

Energy Conservation in CO₂ Removal System of Ammonia Plant

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The selection and design of CO₂ system was the most difficult engineering job of the Phulpur Expansion Project (PEP). Though a repeat of Aonla Expansion Project (AEP), the use of 100 percent naphtha feed in place of 50 percent naphtha + 50 percent natural gas feed (as in AEP) would have resulted in higher CO₂ and a change in raw gas composition. Consequently, a thorough study was required to check the adequacy of this section. Further, the new ammonia plant was consuming higher energy per tonne of ammonia as compared to the design value and the CO₂ removal system was identified as one of the higher energy consuming areas. This paper gives an account of the study carried out to check the adequacy of the CO₂ removal system, the changes incorporated in this system and the efforts made to lower the energy consumption of CO₂ removal system.

Indian Farmers Fertiliser Cooperative Ltd., (IFFCO), with an annual production of over 40 lakh tonnes of fertilisers is considered to be one of the largest manufacturer of fertiliser in the world. During December 1997, IFFCO installed an expansion project comprises of 1350 MTPD ammonia plant designed and engineered by M/s. HTAS and a 2200 MTPD urea plant designed and engineered by M/s. Snamprogetti.

The Phulpur Expansion Project (PEP) is a repeat of Aonla Expansion Project (AEP). However, due to change in geographical layout, most of the battery limit engineering had to be re-done. Since PEP was based on the use of 100 percent naphtha feed in place of 50 percent naphtha and 50 percent natural gas feed (AEP), a new per-hydrodesulphurisation section was added at PEP and certain sections of plants had to be rechecked for adequacy. The sections rechecked for adequacy are (i) steam generation and boiler feed water and process condensate systems, since naphtha plants require higher quantity of steam than natural gas (ii) synthesis gas compressor turbine for higher extraction of medium pressure steam and CO₂ removal system, since higher quantities of CO₂ have to be handled in a naphtha based plant.

Ammonia plant - The Latest Generation Plant

Some of the salient features for energy saving in ammonia plant are as follows:

- Gas turbine drive, with naphtha as fuel, for process air compressor
- Heat recovery unit connected to the gas turbine for generating high pressure steams to meet the requirement of ammonia and urea plants.
- Medium pressure process condensate stripper
- GV - Low energy CO₂ removal system

CO₂ Removal Systems - Problems and Solution

The selection and design of CO₂ removal system was the most difficult engineering job of this project. Though it was a repeat of AEP, the use of 100 percent naphtha feed in place of 50 percent naphtha and 50 percent natural gas feed (used in AEP), would have resulted in higher quantity of CO₂ generation and a change in raw syn gas composition. Consequently a thorough study was carried out to check the adequacy of this system like the adequacy of the existing towers, the performance of the repeat CO₂ blower, the stripper top overhead condenser meeting the duty with respect to CO₂ temperature and cooling water flow rate and the GV pumps giving the required solution flows etc.

CO₂ absorption is more in case of naphtha feed as compared to gas feed, because of higher partial pressure of CO₂ in feed gas. Though the solution flow rates are higher the CO₂ absorbed (Vol. flow) per unit volume of solution is higher in case of naphtha feed and hence the same size of absorber could be used as that of AEP.

The main change envisaged was the change of packing in the absorber bottom bed lower part from IMTP-50 to CMR - 3 (Cascade Mini Rings) due to increase in pressure drop because of higher gas flow rates. These packings have same efficiency as IMTP but offer lower pressure drop. Also the lower layer of the 3rd bed packing have been changed from IMTP - 40 to IMTP-50. The packing volumes remained unchanged with same diameter of absorber. The distributors also remained the same.

For regeneration, the CO₂ liberation due to flashing is more and so the capacity (total tower size) of the regenerators were checked and found suitable.

The process control principles as well as solution composition and physico - chemical characteristics were also checked and found suitable.

CO₂ blower capacity was checked with the vendor. The capacity of the CO₂ blower was increased as it had to handle a higher CO₂ flowrate.

Stripper top CO₂ overhead condensers capacity with respect to CO₂ cooling load, cooling water supply, pipe size etc. were also checked and found to be suitable.

The lean, semilean pumps and the hydraulic turbines were also checked and found to be adequate without any modification.

