NITRIC ACID

1. Introduction

Nitric acid [7697-37-2], HNO_3, also known as *aqua fortis*, azotic acid, hydrogen nitrate, or nitryl hydroxide, is a chemical of major industrial importance. Because of its properties as a very strong acid and a powerful oxidizing agent, as well as its ability to nitrate organics, nitric acid is essential in the production of many chemicals (eg, pharmaceuticals, dyes, synthetic fibers, insecticides, and fungicides), but is used mostly in the production of ammonium nitrate for the fertilizer industry (see FERTILIZERS). By the end of the nineteenth century, its industrial importance had already become established in the production of explosives and dyestuffs. After World War II nitric acid production grew rapidly with the expanding use of synthetic fertilizers. Because of the increased popularity of urea as a fertilizer, production has leveled off in the 1990s. Most growth in demand has come from the production of polyurethanes, fibers, and ammonium nitrate-based explosives. Other uses for nitric acid are in the manufacture of explosives (trinitrotoluene, nitroglycerin, etc), metal nitrates, nitrocellulose, and nitrochlorobenzene, the treatment of metals (eg, the pickling of stainless steels and metal etching), as a rocket propellant, and for nuclear fuel processing.

The first reports of nitric acid have been credited to Arab alchemists of the eighth century. By the Middle Ages it was referred to as *aqua fortis* (strong water) or *aqua valens* (powerful water). From that time onward, nitric acid was produced primarily from saltpeter [7757-79-1] (potassium nitrate) and sulfuric acid. In the nineteenth century, Chilean saltpeter [7631-99-4] (sodium nitrate) from South America largely replaced potassium nitrate. However, at the beginning of the twentieth century newer manufacturing technologies were introduced. In Norway, where electricity was inexpensive, electric arc furnaces were used to make nitrogen oxides, and subsequently nitric acid, directly from air. The commercial life of these furnaces was relatively brief and most were shut down by 1930. At about the same time, a different production method was being developed. In 1908, at Bochum, Germany, Ostwald piloted a 3-t per day nitric acid process based on the catalytic oxidation of ammonia with air. In 1913 the synthesis of ammonia from coal, air, and water was successfully demonstrated using the Haber-Bosch process. With a secure and economical supply of ammonia, ammonia oxidation became firmly established as an industrial route to nitric acid manufacture. Process developments continued and plant scale increased to commercial quantities in both Europe and the United States. The first full-size plant to be built in the United States was installed in 1917 by Chemical Construction Company (Muscle Shoals, Alabama). The process operated at atmospheric pressure and used multiple ammonia oxidation converters. Since those early days, ammonia oxidation has become the basis of all commercial nitric acid production. There have been many advances in plant design leading to improved process performance and higher production capacities at increased operating pressures. More details on the history of nitric acid and development of the manufacturing process are available (1-4).

In the modern ammonia oxidation process, most nitric acid is produced as a weak acid (50–65 wt%). High monopressure processes minimize capital investment, whereas split- or dual-pressure processes optimize ammonia conversion efficiency and catalyst use. Weak acid is suitable for use in the production of fertilizers, but stronger acid (up to 99 wt% acid) is required for many organic reactions of industrial importance. Direct strong nitric (DSN) processes make the acid directly from nitrogen oxides obtained by the oxidation of ammonia. Nitric acid concentration (NAC) processes use extractive distillation to concentrate the weak acid. A dehydrating agent such as sulfuric acid or magnesium nitrate is used to enhance the volatility of HNO_3 so that distillation methods can surpass the maximum boiling azeotrope of nitric acid. Several DSN processes can produce weak and strong acids simultaneously.

2. Physical Properties

Crystals of pure nitric acid are colorless and quite stable. Above the melting point of $-41.6°C$, nitric acid is a colorless liquid that fumes in moist air and has a tendency to decompose, forming oxides of nitrogen. The rate of decomposition is accelerated by exposure to light and increases in temperature. Depending on the concentration of dissolved nitrogen dioxide, the color may range from yellow to red. The normal boiling point of nitric acid is 83.4°C, but when heated the liquid gradually decomposes to form a maximum boiling azeotrope at 120°C and 69 wt% HNO_3 (5).

Nitric acid is completely miscible with water. The freezing point curve for aqueous solutions of nitric acid has two maxima corresponding to melting points for the two hydrates of nitric acid: the monohydrate (77.77 wt% acid) at $-37.62°C$ and the trihydrate (53.83 wt% acid) at $-18.47°C$ (6). Local minima occur at about 32, 71, and 91 wt% acid (7). There is some variability in the data available on partial pressures of acid and water vapor over solutions of nitric acid. This is most evident in the vapor pressure measurements of one component when the solution concentration of that component is very low. The decomposition of nitric acid at high temperatures and concentrations can also lead to some doubt about the accuracy of vapor pressure measurements. The vapor pressure and density of such acid-containing nitrogen dioxide (ie, fuming nitric acid) increase with the percentage of dioxide present. Data that have been subjected to thermodynamic tests and corroborated by the measurements of other studies are therefore the most reliable (5,8-11). The density, viscosity, and thermal conductivity of nitric acid solutions are given in Table 1. A detailed tabulation of densities is available (12). For all temperatures, density increases with acid concentration; viscosity reaches a maximum at ca 60–70 wt% acid (13).

Thermodynamic data for nitric acid are given in Table 2. Properties for the ternary systems sulfuric acid–nitric acid–water (5,14) and magnesium nitrate–nitric acid–water (11,15-17) used in processes for concentrating nitric acid are available.

3. Chemical Properties

Nitric acid is a strong monobasic acid, a powerful oxidizing agent, and nitrates many organic compounds. Until the end of the nineteenth century, it was made by heating a metallic nitrate salt with less volatile concentrated sulfuric acid. Removal of the volatile nitric acid permits the reaction to go to completion. This method is still used for laboratory preparation of the acid.

3.1. Acidic Properties. As a typical acid, it reacts readily with alkalies, basic oxides, and carbonates to form salts. The largest industrial application of nitric acid is the reaction with ammonia to produce ammonium nitrate. However, because of its oxidizing nature, nitric acid does not always behave as a typical acid. Bases having metallic radicals in a reduced state (eg, ferrous and stannous hydroxide becoming ferric and stannic salts) are oxidized by nitric acid. Except for magnesium and manganese in very dilute acid, nitric acid does not liberate hydrogen upon reaction with metals.

3.2. Oxidizing Properties. Nitric acid is a powerful oxidizing agent (electron acceptor) that reacts violently with many organic materials (eg, turpentine, charcoal, and charred sawdust) (19,20). The concentrated acid may react explosively with ethanol (qv). Such oxidizing properties have had military application: nitric acid is used with certain organics, eg, furfuryl alcohol and aniline, as rocket propellant (see EXPLOSIVES AND PROPELLANTS).

Depending on acid concentration, temperature, and the reducing agent involved, any of the following oxidations may occur:

$$4HNO_3 + 2\,e^- \longrightarrow 2\,NO_3^- + 2\,H_2O + 2\,NO_2 \tag{1}$$

$$8HNO_3 + 6\,e^- \longrightarrow 6\,NO_3^- + 4\,H_2O + 2\,NO \tag{2}$$

$$10HNO_3 + 8\,e^- \longrightarrow 8\,NO_3^- + 5\,H_2O + N_2O \tag{3}$$

$$10HNO_3 + 8\,e^- \longrightarrow 9\,NO_3^- + 3\,H_2O + NH_4^+ \tag{4}$$

$$16HNO_3 + 12\,e^- \longrightarrow 14\,NO_3^- + 4\,H_2O + 2\,NH_3OH^+ \tag{5}$$

Concentrated nitric acid favors the formation of nitrogen peroxide, whereas low strength acid favors the generation of nitric oxide. Concentrated acid converts the oxides, sulfides, etc, of most elements in a low oxidation state to a higher level, eg, sulfur dioxide is oxidized to sulfuric acid. As a general rule for metals, those below hydrogen in the electrochemical series yield nitrogen peroxide and nitric oxide. Those above hydrogen react to produce nitrogen, ammonia, hydroxyl amine, or nitric oxide when treated with nitric acid.

Most nonmetallic elements (except nitrogen, oxygen, chlorine, and bromine) are oxidized to their highest state as acids. Heated with concentrated acid, sometimes in the presence of a catalyst, sulfur, phosphorus, arsenic, and iodine form sulfuric, orthophosphoric, orthoarsenic, and iodic acid, respectively. Silicon and carbon react to produce their dioxides.

