Espindesa operating procedures and design alternatives

Several options regarding operating procedures and design alternatives are used by Espindesa to improve the start-up and shutdown of nitric acid units[4].

Undesirable NOx emissions during the start-up of nitric acid units are formed due to several factors, the most relevant being the lack of pressure in the absorption tower that leads to a lower absorption efficiency. Other significant factors include: chiller water that is too warm and ammonium nitrate deposition.

Most nitric acid units use chilled water for higher efficiency of the absorber in normal operation; this chiller water is obtained by ammonia vaporisation (Fig. 23). During shutdown, but mainly during start-up, the temperature of the chilled water can be too high, especially in warmer climates as the temperature of the weather and solar radiation over chilled water pipes increases the temperature of the chilled water, bearing in mind that during these periods the ammonia vaporiser is not in use and will not be cooling the water. The situation is not so critical in colder climates where chilled water temperatures can be maintained.

The risk of ammonium nitrate deposition over expander blades is another factor. Most modern nitric acid units are provided with a NOx abatement system before the expander, however, to avoid ammonium nitrate and ammonium nitrite deposition on the expander blades a minimum temperature at the expander outlet is needed, this minimum temperature depends on the NOx and NH_3 content in the gas and ranges between 60-90°C. During plant start-up or shutdown if the required temperature at the expander outlet cannot be achieved to operate the NOx abatement system in operation, deposition of nitrates takes place.

To minimise these effects during start-up and shutdowns several developments have been made, a brief description of some common practices are mentioned below. In general, there are 20-30 critical minutes immediately after ammonia ignition until absorption sets stable and expander outlet temperatures are achieved.

The actions suggested to improve the start-up and shutdown can be categorised into operational procedures and design issues.

Issues related to operating procedures:

- Ammonia-air ratio control: During start-up the ammonia-air ratio increases from 0%, when there is no ammonia in the reaction, to the required 9-12% as required by the process, depending on the ammonia oxidation pressure. The ratio should be increased fast enough to avoid damage to the platinum gauzes due to rhodium oxidation, and to pass the limit for high rhodium oxidation as fast as possible, but not so fast

Fig. 23: **Chilled water system**

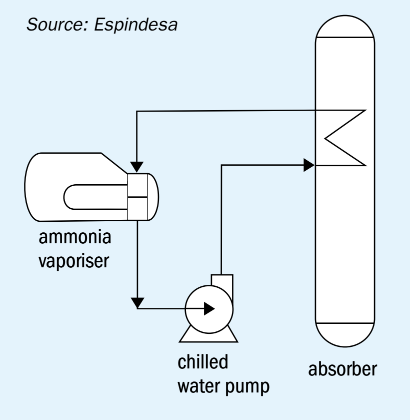
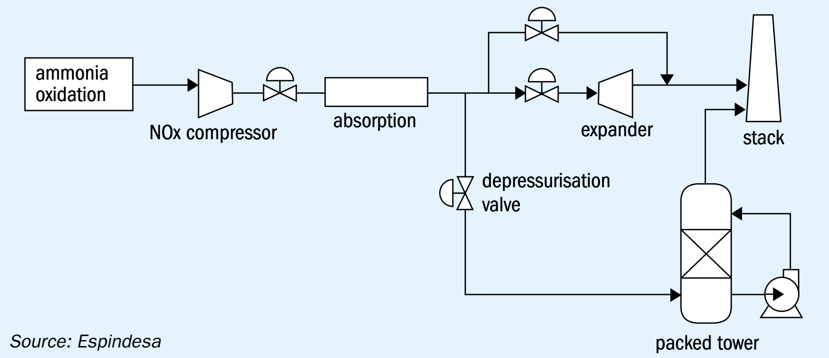


Fig. 24: **Nitric acid absorption tower**

SOURCE: ESPINDESA

Fig. 25: **Enclosed NOx system**



Source: Espindesa

that the expander does not reach the required temperature for NOx abatement. When possible it is good practice to increase the ratio quite quickly until the temperature of the gauzes reaches about 810°C (to minimise rhodium oxide) and then continue at a lower rate until the reaction temperature achieves the nominal value in order to stabilise absorption and provide sufficient time for the tail gas to the expander to achieve the required temperature. The typical residence time from reaction to expander to warm the full unit is in the range from 15-30 minutes.

- Water flow to the absorber: The absorber is, in fact, a buffer for start-up and shutdown. It is therefore possible to maintain higher water flow during start-up and shutdown to maximise the buffer effect, the secondary effect on the unit being that it will handle a little more off-spec acid (more diluted) than can be reprocessed in normal operation.
- NOx abatement buffer effect: It is known that the NOx abatement catalyst retains ammonia during operation that will be useful for abatement at start-up. However, this effect is not suitable for longer shutdown periods[5] as the adsorbed ammonia over the catalyst will be released.

Design issues:

- Extended absorption: The absorption tower can be designed to obtain higher NOx content after absorption during normal operation (about 500 ppmv NOx) which will lead to very high emissions during start-up and shutdown. Alternatively, absorption towers (Fig. 24) can be designed for lower emission during normal operation (about 180 ppmv), which can also control the visual effect of NOx emissions during start-up and shutdown by maintaining the water flow to the absorber. The difference between the two concepts are about 10 m of absorption tower length.
- Increasing tail gas temperature: It is possible to increase the tail gas temperature during start-up and shutdown period by using in-line burners with natural gas to achieve the required temperatures of the NOx abatement system and expander in order to allow the NOx abatement system to be started at any time
- Hydrogen peroxide dosing: the benefits of using hydrogen peroxide (H_2O_2) for NOx abatement have been known since the 1970s[6] and in the past Espindesa has designed NOx absorption system for nitro compounds in Spain and France for cases where NOx fluctuations widely (making it difficult to control with a SCR system). This system can also be effectively used for absorption towers during start-up to increase the buffer effect. Peroxide dosing is optimised and only used during start-up periods to minimise costs. This system has to take into account the ratio between hydrogen peroxide and nitric acid concentration to avoid the risk of explosion[7] when the acid concentration is higher than 55%. However, the dilution of H_2O_2 is usually high enough to avoid any concern.
- Enclosing NOx: During the 1970-1980s, one of Espindesa's designs involved enclosing the NOx in the unit by shutdown valves (Fig. 25). To avoid further corrosion by the enclosed NOx, this system requires an additional absorber (packed tower) with ammonia, dolomite solution dolomite or caustic to abate the NOx to low levels, and nowadays, expanders with higher speed would also require a source of plant air to avoid overheating during shutdown.
- NOx abatement after the expander: Some units use a NOx abatement system after the expander, but due to the low tail gas pressure a heating system as well as a higher volume of NOx abatement catalyst is needed.

Espindesa typically optimises the operating procedures, together with extended absorption, to achieve high reliability of the unit and provides the possibility to implement H_2O_2 abatement in the future. ■

References

4. Ferrer J.R. (ESPINDESA): "Better nitric acid plant start-up and shutdowns", written for Nitrogen+Syngas (Dec 2018).
5. Miggelbrink J, Maaskant O , Stopping the smoke-screen. How technology can be used to clear a colored stack plume. ANNA conference 2010
6. Japanese Patent 4815766 to Kanto Denka, Kogyo Co, N-Oxide removal from Exhaust Gas, February 1973
7. Solvay Chemical 2005 TDS HH-1064 Revised 1-28-05 Solvay Chemical.