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Sustainable N_2O Abatement Technology for Nitric Acid Plants

PARTHA PRATIM CHOWDHURY
Sr. Technical Advisor, Nitric Acid and Fertilizers Technology Portfolio

RIT DESAI
Manager of Nitric Acid and Fertilizers Technology Portfolio

KBR
New Delhi, Delhi, India

In 2019, nitrous oxide (N_2O) accounted for nearly seven per cent of all greenhouse gas emissions resulting from activities like agriculture, fuel combustion, wastewater management, and industrial processes in the U.S. Besides, N_2O molecules remain in the atmosphere for an average of 114 years unless removed by a sink or destroyed through chemical reactions. The greenhouse impact of N_2O is ~300 times more than that of CO_2.

Industrial nitrous oxide is generated as a byproduct during the production of chemicals such as nitric acid, which is used to manufacture fertilizers, and in the production of adipic acid, which is used to produce fibers like nylon, and other synthetic products.

KBR's N_2O abatement process employs installation of a catalytic reactor upstream of tail gas expansion unit in a nitric acid plant. At an operating temperature range of 350°C to 660°C the KBR process achieves more than 95% N_2O removal efficiency by use of a proprietary catalyst. By operating at a higher temperature range up to 660°C, the increased energy efficiency at the expander is an added advantage for the KBR process. KBR's proprietary reactor is designed to withstand severe operating conditions and have a design life up to 25 years. With relatively easier installation, the KBR process is the best value proposition for grassroots and brownfield retrofits.

In this paper KBR will present how KBR's tertiary N_2O abatement system has been able to help clients nitric acid producers worldwide meet the governmental environment regulations and keep the planet clean and green.

GLOBAL CLIMATE CHANGE AND N_2O ABATEMENT

Nitrous oxide (N_2O) accounts for 457.14 million metric tons (~7%) of total U.S. greenhouse gas emissions of 2019[$]. Of the total N_2O emission, 21.08 million metric tons accounted from various industrial sources[$]. Nitric acid production is a major industrial process attributing to this emission. Industrial nitrous oxide is generated as a byproduct during the production of chemicals such as nitric acid, which is used to manufacture fertilizers, and in the production of adipic acid, which is used to produce fibers like nylon, and other synthetic products.

The below table shows emission of N_2O per tonne of nitric acid produced.

Table 1. Default N2O Emission Factors

Production Process	Approximate Pressure (atm)	N_2O Emissions (kg N_2O/ metric ton Nitric Acid)		
		Low	Average	High
Plants with NSCR		1.9	2.0	2.1
Plants with process-integrated or tailgas N2O destruction		2.25	2.5	2.75
Atmospheric pressure (low pressure)	1	4.5	5.0	5.5
Medium pressure plants	4-8	5.6	7	8.4
High Pressure plants	8-14	5.4	9	12.6

Source: IPCC 2006 Guidelines for National GHG Inventories & https://www.epa.gov/sites/default/files/2015-12/documents/nitricacid.pdf

Table 2. Uncontrolled N2O Emissions – Clean Development Mechanism Projects

Type of Control	Number of Test Reports	Range (kg N_2O /metric ton HNO_3)	Average (kg N_2O /metric ton HNO_3)
Secondary	38	4.0-19	8.5
Tertiary	11	6.2-15.7	10
	49	4.0-19	8.9

Source: Clean development maechanism projects & https://www.epa.gov/sites/default/files/2015-12/documents/nitricacid.pdf

KBR's N_2O abatement process employs tertiary abatement technology and achieves ~95% removal efficiency.

Table 3. Reference data of N2O Abatement in KBR Technology

Plant Capacity (MTPD)	N2O at inlet (lb/hr)	N2O at outlet (lb/hr)	Abatement Efficiency (%)
624	170.1	8.5	95
835	281	4.9	98.3
1200	409.2	7.2	98.3

NITRIC ACID PRODUCTION PROCESS

The raw materials for producing nitric acid are atmospheric air and gaseous ammonia. The materials are reacted at elevated pressure and various temperatures in several stages to produce nitric acid. In the first stage reaction, the ammonia reacts with oxygen from the air on the platinum and rhodium gauze to produce nitric oxide.