Nitric acid reacts with all metals except gold, iridium, platinum, rhodium, tantalum, titanium, and certain alloys. It reacts violently with sodium and potassium to produce nitrogen. Most metals are converted into nitrates; arsenic, antimony, and tin form oxides. Chrome, iron, and aluminum readily dissolve in dilute nitric acid but with concentrated acid form a metal oxide layer that passivates the metal, ie, prevents further reaction.

3.3. Organic Reactions. Nitric acid is used extensively in industry to nitrate aliphatic and aromatic compounds (21). In many instances nitration requires the use of sulfuric acid as a dehydrating agent or catalyst; the extent of nitration achieved depends on the concentration of nitric and sulfuric acids used. This is of industrial importance in the manufacture of nitrobenzene and dinitrotoluene, which are intermediates in the manufacture of polyurethanes. Trinitrotoluene (TNT) is an explosive. Various isomers of mononitrotoluene are used to make optical brighteners, Herbicides (qv), and insecticides. Such nitrations are generally attributed to the presence of the nitronium ion, NO_2^+, the concentration of which increases with acid strength (see NITRATION).

$$HNO_3 + H^+ \rightleftharpoons NO_2^+ + H_2O \tag{6}$$

$$ArH + NO_2^+ \longrightarrow ArNO_2 + H^+ \tag{7}$$

Alcohols and glycerols are nitrated by esterification in a mixture of concentrated nitric and sulfuric acids. This reaction is of importance in the production of nitroglycerin from glycerol and nitrocellulose from cellulose.

$$ROH + HONO_2 \longrightarrow RONO_2 + H_2O \tag{8}$$

Dilute nitric acid can be used to oxidize an aliphatic hydrocarbon. For example, a significant use for nitric acid is the oxidation of Cyclohexanol and Cyclohexanone (qv) to produce Adipic Acid (qv). Most adipic acid is used for the production of nylon-6,6.

$$3C_6H_{11}OH + 3\ C_6H_{10}O + 14\ HNO_3 \longrightarrow 6\ HOOC(CH_2)_4COOH + 14\ NO + 10\ H_2O \tag{9}$$

4. Manufacture and Processing

Almost all commercial quantities of nitric acid are manufactured by the oxidation of ammonia with air to form nitrogen oxides that are absorbed in water to form nitric acid. Because nitric acid has a maximum boiling azeotrope at 69 wt%, the processes are usually categorized as either weak (subazeotropic) or direct strong (superazeotropic). Typically, weak processes make 50–65 wt% acid and direct strong processes make up to 99 wt% acid. Strong acid may also be made indirectly from the weak acid by using extractive distillation with a dehydrating agent. Nitric acid concentration processes use a dehydrating agent such as sulfuric acid or magnesium nitrate to enhance the volatility of HNO_3 so that distillation methods can surpass the azeotropic concentration of nitric acid.

4.1. Weak Acid Process. Historically, different design philosophies between the United States and Europe have led to the development of two basic types of weak acid plant: the high monopressure and the dual-pressure processes. The high monopressure process has been favored in the United States because of its lower capital cost and traditionally lower energy and ammonia prices. In Europe, where allowable capital payback periods and energy costs have traditionally been higher, the dual-pressure process evolved. In the 1990s, these processes continue to advance in design and are competitive on a worldwide basis (22). Many licensors offer both designs. Figures 1 and 2 show examples of the two kinds of processes. The different types of NO_x abatement systems illustrated in these diagrams are interchangeable for either process.

Monopressure Process. Monopressure processes are either medium pressure, 0.3–0.6 MPa (3–6 atm), or high pressure, 0.7–1.2 MPa (7–12 atm). The high pressure process has been the most prevalent design. Higher operating pressures reduce equipment size and capital cost. The capital cost of the high monopressure process is about 10–14% lower than that of the dual-pressure process. Higher gauze temperatures and operating pressures accommodate a more efficient recovery of process energy, either as steam or as reheated tail gas, providing power for air compression. One licensor (23) has found additional cost advantages by going to a vertical equipment layout, resulting in a smaller process footprint, less piping, and the elimination of weak acid pumps.

Dual-Pressure Process. Dual-pressure processes have a medium pressure (ca 0.3–0.6 MPa) front end for ammonia oxidation and a high pressure (1.1–1.5 MPa) tail end for absorption. Some older plants still use atmospheric pressure for ammonia conversion. Compared to high monopressure plants, the lower oxidation pressure improves ammonia yield and catalyst performance. Platinum losses are significantly lower and production runs are extended by a longer catalyst life. Reduced pressure also results in weaker nitric acid condensate from the cooler condenser, which helps to improve absorber performance. Due to the split in operating conditions, the dual-pressure process requires a specialized stainless steel NO_x compressor.

Process Description. Air is supplied to the process from a compressor that is powered by an expander and a makeup driver, all having a common shaft. The expander is a turbine that recovers energy from spent process gases as they are reduced to atmospheric pressure. The makeup driver, usually a steam turbine or electric motor, meets the balance of any power requirement for air compression. Ammonia and air are mixed such that there is an excess of oxygen and are passed over a platinum catalyst to produce nitric oxide, NO, water vapor, and much heat. The resulting gases are cooled, thus generating steam that can be exported or used to power the steam turbine. As the process gases cool, nitric oxide is further oxidized to form nitrogen dioxide, NO_2, in equilibrium with its dimer, dinitrogen tetroxide, N_2O_4. Because hot liquid nitric acid is corrosive, the extent to which heat can be usefully recovered from the hot process gas in the heat train is limited by a need to remain above the dew point for HNO_3. After leaving the heat train, the process gases are further cooled in a cooler–condenser to remove condensate. This exchanger uses expensive materials of construction that are resistant to corrosion by hot acid. The process gases then enter a column where the equilibrium mix of NO_2 and N_2O_4, known as nitrogen peroxide, is absorbed into water, producing nitric acid. Nitric oxide, released by formation of the nitric acid, must be oxidized to complete the conversion of nitrogen oxides to nitric acid. Spent gases from absorption contain residual levels of nitrogen oxides, NO_x, which for environmental reasons have to be removed before discharge to the atmosphere.

Compression and Expansion. For many reasons the compressor–expander set may be considered the heart of a nitric acid process. To a large extent it sets the energy efficiency and operating flexibility of the process and represents about 35% of total equipment cost. Air compressors are typically multistage centrifugal units with intercoolers, while for large-capacity plants axial flow compressors are often used for the initial stages of compression. A high pressure process may use as much as 470 kWh/t of HNO_3 for air compression, with over 80% of this energy provided by power recovery in the expander. For a given flow, the amount of energy available for recovery is set by its absolute temperature. The fraction of available energy actually recovered by an expander is a function of its polytropic or adiabatic efficiency and the pressure expansion ratio. The upper limit for temperature is primarily determined by an expander's mechanical design. Hot expanders are of a multistage gas turbine design and construction, permitting operation at temperatures up to 680°C. The less expensive cold expanders operate below ca 540°C and are of simpler design, eg, steam turbine designs modified for operation with nitric plant tail gas. Hot expansion maximizes the power provided by an expander for air compression. Being more energy efficient than a typical steam turbine makeup driver, a hot versus a cold expander can increase steam for export by as much as 0.5 t/t of HNO_3. Steam export can also be enhanced by replacing the steam makeup driver with an electric motor. Every ton of steam thus saved increases electrical consumption by ca 200 kWh.

Both the compressor and expander are carefully matched to the process and its design capacity. The rate of oxidation of nitric oxide dictates that production capacity is proportional to pressure cubed. The expander, however, varies plant operating pressure linearly with gas flow rate. Consequently, the range of energy efficient operation is limited and most nitric plants can turn down to only about 70% of design capacity. Reduced rates often require back-pressuring of the process to maintain a suitable operating pressure. This results in a loss of expander energy recovery. Maintaining pressure at reduced flow rate brings operation of the compressor closer to its surge point. A portion of compressed air is sometimes vented to atmosphere to increase flow rate and avoid surge conditions with a resulting loss in process energy efficiency. Various schemes have been used to increase the range of efficient turndown. Flow rate can be increased by bypassing some air around part of the process and into the expander (24). Selection of compressors and expanders with adjustable stators and nozzle sizes can also help extend the range of efficient turndown (25).

