AMMONIA

1. Introduction

Most people associate the pungent smell of ammonia (NH_3) with window cleaners or smelling salts. However, the use of ammonia in these two products represents only a small fraction of the total global ammonia production, which was around 200 million metric tons in 2016.

The preparation of ammonium salts dates to the early Egyptians in the fourth century BC. Ammonia gas was first produced as a pure compound by Priestly in 1774.

In 1840, Justus von Liebig outlined the theoretical principles of plant nutrition and the role of fertilizers as essential plant nutrients. The second half of the century witnessed increasing use of fertilizers; however, nitrogen sources were limited. Ammonium sulfate (a by-product of coke ovens), Chilean saltpeter, Peruvian guano, crop rotations, and other natural nitrogen sources were the main nitrogen fertilizers during this time.

2. Physical Properties

Ammonia (NH_3) is a colorless gas at atmospheric temperature and has a pungent, penetrating odor. Ammonia can be liquefied at ambient temperatures under moderate pressures.

Ammonia boils at −33°C and freezes to a white crystalline mass at −77°C. When heated above its critical temperature of 134°C, ammonia exists only as a vapor regardless of the pressure. Between the melting and critical points, liquid ammonia exerts a vapor pressure, which increases with rising temperature.

3. Chemical Properties

The flammable limits of ammonia in air are 16–25% by volume; in oxygen, the range is 15–79%. Such mixtures can explode although ammonia–air mixtures are quite difficult to ignite. The ignition temperature is about 650°C.

Ammonia is readily absorbed in water to make ammonia liquor. Considerable heat is evolved during the dissolution of ammonia in water: approximately 2180 kJ (520 kcal) of heat is evolved upon the dissolution of 1 kg of ammonia gas.

Ammonia is an excellent solvent for salts and has an exceptional capacity to ionize electrolytes. The alkali metals and alkaline earth metals (except beryllium) are readily soluble in ammonia. Iodine, sulfur, and phosphorus dissolve in ammonia. In the presence of oxygen, copper is readily attacked by ammonia. Potassium, silver, and uranium are only slightly soluble. Both ammonium and beryllium chloride are very soluble, whereas most other metallic chlorides are slightly soluble or insoluble. Bromides are, in general, more soluble in ammonia than chlorides, and most of the iodides are soluble. Oxides, fluorides, hydroxides, sulfates, sulfites, and carbonates are insoluble. Nitrates (eg, ammonium nitrate) and urea are soluble in

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both anhydrous and aqueous ammonia, making the production of certain types of fertilizer nitrogen solutions possible. Many organic compounds, such as amines, nitro compounds, and aromatic sulfonic acids, also dissolve in liquid ammonia. Ammonia is superior to water in solvating organic compounds such as benzene, carbon tetrachloro iodide, and hexane.

4. History of Ammonia

In 1913, BASF (then Badische Anilin und Soda Fabrik) began operation of the world's first commercial ammonia plant in Oppau, Germany, 3 km north of the company's large Ludwigshafen site. The Oppau plant used what is now called the Haber-Bosch process to synthesize ammonia by a reaction of hydrogen and nitrogen over an iron-based catalyst. The initial plant capacity was 30 t/d of ammonia. Coal and coke were used to produce steam and coke oven gas, which was purified and compressed ahead of ammonia synthesis.

The engineering development of ammonia technology has been described as "Detonation of the Population Explosion," which through application of synthetic fertilizers for food production facilitated the growth in the number of human beings on Earth from about one billion in 1900 to about seven billion in 2000. It has been stated that a world without synthetic fertilizers would only sustain a world population of about four billion.

4.1. The Haber-Bosch Process.

Fritz Haber, an industrial chemist, and Carl Bosch, a chemical engineer, have been named as the world's most influential scientists of all time by readers of the UK Institute of Chemical Engineers' magazine *The Chemical Engineer* in March 2010. The German duo were responsible for devising the Haber-Bosch process, perhaps the most recognized chemical process in the world, to capture nitrogen from the air and convert it into ammonia for use in fertilizers. While Haber developed a high temperature, 450°C, high pressure, 300 bar, process to break the triple bonds of atmospheric nitrogen, Bosch was responsible for scaling up the process, finding cheaper ways of producing hydrogen, developing a new catalyst, and designing and building a reactor that could withstand both the temperature and pressure requirements of the reaction.

The Haber-Bosch process was certainly the key to accessing the large amount of fertilizer needed to boost crop output to fight hunger and has proved to be an enduring invention since that time. More than 180 million tonnes of nitrogen-containing fertilizers are now produced by this process annually, helping to feed more than 40% of the earth's population.

During 1898, Frank, Caro, and Tothe found that N_2 could be fixed by calcium carbide to form calcium cyanamide, which could then be hydrolyzed with water to form ammonia.

$$CaO + 3C \leftrightarrow CaC_2 + CO \tag{1}$$

$$CaC_2 + N_2 \leftrightarrow CaCN_2 + C \tag{2}$$

$$CaCN_2 + 3H_2O \leftrightarrow CaCO_3 + 2NH_3 \tag{3}$$

Following this discovery, many people started working on commercialization. The high electrical energy consumption of the cyanamide process led to work on processes with lower energy requirements. The most important toward the development of the modern ammonia industry was the work done by Fritz Haber. He first became interested in nitrogen fixation to produce ammonia and nitrogen oxides while visiting the Niagara Falls, New York, cyanamide-based ammonia plant in 1902. At that time, he was a chemistry professor at the Karlsruhe Engineering College, Germany. The Margulies brothers of Vienna contracted Haber to do research on the production of ammonia from the elements. One of his students, Gabriel van Oordt, worked with him to synthesize ammonia in the laboratory from N_2 and H_2. Walther Nernst, professor of physical chemistry at the University of Berlin, competed with Haber to develop a process to make ammonia from N_2 and H_2. In 1901, Le Chatelier in France developed a high pressure synthesis route to ammonia. He received a patent for his work. Unfortunately, his work eventually led to an explosion that ended his work on the ammonia process.

Both Haber and Nernst adopted the high pressure route to produce ammonia over a catalyst. Haber, working with research assistant, Robert Le Rossignol, and a mechanic named Kirchenbauer—whose work was invaluable in the difficult task of designing and building the equipment required to withstand high temperature and pressure—finally developed a process for producing commercial quantities of ammonia. In 1906, Haber was able to produce a 6% ammonia concentration in a reactor loaded with an osmium catalyst. This is generally recognized as the turning point in the development of a practical process to produce ammonia in commercial quantities.

Haber also realized that the amount of ammonia formed in a single pass through a converter was far too low to be of commercial interest. To produce more ammonia from the makeup gas (MUG), he proposed a recycle system and received a patent for the concept. Haber's recycle idea changed the static conception of process engineering in favor of a more dynamic approach. For the first time, reaction kinetics was considered as well as the thermodynamics of the system. In addition to the chemical reaction equilibrium, Haber recognized that for the technical realization, reaction rate was a determining factor. Instead of simple yield in a once-through process, he concentrated on space time yield in a recycle system. BASF purchased Haber's patents and started development of a commercial process. Carl Bosch and Alwin Mittasch along with BASF chemists developed a promoted iron catalyst to produce ammonia in 1910.

The next problem, development of equipment, was an extremely difficult one. Ordinary steel did not last very long at the high temperature and pressure needed for production of ammonia across an iron catalyst. An early mild steel reactor only lasted 80 hours before failure due to decarbonization. Lining mild steel reactors with soft iron, which was not subject to decarbonization, and adding grooves between the two liners to release hydrogen that had diffused through the soft iron liner solved this problem. Other major challenges were the design of a heat exchanger to bring the inlet gas to reaction temperatures and cool the exit gas and a method to bring the catalyst to reaction temperature.

These problems were finally solved, and the first commercial ammonia plant based on the Haber-Bosch process was built by BASF at Oppau, Germany, which is located just 3 km north of BASF's Ludwigshafen plant complex. The plant went onstream on September 9, 1913, with a production capacity of 30 tons/day.

Another German plant was built at Leuna and started up during April 1917, producing 36,000 tons of ammonia per year. By the end of World War I, it had been expanded to produce 240,000 tons per year. A flow sheet of the first commercial ammonia plant is shown in Figure 1. The reactor contained an internal heat exchanger in addition to those shown in the figure.

While BASF was developing the Haber-Bosch process in Europe, interest was also growing in the United States to produce ammonia from the elements. Companies and organizations such as the General Chemical Company and the U.S. Department of Agriculture began research on ammonia synthesis from H_2 and N_2 with one objective to develop a method that would not infringe BASF patents. The de Jahn process was patented and developed and commercialized during the 1920s. Due to the urgent need for nitrates during World War I, the U.S. government contracted with General Chemical in 1917 to build a plant in Muscle Shoals, Alabama. The plant was constructed and completed in record time. The first steel was set on June 4, 1918, with the first ammonia produced on September 16, 1918. The plant was called U.S. Nitrate Plant No. 1. It ran until the end of the war.