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O \text{ (Reaction No. 1)}$$

The heat generated by reaction one is removed by passing the resultant process gas through a series of heat exchangers. As the process gas is cooled by the heat recovery equipment, the nitric oxide combines with additional oxygen to produce nitrogen dioxide.

$$2\ NO + O_2 \rightarrow 2\ NO_2 \text{ (Reaction No. 2)}$$

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO \text{ (Reaction No. 3)}$$

As the process gas enters the cooler condenser, nitric acid is formed when nitrogen dioxide combines with the water produced in Reaction No. 1. The reaction continues in the absorber where additional water is added to produce nitric acid.

The nitric oxide formed in Reaction No. 3 reacts again in accordance with Reaction No. 2. Excess oxygen is supplied by the bleach air to promote conversion of nitric oxide to nitrogen dioxide. Reaction Nos. 3 and 2 keep recurring up through the absorber trays producing nitric acid until the quantity of nitrogen oxides in the gas reaches approximately 500 ppm NOx (by volume). Plant cooling water is fed through the cooling coils on the absorber trays to remove the heat of reaction for both the nitric acid and oxidation reactions.

While above are the desired reaction for production of Nitric Acid, there are some undesirable side reactions which occur during this process. These undesirable reactions produce N2O.

In the ammonia oxidation catalyst gauze

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O$$

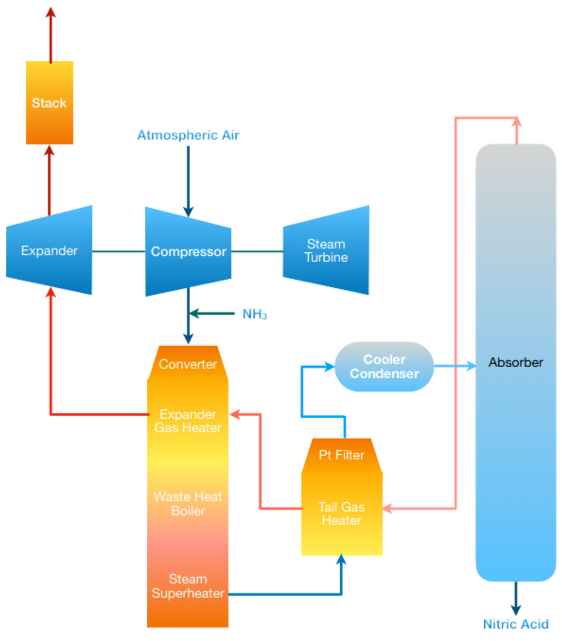

Fig. 1: KBR Nitric Acid Production Process

PRIMARY ABATEMENT

Primary abatement systems conceptually try to reduce N_2O generation during NH_3 oxidation at the Converter. This is basically spontaneous destruction of N_2O by high temperature and time. This is a relatively slow destruction process and with longer residence time we can destroy the N_2O more. Old KBR-Weatherly nitric acid plants with horizontal train had more residence time compared to newer vertical train. This is because in horizontal trains the gas passes through an elbow before entering the heat exchanger. This elbow allows increased residence time leading to primary abatement of N_2O.

Since it is not desirable to keep the hot gas at such high temperature, an exchanger is connected at immediate downstream to bring the gas temperature down. This design is followed in current KBR vertical train nitric acid plants. This addresses the maintenance issues faced by the mechanical components exposed to the high temperature.

Certain other process depends on modified reactor/converter design with higher residence time between the platinum gauge to the first heat exchanger. Also, a modified platinum catalyst is developed, and operating conditions are optimised to reduce the undesired reactions at the platinum gauge.

However, abatement of N_2O by these primary measures are limited and the process has limited efficacy to achieve the acceptable emission norms.