In the split- or dual-pressure process, low to medium pressure gases (ca 0.3–0.6 MPa) containing nitrogen oxides are compressed to ca 1.1–1.5 MPa for efficient absorption in water to make nitric acid. Stainless steel is used for construction in this corrosive environment and, because of the potential for unreacted ammonia from the converter combining with nitric acid to form ammonium nitrate, there can be additional operating and safety considerations caused by the accumulation of ammonium nitrate solids. Successful operation of dual-pressure processes has shown that these problems have been overcome. One reported solution to the buildup of ammonium nitrate solids is a periodic injection of steam to parts of the compressor (26).

Conversion of Ammonia. Ammonia [7664-41-7], mixed with air and having an excess of oxygen, is passed over a platinum catalyst to form nitric oxide and water (eq. 10). The $\Delta H_{298\ \mathrm{K}} = -226$ kJ/mol of NH_3 consumed (−54 kcal/mol). Heats of reaction have been derived from heats of formation at 25°C (18).

$$NH_3 + 1.25\ O_2 \longrightarrow NO + 1.5\ H_2O \tag{10}$$

Various metal oxides can and have been used as catalysts for this reaction, but none have found wide use in industry. Interest in finding a less expensive material than platinum continues, with most recent activity centering on cobalt catalysts (26,27). In the 1990s, platinum remains the catalyst of choice. Used as multiple layers of a fine wire mesh or gauze, it typically contains 5–10 wt% of rhodium for increased strength and improved reaction yield. Use of up to 5 wt% palladium reduces the overall cost. Using such platinum-based catalysts, the conversion of ammonia to nitric oxide is high (93–98%). The optimum reaction temperature for conversion efficiency increases with operating pressure. Overall, the combination of higher operation pressure and temperature results in decreased conversion efficiency. At typical gauze temperatures of 800–940°C, nitric oxide is thermodynamically unstable and slowly decomposes into nitrogen and oxygen. Decomposition losses are minimized by avoiding excessive catalyst contact time and rapidly cooling the gases as they exit the converter. Fortunately, the conversion of ammonia to NO is very rapid and catalyst contact time is ca 10^{-3}–10^{-4} s. The formation of nitrogen by direct combustion of ammonia usually represents the most significant yield loss (eq. 11), where $\Delta H_{298\mathrm{K}} = -317$ kJ/mol of NH_3 consumed (75.8 kcal/mol). Small amounts of nitrous oxide N_2O are also formed but much lower reaction temperatures of around 500°C are required for N_2O to become a significant yield loss.

$$NH_3 + 0.75\ O_2 \longrightarrow 0.5\ N_2 + 1.5\ H_2O \tag{11}$$

Besides the direct oxidation of ammonia, various theories have been postulated for the reaction mechanism, including the formation of an intermediate imide (NH), nitroxyl (HNO), or hydroxylamine (28). Parameters affecting the conversion efficiency of ammonia to nitric oxide have also been studied (28-34). Gas velocity (linear, space, and mass), catalyst (composition, surface area, and age), operating conditions (pressure and temperature), and converter design (mixing and flow distribution) all have a significant effect on conversion efficiency. Reduced ammonia feed concentration and operation at low pressure are reported to improve nitric oxide yield. The greater selectivity toward nitric oxide formation under such conditions is probably caused by operating under gas-phase, mass-transfer limiting conditions for ammonia, which results in low concentrations of ammonia at the catalyst surface. Reactions involving the formation of N_2 and N_2O at the catalyst surface are thought to be one order higher in ammonia concentration than the desired reaction for NO. Decomposition of NO at the catalyst also appears to be enhanced by pressure, because the reaction is second order in the partial pressure of NO (32). Operation at atmospheric pressure is generally credited with a 3% yield benefit over operation at high pressure, ca 1.0 MPa (10 atm). Because low ammonia feed concentration improves yield, air and ammonia are often preheated so that an optimum feed concentration and temperature can be attained for the desired reaction. Most commercial processes operate with ammonia feed concentrations of between 10.5 and 12.0 vol%; the lower explosive limit for ammonia in air is 13.8 vol% at 0.1 MPa, diminishing to 12.4 vol% at 0.8 MPa (33,34). Industrial experience has shown that significant yield losses can result from impurities such as oil and rust present in feedstocks, so various methods of impurity removal, including filtration (ie, of the air, ammonia, and ammonia–air mixture) are commonly employed (35-37). Particles of rust and equipment made of mild steel promote the decomposition of ammonia even before it reaches the gauze.

The performance of a platinum gauze catalyst varies with its age. Changes in efficiency are affected by structural and compositional changes to the catalyst. A new gauze has smooth rounded wires of catalyst. After a short period of operation, conversion efficiency increases as the surface roughens and metal migrates to the surface to form small metal growths that increase surface area of the catalyst. As these growths increase, the catalyst structure is weakened and catalyst is lost. The catalyst surface becomes enriched with inactive rhodium oxide, Rh_2O_3, and ammonia conversion efficiency begins a gradual decline. Platinum is lost preferentially to palladium or rhodium. The rate of metal loss is a strong function of temperature; as much as a tenfold increase has been reported for a temperature change from 820 to 920°C (34). The amount of precious metal loss is financially significant and various methods, such as downstream glass fiber filters, are used to recover lost particles of catalyst.

Volatilized platinum oxides may be recovered on noble metal catchment gauzes that are placed immediately below the platinum oxidation gauze. Catchment gauzes are made from palladium or palladium combined with a base metal (38,39). Platinum recovery rates, reported to be as high as 70–85%, are to some extent offset by losses of palladium. Newer specialized designs of gauze have become available that reach optimum conversion efficiency in a matter of hours rather than days of plant operation and, overall, provide a higher conversion efficiency (38). Such gauzes replace only a portion of the standard converter gauze sheets and provide an easy light-off because they have a lower ignition temperature. This approach is similar to the well-known practice of placing a few used catalyst sheets on top of a new gauze pack to facilitate easy light-off and improved initial catalyst performance. Other gauze designs use knitted wire construction rather than a weave (39). The increased surface area per unit mass of catalyst is reported to improve ammonia conversion and possibly increase catalyst life because of reduced migration of rhodium to the catalyst surface. Knitted gauzes are approximately 75% lighter than conventional gauzes (four knitted sheets are equivalent in weight to one woven sheet).

Actual converter design and performance vary with the operating conditions. Single-train capacities of up to 2500 t/d HNO_3 for a high pressure process and 1500 t/d for a medium pressure process are claimed, but most large-capacity processes have used multiple converters, each with capacities of ca 600–1000 t/d HNO_3 and diameters of up to 6 or 7 m. Catalyst loading for most plants is reported (22) to be in the range from 1.5 to 1.9 kg per t/h of nitric production and probably lowest for high pressure operation (34). In approximate terms, gauze diameter varies inversely with pressure and the number of layers of gauze varies from four at atmospheric pressure to 24–45 layers for high pressure operation. Ammonia conversion efficiency and optimum gauze temperature vary with operating pressure. Typical values for atmospheric operation are a 97–98% conversion efficiency at 790–850°C. High pressure operation, ie, at 1.0 MPa (10 atm), provides a 94–95% conversion efficiency at about 940°C. Gross catalyst losses increase from around 0.05–0.10 g/t for atmospheric to medium pressure plants up to 0.2–0.4 g/t HNO_3 for high pressure processes. The greater catalyst loss for high pressure operation has encouraged the development and use of recovery catchment gauzes and mechanical filters. High efficiency mechanical filters recover as much as 50% of such losses. The combined use of catchment gauzes and filters is credited with 70% or greater recovery when used in a high pressure process (23). A gradual deterioration in gauze efficiency limits plant operating time. Operating time is shortest for high pressure operation at 2–3 months. This increases to 4–6 months for medium pressure plants and 8–12 months for low pressure combustion. The advantages of low pressure operation are offset by the capital cost for larger process equipment.

Oxidation of Nitric Oxide. Nitric oxide [10102-43-9] reacts slowly with oxygen to yield nitrogen dioxide [10102-44-0] according to the reversible reaction (eq. 12) for which $\Delta H_{298\ \mathrm{K}} = -57$ kJ/mol of NO consumed (13.6 kcal/mol).

$$2NO + O_2 \rightleftharpoons 2NO_2 \tag{12}$$

Low temperatures strongly favor the formation of nitrogen dioxide. Below 150°C equilibrium is almost totally in favor of NO_2 formation. This is a slow reaction, but the rate constant for NO_2 formation rapidly increases with reductions in temperature. Process temperatures are typically low enough to neglect the reverse reaction and determine changes in NO partial pressure by the rate expression (40-42) (eq. 13). The rate of reaction, and therefore the time required to achieve a given extent of oxidation, is proportional to pressure cubed. This is of great significance in plant design and economics. The volume or size of equipment needed to oxidize the nitric oxide is inversely proportional to pressure cubed.

$$d(P_{\mathrm{NO}})/dt = -k(P_{\mathrm{NO}})^2(P_{\mathrm{O2}}) \tag{13}$$

Nitrogen dioxide rapidly forms an equilibrium mixture with its dimer, dinitrogen tetroxide ($\Delta H_{298\ \mathrm{K}} = -28.6$ kJ/mol of NO_2 consumed). The formation of tetroxide is favored by low temperature and high pressure.

