed thermocouples, Fig. 2.

The plant thereafter continued to operate with the stated anomalous indications for another eight months when the plant personnel concluded that it would be necessary to replace the HTS catalysts on the ground that the catalyst might have lost activity, the bottom of the bed being only active, and channeling of flow in the bed. At this stage, a study was undertaken to evaluate the performance of HTS converter and its catalyst without interrupting the plant operation[1].

Study and Analysis of HTS Converter Problems

The study began with the plant visit from 19-21 February, 1992. Literature on the catalyst C-12 in use and operating data of HTS converter since its commissioning were collected. The integrity of the thermocouples was checked by disconnecting them at the control room and the thermocouples were found satisfactory. The issue to be settled was how to establish that there existed an axial temperature gradient inside the bed (the catalyst bed still active) assuming that for some reasons channeling had taken place along the full length of the thermowell resulting in identical temperature indications by all four thermocouples so that activity of the catalyst be ascertained [1].

It was decided to measure the skin temperature of the HTS converter vessel at several locations to check whether the catalyst bed had truly attained a uniform temperature or not. This required removal of insulation at specified locations and would need some preparation. Instead of waiting further, it was decided to measure temperatures of the three nozzles (C, D and E) located along the converter vessel, Fig. 1 at the bare flanged end and nozzle surface (which were exposed). Table below lists the measured temperature.

Bed depth from top (mm)	Nozzle surface Temp °C	Flange end Temp °C
694	138	110
1994	151	117
3294	158	126

Although these temperatures were much lower than the bed temperatures at the corresponding depths, it was clear that a temperature gradient existed. This was a great relief for the plant personnel, although some explanation was needed for the bed thermocouples readings. Immediately arrangements were made to measure vessel skin temperatures at several locations. Table 1 lists the measured skin temperatures, nozzle temperatures, bed temperatures and inlet/outlet gas temperatures of HTS converter [1].

The skin temperatures measured at the same heights as the nozzles C, D, E (Fig. 1) at various radial positions F and G indicated that there existed a temperature gradient along the bed. The thermocouples F and G at the same radial position showing different temperatures might be due to disturbance of the bed, channeling of flow or loss of activity. It was evident that the catalyst bed was active and not exhausted. However, it was not possible to explain the anomalous readings (about the same reading) of the four bed thermocouples.

To find whether there had been breakage of catalysts due to thermal shock, steam condensates were collected from downstream of HTS converter for checking the presence of iron. No iron was detected in the laboratory analysis.

Examination of the operating data after the cyclone revealed that the observed increase of pressure drop had been decreasing gradually since its sudden increase and the concentration of CO in the HTS converter outlet remained close to 4 mole % against the design value of 3.12 mole %. However, LTS converter was able to process the gas containing 4 mole % CO by producing an exit stream containing less than 0.4 mole % CO which was close to the design value of 0.30 mole % [1].

Moreover, examination of the operating data of HTS and LTS converters since commissioning up to the March 1992 revealed that ΔT (temperature rise) in each converter as well as total ($\Delta T_{HTS} + \Delta T_{LTS}$) were consistent and nothing alarming happened since the cyclone. In respect of CO content in the outlet streams from both HTS and LTS converters, there was nothing serious to be alarmed, Fig. 3.

On the basis of material-energy balances for HTS and LTS taken together it was evident that LTS had the capacity to handle the extra CO coming from HTS including increased temperature rise therefore. These units with some built-in design margin would perform within design limits with additional CO entering LTS provided the shift converters were closely monitored.

Recommendations

The study presented the following recommendations:

1. The HTS converter catalyst bed was active and the change of catalyst not required immediately. The change could be made at the time of next scheduled overhauling due in October next.
2. The performance of HTS catalyst bed would be monitored (inlet/outlet temperatures of HTS gas plus skin temperatures of the converter regularly).
3. By adjusting parameters such as temperatures and steam flow, CO level could be managed if LTS converter operated by monitoring closely.

Achievements

1. The plant continued operation at load above 96% up to October 1992, the time for scheduled overhauling without difficulty.
2. There was no need to buy about 50,000 t urea during the peak urea demand season for the shutdown of the plant for replacing HTS converter catalyst in March '92 as envisaged by the plant operators.