During the 1920s, research and development was continued by the Atmospheric Nitrogen Corporation and the Fixed Nitrogen Research Laboratory in the United States. A better ammonia synthesis catalyst was developed, and a plant was built in Syracuse, New York, in 1921. This successful plant was followed by a very large installation built by Atmospheric Nitrogen in Hopewell, Virginia. The American process developed by the Fixed Nitrogen Research Laboratory was represented by a plant built in Niagara Falls by the Mathieson Alkali Works during 1922. The Niagara Ammonia Company built a plant in Niagara Falls, New York, in 1924 using European technology. This was followed by a DuPont plant in Belle, West Virginia, in 1926, and Shell Chemical at Long Beach, California, using the same technology. Various other plants were built with the ammonia industry thriving in the United States by 1930.

The American ammonia technology was also exported to Europe. The Nitrogen Engineering Corporation (NEC) was commissioned by Kuhlmann in France to build an ammonia plant near Paris in 1928. Thereafter, NEC built plants all

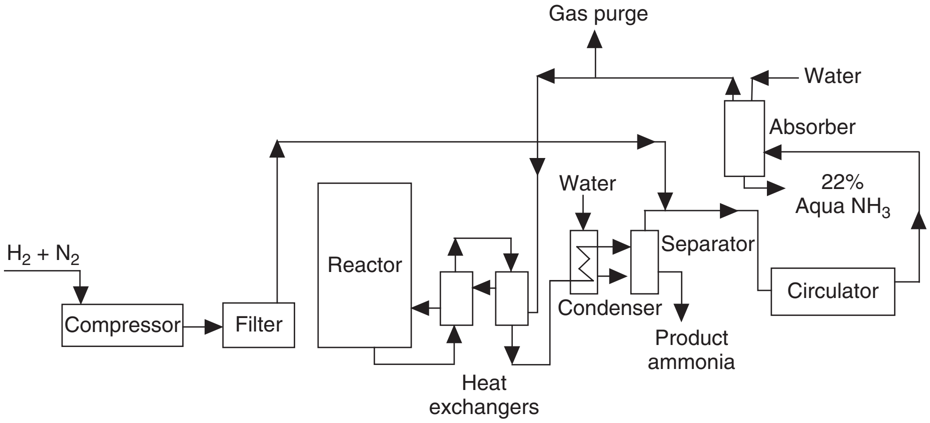


Fig. 1. First commercial plant built by BASF Corporation.

over the world, including Russia and the Far East. NEC was later taken over by the Chemical Construction Corporation (Chemico), who built many plants around the world up to the late 1970s.

BASF continued process development and plant expansions in Europe. Other organizations such as Casale, Fauser, Claude, and Mont Cenis also entered the field of design and construction of ammonia plants. Their plants differed from the Haber-Bosch process in various ways. For example, Casale built a plant in Terni, Italy, during the 1920s with a synthesis loop operating at almost 775 bar.

In the decades after 1930, further improvements were made in ammonia production technology. However, the synthesis section design remained essentially the same. Reactor capacity increased; however, few were built with capacities higher than 100 tons/day. Various "named" processes were used in new plants without much change from older ones.

Although the technology changed very little during this period, production capacity increased significantly driven by nitrogen products demand during World War II. In 1932, there were only ten ammonia plants in the United States. By the early 1940s, 10 more plants had been built in the United States with a total capacity more than twice that were in 1932.

World production was also increasing rapidly. By 1945, about 125 plants were reported to be in operation with a capacity of over 4.5 million tonnes of nitrogen per year. Production had increased fourfold, from about 900,000 tonnes of nitrogen in 1930 to 3,650,000 tonnes in 1950. This compares to a production of about 4,000 tonnes per year in 1914, 100,000 in 1920, and 400,000 in 1925.

The growing need for nitrogen fertilizers brought about a rapid expansion of ammonia production between 1950 and 1980. One of the developments that helped make this possible was the development of methanation catalyst to remove carbon oxides from synthesis gas.

Early ammonia plants utilized the copper liquor process for purification of the synthesis gas to the ammonia loop. The copper liquor process can be described as follows:

$$\mathrm{Cu(NH_3)_2A + CO + NH_4OH \leftrightarrow Cu(NH_3)_3A \cdot CO + H_2O} \tag{4}$$

$$\mathrm{2NH_4OH + CO_2 \leftrightarrow (NH_4)_2CO_3 + H_2O} \tag{5}$$

The scrubbing system contained both cupric and cuprous ammoniacal salts of acids such as formic, acetic, or carbonic plus an excess of ammonia. In operation, these salts form complexes with CO and hold it loosely. Absorption is carried out at high pressure, typically 120 bar, and low temperature, typically 0°C. The copper liquor process is no longer used in the ammonia industry due to the difficulty to control and environmental unfriendliness. The last plant in North America utilizing copper liquor for CO removal was shut down in the 1970s.

Girdler Corporation located in Louisville, Kentucky, built H_2 plants for industry starting in the 1930s. During World War II, Girdler began producing catalysts for these plants due to the lack of supply from other sources. When the companies started building ammonia plants during the 1940s, they recognized that they needed a process to remove carbon oxide to replace the copper liquor process. Work started in Girdler R&D lab where they developed and commercialized high nickel, high activity methanation catalyst with the first charge

Fig. 2. C13 spherical methanation catalyst.

produced in 1948. The first ammonia plant with a methanator instead of copper liquor was built by Girdler Engineering for Mississippi Chemical Corporation in Yazoo City, Mississippi, in 1949. Other plants soon followed. Girdler's G-65 series of methanation catalysts allowed more stable operation of the plant, leading to better onstream factors and better energy efficiency. Girdler produced high nickel methanation catalysts until the early 1960s. At that time, Catalysts and Chemicals Inc. (CCI), commonly known as CCI, introduced C13, a low nickel, high activity methanation catalyst in the form of spheres. Production as spheres allowed optimization of the pore structure of the particle, making lower nickel levels possible. This spherical methanation catalyst (Fig. 2) has been the preferred catalyst of the ammonia industry for more than 40 years. Many charges that have been onstream for 15–20 years continued to perform well after surviving severe upset conditions with no impact on performance.

Due to Girdler's success in producing catalysts for the plants that they engineered and built, the company started selling catalysts used to produce NH_3 in 1947. This was essentially the beginning of the commercial syngas catalyst business in North America.

5. Global Ammonia Production Rates

Ammonia production has developed into one of the most important industries in the world. Without the crop yield made possible by ammonia-based fertilizers and chemicals, the global population would be at least two to three billion less than it is today. Ammonia production has increased steadily since 1946 (Fig. 3), and it is estimated that the annual production of ammonia is worth more than $100 billion, with some plants producing more than 3000 metric tons per day (mtpd) of NH_3.

In 1983, on the 75th anniversary of the American Institute of Chemical Engineers (AIChE)'s Foundation, a blue-ribbon panel of distinguished chemical engineers named what they believed to be the world's ten greatest chemical

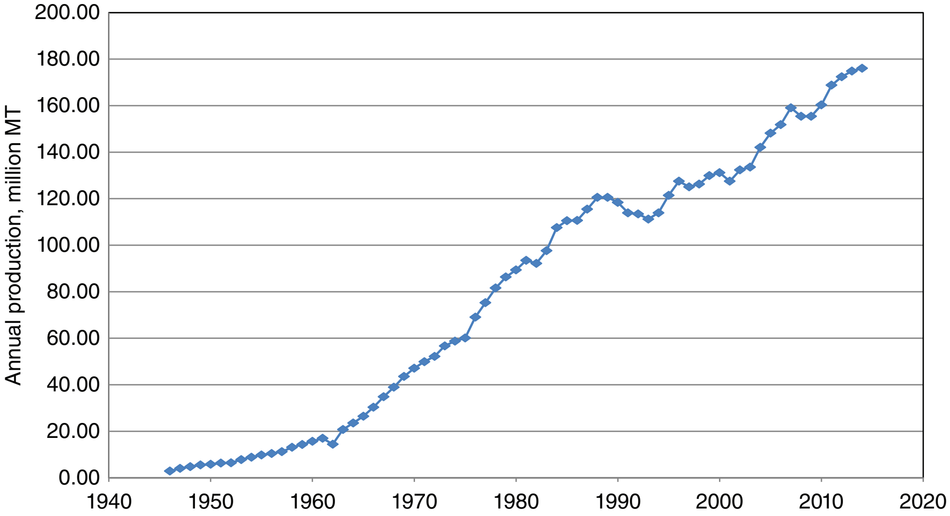


Fig. 3. Worldwide ammonia production has steadily increased from 1946 to 2014.

engineering achievements. Embracing feats such as wonder drugs, synthetic fibers, and atomic energy, the citation also included the breakthrough that permitted the production of large quantities of ammonia in compact, single-unit plants.

Within the past decades, chemical engineers have succeeded in creating processes that make vast amounts of ammonia at relatively at low costs. As recently as 80 years ago, the total annual production of synthesized ammonia was just over 300,000 tons. Thanks to chemical engineering breakthroughs, one modern ammonia plant can produce more than a million tons per year.

Approximately 88% of ammonia made annually is consumed in the manufacturing of fertilizer. Most of the remainder goes into the manufacture of other chemicals. China produced about 32.6% of the global production in 2014, while Russia, India, and the United States produced 8.1%, 7.6%, and 6.4%, respectively. While most of the global production of ammonia is based on steam reforming of natural gas, significant quantities are produced by coal gasification; most of the gasification plants are in China.

6. Modern Ammonia Manufacture

The growing need for fertilizer nitrogen brought about a rapid expansion of ammonia production between 1950 and 1980. Worldwide consumption of ammonia almost doubled between 1964 and 1968 from about 23 million to about 41 million tons. Today, the consumption of ammonia exceeds 200 million tons per year.