CO₂ Removal System and its Chemistry

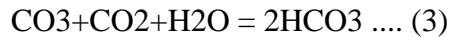
In the GV CO₂ removal system, carbon-di-oxide is removed from the process gas by absorption in an aqueous hot potassium carbonate solution (HPC solution) containing approx. 30 wt. percent potash (K₂CO₃) partly converted into bicarbonate (KHCO₃). The solution also contains glycine and a tertiary amine DEA as activator and Vanadium Penta Oxide as corrosion inhibitor. The reason for keeping the solution hot is to increase the rate of absorption and keep the bicarbonate dissolved.

A scheme of CO₂ removal system is illustrated in Figure 1.

The process gas from the shift reactors is passed to the CO₂ absorber (F 3303). In the absorber the gas flows upwards against a descending stream of hot potassium carbonate solution. Approximately 15 percent of the solution is introduced above the top bed at 70 deg. C whereas the remainder is introduced at about 106 deg C below the two top beds.

The CO₂ absorption occurs according to the following reaction mechanism:

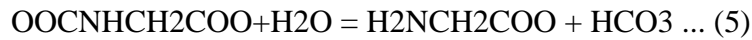




The reaction rate of step 3 is determined by step 1 which is the slower of the steps 1 and 2. The activator action resulting in an increased rate is caused by the quick transfer of gaseous CO₂ into the liquid phase by means of the glycine carbamate formation according to the reaction.



The activator effect is much higher than the one relating to carbamate concentration . At higher temperature and in the presence of OH the carbamate is hydrolysed and the activator is restored according to the reaction :



The sum of steps 4 and 5 gives 1. As reaction 4 and 5 takes place continuously, it means that the glycine acts as a CO₂ carrier. Reaction 5 is the hydrolysis of glycine carbamate. The reaction is catalysed by a small amount of DEA in the solution .

The absorption takes place in two stages in F 3303. In the first stage, where the bulk of CO₂ is absorbed, the high temperature increases the reaction rates of 5 and 3. This is done by using the normal regenerated solution (semi lean) from the second regenerator, F3302.

In the second stage, a stream of strongly regenerated solution (lean solution) is utilised. At the lower temperature, the CO₂ vapour pressure of the solution is further reduced to meet the low CO₂ slippage in the purified gas (about 0.05 mole % dry CO₂).

The solution leaving the absorber bottom is loaded with CO₂ and is referred to as the rich solution. The rich solution is depressurised through the hydraulic turbines, TX 3301 A/B driving the semilean solution pumps P 3301 A/B.

Downstream the hydraulic turbines, the rich solution enters the top of the first regenerator, F3301 working at a pressure of about 1.0 Kg/cm²g.

A stream of rich solution extracted from the top of F3301 is depressurised through a control valve and enters the top of the second regenerator, F 3302, working at a low pressure (0.1 Kg/cm²g). The semilean solution extracted from the intermediary tray of F3301 at 124 deg C is flashed across the level control valves and fed into F 3302. In F 3302 the semilean solution is collected on a take-off tray feeding the semilean pumps, P 3301 A/B/C. The lean solution extracted from bottom of F3301 at 127 deg. C is flashed across the level control valves and enters F 3302 below the semilean solution take-off tray feeding the semilean pumps, P 3301 A/B/C. The lean solution extracted from bottom of F3301 at 127 deg. C is flashed across the level control valves and enters F 3302 below the semilean solution take off try. The lean solution is collected in the bottom of F3302 and fed to the lean solution pumps, P3302 A/B. The steam developed by flashing of the lean and semilean solutions is used as stripping steam to regenerate

the rich solution entering the top of F 3302. In this way more than half of the stripping steam supplied to F3301 is recovered by flashing and works in double effect in F 3302. The semilean solution is pumped by P3301 A/B/C and sent to the lower part of the absorber (F3303) at a temperature of 106 deg. C Lean solution is drawn from the bottom of F 3302 at a temperature of 109 deg C and cooled by the DMW preheater E 3306 A/B to a temperature of 70 deg C. From E 3306 A/B, the cooled lean solution is fed into the top of F 3303 by P 3302 A/B.

The gas cooling arrangement is illustrated in Figure 2.

Before absorption of carbon dioxide, the shifted process gas is cooled from about 163 deg C to about 104 deg C.

First step is cooling from about 163 deg C to 132 deg C in the parallel operated vetrocoke reboilers, E 3302 A/B, and thereby providing a part of the heat required for the first regenerator, F 3301.

The process gas from E 3302 A/B is then cooled from about 132 deg C to 122 deg C in the LP boiler, E 3303. The steam produced in E 3303 is by means of the ejector, X 3301, injected into the first regenerator, F 3301 as stripping steam.

The process gas is further cooled to 104 deg C in the DMW preheater, E 3304 before the process gas enters the CO₂ absorber, F 3303.

