HP Scrubber operational experiences in a Chinese CO_2 stripping Urea Plant

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1. Introduction

The Urea plant of the Chemical Company of Qinghai Salt Lake Industry Group Co. uses the off-gas from the acetylene production applying natural gas partial oxidation process as feedstock and has a urea production capacity of 330,000 t/a. This urea plant utilizes CO_2 stripping of traditional modification process (remark UreaKnowHow.com: this process is similar to the typical Stamicarbon falling film CO_2 stripping urea process of the 1990's).

The differences between this process and those of formerly imported urea plants are:

- At the inter stage of the CO_2 compressor unit, a hydrogen converter is installed for removing hydrogen from CO_2 feed gas; (remark UreaKnowHow.com: the ammonia feed also can contain some hydrogen)
- A packed bed with pall rings is arranged at the absorber part of the HP scrubber
- HP scrubber off-gas is sent to the LP absorber (0.4MPa) for further absorption before being vented to atmosphere

Please refer to the figure below for the schematic diagram of the HP scrubber.

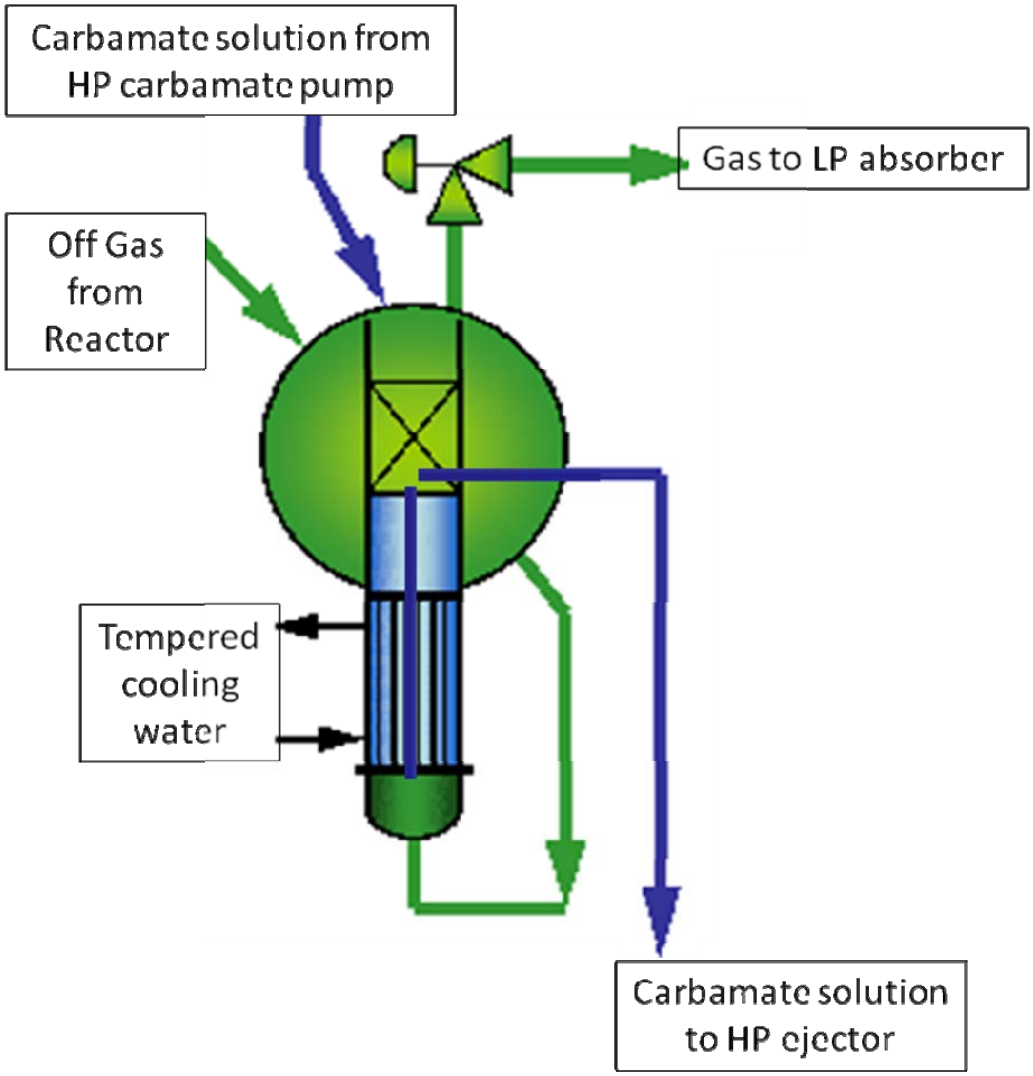

Figure 1: Schematic diagram of the HP scrubber

The purpose of the HP scrubber is to condense and absorb ammonia and CO_2, present in the off gas from the urea reactor, in a heat exchanger part and an absorber part with help of the carbamate recycle solution from the LP recirculation section. The carbamate recycle solution sent by the HP carbamate pump passes through the packing section at the absorber part of the HP scrubber and then through the heat exchanger part of the HP scrubber where it reaches the bottom. Here it is mixed with the off gas from the urea reactor, which first passes through the hemisphere and the U shaped line.
The mixture thus formed flows upwards through the heat exchanger tubes, during which ammonia and CO_2 in the gas are condensed and absorbed, while the heat is removed by the tempered cooling water on the shell side. Unabsorbed ammonia and CO_2 then contact counter-currently with the carbamate solution sent by the HP carbamate pump in the packing section of the HP scrubber for heat exchange and mass exchange.
Inert gases going out of the HP scrubber and a small quantity of ammonia and CO_2 are absorbed in the LP system and then vented to atmosphere. The inert gases origin from the inerts present in the feed plus the air added to the CO_2 feed for the operation of the hydrogen converter and for the

passivation of the applied stainless steels in the urea plant. This means oxygen is present in the off gases and like in any other urea process proper attention need to be paid to avoid explosion risks.

2. Process operation of the HP Scrubber