This tremendous increase in demand plus a better distribution system led to the building of larger, more energy-efficient plants. The new technology of these plants began in the early 1950s. Developments included the use of centrifugal compressors to replace the more cumbersome and expensive to operate reciprocating compressors and an increased recovery of process energy that was used directly to supply part of the plant energy requirement. There was a change in design philosophy. Until this time, an ammonia plant was regarded as an assembly of unrelated units such as gas preparation, gas purification, gas compression, and ammonia synthesis. New developments were based on an integral design that would tie the units together in the most effective and energy-efficient way.

A typical flow sheet for these new type plants is shown in Figures 4–6.

Although these flow sheets are typical, many minor departures are encountered. The heat recovery system is especially subject to variation with different

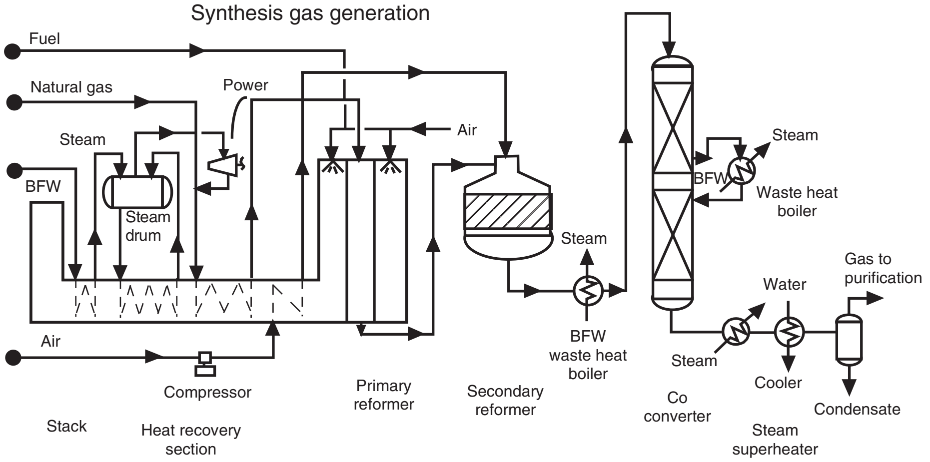


Fig. 4. Integrated ammonia process: synthesis gas generation.

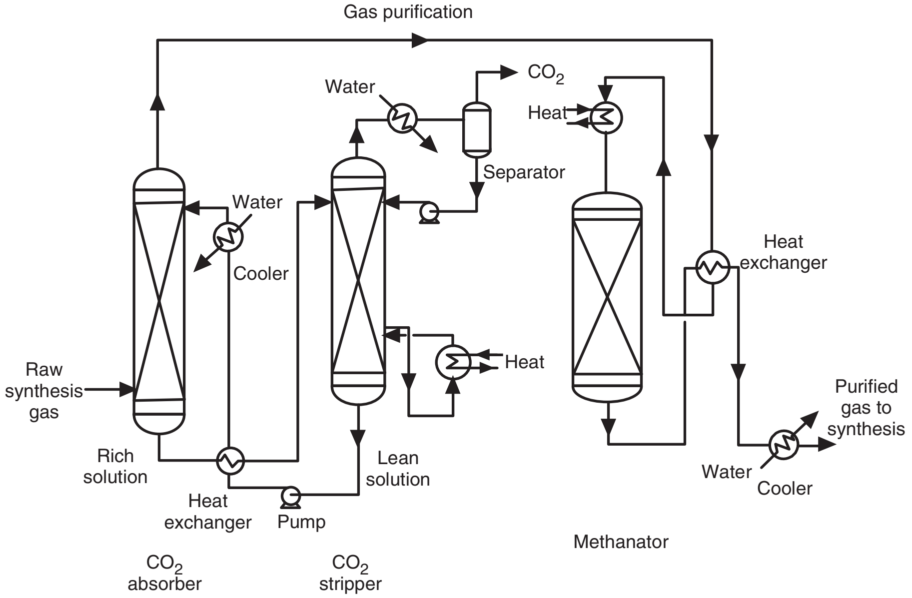


Fig. 5. Integrated ammonia process: synthesis gas purification.

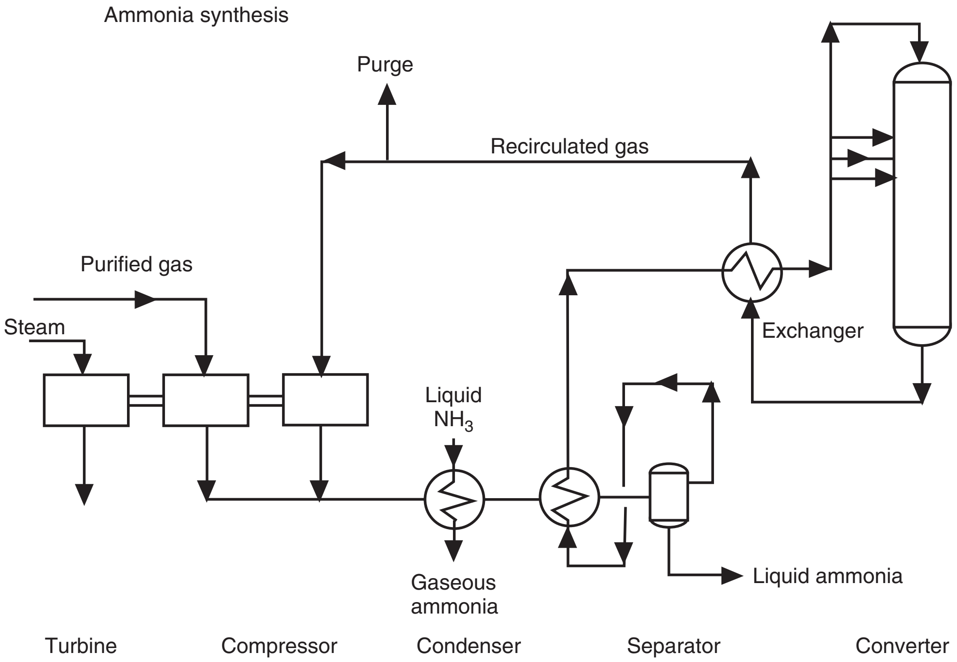


Fig. 6. Integrated ammonia process: ammonia synthesis loop.

combinations of waste heat boilers and heat exchangers. However, all designs are aimed at high energy efficiency or lower energy consumption.

6.1. Single-Train Ammonia Technology. *Concept of Singe-Train Ammonia Plants—MW Kellogg*. The MW Kellogg Company had received the prestigious Kirkpatrick Chemical Engineering Achievement Award in 1967, and the special credit went to a team of 12 persons who formed the nucleus of the development effort for a large-capacity, energy-integrated, single-train synthetic ammonia plant—a development that was to revolutionize the fertilizer industry. Those 12 members of Kellogg team were Len Axelrod, Jack Dwyer, Gunther Eschenbrenner, Jim Finneran, Benn Jesser, Bob Malthaup, Fritz Peterson, Lanny Quartully, Herman Rickerman, Ron Smith, Joe Yarze, and Hays Mayo who died in October 2008.

The innovative single-train concept was a technical and economical breakthrough and triggered a tremendous increase in world ammonia capacity. No parallel lines even for high capacity and a highly efficient use of energy, with process steps in surplus supplying those in deficit, were the main features.

An ammonia plant designed in 1960, just over a half century after Fritz Haber and Carl Bosch had made their important discovery, would have been based on steam reforming at 14 bar, synthesizing ammonia at 324 bar, thus limiting single-train capacity to between 300 and 400 TPD. It would have utilized three 50% capacity reciprocating machines operating in parallel for the compression needs, driving this machinery with gas engines or electric motors using imported energy and recovering only a minimal amount of waste heat generated by the process.

The MW Kellogg Company pioneered the large-scale single-train ammonia plant design in the early sixties, and there was some amazing work behind the development.

In 1962, American Oil Company (Amoco) asked Kellogg, Foster Wheeler, and Chemico to bid for the design and construction of a 600-TPD ammonia plant at their Texas City refinery.

The Project Management Department of MW Kellogg appointed Hays Mayo to lead the study. Hays Mayo was educated as an electrical engineer and experienced in the application and utilization of rotating machinery such as compressors, motors, gas engines, and turbines. Before his move into project management, he had headed Kellogg's Machinery Division.

Prior to the issue of the bid, Amoco had asked how large a single-train ammonia plant Kellogg could build. After a quick study by their process department, Kellogg came up with a capacity over 750 TPD. Amoco's inquiry document specified that the 600-TPD unit had to be a single train except for reciprocating compressors, which they specified as two 55% capacity, motor-driven reciprocating compressors for each compression service.

Hays Mayo summarized some thoughts for the proposal with a startling variance to the then-standard design. His March 5, 1962 internal memorandum stated that "It is recommended that the proposal be based on the use of a centrifugal compressor for synthesis gas compression to approximately 124 bar (the design was later changed from a three-case machine to a four-case machine raising the discharge pressure to 152 bar). Compression from 152 to 324 bar will then be done with two 55% reciprocating machines operating in parallel. It is further recommended that a centrifugal compressor be used for the recirculator in the synthesis loop."