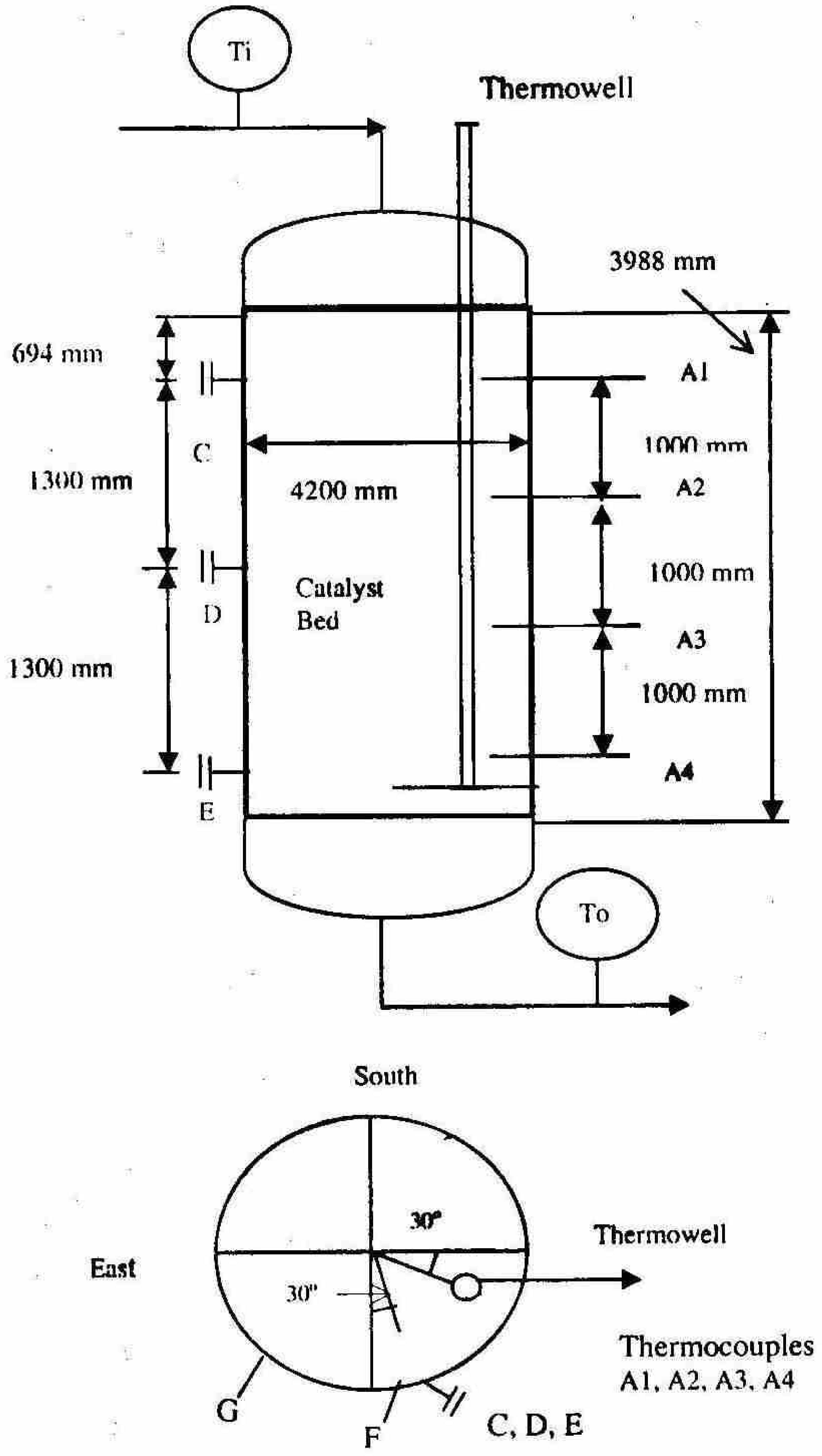
References

1. Report on "High Temperature Shift (HTS) Converter Catalyst of CUFL", submitted to BCIC, April (1992).
2. Fertilizer Manual, Chapter 6 (Production of Ammonia), Kluwer Academic Publishers (1998).
3. Allen, D., Carbon Monoxide Conversion, Ammonia, Part II, edited by A.V. Slack and G.R. James, P3-24, Marcel Dekker (1974).

