

TENDENCIES IN NITRIC ACID PROJECTS

Jose R. Ferrer, ESPINDESA (Técnicas Reunidas Group), Spain, provides a detailed look at the tendencies in the development of nitric acid projects.

The development of a nitric acid project is always linked to the market conditions of downstream units and is influenced in each specific case by different factors. The main market industry for nitric acid has traditionally been the fertilizer industry. Other users of nitric acid include the mining industry (as nitrates are used for civil explosives) and the plastic industry, mainly for isocyanates (MDI, TDI).

Figure 1 shows the typical plant capacities that are being designed for each type of market.

During 2005 – 2012, there were important developments of projects related to the plastic industry, including BASF, Huntsman, Dow-Aramco, Covestro and Yantai Wanhua Polyurethane. These developments have substantially increased the worldwide capacity of isocyanates. It is expected that this market will stabilise before new projects are started. Plant capacities are in two ranges: 500 – 600 metric tpd; or 1000 – 1500 metric tpd (based on HNO_3 100%).

Regarding the fertilizer market, the continuous growth of the world population demands more and more fertilizers. Nevertheless, in some countries, there are restrictions on the use of ammonium nitrate, and in others, calcium ammonium nitrate continues to be extensively used or partially substituted by urea ammonium nitrate (UAN).

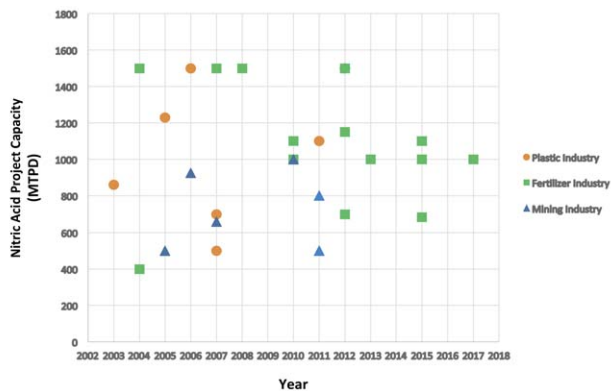


Figure 1. Typical nitric acid plant project capacities.



Figure 2. Nitric acid applications.

Fertilizer demand will suffer cyclic breaks due to economy fluctuations that allow farmers to minimise application of fertilizer for one or even two years.

During the last decade, Henry Hub natural gas price has been maintained in the range of US\$2/million Btu – US\$4/million Btu. It has led to project development based on direct application of natural gas close to natural gas fields and it is called ‘monetisation of natural gas’, especially in North America and recently in Russian or CIS countries. This involves the direct application of natural gas as raw material (without liquefaction which requires high investment) in areas close to gas fields to obtain ammonia for natural gas and from there all downstream units (nitric acid, ammonium nitrate, TDI, MDI or fertilizer). These natural gas ‘monetisation’ projects include typical US projects, such as CFI and IOWA Fertilizer, and are in the range of high nitric acid capacities: 1400 – 1800 metric tpd. These projects also have the advantage of being close to natural sources and farmers.

There are a number of long-term operating nitric acid units in the fertilizer industry (40 – 50 years operation) that are located in Europe, Russia, North Africa and the US, and that are under renovation or being substituted for a new one. Typical capacities are in the medium range of 400 – 600 metric tpd. These types of projects are expected to increase in the coming years.

The other main market still to be reactivated is related to the mining industry, where nitric acid is an intermediate product for low density ammonium nitrate (LDAN), as ammonium nitrate is the base to produce ANFO, probably the most common civil explosive. Typical nitric acid plant capacities for this market are in the range of 400 – 1000 metric tpd. This market related mining has been significantly reduced due to two factors. The first factor is indirectly related to natural gas. Due to cost and environmental concerns, dependency on coal has been reduced as use of

other energy sources increases, and leads to reducing demand for LDAN for coal mining. The second factor is the global economy reduction, which has still not fully recovered for construction and has created a lower demand for metals for construction, such as copper and iron. In this industry, close attention must be paid to the global economy recovery. Many LDAN projects are located close to the mining sites to reduce transport issues and regulations. New mining sites could request a new LDAN project, even when global demand is not increased.

In any case, the expectation for future development of nitric acid units globally is still optimistic. It has historically been a limited market, but it could remain at an average of two nitric acid units per year in the long-term.

Material developments

Nitric acid units experience a wide range of corrosion conditions due to high temperature and/or nitric acid concentration, as well as chloride corrosion from water.

High temperatures include not only stress corrosion, but also the possibility of nitrous gases condensation. For ammonia oxidation catalyst support, high temperature materials have been used from ceramics; for instance, high temperature stainless steel, such as UNS 30815, or high nickel alloys, such as UNS N06230, UNS N06600 or UNS N08810/N08811.

For diluted nitric acid, austenitic stainless steels have been commonly used. However, composition of stainless steel material is critical for the resistance to nitric acid. The following list (from low to high resistance) shows typical materials used in diluted nitric acid (this being in the range of 5 – 68% nitric acid content).

In general, the following elements provide better resistance to intergranular corrosion for nitric acid: nickel, chromium and nitrogen. However, other elements, such as carbon and molybdenum, reduce the corrosion resistance to nitric acid.

- SS321.
- SS304L.
- SS304L with low molybdenum content.
- SS304L with very low carbon and molybdenum content.
- EN 1.4311 with composition equivalent to 304LN.
- SS304L electro slag nitric acid grade.
- SS310 with very low carbon content (nitric acid grade).
- Titanium.
- Zirconium.
- Tantalum.

Most of the austenitic stainless steels resistant to nitric acid have limited resistance to cooling water with chlorides. Still, there are options for development of materials resistant to nitric acid and water with chlorides to avoid using expensive materials, such as titanium, zirconium or tantalum.

Catalyst developments

One of the continuous developments in nitric acid units are the catalysts:

Primary catalyst

The primary catalyst is understood as the platinum gauzes for ammonia oxidation and palladium gauzes for platinum recovery. In the past, they were two separate sets of gauzes.



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Figure 3. Nitric acid plant view.

Nowadays, however, they have been developed as a common package, which can be personalised for specific operating conditions, adjusted for platinum and palladium losses depending on market prizes, and that can minimise N_2O formation.

Secondary catalyst

The second catalyst system developed for nitric acid units are the NO_x abatement catalysts, which maximise NO_x abatement and reduce NH_3 slip. Nowadays, the NO_x emission is easily achievable below 30 ppm vol. and ammonia slip below 1 ppm vol. in the stack.

Third catalyst

The third catalyst development is the N_2O abatement system, which has been developed in two ways: through the secondary abatement system, below platinum-palladium gauzes; and the tertiary abatement that is placed in the tail gas. Historically, there was a considerable gap between secondary and tertiary, but this gap has been reduced. It is possible, depending on operating conditions, to achieve a secondary catalyst with abatement in the range of 90 – 97% and tertiary in the range of 97 – 99%.

Summary

Although from a technical point of view, nitric acid units are a mature technology, there are still developments underway regarding catalysts (for improving environmental emissions, or reducing catalyst losses) and in material selection. From a market point of view, nitric acid projects are being developed close to natural gas fields and close to mining areas. **WF**



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