Most of the personnel operating a newly built urea plant are not so experienced in the process operation of the HP scrubber. Various abnormal situations might occur during the startup, shutdown and even during normal production of the plant. In view of this, the following analyses are made on the process operation of the HP scrubber:

2.1 Normal operation mode

Why should the carbamate solution outlet temperature of the HP scrubber be controlled above 155 ^{o}C during normal operation? And how to control?

Assuming that the carbamate solution at the outlet of the HP scrubber is in equilibrium with the gas stream in the bottom section of the packed bed, the temperature of this carbamate solution is influenced by the percentage inerts present in the gas phase. The higher the percentage inerts, the higher the inert pressure, the lower the system pressure (= partial pressure of NH_3, CO_2 and H_2O) and the lower its boiling temperature.

In order to maintain non-explosiveness of the off-gas of the HP scrubber, inert gas content in the off-gas should be less than 36%. It can be found from NH_3-CO_2-H_2O ternary diagram in terms of temperature, pressure and composition that this means that the partial pressure of NH_3+CO_2 should not be less than 8.29 MPa when the operating pressure is 14.4 MPa, which corresponds to a carbamate solution temperature of 155 ^{o}C. If the H_2O content in the carbamate solution increases, the outlet fluid temperature should be increased accordingly so as to maintain the same partial pressure.

Remark UreaKnowHow.com: The carbamate solution temperature can be controlled by means of the HP inert valve. When opening this valve the temperature will increase.

2.2 Start up and shut down operation modes

Blocking U-shape gas line

During a blocking in shutdown of the HP scrubber the gas in the U-shaped line from the hemisphere to the bottom of the heat exchanger may crystallize and cause plugging. For example when the power supply of the plant is shut down and the emergency power supply fails to start and the steam supply for the plant is unavailable, etc.). Remark UreaKnowHow.com: or when the tracing and insulation is in bad condition.

As a result a large pressure difference between the inside and outside of the cylinder in the hemisphere occurs and might become damaged.

Signals are:

- The pressure of the HP synthesis system rises rapidly

- Temperature difference of the HP scrubber gradually reduces with zigzag fluctuation
- The vented quantity of off gases increases.

Temperature of tempered cooling water is too low

During the startup of the HP scrubber, when the temperature of the tempered cooling water is controlled too low, the carbamate solution in the tubes of the heat exchanger may crystallize and block the tubes. This again might cause a damage to the cylinder in the hemisphere.