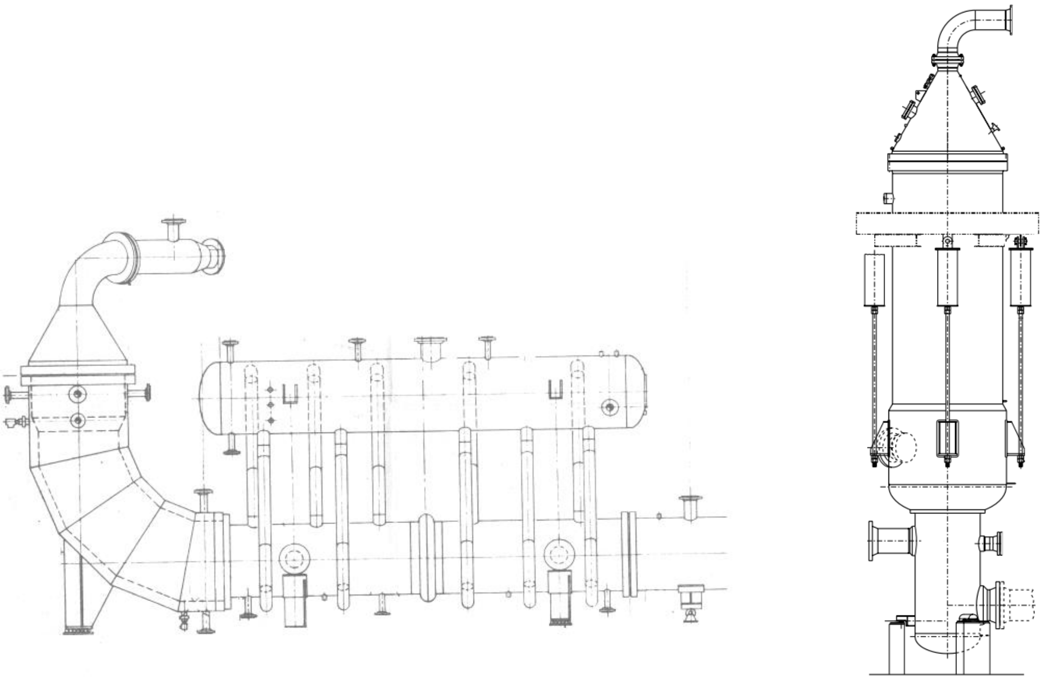

Fig. 2: KBR Heat Train Horizontal vs Vertical

SECONDARY ABATEMENT

Secondary abatement systems work on the principle of installing abatement catalyst after the platinum gauge. This targets to reduce the N_2O from the process stream from NH_3 oxidation stage to HNO_3 production stage. The catalyst undergoes several extreme thermal exposures and is susceptible to damage/cracking. The performance of the catalyst has not been very successful at these operating conditions. KBR has not yet guaranteed any removal efficiency with the secondary abatement, even though there are KBR plants where these are in operation.

TERTIARY ABATEMENT

KBR's N_2O Abatement system which is Tertiary Abatement has a catalytic reactor upstream of tail gas expansion unit. The below figure shows two possible locations of the Abator vessel. In Tertiary control system, N_2O is catalytically decomposed into N_2 and O_2 as in following:

$$N_2O \rightarrow N_2 + \frac{1}{2} O_2$$

The process uses proprietary Fe/Zeolite based catalyst. This catalyst can be bought in pellet form or as monolith bricks. The tertiary N_2O abatement can remove up to 98% of the N_2O content in the tail gas stream. The catalyst will be housed in a pressure vessel suitable for continuous operation. It is expected that the catalyst will remain active for a period of 5 to 7 years.

The biggest advantage of the catalyst is that it is highly efficient in N_2O abatement up to an operating temperature of 660°C. The nitric acid plants designed by KBR features the unique expander gas heater that heats the tail gas up to 650°C. The high tail gas temperatures improve the power recovery in the expander and maximise the steam export, making the KBR design very energy efficient. This enables retrofit of a N_2O abatement system between the expander gas heater and the expander.

Alternatively, a unit can be placed upstream of the expander gas heater thus reducing the operating temperature of the abatement system.