To reduce capital and operating costs, Kellogg proposed the bid with the following features:

- Single-train, steam-turbine-driven centrifugal air compressor
- Single-train electric-motor-driven centrifugal refrigeration compressor
- Two 55% motor-driven reciprocating synthesis gas compressors with a single circulator cylinder on each
- Two 55% motor-driven reciprocating product rundown refrigeration compressors located at the ammonia storage tanks

Lower capital costs came largely from the use of centrifugal compressors instead of reciprocating compressors for air and refrigeration services. Lower operating costs were due to more intensive waste heat recovery via high pressure steam generation and utilizing that steam to power compressors. In fact, the waste heat recovered from the reformer furnace flue gases increased thermal efficiency to a creditable 85 percent.

With a creative proposal using a gas turbine to drive the syngas compressor, the bid was awarded to Kellogg and the plant went into production in December 1963. All major items of equipment were the largest that had ever been used. Onstream efficiency of the plant proved to be extremely good, and the soundness of a large, single-train ammonia plant had been confirmed.

While there were several “firsts” on the Amoco design, in retrospect, the following evolutionary steps seem the most significant in advancing the concepts that would eventually become part of the award-winning, large-scale ammonia plant design:

1. Extending single-train design to 600 TPD
2. Using centrifugal compressors as part of the synthesis gas compression
3. Establishing the concept of maximizing the recovery of waste heat from the process
4. Generating steam from the waste heat for use in steam turbine drivers
5. Utilizing the refrigeration compressor for rundown and atmospheric refrigeration

In late 1962, MW Kellogg received another inquiry from Imperial Chemical Industries (ICI) for a 600-TPD ammonia plant to be located at Severnside, England. Ron Smith, then senior vice-president of Operations, took a special interest in the ICI project and asked his team to make improvements over the Amoco design. Ron challenged his team with a question “why we couldn’t eliminate reciprocating compressors completely for syngas compressors” and “what was wrong in making ammonia at a pressure of 152 bar rather than 324 bar.” But experience with low pressure synthesis was very limited at that time.

The big question was: would the ammonia synthesis reaction work at the lower pressure of 152 bar? From the Amoco studies, there was confidence by the MW Kellogg team that it would work at lower pressures, but reaction kinetics data at 152 bar were needed. Other challenges were whether a low pressure system would require such a large catalyst volume that it could make such a design economically impractical. The cost of a huge converter, the problems of designing a full-diameter closure that would not leak, obtaining an equal flow distribution over a large-diameter bed, the cost of the additional catalyst, and the cost of a much larger recycle compressor were all haunting concerns.

The Collier Carbon and Chemical plant at Brea, California, had a Mont Cenis synthesis section operating at 104 bar and the catalyst had been replaced by a Topsoe catalyst. Since kinetic data were not easily measured in a laboratory without elaborate apparatus, it was not feasible for Kellogg to gear up for such a program within the time frame required. Therefore, Kellogg contacted Haldor Topsoe to visit Topsoe’s laboratory in Copenhagen, Denmark. Topsoe had not only more data on the Brea plant but also data covering the entire pressure range of interest to Kellogg. In addition, they had a computer program for calculating the quantity of catalyst required, which Topsoe permitted Kellogg to use.

The catalyst requirement at 152 bar versus 324 bar essentially doubled the size of ammonia synthesis converter, an increase that seemed economically feasible. Although the converter would be larger, needing twice the volume, the operating pressure was more than halved, thus reducing the thickness of the pressure shell. As a result, the weight of metal required for the converter (and hence the cost) remained about the same. It certainly appeared that a low pressure synthesis loop was feasible for the Severnside bid, and hence load sheets for a 152-bar ammonia synthesis were produced in September 1962.

Topsoe's cooperation and overall contribution cannot be overemphasized. Only a few months later Kellogg approached them about participating in a "technology transfer" so that Kellogg could determine the converter size on its own. The Kellogg team worked with Topsoe engineers for several days and calculated catalyst volumes and thus the size of the converter. Kellogg did more work in integrating process and energy requirements and developed waste heat recovery from reformer flue gases, raising steam system pressure and temperatures, and through this a low energy single-train concept became a reality.

So, finally, the single-train revolutionary ammonia process was conceived with the following features:

1. Reducing synthesis gas conversion pressure level to 152 bar thus making all compression duty possible with centrifugal compressors
2. Fully utilizing waste heat recovery for steam generation
3. Using steam turbines for all drivers
4. Producing steam at a substantially higher pressure than required for process needs, which improved the overall efficiency of the process
5. Expanding the large quantities of high pressure steam through the turbines to the pressure levels of the process, thereby developing nearly half of the horsepower required for the plant essentially at no extra cost for the steam generation
6. Fulfilling horsepower requirements by expanding additional steam to vacuum condensing

A typical flow sheet for a single-train, large ammonia plant such as those designed and built by the M.W. Kellogg Company is shown in Figure 7.

6.2. Ammonia Technologies—KBR. In 1998, Kellogg Brown & Root (KBR) was formed by a merger of The MW Kellogg Company and Brown & Root Inc. Brown & Root had previously acquired CF Braun & Co. These acquisitions and mergers resulted in the ability of KBR to offer the combined ammonia technology, engineering, and construction experience of MW Kellogg, Brown & Root, and CF Braun. Some historical milestones of KBR in the ammonia industry can be summarized as follows:

1948	first conventional KBR plant
1966	first purifier plant
1966	first centrifugal plant
1967	first 1000-tpd plant
1968	first 1500-tpd plant
1987	first 1750-tpd plant
1998	first 1850-tpd plant
2005	First 2200-tpd plant

Most plants built between 1963 and 1993 had large, single-train designs with synthesis gas production at 25–35 bar and ammonia synthesis at 150–200 bar. Another variation by Braun (now KBR) offered slight modifications to the basic

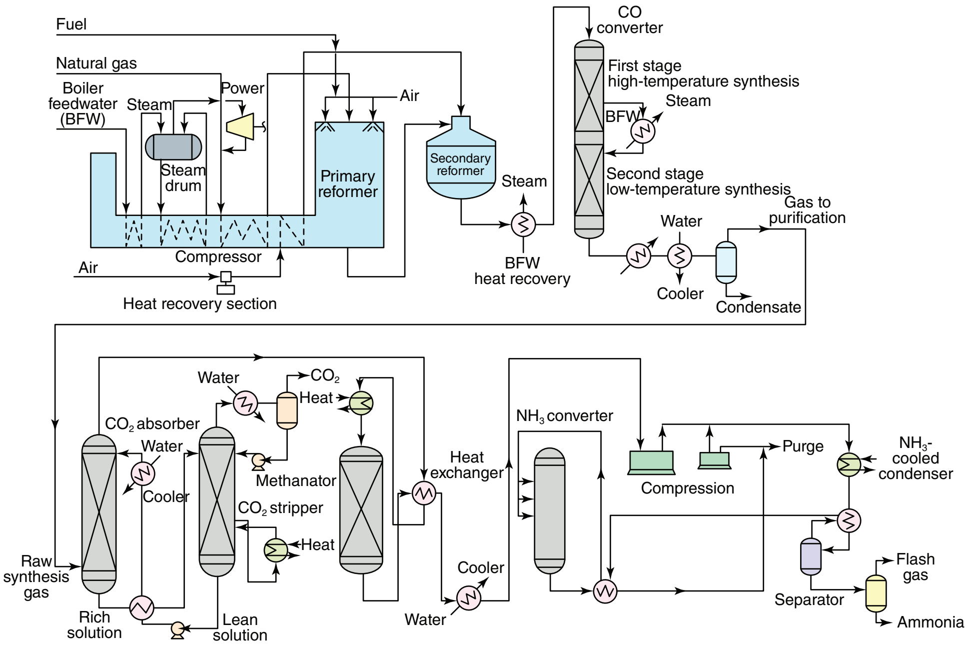


Fig. 7. M.W. Kellogg designed first single-train, large capacity ammonia flow sheet.

design. Braun Purifier plants utilized a primary or tubular reformer with a low outlet temperature and high methane leakage to reduce the size and cost of the reformer. Excess air was added to the secondary reformer to reduce the methane content from the primary reformer to a level of 1–2%. Excess nitrogen and other impurities were removed downstream of the methanator using a Purifier unit with cold box. Because the synthesis gas was essentially free from impurities, two axial-flow ammonia converters could be used to achieve a high ammonia conversion.

6.3. UHDE. Uhde now known as tkIS (ThyssenKrupp Industrial Solutions) is another company with a long innovative history in the ammonia industry with their first ammonia plant built in 1928. Uhde developed its dual-pressure process for large-scale plants in late 2001. The first plant based on this technology was the SAFCO IV ammonia plant in Saudi Arabia, which was commissioned in 2006.

Uhde pushed the capacity of a single-train ammonia plant by using proven contemporary equipment made possible by having the final synthesis in two stages running at different pressures. Uhde's technology for large capacity is based on currently available technology and catalysts. Their new flow sheet delivers a capacity of 3300 mtpd using well-tried and tested equipment.

Several options for scale-up of the synthesis loop have been evaluated. The simplest option of using two loops in parallel was not acceptable because it didn't not achieve the economy of scale.