Absorption of Nitrogen Oxides. There have been numerous studies and reports on the reaction mechanisms and rate-controlling steps for the absorption of nitrogen oxides into water (43-46). The overall reaction to form nitric acid may be represented by equation 14, where $\Delta H_{298\ \mathrm{K}} = -46$ kJ/mol of NO_2 consumed.

$$3NO_2(g) + H_2O(l) \rightleftharpoons 2\ HNO_3(aq_\infty) + NO(g) \tag{14}$$

Equilibrium for this reaction, expressed in terms of the constituent partial pressures, is a function of temperature, with low temperature favoring the formation of nitric acid (43). The equilibrium for reaction 14 has been more commonly reported in terms of the partial pressure of nitrogen oxides as a strong function of acid strength. Replacing the partial pressure of NO with that of N_2O_4 by use of the equilibrium expression for NO_2-dimer formation eliminates temperature as a significant variable for typical absorption applications (44). Besides equilibrium, models used to simulate or design the absorption process (45-51) must also account for large changes in absorption efficiency, ie, the approach to equilibrium, with acid strength. The mechanisms and rate-controlling steps for acid formation change with concentration and extent of oxidation to nitrogen peroxide. At high concentrations of nitrogen peroxide (>40 wt%), ie, for nitric acid concentrations, N_2O_4 is the principal route to acid formation. At lower concentrations of nitrogen peroxide, a combination of mechanisms involving NO_2, N_2O_3, and HNO_2 become more important (45,50).

Before entering the absorption column, the process gases are cooled in a cooler–condenser to remove condensate. Because most of the water for absorption comes from the combustion of ammonia, it is important to remove the condensate with a minimum content of nitric acid. This optimizes the height at which condensate may be fed to the column. If the condensate contains too much nitric acid, the column may not be able to provide the desired product acid strength. It is therefore important not to oversize the cooler–condenser. For condensation at atmospheric pressure, it is possible to remove water containing less than 10 wt% acid. At higher pressures of up to 0.9–1.4 MPa (9–14 atm), the condensate typically contains 45–50 wt% acid. Formation of nitric acid in the condensate generates nitric oxide, which lowers the extent of oxidation to NO_2. To make product acid of high strength, the nitrogen oxides must be fully oxidized before entering the absorption column. Air, used to strip dissolved NO_x in the product acid, is mixed with the process gas to enhance the oxidation process. As the gases are cooled and oxidized, further conditioning of the gas stream is caused by staged contacting with the acid condensate. Nitric oxide reacts with nitric acid per equation 14 to restore equilibrium forming the dioxide and water.

The design of nitric absorption columns is a specialized process requiring the individual tailoring of each tray for its cooling requirements and the gas volumes needed for oxidation of the nitric oxide. A good summary of absorber design aspects is available (52). Modern processes use columns having bubble cap or sieve trays. Capacities of around 1800 t/d HNO_3 have been achieved in a single column. Columns are up to 6 m in diameter, 80 m high, and contain as many as 30–50 trays. Discounting NO_x abatement requirements, the economic optimum for absorber efficiency results in tail gas NO_x concentrations of ca 1500–2500 ppmv. For abatement reasons single absorption columns reach tail gas NO_x compositions of ca 200 ppmv. The need to make processes more efficient and to meet environmental regulations has led to new advances in understanding absorption chemistry. One such development is the High Efficiency Absorption (HEA) technology developed by Rhône Poulenc. The specifics of this technology are not well known, but it can reduce the size of an absorber column by up to 35% (53). HEA is reported (54) to be applicable in regions in which the gas-phase concentration of NO_x is low (<8000 ppm) and the rate-limiting step for nitric acid formation is typically the gas-phase oxidation of NO. By directly oxidizing nitrous acid in the liquid phase to nitric acid, the usual decomposition of nitrous acid into nitric oxide and acid is circumvented and the large oxidation volumes needed to regenerate NO_2 from NO are greatly reduced.

NO_x Abatement. Source performance standards for nitric acid plants in the United States were introduced by the U.S. EPA in 1971 (55). These imposed a discharge limit of 1.5 kg of NO_x as equivalent nitrogen dioxide per 1000 kg of contained nitric acid, which corresponds to about 200–230 ppmv of nitrogen oxides in vented tail gas, whereas concentrations after absorption may contain as much as 2000–3000 ppmv of nitrogen oxides. Regulations and a review of abatement methods used in the EC are available (56). Various methods have been used to reduce tail gas NO_x concentrations to an acceptable level for discharge to the atmosphere (57). The most commonly employed methods are extended absorption, selective catalytic reduction (SCR), and nonselective catalytic reduction (NSCR).

Extended absorption uses an additional column to oxidize and react the nitrogen oxides with water to form acid. Bubble cap trays hold their liquid seal on shutdown and are therefore preferred for minimizing NO_x abatement problems during start-up and shutdown. Low partial pressures of nitrogen oxides lead to low rates of oxidation and a need for large amounts of gas-phase holdup. Extended absorption requires relatively few trays but large oxidation volumes, and often employs refrigeration to promote the oxidation process and minimize column size. This method of abatement is most effective for high pressure absorption in which abatement to less than 200 ppmv NO_x can be achieved in a single column. In general, medium pressure plants use two absorption columns to achieve concentrations of ca 500 ppmv NO_x. Cold tail gases are reheated by heat exchange with hot process gas to increase power recovery in the expander.

Selective catalytic abatement uses a catalyst and ammonia fuel to selectively reduce nitrogen oxides in preference to combustion with the much higher levels of oxygen in the tail gas. This method can operate over a wide range of pressures but requires temperatures to be 210–410°C. For effective abatement, a slight excess of ammonia is used, leaving 5–20 ppmv in the treated tail gas. Higher concentrations of ammonia present a potential safety hazard that has to be avoided by the use of good process controls. Ammonia at low temperatures can form ammonium nitrate and nitrite, which might accumulate in downstream equipment and pose an explosion hazard upon being heated. Base metal oxides (titanium and vanadium) are commonly used as the catalysts, although platinum, palladium, or zeolites may also be used. The catalysts are usually shaped as honeycombs or flat parallel plates. The treated tail gases are also reheated for improved expander energy recovery.

Nonselective abatement uses a catalyst and fuel (gaseous hydrocarbon such as propane or natural gas) to reduce nitrogen oxides to nitrogen and, in the process, combust any remaining free oxygen in the tail gas. This consumes significantly more fuel than a selective reduction system, but the energy thus generated is mostly retrieved as power in the expander. Platinum, palladium, and rhodium, either in the form of pellets or as a honeycomb, are typically used as catalysts in these systems. The minimum temperature for inlet tail gas depends on the fuel in use and its ignition temperature. Hydrogen, which has the lowest ignition temperature, requires about 150–200°C. A large temperature rise due to combustion, about 130°C for every volume percent of oxygen, places a limit on total oxygen content for tail gas exiting the absorber. Free oxygen tends to be consumed preferentially and fuel must be fed in slight stoichiometric excess to the oxygen. Leftover hydrocarbons are discharged to the atmosphere, including small amounts of carbon monoxide and hydrogen cyanide. Relatively few nitric acid plants use this method of abatement, which was one of the first available when source performance standards were introduced in 1971.

In an economic comparison of these three common abatement systems, a 1991 EPA study (58) indicates extended absorption to be the most cost-effective method for NO_x removal, with selective reduction only matching its performance for small-capacity plants of about 200–250 t/d. Nonselective abatement systems were indicated to be the least cost-effective method of abatement. The results of any comparison depend on the cost of capital versus variable operating costs. A low capital cost for SCR is offset by the ammonia required to remove the NO_x. Higher tail gas NO_x concentrations make this method less attractive. The investment required for extended abatement is partially recovered by increased yield of nitric acid product. Other methods of abatement have been proposed but for various reasons have not found general commercial acceptance. They include scrubbing (eg, with ammonia, urea, and caustic chemicals) as well as molecular sieve adsorption (57,59). One chemical absorption method (60) uses weak acid (25–30 wt%) to remove nitrogen oxides from the tail gas to form nitrous acid, HNO_2. Steam stripping regenerates the clean acid for recycle. The removed NO_x is compressed and fed to the plant's main absorption column. Environmental regulations may reasonably be expected to become stricter in the future. This could lead to plant designs using a combination of NO_x abatement methods, eg, extended absorption with SCR.