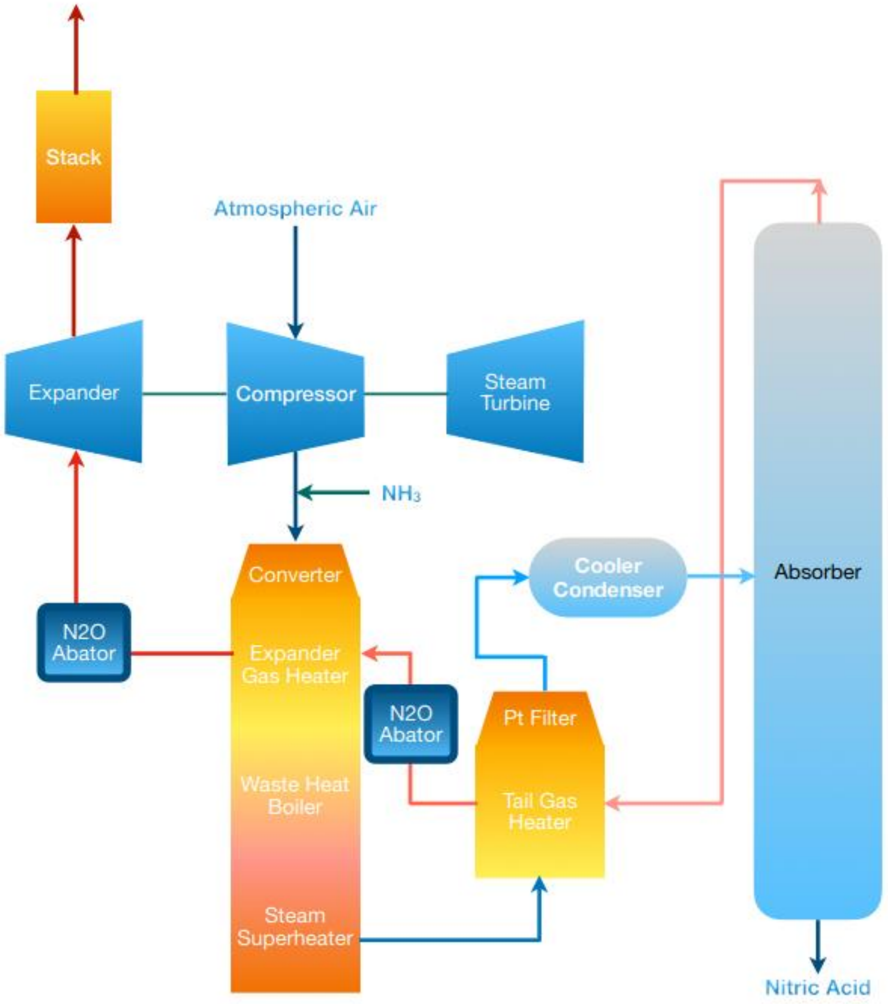

Fig. 3: N2O Abator Vessel and Process Flow

A significant feature of the design is the low-pressure drop in the tertiary N_2O abatement system, approximately 20 kPa or less. This is further improved if a radial flow design is used. However, this leads to higher mechanical cost due to to intricate internal basket design inside the vessel.

The N_2O Abatement System can be coupled with NO_x Abatement System if there is a process requirement. The NO_x Abatement system can be independent equipment or can be combined in a single reactor with N_2O Abatement.