Table-1: Skin Temperatures, Nozzle Temperatures and Other Temperatures (^{O}C)

Dates	Nozzle Flange/ Nozzle Surface			Skin Positions*			Bed Thermocouples				HTS inlet/outlet
	C_F/C_S	D_F/D_S	E_F/E_S	F1/G1	F2/G2	F3/G3	A1	A2	A3	A4	
2.3.92	111	120	125	329	366	371	433.2	433.5	435.1	435.1	370
	137	157	166	315	327	372					426
5.3.92	114	127	132	335	356	371	436	436.4	37.6	437.7	375
	143	155	175	316	330	370					428
10.3.92	113	128	135	327	368	370	436	436.7	438	438	375
	145	159	181	305	321	359					427

*On the same height as the nozzles but different radial positions $\underline{C_F, C_S, F_1, G_1}$; $\underline{D_F, D_S, F_2, G_2}$; and $\underline{E_F, E_S, F_3, G_3}$.



C, D, E : Spare Nozzles with blind flanges
A1, A2, A3, A4 : Axial Bed Thermocouples
Ti, To : Inlet and Outlet Thermocouples
G, F : Skin Thermocouple Positions shown radially at same spare nozzle levels

Fig. 1: Schematic Diagram of HTS Converter

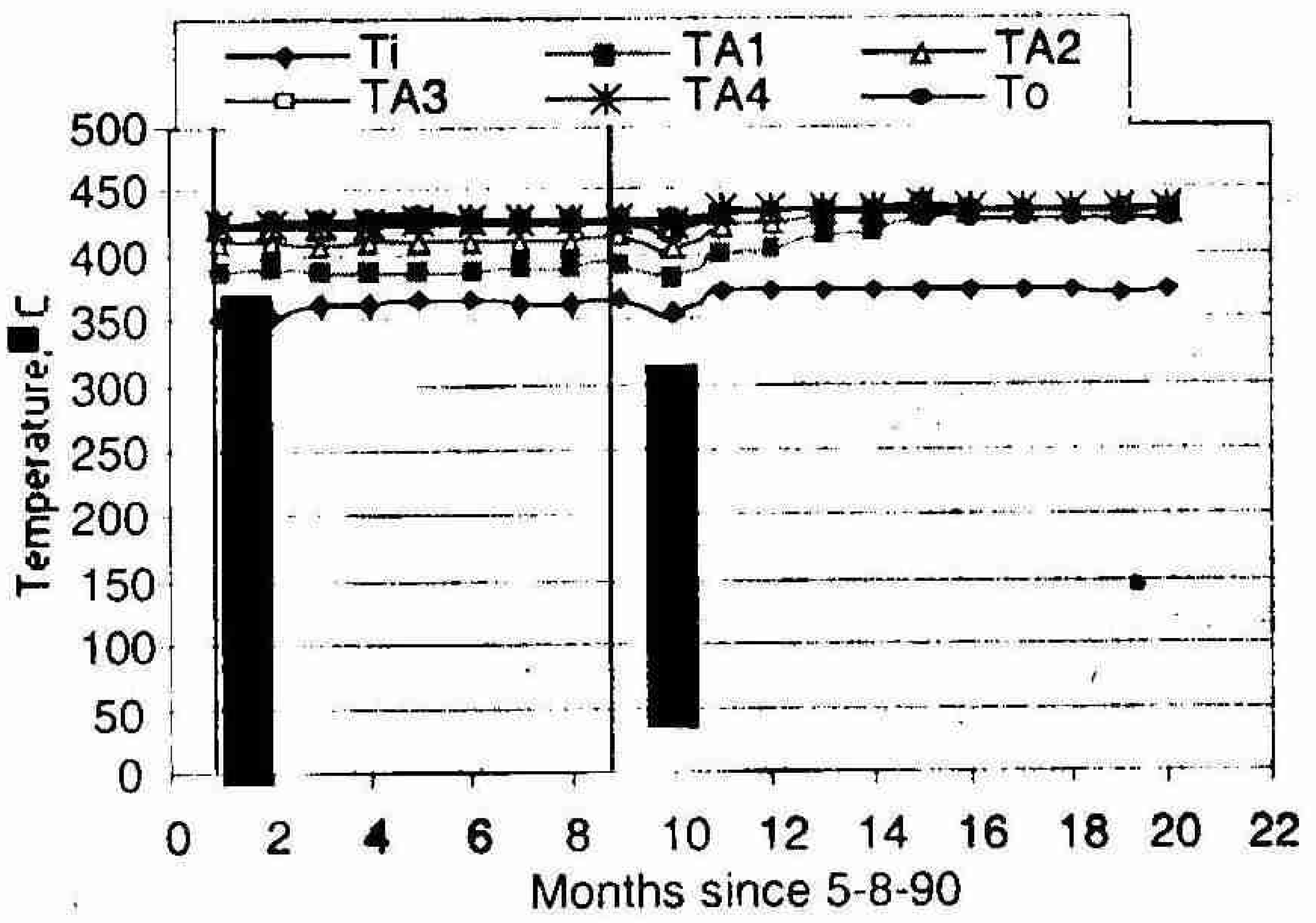


Fig.2: Temperature Profile of bed Thermocouples T_{A1}, T_{A2}, T_{A3}, T_{A4} and HTS inlet and outlet temp T_i and T_o