4.2. Direct Strong Nitric Processes. Direct strong nitric (DSN) processes use many of the production steps described for weak acid production. Ammonia and air are combusted over platinum and the process gas stream is cooled to the point at which weak acid condensate is formed. Tail gases are reheated by hot process gas and provide energy recovery in a gas expander. DSN processes differ from weak acid plants in the additional processing steps required to achieve superazeotropic strengths of nitric acid. The combustion of ammonia and cooling of process gas are often carried out at atmospheric pressure. Excess water can then be directly removed as process condensate containing only 1–3 wt% nitric acid. Processes using medium or high pressure ammonia combustion have a 45–50 wt% nitric condensate, requiring either a rectification step to remove excess water from the plant or the co-production of weak acid. The dehydrated process gases are usually compressed, mixed with air and nitrogen peroxide obtained from the bleaching of product acid, and then cooled to promote the full oxidation of nitric oxide to nitrogen peroxide. The gases are sometimes contacted with weak to azeotropic strength acid so that the nitric oxide can react with nitric acid per equation 14 to restore chemical equilibrium by forming the dioxide and water.

The key to producing strong acid is obtaining high partial pressures of nitrogen peroxide. In older processes such as HOKO (61), nitrogen peroxide is absorbed in chilled 98 wt% acid, distilled off, and condensed. The peroxide is mixed with oxygen and weak nitric acid in an autoclave at 5 MPa to produce strong acid. Processes such as SABAR generate strong acid by azeotropic rectification (62). Nitrogen peroxide in the process gas is chemically absorbed into azeotropic or greater strength acid. Air stripping and rectification of the resulting acid stream produces strong acid of 98–99 wt% strength. Various process schemes (63-65) fall between these two examples, some of which co-produce both strong and weak acid. Flow schemes for many of the DSN processes, as well as nitric concentration (NAC) plants, are available (66,67).

DSN plants have found little application in the United States, but several have been built in Europe. Some older-style HOKO processes, although more capital-intensive and less economical than later DSN processes, continue to operate in the 1990s.

4.3. Nitric Acid Concentration. Nitric acid has a maximum boiling azeotrope at 69 wt%, so it is not possible to obtain greater concentrations by the simple distillation of the weak acid. Nitric acid concentration (NAC) processes use extractive distillation to concentrate weak acid up to 99 wt%. A dehydrating agent, such as sulfuric acid or magnesium nitrate, is used to enhance the volatility of HNO_3 so that distillation methods can surpass the azeotropic concentration of nitric acid. Weak acid and dehydrating agent are fed to a distillation column. Water removed from the acid dilutes the dehydrating agent, which is removed as a bottom stream and later concentrated for reuse in the process. Superazeotropic acid vapors pass to the bottom of a rectification section in which the acid is concentrated up to 99 wt%. The strong nitric vapors are condensed overhead and a portion of the acid is returned to the column as reflux.

One of the most commonly practiced NAC technologies uses sulfuric acid of 82–96 wt% as the dehydrating agent (66,67). The spent dilute sulfuric acid, typically ca 65–70 wt%, often requires multiple vacuum-stage evaporation for reconcentration and use in the NAC process. Sulfuric acid is sufficiently strong dehydrating agent that at high feed concentrations of ca 93–96 wt% H_2SO_4 the rectification section can be eliminated. The resulting higher operating temperatures can lead to increased decomposition of the nitric acid product. One licensor reduces sulfuric acid use by preconcentrating the weak nitric acid (eg, to ca 67 wt%) by simple distillation without a dehydrating agent. Some processes use live steam injected into the base of the column to remove any residual nitric acid from the spent sulfuric acid.

Magnesium nitrate has become popular as a dehydrating agent in commercial NAC processes (17,68). At high concentrations, magnesium nitrate solutions are quite viscous and have high melting points, so feed concentration is typically restricted to around 72 wt%. Recovered nitrate, ca 68 wt%, is concentrated for reuse in a single-stage, steam-heated vacuum flash drum. The ease of concentrating aqueous magnesium nitrate solution and the use of less expensive materials of construction make magnesium nitrate NAC technology less capital intensive than the sulfuric acid method. Magnesium nitrate at 72 wt% is a less effective dehydrating agent than sulfuric acid, which has a lower melting point and viscosity and so can be used in higher concentrations. Therefore, processes using magnesium nitrate use rectification to increase the concentration of nitric acid up to 99 wt%.

Because of restrictions in equipment size, magnesium nitrate processes were initially limited to small plants. Improvements in the materials of construction have led to increased capacities and a lower capital cost. Sulfuric acid processes are usually preferred when reconcentration of the sulfuric acid is not required, ie, when the dilute sulfuric can be used to make another product.

4.4. Other Processes.

Most other routes for making nitric acid involve the formation of nitrogen oxide directly from the air using various energy sources, such as electric arc furnaces and shock waves (4). Air heated to extremely high temperatures forms nitric oxide (ca 8 vol % at 4000 K), which must then be rapidly quenched to avoid decomposition of the nitric oxide on cooling. In Norway an electric arc process found successful application until ca 1930. The Wisconsin process, developed during World War II, heated air to >2000°C by contact with a bed of fuel-heated magnesia pebbles. Rapid quenching by contact with a second cold bed yielded 1–2 wt% nitric oxide. Later, a method using three beds of silica gel in series was developed to recover the nitric oxide. The first bed dehumidified the gas, while the second catalytically oxidized the nitric oxide to dioxide and the third adsorbed the nitrogen dioxide, which then could be stripped in a highly concentrated form (69,70). A small plant was built in 1953 for the U.S. government to demonstrate the technology. The plant operated successfully for 18 months, but the process did not prove its economic viability (71).

Alternative approaches to nitric oxide formation include irradiation of air in a nuclear reactors (72) and the oxidation of ammonia to nitric oxide in a fuel cell generating energy (73). Both methods indicate some potential for commercial application but require further study and development.

The Kleiner method is a new chemical process for the manufacture of nitrogen dioxide, nitrogen oxide, and nitric acid. The major chemical reactions take place at the surface of the water medium where the nitrogen dioxide and nitrogen oxide are produced. Nitric acid remains in a liquid state in the deep layer (74).

5. Materials of Construction

Early nitric acid plants were severely restricted in design by the available materials of construction. Until high chromium content iron was developed in the 1920s, commonly used construction materials were acid brick, earthenware, and Glass (qv). As better materials of construction came along, nitric acid process design could be improved. Higher operating pressures resulted in lower plant capital costs. The following is an overview of the materials of construction used in modern processes. More detailed information concerning the application and corrosion resistance of specific materials can be found (4,77).

5.1. Weak Acid.

Stainless steels (SS) have excellent corrosion resistance to weak nitric acid and are the primary materials of construction for a weak acid process. Low carbon stainless steels are preferred because of their resistance to corrosion at weld points. However, higher grade materials of construction are required for certain sections of the weak acid process. These are limited to high temperature areas around the gauze (ca 900°C) and to places in which contact with hot liquid nitric acid is likely to be experienced (the cooler condenser and tail gas preheater).

Catalyst baskets and gauze supports must be resistant to oxidation, nitriding, and distortion from high temperatures. Typical materials of construction are high strength alloys made of iron–nickel–chromium and nickel–chromium. Alloys made of nickel–chromium–tungsten–molybdenum are also finding application in such service.

High chromium (20–27%) SS provides better corrosion resistance to nitric acid at elevated temperatures than low carbon SS. It has been used to replace low carbon steel in cooler condenser and tail gas preheater service, providing sufficiently extended life to justify its additional cost.

Zirconium has seen increasing use with nitric acid. The excellent corrosion resistance of zirconium is a result of the formation of a strongly adhering inert oxide film. The film is diffusion-bonded to the metal and has the ability to repair itself should it be damaged. Zirconium rivals tantalum in its corrosion resistance to nitric acid (76), having low corrosion rates at all concentrations up to the boiling point. Its resistance extends up to 230°C and 65 wt%. It is susceptible to stress corrosion cracking, which can be prevented by avoiding high, sustained tensile stresses (78). Zirconium is used in nitric acid service for cooler condensers, tail gas preheaters, and reboilers.