Signals are:

- The tempered cooling water shows no temperature difference between in and outlet of the heat exchanger
- The temperature of the off gas of the HP scrubber rises rapidly
- Temperature of the carbamate solution outlet of the HP scrubber drops
- The temperature at the outlet of the HP carbamate ejector drops rapidly
- CO_2 conversion rate in the reactor decreases
- Steam consumption of the HP CO_2 stripper increases
- Steam consumption of the first-stage evaporation heater increases

Another problem which may occur when the temperature of the tempered cooling water of the HP scrubber is controlled at a too low level, is that NH_3 and CO_2 are excessively condensed in the HP scrubber, causing that the off-gas may fall into the explosion zone.

Hydrogen content too high

When the hydrogen converter fails or due to a problem in the ammonia plant too much hydrogen is present in the feed, the off gases of the HP scrubber may fall into the explosion zone.

Signals are:

- Hydrogen content of the hydrogen analyzer increases
- N/C ratio increases
- CO_2 conversion rate decreases
- Steam consumption of the HP CO_2 stripper increases
- Temperature of the liquid outlet of the HP carbamate condenser drops
- Pressure of the HP synthesis system rises.

Carbamate solution temperature too low

We have observed that all HP scrubber off-gas fires during the start up occur within 10-15 minutes after overflow of the urea reactor. Why would the off-gas become explosive at this moment ? Observations from each plant show that it is caused by a sudden drop of the temperature of overflow liquid from the HP scrubber. We have made a comparison between good operation and bad operation practice. The minimum carbamate liquid overflow temperature of the HP scrubber is above 155 ^{o}C in the good operation practice while the minimum temperature drops to 136 ^{o}C in the bad operation practice. When the overflow temperature is lower than 150 ^{o}C the off-gas may enter into the explosive zone.

Why there is a low point of the temperature of overflow fluid at that moment: the reason why the off-gas of the HP scrubber may enter the explosive zone when the urea reactor is at overflow condition is that the temperature of the reactor solution is lower during the overflow. When the temperature of the reactor solution is lower, the NH_3 and CO_2 contents of the off gas of the reactor, which is in equilibrium with the reactor solution, decreases. As the off-gas discharge amount remains unchanged (remark UreaKnowHow.com: as the off gas discharge amount is determined by HP inert valve position), the available NH_3 and CO_2 to be absorbed by the HP scrubber decreases, thus the reaction heat generated from the condensation in the HP scrubber decreases, causing the temperature of the overflow fluid of the HP scrubber to drop down.

2.3 Other analysis

Cause of damage to rupture disc shell side heat exchanger cylinder during the startup

Tightly close the inert gas vent valve at the high point of the shell side (tempered cooling water side) of the heat exchanger when starting up the tempered cooling water system circulation. Introduce steam from the tempered cooling water jacket for heating up the tempered cooling water system during this process. Balance cannot be reached if the balancing makeup water valve between MP steam drum and the tempered cooling water system has not been opened in time. As the compressibility of water is very small (compression coefficient of liquid water: 5×10^{-5}atm), water expands in its volume after being heated (expansion coefficient of liquid water: 0.21×10^{-3}K). However, because the whole system is tightly closed, the pressure of the tempered cooling water system rises instantly, ultimately causing a damage of the rupture disc on the shell side.

Result of sudden temperature drop of the carbamate liquid outlet from the HP scrubber during startup

The reason why the carbamate liquid outlet temperature of the HP scrubber drops is that the ammonia and CO_2 in the off gas from the urea reactor have not been condensed and absorbed in the HP scrubber. This is caused by the internal crystallization which plugs tubes of the heat exchanger. Then the pressure of the HP synthesis section rises continuously, causing rupture of the internal cylinder of the HP scrubber. Then the vented quantity of off-gas from the HP scrubber increases and the gas-phase temperature at the outlet rises.