Circulation in the synthesis loop is a function of the conversion per pass across the ammonia converter. A high conversion per pass can be obtained by reducing the ammonia separator temperature, by reducing the inerts level, and by increasing the catalyst volume. However, there is only limited scope for increasing the conversion per pass because of the reaction equilibrium constraint.

Uhde's synloop design comprises compression of the MUG followed by once-through conversion of hydrogen and nitrogen to ammonia before the part-converted MUG is introduced into the synthesis loop. The ammonia produced in the once-through converter is separated before adding the remaining MUG to the synthesis loop.

A production rate of 3300 tpd could be produced using the Uhde dual-pressure process with all the equipment needed in the synthesis loop and compressor already proven. The primary and secondary reforming front end of the plant operated at proven process conditions. Scale-up of the reforming section was straightforward when using a top-fired box reformer with a cold outlet manifold system. The size of the reformer is much smaller than reformers currently designed for large-scale methanol projects.

Uhde Dual-Pressure Ammonia Process: Features and Benefits.

- Reduces load on both the synthesis gas compressor and the synthesis loop
- Significant increase in plant capacity (+65%)
- Reduction of scale-up risk by use of proven equipment
- A 3300-tpd plant can be built with no critical high pressure equipment exceeding the sizes of a current 2000-tpd plant
- Energy consumption decreased by 4%
- Specific production cost per ton of ammonia reduced considerably

Milestones in Uhde ‘s Ammonia History.

1928	first ammonia plant on stream, 100 t/d, loop pressure 100 bar
1962	first 3-bed ammonia converter with indirect heat exchange
1967	introduction of the reformer “cold “outlet manifold system
1970	single-train 880 t/d with turbo compressor, 32 GJ/t ammonia, HP steam boiler in front-end and synthesis section.
1982	first radial-flow ammonia converter with indirect heat exchange
1989	BASF ammonia plant, 1800 t/d, 28 GJ/t ammonia
1999	ammonia Partnership with Johnson Matthey
2001	dual-pressure process presented
2006	largest ammonia plant of the world commissioned (3300 t/d)

6.4. Haldor Topsøe. Topsøe offers two process versions. The first operates at a steam/carbon ratio of 3.3 with high methane content from the secondary reformer. Shift conversion is conventional, Benfield or aMDEA is used for CO_2 removal, and the synthesis pressure depends on the plant size ranging between 140 and 220 bar when the proprietary Topsøe two-bed radial converter S-200 is used.

The second version operates with a steam to carbon ratio of 2.5 and shift conversion with medium and low temperature catalysts, both copper based. For CO_2 removal, aMDEA is chosen. The synthesis section runs at a pressure of 140 bar with a Topsøe two-bed S-200 radial converter followed by a single-bed S-50 converter (S-250 configuration). After the synthesis converters, high pressure steam is generated and/or superheated. An additional proprietary item is the side-fired reformer.

As indicated earlier in this article, Topsøe contributed to the development of the large–scale, single-train ammonia process by developing kinetic data for the synthesis catalyst so that a low pressure loop was possible. The data were available because Topsøe had been producing NH_3 with synthesis catalyst since 1947. Topsøe also introduced their first radial-flow converter, S-100 in 1966, followed by the S-200 converter in 1976, and the S-300 converter in 1999.

Milestones in Topsøe Ammonia History.

1947	first charge of ammonia synthesis catalyst
1957	first Topsøe side-fired tubular reformer
1966	first Topsøe radial-flow converter
1967	commissioning of first Topsøe grassroots ammonia plant
2000	commissioning of ammonia plants 2000 and 2050 TPD
2007	basic Engineering for 2200 TPD ammonia plant

6.5. Linde. The Linde Ammonia Concept (LAC) is an established technology process scheme with over 25 years of operation experience in plants with capacities from 200 mtpd to over 1350 mtpd. The LAC process scheme replaces the costly and complex front end of a conventional ammonia plant with two well-proven, reliable process units:

- Production of ultra-high purity hydrogen from a steam-methane reformer with PSA purification
- Production of ultra-high purity nitrogen, by means of a cryogenic nitrogen generation unit, also known as an air separation unit (ASU)

6.6. Casale. Ammonia Casale's plant design has a production rate of 2000 mtpd. One of the key features of this design is axial–radial technology in the synthesis converter (Fig. 8). In an axial–radial catalyst bed, most of the synthesis gas passes through the catalyst bed in a radial direction, creating a very low pressure drop. The rest of the gas passes down through a top layer of catalyst in an axial direction, eliminating the need for a top cover on the catalyst bed. Casale's axial–radial catalyst bed technology is used in both high temperature and low temperature shift (LTS) converters, as well as in the synthesis converter.

6.7. Other Technologies. Gas-heated reformers (GHRs) have been offered by some technology suppliers for production of ammonia in small capacity plants or for capacity increases. Unlike conventionally designed plants utilizing a primary reformer and secondary reformer operating in series, plants with GHRs

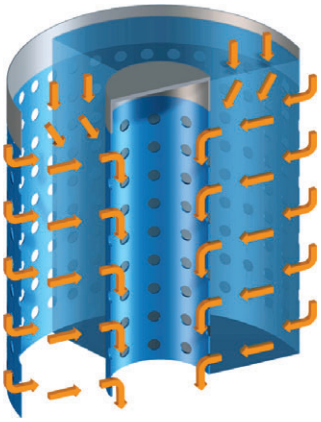


Fig. 8. Ammonia Casale's axial–radial ammonia synthesis converter.

use the hot process gas from the secondary reformer to supply heat for reforming in the primary reformer. This reduces the size of the primary reformer in addition to eliminating CO_2 emissions from the primary reformer stack, making the process more environmentally friendly.

Even though some ammonia producers advocate for distributed production of ammonia in small ammonia plants, most companies prefer to build large facilities near cheap raw material sources and transport the product by ship, rail, or pipeline to the consumers.

7. Ammonia from Coal

China produces more ammonia than any other country and produces most of its ammonia from coal.

The basic processing units in a coal-based ammonia plant are the ASU for the separation of O_2 and N_2 from air, the gasifier, the sour gas shift (SGS) unit, the acid gas removal unit (AGRU), and the ammonia synthesis unit. Oxygen from the ASU is fed to the gasifier to convert coal into H_2, CO, CO_2, and CH_4. There are many gasifier designs, but most modern gasifiers are based on fluidized beds that operate above atmospheric pressure and could utilize different coal feeds. Depending on the design, CO levels of 30–60% by volume may be produced.

After gasification, any particulate matter in the synthesis gas is removed and steam is added to the SGS unit. The SGS process typically utilizes a cobalt and molybdenum (CoMo) catalyst specially designed for operation in a sulfur environment.

After reducing the CO concentration in the synthesis gas to less than 1 vol%, the syngas is fed to an AGRU, where a chilled methanol scrubbing solution (eg, Rectisol) removes CO_2 and sulfur from the synthesis gas. The CO_2 overhead is either vented or fed to a urea plant. The sulfur outlet stream is fed to a sulfur recovery unit (SRU).

Syngas that passes through the AGRU is typically purified by one of the two methods:

- a N_2 wash unit to remove residual CO and CH_4 from the syngas before it is fed to the synthesis loop
- a PSA system for CO and CH_4 removal

8. Carbon Dioxide Removal

Ironically, this part of ammonia process technology is one of the substantial changes during the last 100+ year of operation of the Haber-Bosch ammonia process.

Many solvents were used for the removal of CO_2 from synthesis gas from the early days of ammonia production. Some of them are discussed in the following sections:

8.1. Water Scrubbing. The oldest method, water scrubbing, is practically abandoned in many plants. The CO_2 is absorbed in water under pressure, and the water is regenerated by a release in pressure. Most of the energy contained in the high pressure water is recovered by a water turbine coupled to the motor of the high pressure water pump. Although this method is simple and inexpensive, hydrogen is dissolved along with the CO_2, so that the H_2 loss is appreciable, amounting to 1.5–2.5% when the scrubber is operated at about 7.2 bar. Several schemes were proposed for recovering H_2, but these required additional equipment and increased investment couldn't justify the value of the recovered hydrogen.

8.2. MEA Absorption. The first generation of single-train plants often used monoethanolamine (MEA) with a high demand of low grade heat for solvent regeneration. With corrosion inhibition systems, amine strength could be raised, and solvent circulation reduced, saving heat and mechanical energy.

8.3. Selexol. This process uses polyethylene glycol dimethyl ether as solvent, which is stable, noncorrosive, not very volatile, but has a rather high capacity to absorb water. For this reason, a relatively dry gas is required, which is achieved by chilling.

8.4. Rectisol. This process seems to be the prime choice in partial oxidation plants, which is very versatile and allows several different configurations.

8.5. Sulfinol. The Sulfinol process uses a mixture of sulfolane and diisopropanolamine (DIPA).

8.6. Hot Potash Systems. Commercial hot potash systems differ in the type of activator used to increase the reaction rate between the CO_2 and the solvent. The activators enhance mass transfer and thus influence not only the regeneration energy demand but also the equipment sizing. The various hot potassium solvents were as follows:

- Benfield Loheat process with DEA as activator.
- Catacarb process with amine and borate as activator.
- Giammarco-Vetrocoke process with glycine and various ethanol amines as activators.