Duplex stainless steels (ca 4% nickel, 23% chrome) have been identified as having potential application to nitric acid service (75). Because they have a lower nickel and higher chromium content than typical austenitic steels, they provide the ductability of austenitic SS and the stress–corrosion cracking resistance of ferritic SS. The higher strength and corrosion resistance of duplex steel offer potential cost advantages as a material of construction for absorption columns (see CORROSION AND CORROSION CONTROL).

5.2. Strong Nitric Acid. Materials of construction commonly used in the production of strong acid (98–99 wt%) are aluminum, tantalum, borosilicate glass, glass-lined steel, high silica cast iron, and high silica stainless steels. Stainless steel is often used for the storage and shipment of up to 95 wt% nitric acid. At higher concentrations, corrosion rates for stainless steel become excessive and aluminum is the commonly accepted material of construction. The use of aluminum alloys is restricted to high acid concentrations of 80–100 wt% and moderate temperatures of less than 38°C. High silica stainless steels (ca 4–7 wt% silicon) have demonstrated good corrosion resistance to concentrated nitric acid. However, corrosion resistance does not significantly extend to weaker strengths of acid. These steels are commonly used in direct strong acid processes and apparently played a key role in making such processes successful. High silica cast iron also displays good corrosion resistance to strong acid, but is more commonly used in columns and pump casings.

Titanium is resistant to nitric acid from 65 to 90 wt% and dilute acid below 10 wt%. It is subject to stress–corrosion cracking for concentrations above 90 wt% and, because of the potential for a pyrophoric reaction, is not used in red fuming acid service. Tantalum exhibits good corrosion resistance to nitric acid over a wide range of concentrations and temperatures. It is expensive and typically not used in conditions where other materials provide acceptable service.

Tantalum is most commonly used in applications where the nitric acid is close to or above its normal boiling point.

Glass offers good resistance to strong acid at high temperatures. However, it is subject to thermal shock and a gradual loss in integrity as materials such as iron and silica are leached out into the acid. Nonmetallic materials such as PTFE, PVDC, PVDF, and furan can be used for nitric acid to a limited degree, but are mainly restricted to weak acid service at ambient to moderate temperatures.

6. Economic Aspects

World nitric acid production in 2002 was estimated at 46×10^6 t with an fob market value in excess of $\$10 \times 10^9$. The merchant portion is only about 10% of the total. The world's average operating rate fluctuates around 80% level (79).

World demand is largely dependent on solid ammonium nitrate fertilizers and nitrogen fertilizers that incorporate ammonium nitrate. There is a trend towards the use of urea that has resulted in a negative growth in use of ammonium nitrate solid fertilizers.

Western Europe, the United States, the former USSR, and Eastern Europe accounted for 74% world capacity, 79% production, and 80% consumption. World production and consumption declined by about 12% between 1990 and 2002, but is expected to increase marginally through 2008. The declines occurred in the dominant countries, but were partially counteracted by increases in other regions, particularly Africa. Only Western Europe is expected to record a marginal decline. All other countries are expected to show some growth (79).

United States producers of nitric acid and their producers are listed in Table 3 (80).

7. Specifications and Standards

7.1. Shipment.

The Department of Transportation (DOT) classifies nitric acid as a hazardous material requiring proper packaging, labeling, and shipping documentation for transportation. The DOT defines three categories of nitric acid: (*1*) nonfuming, more than 70 wt% acid; (*2*) nonfuming, less than 70 wt% acid; and (*3*) red fuming nitric acid. All are in Hazards Class 8, meaning corrosive material, and must be labeled "corrosive." Red fuming nitric acid must also be labeled "oxidizer" and "poison." Each category of nitric acid has its own packaging authorization number (ie, packaging requirements) for both bulk and nonbulk shipping. Depending on these packaging requirements, nitric acid may be shipped in either stainless steel or aluminum. Bulk nitric acid can be shipped by railcar, tank truck, or portable tank. Nonbulk packaging includes drums. For other than red fuming acid, a variety of smaller containers are permitted, all of which require various forms of individual packaging, depending on acid strength and mode of transportation. Packages are mostly glass or earthenware containers ranging in size from 0.5 to 2.5 l. Transportation on passenger aircraft or railcar is forbidden for all categories of nitric acid. Red fuming acid is forbidden on cargo aircraft. The full DOT requirements for packaging and shipping nitric acid are available (81).

7.2. Standards. The ACS defines two grades of reagent acid (82): nitric acid, having a concentration of 69.0–71.0 wt% HNO_3, and nitric acid, 90%, having a concentration of $\geq$90 wt% HNO_3. Both have maximum allowable levels of chlorides, sulfates, arsenic, heavy metals, iron, and residue after burning. Impurity limits defined for the 90% grade are the least stringent. Nitric acid must be colorless and free from suspended matter, whereas the 90% grade has a maximum content for dissolved oxides as N_2O_3. The USP (83) has definitions that refer to those of the ACS.

Commercially, nitric acid concentrations are graded in terms of degrees Baumé as follows:

Degrees Baumé	Approximate wt % HNO_3
36	52.3
38	56.5
40	61.4
42	67.2

8. Analytical and Test Methods

8.1. Qualitative Analysis. Nitric acid may be detected by the classical brown-ring test, the copper-turnings test, the reduction of nitrate to ammonia by active metal or alloy, or the nitrogen precipitation test. Nitrous acid or nitrites interfere with most of these tests, but such interference may be eliminated by acidifying with sulfuric acid, adding ammonium sulfate crystals, and evaporating to a low volume.

In the brown-ring test, concentrated sulfuric acid is carefully poured down the side of an inclined test tube to form a separate layer beneath the solution to be tested. After the two layers have been cooled without mixing, a few drops of a ferrous sulfate solution are placed inside the inclined tube and drained down to the interface. The appearance within a few minutes of a brown layer of ferronitrosulfate, $(Fe(NO))SO_4$, at the junction of the two liquids shows the presence of nitrates. Nitric acid or nitrates may be detected after the removal of nitrous acid by warming a mixture of the material to be tested, a 1:1 solution of sulfuric acid, and copper turnings in a test tube. The evolution of brown fumes indicates the presence of nitrates. Nitrates are easily reduced by active metals or alloys in alkaline solution to give ammonia. Suitable reducing agents are aluminum, zinc, or Devarda's alloy (50 wt% Cu, 45 wt% Al, 5 wt% Zn).

Nitric acid may be precipitated by nitron [2218-94-2] (4,5-dihydro-1,4-diphenyl-3,5-phenylimino-1,2,4-triazole). The yellow precipitate may be seen at dilutions as low as 1:60,000 at 25°C or 1:80,000 at 0°C. To prevent nitrous acid from interfering with the test results, it may be removed by treating the solution with hydrazine sulfate, sodium azide, or sulfamic acid.

8.2. Quantitative Analysis.

The total acidity of nitric acid solution may be determined by conventional titration using phenolphthalein as the indicator.

Other Acidic Impurities.

Sulfuric Acid. The sample is evaporated to dryness on a steam bath. The residue is removed with water, and evaporation is repeated until the sample is free from nitric acid fumes. The residue is diluted with water and titrated with standardized sodium hydroxide solution using phenolphthalein as an indicator.

Hydrochloric acid. is determined gravimetrically as silver chloride.

Nitrous Acid. Lower oxides of nitrogen and nitrous acid [7782-77-6] generally are determined and reported as NO_2. In the absence of organic matter or other reducing agents, the determination may be made by titrating with potassium permanganate solution. A sharp end point is achieved by rapidly adding the permanganate solution to the solution containing the oxide of nitrogen or nitrous acid. If the addition of permanganate solution is low, some oxidation of the sample by dissolved air occurs resulting from the dilution of the solution with water.

Other Methods. Ion chromatography using conductance detection can be used to measure low ($<1\%$) levels of nitrite, chloride, sulfate, and other ions in nitric acid. Techniques for ion chromatographic analysis are available (84).

Ferrous Sulfate Titration. For determination of nitric acid in mixed acid or for nitrates that are free from interferences, ferrous sulfate titration, the nitrometer method, and Devarda's method give excellent results. The determination of nitric acid and nitrates in mixed acid is based on the oxidation of ferrous sulfate [7720-78-7] by nitric acid and may be subject to interference by other materials that reduce nitric acid or oxidize ferrous sulfate. Small amounts of sodium chloride, potassium bromide, or potassium iodide may be tolerated without serious interference, as can nitrous acid up to 50% of the total amount of nitric acid present. Strong oxidizing agents, eg, chlorates, iodates, and bromates, interfere by oxidizing the standardized ferrous sulfate.