Causes of liquid entrainment of gas-phase at the outlet of HP scrubber

Reasons for liquid entrainment at the gas outlet of the HP scrubber may be as follows:

- Packing of the HP scrubber is corroded
- Internal distributors are blocked
- Liquid seal trough at the lower head of the HP scrubber is displaced
- Pressure difference between the inlet and outlet of the HP ejector is small or pumping capacity decreases due to severe corrosion of the nozzle, thus carbamate solution in the HP scrubber cannot be pumped away or only a small amount can be pumped away
- Rotating speed of the HP carbamate pump is higher. The sudden increase in rotating speed of the HP carbamate pump will cause the flow of the carbamate solution in the HP scrubber to suddenly increase without adjusting other operating conditions
- Liquid overflow line or its valve is blocked, which may occur during the startup after a shutdown (in

case pipelines are blocked by crystallization due to incomplete flushing or draining). Crystallization and plugging may also occur in the overflow line when the temperatures of the heat exchanger of the HP scrubber is controlled too low, causing blockage of the carbamate solution flow

- N/C ratio in the urea reactor is improper and conversion rate is too low, therefore, the load of the HP scrubber is large
- The cylinder in the HP scrubber is damaged and short circuit of gas phase occurs, causing off-gas in the HP scrubber to increase greatly, causing flooding occur in the packing section of the scrubber
- If the temperature of the tempered cooling water is controlled too high or heat exchange duty is poor, then the condensation and absorption of NH_3 and CO_2 is poor, the amount of gas phase going out of the HP scrubber is large and flow rate becomes higher, thus causing flooding in the packing section
- During HP startup, inaccurate judgment of the level in the urea reactor causes the urea reactor to be fully filled with fluid, reaching up to the HP scrubber, thus causing liquid entrainment of gas-phase in the HP scrubber

Liquid entrainment of the HP scrubber will cause that the vented off-gas will contain a large quantity of carbamate solution, meanwhile, pressure control of the high pressure synthesis fluctuates.

3. Recommendations

Under normal production conditions, strictly control the carbamate solution outlet temperature of the HP scrubber above 155 ^{o}C by controlling the temperature of the tempered cooling water to be higher than 120 ^{o}C, adjusting the opening of the HP inert vent valve of the HP scrubber and the flow rate of the carbamate recycle solution of the HP carbamate pump to be consistent with corresponding production load, so as to allow the compositions of the HP scrubber off-gas to be outside the explosion zone.
Remark UreaKnowHow.com: Some Stamicarbon CO_2 stripping plants operate HP scrubbers with a tempered cooling water inlet temperature of 80 ^{o}C without any problems.

During blocking-in shutdown of the urea synthesis, control the temperature of tempered cooling water above 125 ^{o}C, completely drain the Y-shape line between the hemisphere the bottom of heat exchange in time and use water for flushing the drained pipeline.

Properly control hydrogen content of the feed to be below 50 ppm.

In order to prevent or reduce the temperature drop of the liquid overflow the HP scrubber after overflow of the reactor during startup, the most important thing is to increase the temperature of the reactor solution during overflow (i.e. control the pressure of the LP steam drum at high limit to condense more NH_3 and CO_2 in the urea reactor for increasing the temperature of the reactor solution) and normalize the operation as soon as possible. After the reactor solution level is indicated, such auxiliary adjustments as increasing the quantity discharged or vented, etc. can be applied in a short time so as to have more inert gases discharged, thus increasing the temperature of overflow liquid flowing out of the HP scrubber. It is strictly forbidden to open or close violently the HP inert control valve of the HP scrubber because this will easily generate electrostatic spark and cause explosion risks.

Factors causing liquid entrainment as mentioned above are those occurred under abnormal operating conditions. The main cause of liquid entrainment under normal operating conditions is that an excessive amount of carbamate solution is added at higher loads. Thus the fluid cannot flow downwards smoothly, causing liquid entrainment of the HP scrubber. The solution for solving this problem is to properly reduce the speed of the carbamate pump and decrease the amount of

carbamate solution added to the HP scrubber and then the system will return to normal condition in a short time.

4. Conclusions

Corresponding countermeasures have been proposed through analyzing the process disturbances under different operating conditions, which is not only a way to determine a operation procedure, but also an approach for exploring optimum process conditions in the future. Energy-saving and consumption reduction as well as safety of human and equipment can be realized only through constant optimization of operating conditions.

Translator notes:
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