8.7. aMDEA (OASE). A leading process today is the BASF's activated methyl diethanol amine (aMDEA) with a special activator. Because of the low vapor pressure of aMDEA solvent, the solvent losses are at a minimum. The CO_2 binds much less strongly to MDEA than to MEA and hence requires less energy for regeneration. Many MEA solvent systems were revamped by swapping the solvent without a need of changing the process equipment.

9. Catalyst Developments

- In general terms, a catalyst is described as a substance that *increases* the rate of a reaction without being *consumed* by the reaction.
- Most commercially important reactions are just not *fast* enough to be viable without the use of a *catalyst*.

9.1. The 1960s. Reforming catalysts based on calcium aluminate cement operated very well for many years until the introduction of high heat flux, high pressure reformers by the MW Kellogg Company during the mid-1960s. These reformers utilized tubes with internal diameters of 72 mm, operating pressures as high as 35 bar, and heat flux rates as high as 100,000 W/m^2. With cocurrent flow of process gas and flue gas, localized flux rates in the top of these furnaces could exceed 120,000 W/m^2. This led to excessive tube metal temperatures with existing catalysts. To solve this problem, CCI introduced alpha-alumina-based reforming catalyst in the late 1960s. CCI's C11-9 alpha-alumina reforming catalyst with its excellent physical properties could be made in sizes as small as 16 × 6 × 6 mm rings (Fig. 9). The higher activity of this smaller size resulted in much cooler tube metal temperatures and longer catalyst life.

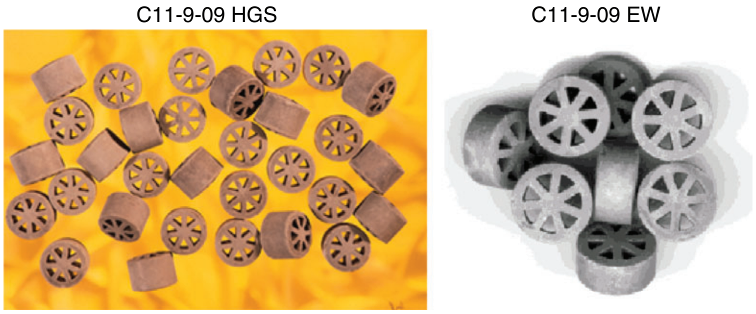
Another catalyst development that significantly reduced the energy consumption of NH_3 plants was commercialized during the 1960s. It was called low temperature shift (LTS) catalyst because it operated at temperatures lower than high temperature shift (HTS) catalysts to take advantage of better equilibrium. The first patents for LTS catalyst were issued in 1928. However, the first charge did not go onstream until 1962. Producers of LTS catalysts during this period used them in their own plants, so they were not available commercially. To reduce the overall energy consumption of ammonia and hydrogen plants, CCI started making and selling copper-/zinc-based LTS catalysts in 1964. Initial charges were placed in plants without LTS catalysts or into plants that utilized two HTS reactors with two CO_2 removal systems. A reduction in the CO concentration from 0.5–1.5% (HTS) to 0.18–0.20% in plants switching to C18 LTS catalyst produced by CCI increased production by 5–15%. Because of the benefits of low temperature CO conversion, most plants that have been built since 1964 have utilized LTS catalysts.

CCI also started producing ammonia synthesis catalyst through a license from Norsk Hydro in 1965. The catalyst that was produced, C73, enjoyed great success in the NH_3 industry and was installed in many plants around the world through the mid-1980s. Due to its activity and robustness, there are several charges of C73 still onstream today even after operating for more than 25 years.

Fig. 9. C11-9-02 alpha-alumina reforming catalyst.

9.2. The 1970s. Small raschig ring alpha-alumina-based catalysts were utilized in most reforming applications throughout the early and mid-1970s. However, as plants continued to upgrade equipment and introduce new technology to achieve higher operating rates, the need for an even more active reforming catalyst was identified. In 1978, United Catalysts (formed by the merger of CCI and Girdler) introduced C11-9-09 HGS (later EW), which was the first “shaped” reforming catalyst in the synthesis gas industry. This catalyst was alpha-alumina based and very quickly became known as “Wagon Wheels” due to its distinctive shape (Fig. 10). During the next seven years, United Catalysts’ C11-9-09 HGS became the most widely used reforming catalyst in the Western Hemisphere. Most plants were able to increase their run length by 50–100% with no loss in efficiency due to either excessive tube metal temperatures or methane approaches to equilibrium. Other manufacturers soon introduced their own version of multihole rings that are in use today.

To prevent premature plant shutdowns due to high CO leakage from the LTS converter, many plants added a LTS guard reactor ahead of their existing LTS reactor. LTS guard beds contained 25–50% of the volume of catalyst contained in the LTS main bed. Because LTS catalyst is poisoned by trace concentrations of sulfur and chlorides in the feed, the concept was to trap poisons in the guard bed



C11-9-09 HGS

C11-9-09 EW

Fig. 10. UCI's "wagon-wheel"-shaped catalysts.

to extend the life of the main bed. Since the guard bed catalyst could be changed while the plant was still running, block valves were used to isolate the bed during catalyst replacement and the subsequent reduction. United Catalysts' C18-HC was widely used in guard beds due to its ability to efficiently trap poisons, thereby protecting the main bed so that it could be run for up to 10 year between replacement.

During the 1970s, reformer tube metallurgy changed. Instead of just supplying high alloy HK-40-type tubes, manufacturers began to custom formulate tubes to balance rupture and creep strength, carburization resistance, ductility, toughness and weldability to suit varying operating conditions. New alloys such as HP Modified were introduced, which allowed plants to reduce the tube wall thickness of reformer tubes. This led to better heat transfer and lower tube wall temperatures. Today, new microalloy materials with even better properties are available to improve the performance of tubular reformers.

9.3. The 1980s. Prior to the mid-1980s, most of the natural gas in North America used for synthesis gas production was rich in methane with only small concentrations of heavier hydrocarbons. Natural gas "stripper" plants cryogenically removed most C3+ hydrocarbons since they were more valuable as refinery and chemical plant feedstocks. This was not as common in other parts of the world where heavier natural gas streams were commonly used. With high methane content natural gas, coking or "hot banding" in top-fired high heat flux reformers was not a problem. However, as natural gas streams became heavier and plants decreased their S/C ratio to save energy, "hot banding," which had not been a significant problem since the introduction of high geometric surface area reforming catalysts, began to appear once again. The good physical properties of C11-9 EW enabled the periodic steam removal of carbon deposition, which caused "hot banding." This, however, required a plant outage and resulted in production losses.

To eliminate unscheduled outages for steaming, alkalized catalysts were introduced for steam/natural gas reforming. Heavily alkalized catalysts for naphtha reforming had been introduced years earlier, but the inherent problems in potassium and silica carry over to waste heat boilers and shift converters making them unsuitable for NG-based plants. The initial catalysts that were used were raschig rings derived from naphtha reforming catalyst with lower potassium contents. While they solved "hot banding" problems in high flux reformers, they were less active than nonpromoted catalysts, resulting in higher tube metal temperatures and methane approaches to equilibrium.

To solve this problem, shaped alkalized reforming catalysts such as United Catalysts' G-91 were introduced during the 1980s. The higher geometric surface area and activity of G-91 resulted in low tube metal temperatures and methane approaches to equilibrium. The G-91 formulation is still used in the synthesis gas industry for reforming of natural gases and heavier hydrocarbon streams.

During the mid-1980s, many plants decided to reduce their reformer S/C ratio to reduce pressure drop and improve energy efficiency. Because of this, overreduction of the iron/chrome HTS catalyst leading to Fischer-Tropsch synthesis occurred. Fischer-Tropsch synthesis across the HTS catalysts reduced the efficiency of the plant and eventually resulted in replacement of the catalyst due to a loss in physical strength. By 1985, Süd-Chemie recognized this problem and had a replacement catalyst available, which would eliminate or delay the onset of Fischer-Tropsch synthesis.

The first charges of G-3C and C12-4 copper promoted HTS catalysts went onstream during the late 1980s. Both catalysts essentially eliminated Fischer-Tropsch synthesis in most plants even at reformer S/C ratios less than 3.0. Another positive benefit of the addition of copper was an improvement in the activity of the catalyst so that plants could operate with inlet temperatures in the range of 300–320°C. This reduced the CO leakage due to more favorable equilibrium leading to lower CO leakages from the LTS converter. Copper-promoted HTS catalysts such as Clariant's ShiftMax 120 are still used today in synthesis gas plants operating with reformer S/C ratios as low as 2.5.

Another improvement in plant design that is indirectly related to the performance of the reforming section of the plant was introduction of purge gas recovery systems. The concept was to recover H_2 from the purge gas and reinject it into the MUG going to the loop. This allowed plants to reduce firing on the primary reformer and increase the air/gas ratio in the secondary reformer. Since the secondary reformer was required to do more work, the primary reformer catalyst had to continue operating at equilibrium at lower exit temperatures, while the secondary reforming catalyst had to operate at higher temperatures in the top of the reactor. This led to a reduction in the volume of secondary catalyst to allow more mixing space in the top of the reactor. Since the secondary reformer volume was reduced, smaller size alpha-alumina catalyst had to be used to achieve equilibrium conversion. Up until that time, large calcium aluminate cement-based catalyst was commonly used.