Mechanical Filtration

The purpose of mechanical filtration is to keep the solution clean and free from solids. These solids may be impurities of the chemicals used for solution preparation and make-up, catalyst dust entrained by the process gas, rust from steel equipment particularly after a long shutdown period or fine dust from poor quality activated carbon. Impurities may also enter the sump tank accidentally.

Two mechanical filters are provided in the plant. The main filter is placed upstream of the activated carbon filter in order to protect carbon filter from solid build-up. The second filter (of smaller surface) is placed downstream of the activated carbon filter in order to retain any fine dust released from poor quality or crashed carbon which can seriously affect the plant's smooth operation. The filtering medium is polypropylene (alkaline resistant) for temperature not exceeding 100 deg C. the solution fed to the main filter is about 5% of the circulating flow while only 50 percent of the solution exiting the filter feeds the activated carbon filter and the downstream mechanical filter.

Activated Carbon Filtration

This filtration is intended for removing any organic substances (active as well as degraded organic activators) from the solution. These substances such as grease, lubricating oil, paints, bitumen, epoxy resins degraded organic compound etc., are saponifiable by the alkaline solution.

They may cause foaming problems and consequent worsening of the CO₂ removal plant's performance. The carbon filter treats the lean and semilean solution streams in similar way. It is placed downstream of the mechanical filter for extending the carbon life. Only a fraction (about 50 percent) of the solution coming out of the mechanical filter feeds the activated carbon filter. The most advisable temperature range for the filtration is 70-110 deg C.

Energy Reduction in GV Section

Whatever calories are used in the fertiliser plant, the lion share is always consumed by the ammonia plant. The new ammonia plant has been running at an energy level higher than the design value. A task force was formed to identify the areas of high energy consumption in ammonia plant and it was found that CO₂ removal system was one of the areas where the energy consumption was very high.

The CO₂ removal system designed by M/s. Giammarco Vetrocoke, Italy, has the following guaranteed parameters at the battery limit.

- a) 0.05 mole% CO₂ (max.) on dry basis at the gas absorber outlet.
- b) The CO₂ product of 45792 Nm³/h (minimum) at 100% ammonia plant load on dry basis coming from solution regeneration will be available at the battery limit.
- c) The pressure of above said CO₂ will be 0.6 Kg/cm² g minimum.
- d) The purity of the above said CO₂ will be minimum 99% (vol.) on dry basis.
- e) The LP steam consumption shall not be more than 9000 Kg/h with a total specific regeneration heat consumption of 660 Kcal/Nm³ of CO₂.

During the ammonia plant guarantee test run, all the parameters were within the guaranteed values except for higher LP steam consumption and hence higher regeneration heat.

Complete operating data, solution analysis, gas analysis etc. were carefully studied and analysed. Following observations were made.

1. The pressure of LP boiler E 3303 was not coming down to the design value of 0.86 Kg/cm² g and always above 1.0 Kg/cm²g even with innumerable manipulations of ejector X 3301 operation even with innumerable manipulations of ejector X 3301 operation.

2. The CO₂ slip from bottom two beds of absorber F3303 was very much within the design limits, but the CO₂ slips from top two beds were not upto the mark, though the final CO₂ slip from absorber was less than 500 ppm.

3. The LP stripper F 3302 was suspected to be performing below its design performance as indicated by higher fractional conversion in lean solution than design.

These observations indicated that ejector was not performing and the suction steam quantity was less and therefore more LP steam was being put in the stripper to meet the solution regeneration heat requirement. The absorption qualities of semilean solution or performance of bottom beds of absorber was excellent, while the absorption qualities of lean solution or absorber top beds performance was bad. The LP stripper was not performing as per design.

The regeneration heat in CO₂ removal system was very high. LP steam to the HP regenerator of GV system was to the tune of 24,000 Kg/h. Any attempt to reduce the steam was causing high CO₂ slip and consequent increase in methanator temperature and loss of valuable potential hydrogen.

The process parameter were tuned to the optimum level like :

1. The solution flow rates were mimimised.
2. The absorber gas inlet temperature was reduced.
3. The semilean solution flow from HP stripper to LP stripper was brought to design value.

With all these efforts the LP steam consumption could be brought down to the tune of 20.0 t/h.

After this, it was decided to check the concentration of chemicals in GV solution.

