Lecture 7
Nitric acid – Part 2

The manufacture process of Nitric acid is continued from previous Lecture

5. *Ammonia Oxidation (converters)*

Ammonia is reacted with air on platinum/rhodium alloy catalysts in the oxidation section of nitric acid plants. Nitric oxide and water are formed in this process. The yield of nitric oxide depend on pressure and temperature:

- Pressure below 1.7 bar, temperature 810-850°C -> NO yield 97%
- Pressure 1.7-6.5 bar, temperature 850-900°C -> NO yield 96%
- Pressure above 6.5 bar, temperature 900-940°C -> NO yield 95%

In this operation combustion takes place with the aid of platinum rhodium catalyst. It consists of several woven or knitted gauzes formed from wire containing about 90% platinum alloyed with rhodium for greater strength and sometimes containing palladium. Heated ammonia (60°C) is mixed with air (at 80°C) in a pipe with a big diameter. The ammonia/air mixture is introduced to the converter. The converter contains two parts, the upper part (of a conical shape) has a pierced disc fitted on its entrance to distribute the mixture on the platinum net equally. The lower part of the converter is a bottom pierced pot filled with pottery rings to distribute the hot gases (evolving from the reaction) on to the coils of the bottom boiler. The ammonia air ratio should be strictly maintained at 12% in case of atmospheric process or 13% in case of dual pressure process.
Ammonia goes through oxidation according to the following reaction

\[ 4\ce{NH_3} + 5\ce{O_2} \xrightarrow{\text{Pt + Rh}} 4\ce{NO} + 6\ce{H_2O} + Q \]

\[ 2\ce{NO} + \ce{O_2} \rightarrow 2\ce{NO_2} + Q \]

Temperature is adjusted in a range 800°-900°C, because above 900 nitrogen oxide will decompose to N\(_2\) and O\(_2\), and below 800° C nitrogen oxide will be formed which does not produce nitric acid when dissolved in water. The heat released from those highly exothermic reactions is mostly recovered by the waste heat boiler (WHB) fitted in the ammonia reaction (burners) in the form of superheated steam for running the NO\(_x\) and air compressors.

Air pollution and contamination from the ammonia can poison the catalyst. This effect, as well as poor ammonia-air mixing and poor gas distribution across the catalyst, may reduce the yield by 10%. Maintenance of the catalyst operating temperature is very important for the NO yield. This is achieved by adjusting the air/ammonia ratio and ensuring that the lower explosive limit for ammonia in air is not exceeded. The preheated ammonia is thoroughly mixed with preheated air and subjected to further filtration to avoid contaminants from entering to the catalyst. The ratio of ammonia air mixture is controlled by a high precision ratio controller which is considered as the safeguard for protecting arising from:

1. Catalyst temperature exceeds 850° C
2. Ammonia/ air ratio exceeds 12.5 % (in atmospheric oxidation) or 10 % (in case of pressure oxidation)
3. Failure of air compressor or NO\(_x\) compressor …etc
The water produced in oxidation is then condensed in a cooler-condenser and transferred to the absorption column. Nitric oxide is oxidized to nitrogen dioxide as the combustion gases are cooled. For this purpose secondary air is added to the gas mixture obtained from the ammonia oxidation to increase the oxygen content to such a level that the waste gas leaving the plant has a normal oxygen content of between 2 - 4 %.

6. Energy Recovery

The hot reaction gases are used to produce steam and/or to preheat the waste gas (tail gas). The heated waste gas is discharged to the atmosphere through a gas turbine for energy recovery. The combustion gas after this heat transfer for energy recovery, has a temperature of 100 to 200º C, depending on the process and it is then further cooled with water.

i. Cooling

Exit gases (NOx, excess air and water vapour) are cooled through a water cooler in two stages, where nitrogen oxides are then dissolved in the water condensate to form a very diluted nitric acid (about 2% conc.) which is collected in a tank. The collected diluted acid is withdrawn by pumps and discharged to the bottom of the absorption tower. The remaining gases are withdrawn, together with excess air, by compressing turbines to the absorption towers.

ii. Absorption:

The absorber is operated with a counter-current flow of water. the absorption of the nitrogen dioxide and its reaction to nitric acid and nitric oxide take place simultaneously in the gaseous and liquid phases. The main reaction taking place is as follows:

\[
\begin{align*}
2\text{NO} + \text{O}_2 & \rightarrow 2\text{NO}_2 \\
3\text{NO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3 + \text{NO} \\
2\text{NO}_2 & \rightarrow \text{N}_2\text{O}_4
\end{align*}
\]
These reactions depend on pressure and temperature to a large extent and are favored by higher pressure and lower temperature.