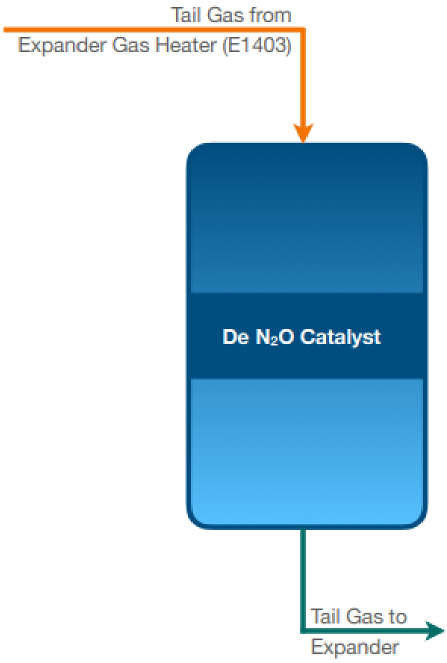

Fig. 4: Standalone N_2O Abator with De N_2O catalyst

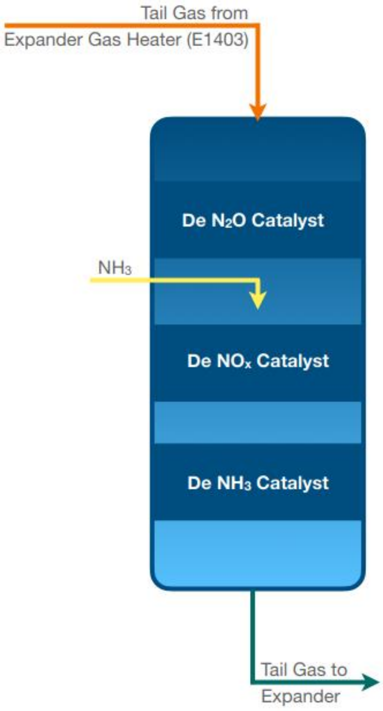

Fig. 5: N_2O Abator coupled with NO_X Abatement using NH_3

EQUIPMENT DESIGN

The N_2O Abator vessel is designed as a hot wall down flow reactor. The tail gas enters the vessel from top and is uniformly distributed over the monolith bed. Computational fluid dynamic analysis helped KBR design the proprietary inlet distributor which ensures smooth distribution of the tail gas above the catalyst bed. This helps in maintaining a uniform operating pressure profile across the reactor bed. Also due to uniform distribution of tail gas, the temperature profile is uniform during startup and shutdown and this enable is lesser thermal loads on mechanical components.

The catalyst bed is supported by the support beam and grid. A 24” man-way is provided above the catalyst bed to allow for easy installation of the monolith bricks and the support grid.

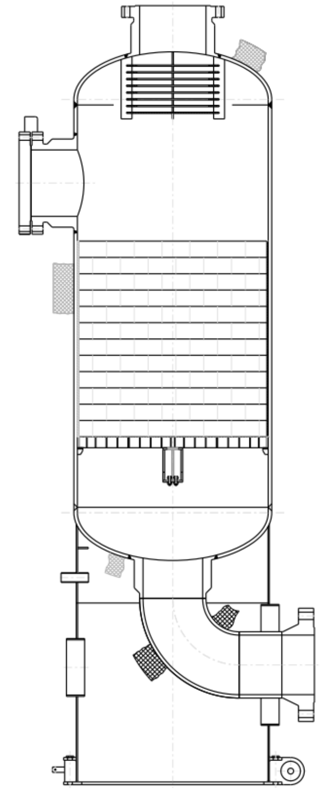

Fig. 6: Typical Sketch of N_2O Abator with De N_2O catalyst

The equipment is made of special stainless steel with stringent chemistry restrictions. This enables a longer life suitable for the harsh operating conditions including temperature and pressure cycles. Being in cyclic service the equipment is subjected to fatigue stresses. This is carefully addressed by mechanical design with compliance to all ASME requirements. The support skirt is designed with hot box to address the thermal cycles. The inlet and outlet nozzle design addresses the temperature and pressure cycles for a life of 20 years as minimum.

The benefit of the proven hot wall design is the reduction in weight compared to cold wall refractory lined design. KBR can provide a cold wall design if requested by client. This will however lead to higher capital cost due to higher weight and more complex design.

While radial flow design provides better pressure drop control across the bed, the simpler axial down flow design leads to a reduction in weight by 40%. The axial flow design enables use of monolith brick design catalyst which can be easily installed during turnarounds. The simpler design of the reactor internals offsets the slightly higher cost of a monolith catalyst compared to pelletised extradite catalyst. This translates to lower capital cost for the client for installing a new N_2O abatement unit.

Also based on client requirements, the equipment can be sized or rated for a higher capacity for future. This additional margin can be used later with additional catalyst as and when necessity arises.

CONCLUSION

With multiple units successfully under operation meeting the N_2O emission restrictions, KBR's tertiary N_2O abatement system has been able to help clients meet the governmental environment regulations as well as provide a sustainability commitment to the society in general. With an operating range of 350°C to 660°C the process not only meets the emission restriction, but also leads to higher power recovery at the expander. The technology license is further enhanced by proprietary equipment supply by KBR which meets the best design, fabrication, and quality control industry standards. Thus, KBR can support client with end-to-end solution from design to delivery.

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