The use of molecular sieve dryers to remove moisture and trace CO_2 concentrations from MUG also became widely practiced during the 1980s. In many plants built before 1980, the main NH_3 separator (sometimes referred to as the secondary separator) was located downstream of the recycle compressor. Moisture in the fresh MUG and NH_3 in the recycle gas was removed in the separator before the process gas went back to the converter. Adding molecular sieve dryers downstream of the methanator allowed plants to condense and separate NH_3 from the process gas prior to circulating back to the recycle compressor. In addition to saving energy, molecular sieve dryers prevented CO_2 from passing into the synthesis loop, thus preventing shutdowns due to carbamate formation in NH_3 chillers. Molecular sieve dryers also replaced many of the NH_3 scrubbing systems that were utilized in some plants for feed gas purification.

As energy costs around the world increased during the 1980s, existing ammonia plants continued searching for ways to lower energy costs. In the synthesis loop, individual beds in axial-flow reactors utilizing 6–10-mm-size catalysts were converted into radial-flow or axial/radial-flow beds, which could utilize smaller size catalysts due to less pressure drop. By replacing 6–10-mm-size catalysts with 1.5–3.0-mm-size catalysts, most plants were able to increase the NH_3 concentration exiting the reactor from 12% up to 14.5–15.0%. This increased conversion allowed plants to increase the MUG rate to the loop, thereby increasing NH_3 production. Some 900-MTPD plants were able to increase their production rate to 1360 MTPD after converting their axial-flow converter beds to radial-flow beds. This concept was further enhanced during the 1990s with the advent of internal heat exchangers and variations of the radial-flow concept such as horizontal converters. An example of conversion of a 4-Bed quench converter to a 3-Bed with internal heat exchangers by Ammonia Casale is shown in Figure 11.

Today, most plants operate with 1.5–3.0-mm-size catalysts with an NH_3 concentration of at least 16% exiting the converter and some with as much as 21% NH_3 in the converter outlet stream.

Process air preheat also became widespread during the 1980s as a retrofit for older plants and as standard equipment for new plants. Heat from flue gas exiting the reformer was used to preheat process air to decrease the amount of fuel needed in the reformer. Some newer plants utilized gas turbine exhaust rich in oxygen as process air for the same reason.

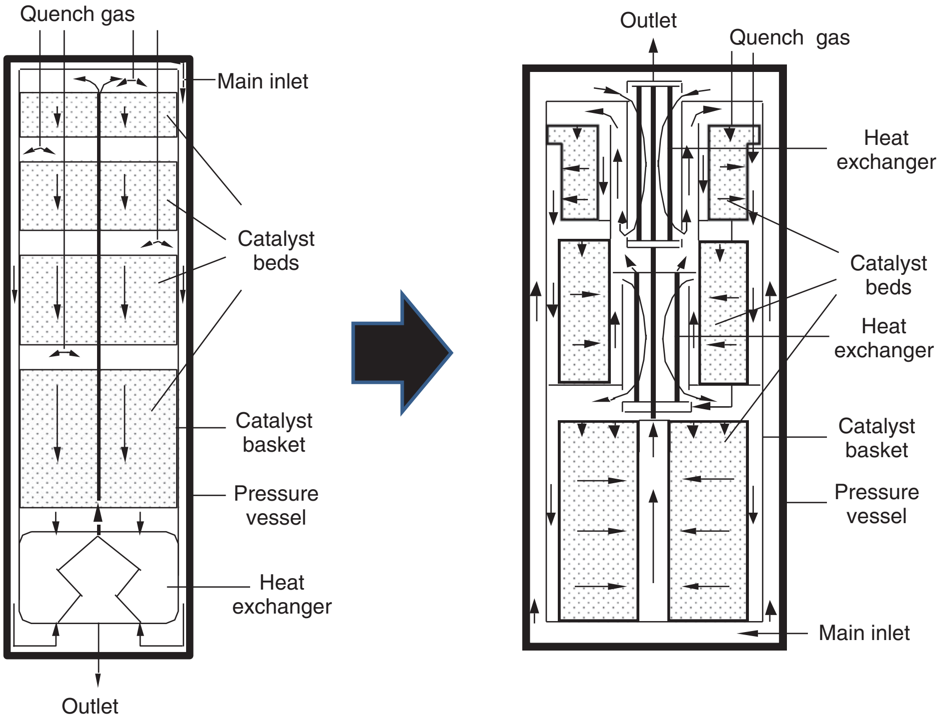


Fig. 11. 4-bed quench converter converter to a 3-bed with internal heat exchange.

9.4. The 1990s. Energy consumption and environmental regulations continued to drive improvements in NH_3 plant design and operation during the 1990s. As 900-MTPD plants increased capacity to 1400 MTPD or higher, pressure drop across the reformer became a bottleneck. Even after new developments in tube metallurgy that allowed plants to increase tube IDs from 72 mm up to 100 mm or larger, pressure drop across the reformer remained a major energy consumer. Operators either had to compress feed gas to a higher level or consume more power to compress MUG going to the synthesis loop.

Süd-Chemie introduced 10-hole LDP reforming catalyst in 1998 (Fig. 12) to reduce pressure drop across the reformer while maintaining sufficient activity and heat transfer to keep tube wall temperatures and methane leakages at acceptable levels. This shape had the same activity properties of the earlier EW shape; however, pressure drop is about 40% lower than the earlier EW material. A lower pressure drop across the reformer results in less energy needed to compress the reformer feed or allows plants to increase the feed rate to produce more ammonia. Another advantage of the 10-hole shape is enhanced physical properties. Since it is stronger than previously produced catalysts, it can withstand the forces caused by expansion and contraction of the reformer tubes much better, which leads to longer lives.

As governments around the world enacted new environmental regulations on plant operators during the 1990s, by-products made across the LTS converter became an issue. Compounds such as methanol and amines, that are formed across HTS and LTS catalysts, eventually end up in the process condensate or overhead CO_2. Methanol in process condensate that goes to a low pressure condensate stripper usually ends up in the atmosphere with the steam exiting the stripper. Methanol is not as troublesome in plants with a high pressure stripper since the methanol in the overhead steam can be recycled back to the reformer. Methanol in the condensate knock-out overhead usually ends up with the CO_2 exiting the CO_2 removal system. This contamination reduces the value of the CO_2 if it is sold as a feedstock for other processes. In addition, methanol production reduces the efficiency of a synthesis gas plant. For example, in an NH_3 plant, each tonne of methanol that is produced reduces NH_3 production

Fig. 12. ReforMax (CLARIANT) LDP shape.

by 1.1 tonnes. This is equivalent to hundreds of thousands of dollars in lost production every year for a modern NH_3 plant.

Since installation of a high pressure condensate stripper is quite expensive, the Süd-Chemie Group developed a catalyst designated C18-HALM (high activity, low methanol) and introduced this to the industry during the mid-1990s. Conventional catalysts produced about 90% of the equilibrium methanol across an LTS converter, whereas C18-HALM produced only 10% of the equilibrium amount. This allowed plants with low pressure condensate strippers to meet environmental regulations by simply changing their LTS catalyst. Less methanol production also improved the economics for most plants since more H_2 ended up in ammonia instead of undesirable products.

Another catalyst development that was first used during the 1990s in new plants was ruthenium-promoted ammonia synthesis catalyst. Ruthenium-promoted catalyst was developed by KBR and installed in two KAAP plants in the 1990s. The catalyst is much more active than magnetite, which allowed KBR to design the NH_3 loop with an operating pressure of less than 100 bar. Operating at a lower temperature, the catalyst was able to achieve NH_3 concentrations of more than 20% exiting the converter even at this low pressure. Lower operating pressure also reduced the capital cost of the plant since piping, vessels, and other equipment in the loop could be fabricated from thinner wall materials.

GHRs such as KBR's KRES technology and ICI's LCA were also introduced during the 1990s. GHRs reduced the cost of the reformer by utilizing the secondary reformer effluent as the source of heat for the primary reforming reaction. They also reduced energy consumption and CO_2 emissions to the atmosphere. Because of the unique reforming conditions in GHRs, United Catalyst developed special catalysts and catalyst sizes to provide the same type of performance and reliability expected with fired reformers.

9.5. The 2000s. The most significant catalyst development of the 2000s was the introduction by Clariant (then Sud Chemie) of Wustite-based AmoMax-10 for NH_3 synthesis converter. Wustite is a nonstoichiometric iron oxide with properties that produce a catalyst with the following benefits:

AmoMax-10 Features.

- 20% higher activity compared to magnetite Fe_3O_4
- Low temperature, low pressure activity
- Extremely good thermal stability for long life
- East to activate + quick reduction
- High poison resistance
- Very high crushing strength
- Available in oxide and prereduced form

The first charge of AmoMax-10 in a plant with 1000-MTPD capacity went onstream at Liaohe Chemical Fertilizer in December 2003. This charge is currently operating at near start-of-run (SOR) conditions and has led to more than 85 other charges onstream since 2005. AmoMax catalyst is being used in NH_3 plants all around the world. It has been used as a drop-in replacement as well as part of a converter revamp.

10. Energy Consumption

Improvements in converter design such as radial and horizontal catalyst beds, internal heat exchangers, and synthesis gas treatment led to an increase in ammonia concentrations exiting the synthesis converter from about 12% to 19–21%. This increased conversion per pass along with more efficient turbines and compressors led to further reductions in energy consumption. More efficient CO_2 removal solvent, aMDEA has contributed to improved energy efficiency. Most modern plants can produce ammonia with an energy consumption of 28 GJ/t, LHV.