Series of towers with 3.5m diameter and 24m height are used in this stage. The absorber-reactor is a sieve plate or bubble cap unit with cooling coils on each of the 20 to 50 trays. Gas enters at the bottom, dilute nitric acid part way up the column, with cold water entering at the top. In the first tower most of the oxidation operation takes place where NO is converted to nitrogen dioxide. Diluted Nitric acid is then formed, collected in a level tank and discharged to the bleaching operation. Chlorine impurities presents a unique problem in the absorber, they cannot be transferred through the bottom neither can they leave in the top gas. Therefore, they must be excluded from entry or provision made for their purging as the reaction of nitric oxide proceeds during gas flow. Consequently the gases are cooled (remove heat of reaction and promote oxidation reactions to go to completion), against the cold tail gases coming out of the absorption tower to preheat them before entering the tail gas turbine. The preheated tail gas passes through the expansion turbine (part of the NOx compressor drives) to recover the energy and reduce tail gas temperature. Then further cooled before passing through the series of counter-current packed towers.

**iii. Bleaching**

The acid leaving the bottom of the column contains some NOx, mostly as N2O4 (colorless) but some as red NO2. It is therefore sent to a bleaching tower to eliminate its colour. In bleaching operation the acid is sprayed at the top of the tower (about 5.5m height and 90 cm diameter), which is filled with a Raschig rings at the bottom. A counter current air stream is introduced at the bottom of the tower through a screen, to absorb the gases from the acid then withdrawn from the top of the tower. The acid, free from gases, is collected at the bottom of the tower and then cooled in cooling plates and sent to storage tanks. Cooling
plates are essential, especially at the first tower, where the highest quantity of heat is released because most of the oxidation and absorption reactions take place in that tower.

**Major Hazards**

The following hazards may arise during nitric acid production:

- Equipment/piping failure because of corrosion
- Explosion hazard due to the air ammonia mixture
- Explosion of nitrite/nitrate salts.

Corrosion protection is achieved by the well proven use of suitable austenitic stainless steel where condensation can occur and by regular monitoring of conditions. Safety is ensured by the automatic closure of the ammonia control valve and separate shutdown trip valve when too high an air ammonia ratio is measured, either from each individual flow meter or indirectly from the catalyst gauze temperature. The air ammonia ratio should be continuously controlled and kept below the hazardous range. Any free ammonia present in the nitrous gas will have a deposit of nitrite/nitrate in a cold spot. Local washing and well proven operating practices will prevent the hazard.

**Platinum Recovery**

During operation the surface of the catalyst is damaged by abrasion and vaporization. Vaporization loss dominates at the beginning of operation, but vaporization weakness the metal structure and leads to abrasion and erosion.

Platinum from the catalyst passes into the gas stream in the form of very fine particles, and its loss can substantially increase the production cost. Therefore, several methods of
platinum recovery were develop and installed in many plants. Two types of recovery systems – catchment gauzes and mechanical filters – are usually offered.

The principle of catchment gauzes is to collect platinum at a temperature as high as possible while the main portion of the platinum loss is still in vapor form. At these temperatures, platinum atoms strike the metal surface and form an alloy with the catchment metal for subsequent recovery. The system can recover up to 80% of the platinum losses. The catchment gauzes, which are installed at the bottom of the burner, are composed of a mesh screen and two or more metal gauzes. Catchment gauzes are returned together with the catalyst gauzes to the precious metal refining plant.

The mechanical filters, which are composed of glass wool or silica fibers, are commonly installed downstream of the catalyst where the gas temperature is below 300°C. Recovery rates of 50% have been reported.

Construction Materials

The corrosive behavior of nitric acid toward metals requires the proper selection of construction material. The principal material wherever nitric acid or wet nitric oxides are present is chromium-nickel austenitic steel. The carbon content in this steel must be kept as low as possible because chromium forms carbides that are not acid resistant. Alloyed steels are also used for welded parts of pumps, impellers, and rotating elements of compressors. For equipment that handles ammonia, air, and hot, dry gases, normal carbon steel can be used. However, for safety in operation, especially during startup and shutdown operations, nitric acid plants are often equipped with practically all stainless steel equipment. Because they are resistant to nitric acid, various fluorocarbon plastic materials are used for flanges, gaskets, and seals.
Industrial Processes

Industrial plants are classified according to the pressure used.

- Monopressure plants. These plants operate at the same pressure in the ammonia oxidation and absorption sections of the plant. Monopressure plants are classified as low pressure (0.3-0.5 MPa) and high pressure (0.8-1.3 MPa).

- Dual-pressure plants. These plants operate under lower pressure in the ammonia oxidation section than in the absorption section.

In general high-pressure operation permits smaller plant units to be used for a given output and helps to reduce capital costs. High pressure also favor NO₂ absorption; however, high-pressure ammonia oxidation induces greater catalyst losses and also increases power requirements unless additional equipment is installed for power recovery. Because of recent emphasis on pollution control, the ability of high-pressure processes to attain acceptably low Noₓ levels in the tail-gas has favored their adoption. Therefore, most new plants use either mono high-pressure or dual-pressure (medium-pressure combustion, High-pressure absorption) process although some mono-medium-pressure processes are used.

The first nitric acid plants used near-atmospheric pressure throughout. However, practically all modern plants use elevated pressures. The choice of the process always depends on local conditions; however, a general principle may be that lower capacity plants favor the high monopressure alternative. The dual-pressure choice seems to be a compromise between the higher investment costs of mono-medium pressure and higher operating costs of mono-high pressure alternative.