Possible interferences and variation of results from modified techniques can be avoided by titrating the sample in exactly the same way and by employing approximately the same amounts of materials as in the initial standardization of the ferrous sulfate against a known quantity of nitric acid. The ferrous sulfate solution is added in a thin stream until the initially yellowish solution turns brown. The titration is complete when the faint brownish-tinged end point is reached.

Nitrometer Method. The nitrometer method also is used to determine nitric acid or nitrates in mixed acid or oleum. It involves the measurement of the volume of NO gas that is liberated when mercury is oxidized by nitric acid. The method is based on the following reaction:

$$2HNO_3 + 3\ H_2SO_4 + 3\ Hg \longrightarrow 3\ HgSO_4 + 4\ H_2O + 2\ NO \qquad (15)$$

Devarda's Method. Nitrogen in nitrates or nitric acid also may be determined by the Kjeldahl method or by Devarda's method. The latter is both convenient and accurate when no organic nitrogen is present. The nitrate is reduced by Devarda's alloy to ammonia in an alkaline solution. The ammonia is distilled and titrated with standard acid.

9. Health and Safety Factors

Nitric acid and the oxides of nitrogen found in its fumes are highly toxic and capable of causing severe injury and death. It is corrosive and can destroy human tissue. Nitric acid is regulated by OSHA, which lists it as a Process Safety Hazardous Chemical and Air Contaminant. Under SARAH, the EPA lists it as an Extremely Hazardous Substance and Toxic Chemical. Per OSHA and A CGTH, the 1991 permissible exposure limits for nitric acid are 2 ppm (5 mg/m^3) for an 8-h time-weighted average and 4 ppm (10 mg/m^3) for a 15-min short-term exposure (19). Exposure limits may vary according to local and national regulations. Inhalation symptoms may take several hours to appear. They include irritation of the throat and nose, coughing, chest pain, difficulty in breathing, giddiness, nausea, ulceration of the nasal mucous membranes, pulmonary edema, and chemical pneumonia. The symptoms resulting from skin contact vary from moderate irritation to severe burn, depending on contact time and strength of the nitric acid. Signs of contact may include a yellow discoloration of the skin; severe burns may penetrate deeply causing ulceration and the scarring of tissue.

First aid practices for the treatment of exposure to nitric acid should be obtained from a current version of the Material Safety Data Sheet or other appropriate safety literature. Acid in contact with the skin must be removed immediately by washing with large amounts of water for a period of at least 15 min. A 5% solution of triethanolamine should be applied to affected areas of the skin. Continuous flushing with large quantities of water is required for acid burns to the eye; the eyelids should be gently lifted to ensure adequate washing. Medical attention should be sought immediately. For cases of ingestion, a poison control center should be contacted for advice. A conscious and alert victim who is not convulsing should drink several glasses of water for dilution and follow with lime milk or milk of magnesia. Vomiting should not be induced, nor should attempts be made to neutralize the acid with sodium bicarbonate. If exposure occurs by inhalation, the person should be moved to fresh air and given support in breathing as needed. The effects of inhalation can be fatal and may be delayed for several hours. It is important to consult a physician immediately after the administration of first aid. Additional health and safety information is available (19,20,85).

10. Uses

The largest use of nitric acid (ca 74% of total U.S. production) is for the manufacture of ammonium nitrate. About 75% of ammonium nitrate [6484-52-2] is used in fertilizers (qv); the remainder is used for chemicals, explosives, and miscellaneous other uses. Partly because of the increased popularity of urea, the use of ammonium nitrate as a fertilizer has declined. This has been offset to some extent by the growth in the use of ammonium nitrate for explosives and other chemical uses. Overall, the production of ammonium nitrate in the United States is expected to remain flat for several years.

Other uses include preparation of adipic acid, 10%; preparation of toluene diisocyanate, 7%; preparation of nitrobenzene, 6%; metal nitrates, 1%; and other, including metal treatments, 2% (80). Other also includes for preparation of nitrochlorobenzene, cellulose nitrate, introparaffins, nonmilitary, non-ammonium nitrate explosives, uranium processing, and miscellaneous fertilizers.

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Table 1. **Physical Properties of Nitric Acid Solutions at 20°C**

HNO_3, wt%	Bp[a] at 101 kPa,[b] °C	Partial pressures,[c] kPa[b]		Density,[d] g/mL	Specific heat,[e] J/(g·K)[f]	Viscosity,[e] mPa·s(= cP)	Thermal conductivity,[e] W/(m·K)
		HNO_3	H_2O				
0.0	100.0		2.27	0.9982	4.19	1.0	0.60
10.0	102.2		2.12	1.0543	3.73	1.1	0.57
20.0	104.4		1.91	1.1150	3.39	1.2	0.53
30.0	107.3		1.61	1.1800	3.18	1.4	0.50
40.0	110.8	0.01	1.28	1.2463	3.01	1.6	0.47
50.0	114.7	0.04	0.94	1.3100	2.85	1.9	0.43
60.0	118.2	0.12	0.61	1.3667	2.64	2.0	0.40
70.0	119.3	0.37	0.33	1.4134	2.43	2.0	0.37
80.0	112.1	1.22	0.12	1.4521	2.22	1.9	0.34
90.0	96.0	3.57	0.02	1.4826	1.97	1.4	0.31
100.0	83.4	6.20	0	1.5129	1.76	0.9	0.28

[a] Ref. 5.

[b] To convert kPa to mm Hg, multiply by 7.5.

[c] Refs. 8 and 9.

[d] Ref. 12.

[e] Ref. 13.

[f] To convert J to cal, divide by 4.184.

Table 2. **Thermodynamic Properties of Nitric Acid and Its Hydrates**

Property[a]	HNO_3	$HNO_3 \cdot H_2O$	$HNO_3 \cdot H_2O$
nitric acid, wt%	100.0	77.77	53.83
freezing point, °C[b]	−41.59	−37.62	−18.47
heat of fusion, kJ/mol[b]	10.48	17.5	29.12
heat of formation at 25°C, kJ/mol kJ/mol[c]	−174.10	−473.46	−1056.04
free energy of formation at 25°C, kJ/mol[c]	−80.71	−328.77	−811.89
entropy at 25°C, J/(mol·K)[c]	155.60	216.90	346.98
heat of vaporization at 25°C, kJ/mol[c]	39.04		

[a] To convert kJ to kcal, divide by 4.184.

[b] Ref. 6.

[c] Ref. 18.

Table 3. **U.S. Producers of Nitric Acid and their Capacities**

Producer	Capacity, × 10^3 t, 100% HNO_3 basis
Agrium US, Beatrice, Neb.; Kennewick, Wash.; West Sacramento, Calif.	500
Air Products, Pasadena, Tex.	310
ANGUS Chemical, Sterlington, La.	65
Apache Nitrogen Products, Benson, Ariz.	140
Vicksburg Chemical, Vicksburg, Miss.	75
CF Industries, Donaldsonville, La.	680
Coastal Chem, Battle Mountain, Nev.; Cheyenne, Wyo. and St. Helens, Ore.	370
Coffeyville Resources, Coffeyville, Kan.	170
DuPont, Beaumont, Tex. Orange, Tex.; Victoria, Tex.	565
Dyno Nobel, Donora, Pa.; Louisiana, Mo.	385
El Dorado Nitrogen, El Dorado, Ark. Baytown, Tex.; Cherokee, Ala.	1,140
First Chemical, Pascagoula, Miss.	75
Geneva Nitrogen, Geneva, Ut.	80
Hercules Incorporated, Parlin, N.J.	80
J.R. Simplot, Helm, Calif. Pocatello, Idaho	100
Koch Nitrogen, Beatrice, Neb.; Dodge City, Kan.; Enid, Okla.; and Fort Dodge, Iowa	330
LSB Industries, Cherokee, Ala.; Crystal City, Mo.	450
Lyondell Chemical, Lake Charles, La.	170
Mississippi Chemical, Yazoo City, Miss.	955
Mobay, Baytown, Tex.; New Martinsville, W. Va.	135
Nitrochem, Newell, Pa.	75
Orica, Joplin, Mo.; Seneca, Ill.	320
PCS Nitrogen Fertilizer, Augusta, Ga. Geismar, La.	1,405
Royster-Clark, Cincinnati, Ohio; East Dubuque, Ill.	195
Rubicon, Geismar, La.	110
Solutia, Pensacola, Fla.	365
Terra International, Port Neal, Iowa Verdigris, Okla.; Woodward, Okla.	945
TradeMark Nitrogen, Tampa, Fla.	35
Vicksburg Chemical, Vicksburg, Miss.	75
Total	*10,225*