Through investigation revealed that actual active quantity of the activators (DEA and Glycine) was less than the design values. Since no standard analytical method is available for quantifying the degraded quantity of glycine and DEA, and also the standard analysis can give only the total DEA and glycine (active as well as degraded) there was a chance that the actual active quantities of activators may be running low. It was therefore essential to remove the degraded activators. The degraded organic product could be removed only by taking the activated carbon filter in line. But there was problem in taking the carbon filter in line as the mechanical filter downstream of carbon filter was not working and hence the problem was getting aggravated.

The activated carbon filter and its downstream mechanical filter were taken in line and partial solution was filtered for 24 hrs. to remove the degraded organic compounds of activators. After filtration the foaming of solution was reduced considerably.

In the next step the solution composition was checked.

The GV operating manual reports the average composition of the circulating solution. The composition does not refer to any specific zone in the plant. Yet, on the grounds of the lab analysis at lean and semilean pump suction, the average value can be assessed.

As a rule, the concentration of K_2CO_3 , $KHCO_3$, V_2O_5 , V_5 Glycine, DEA, Chloride and Fe is analysed in the sample withdrawn at lean pump suction. While only K_2CO_3 and $KHCO_3$ is determined in the sample withdrawn at semilean pump suction.

The fractional conversion and equivalent K_2CO_3 of each sample can be inferred from the values of K_2CO_3 and $KHCO_3$. From the K_2CO_3 equivalent of each sample it is possible to determine the K_2CO_3 equivalent of the overall solution by means of the weighted average of the relevant flow rates.

Finally, from the K_2CO_3 equivalent in the overall solution and the K_2CO_3 equivalent of lean solution; and the concentration of Glycine, DEA, V_2O_5 etc. in the lean solution, it is possible to determine the concentration of the Glycine, DEA, V_2O_5 etc. in the overall solution as shown in the example given below.

As can be seen from the given example that though the analysis of solution indicates a high percentage of DEA and Glycine (0.9% Glycine and 1.12% DEA), in fact their concentration is very low i.e. DEA 0.93 % and Glycine 0.75 % only.

After achieving the guaranteed steam consumption, it was decided to have a closer look at the performance of ejector X 3301 and performance of LP stripper F 3302.

Due to the poor performance of the ejector, the pressure in LP boiler E 3303 was much higher than design and the process gas exited LP boiler E 3303 at much higher temperature than design. This means that the process gas heat transferred to the CO_2 removal section was less than design and therefore less heat of regeneration was being provided to GV solution through process gas. The process gas heat which should have gone to CO_2 removal system was getting transferred to DM water heating and, therefore, excess external energy (in the form of LP steam) had to be provided in CO_2 removal system to meet the regeneration requirement. Operating data around the ejector under various conditions were collected and communicated to the ejector designer in (Table 1).

Following facts were established based on the analysis and perusal of operating parameters around LP stripper F 3302.

1. The Fractional conversion of 0.12 of the lean solution exit HP stripper F 3301 was much better than the FC of 0.26 of lean solution at the exit of LP stripper F3302.
2. Value LV-9 for regulation of the lean solution between HP and LP strippers was open by 25% (a very low value which is not found in similar plants), whereas valve LV-7 for regulation of the semilean solution between HP and LP strippers was fully open.

3. Compared to the first stage (bottom two bed) exit (CO₂ slip of <5000 ppm), the CO₂ slip at Absorber 2nd stage (top two bed) exit was too high (450 ppm).

4. There is a difference of only 2 deg. C (vs 3 deg C of design) in the boiling temperature of lean and semilean solutions from the LP stripper.

All the above observations have pointed towards leakage of semilean solution in the LP stripper to the lean solution. The the LP stripper to the lean solution. The leakage point appears to be the semilean solution draw off tray. The stoppage of the leakage will improve the final CO₂ slip from the absorber, which is expected to decrease to about 200 ppm. This will result in remarkable increase of ammonia production with same process feed. Moreover, it will be easier to correct the solution flowrates and the valve on the lean solution piping between HP and LP stripper will sensibly open allowing to control the levels better.

After having performed the above studies, the operating parameters around CO₂ removal system were collected and the regeneration energy was calculated. The calculated regeneration energy came down from more than 800 Kcal/Nm³ of CO₂ to approximately 661 - 674 Kcal/Nm³ of CO₂ remove. The LP steam consumption also had come down to 9000 Kg/h.

With sincere efforts and study of operating data of plant. the energy has been brought down very close to the guaranteed value of 660 Kcal/Nm³ of CO₂. It is expected that once the suspected leakage in LP stripper is stopped and the ejector performance is improved, the regeneration energy may come down much below the guaranteed value.