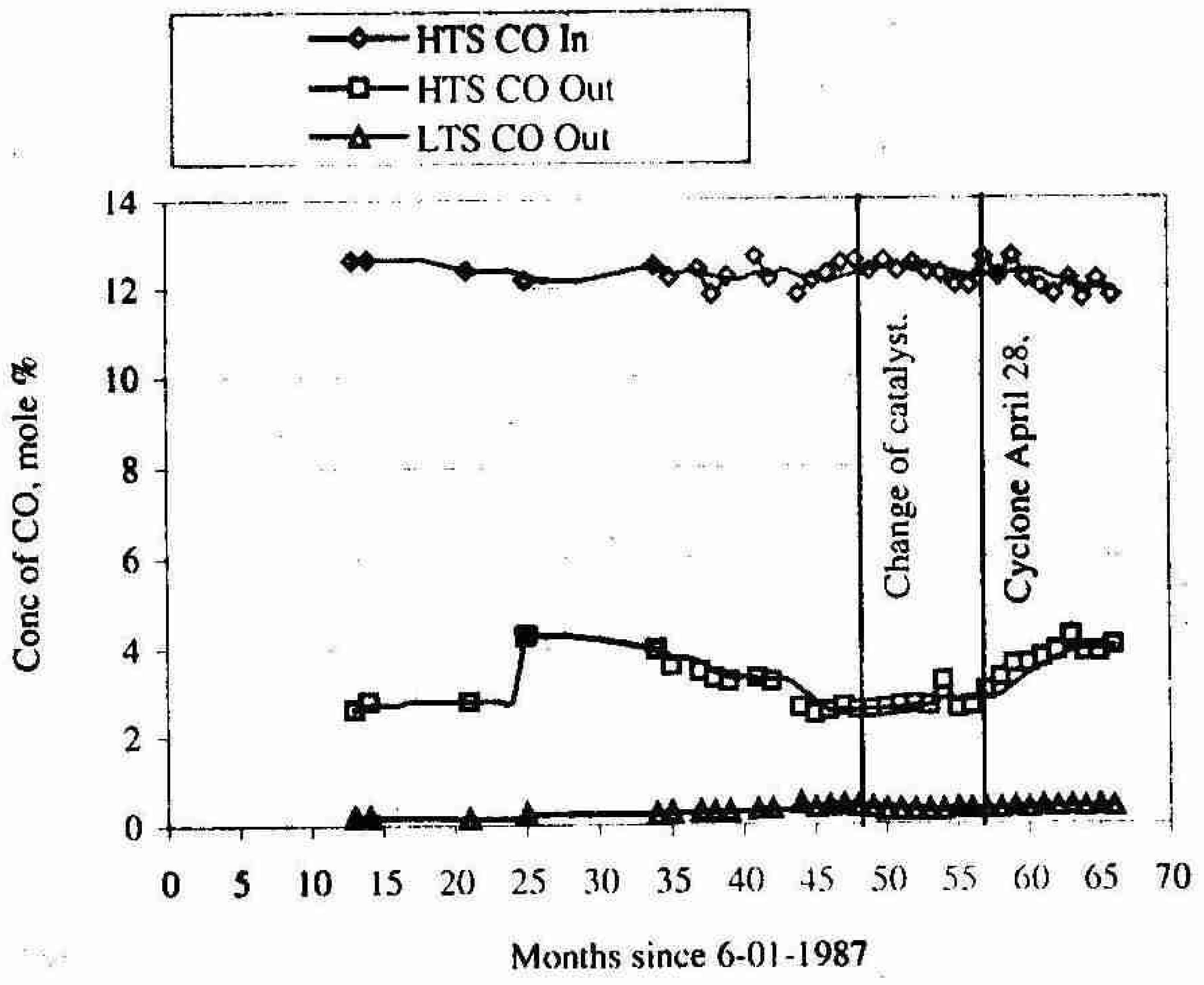


Fig 3: Historical Data on CO at HTS inlet, outlet and LTS outlet