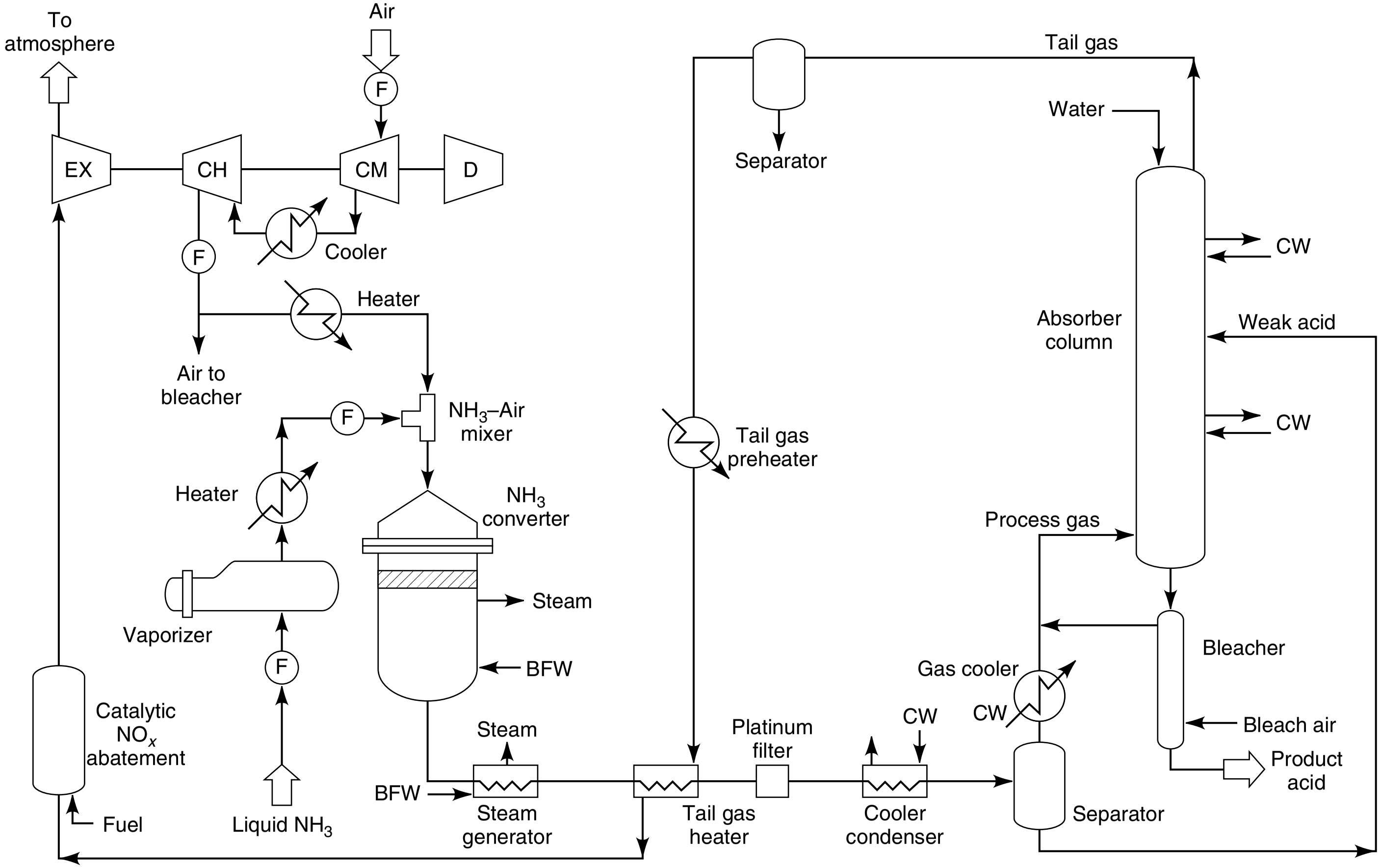

Fig. 1. Monopressure process using catalytic NO_x abatement, where BFW = boiler feed water, CH = high level compression, CM = medium level compression, CW = cooling water, and D = makeup driver, EX = expander, and F = filter.

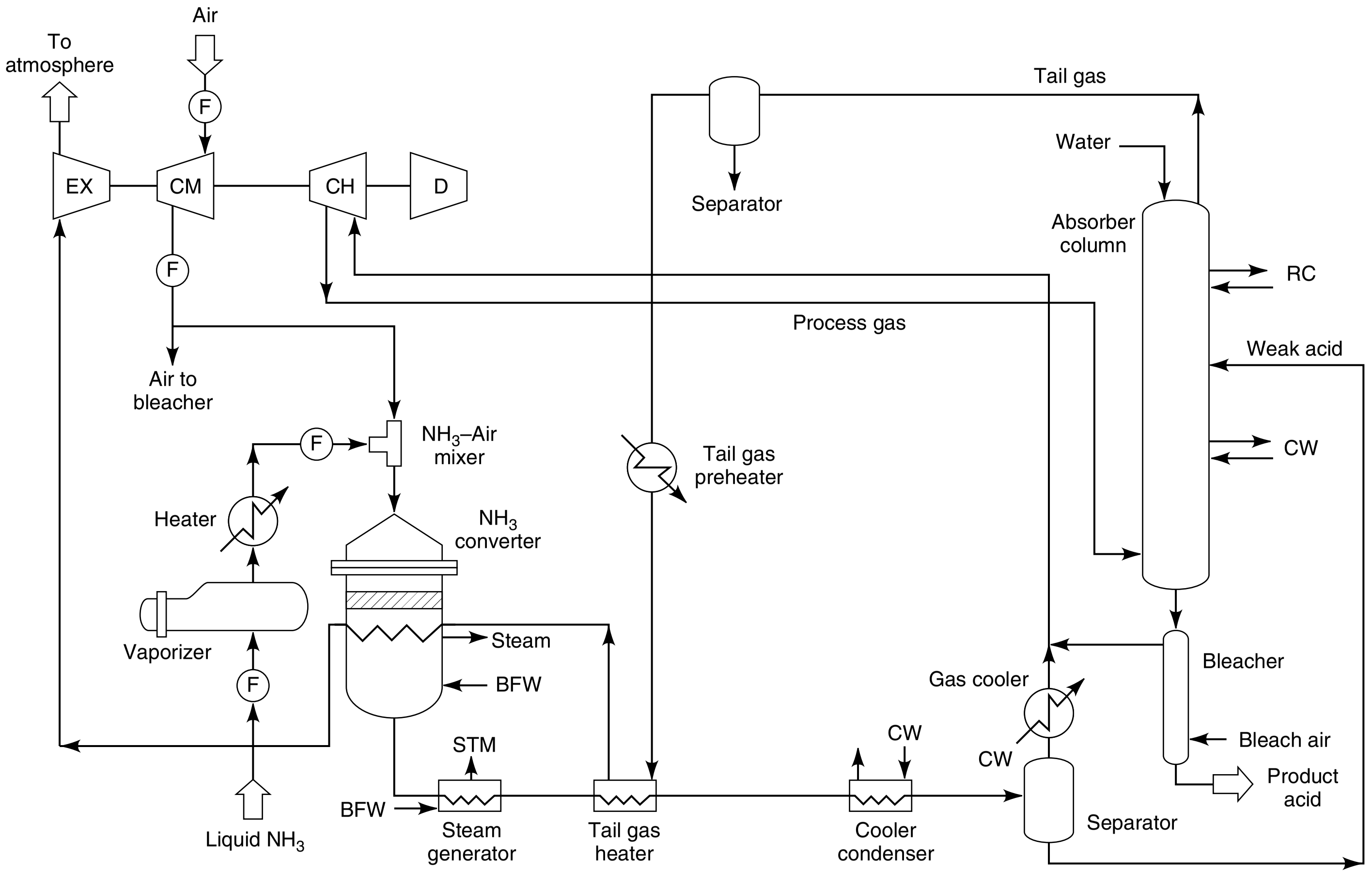

Fig. 2. Dual-pressure process using extended absorption for NO_x abatement. RC = refrigerated cooling; see Figure 1 for other definitions.