Over the last 25–30 years, the ammonia plant net specific energy consumption has been reduced by approximately 30%. The current nominal energy consumption is now just 30% above the theoretical minimum.

11. Storage and Shipment

Storage of liquid ammonia had been a practice for almost 100 years right from the time ammonia was made on an industrial scale. In the earlier stage of ammonia production, ammonia was stored in pressurized systems such as bullets and in Horton spheres. Typically, spheres were used to store up to 2000 tonnes, whereas atmospheric ammonia storage tanks are used to store up to 50,000 tonnes at plant sites and at separate distribution terminals near to where liquid ammonia is applied directly.

Low pressure ammonia storage has been widely accepted for two reasons. First, it requires much less capital per unit volume. Second, it is safer than sphere and bullet storage using pressures higher than atmospheric. With the large-scale industrial production of ammonia, it has become common to store ammonia at atmospheric pressure and at −33°C.

11.1. Types of Ammonia Tanks. The main types of atmospheric tanks operating at −33°C are as follows:

- Single-wall steel tanks with external insulation, commonly known as single-wall tanks (Fig. 13). Some of these tanks have concrete bunds surrounding the tank to contain the full contents of the tank.
- Steel tanks with double walls and perlite insulation in between the walls are known as double-wall tanks or double-containment tanks (Fig. 14).

There are two types of double-wall, double-integrity (DWDI) tanks: those with insulation in annular space (Fig. 15) and DWDI tanks with insulation on the outer tank (Fig. 16).

The main difference between the two types of DWDI tanks is that the one with insulation on the outer tank can be operated for a longer time in the case of an inner tank failure, whereas the one with insulation in the annular space needs to be decommissioned upon inner tank failure as its outer tank is not insulated. DWDI tanks with insulation in the annular space cost less than the tanks built with insulation on the outer tank. All the double-wall style tanks are designed to

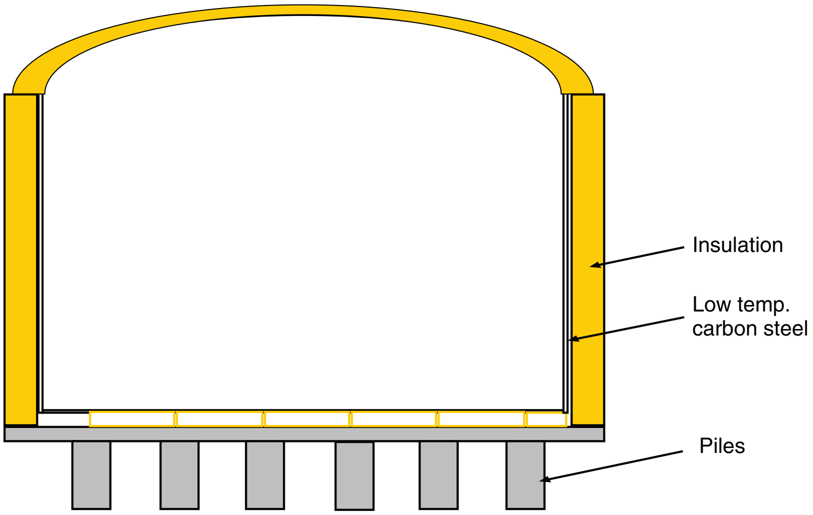


Fig. 13. Single-wall tank.

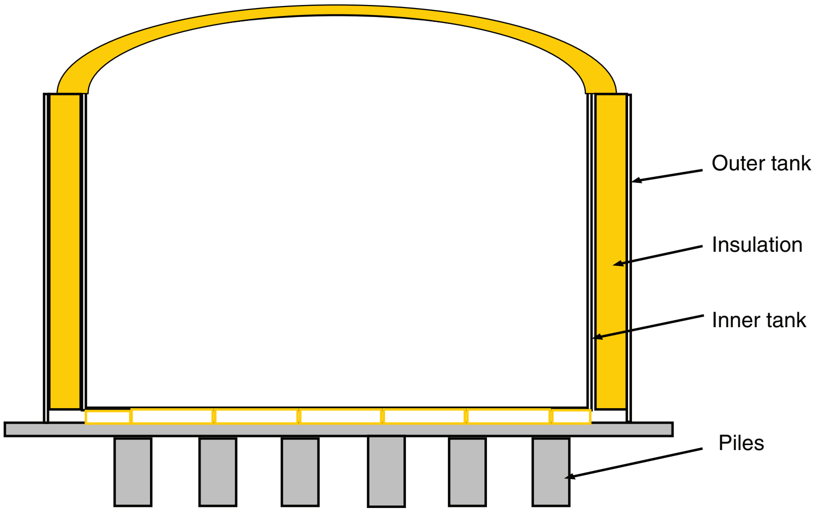


Fig. 14. Double-wall tank (double containment).

contain the full contents within the inner tank, and both styles of DWDI tanks are designed with the same materials of construction.

In the figures, the different tank designs are shown standing on piles. This is the generally accepted standard for newly designed tanks. However, single-wall tanks have been known to be placed directly on compacted soil/sand foundations, which then require under-tank heating coils (foundation heaters) to prevent frost lens and possible ground heaving.

Single-wall tanks were built at many sites in the past, but the current practice, based on quantitative risk assessment (QRA), recommends that DWDI tanks be used for bulk storage to achieve an “As Low as Reasonably Practicable” (ALARP) risk level. Note that the failure rate for DWDI full-containment tanks

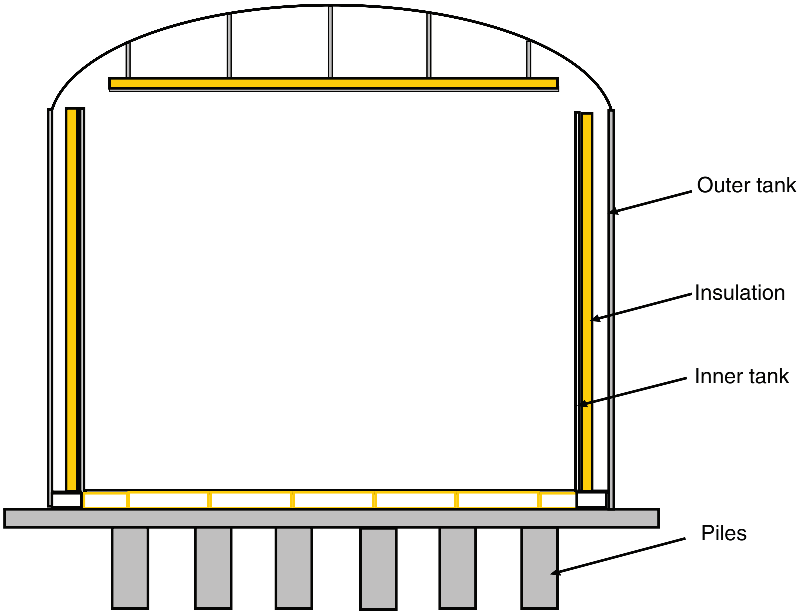


Fig. 15. Double-wall, double-integrity tank (full containment) with insulation in annular space.

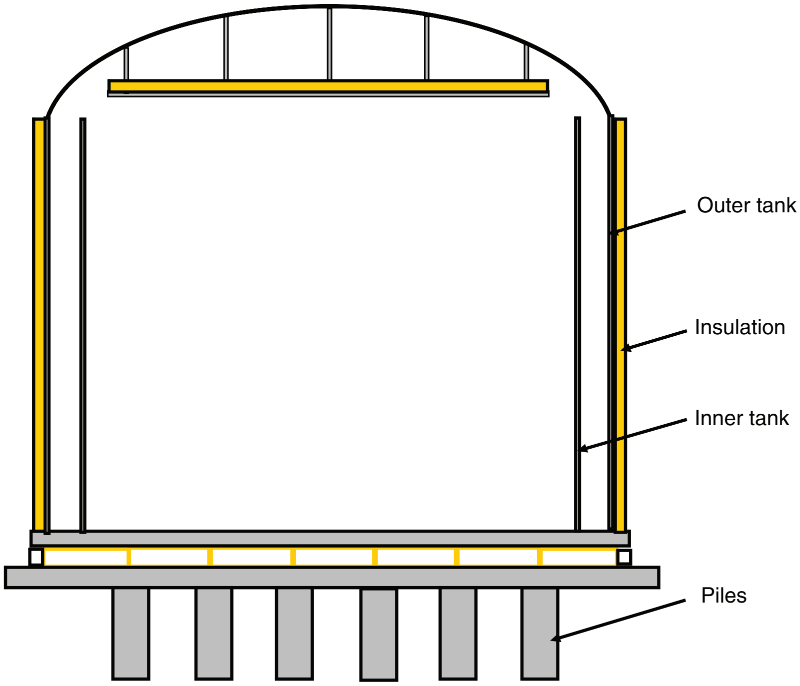


Fig. 16. Double-wall, double-integrity tank (full containment) with insulation on the outer tank.

is nearly one hundredth of that for single-wall tanks (based on failure rates published by HSE UK, Purple Book /SGS 3 published by VROM, Netherlands, and the Failure Rates Handbook by Belgium). Atmospheric ammonia tank standards are still evolving. For example, risk assessment was not previously included in the above-noted standards. Now API 625, which cross references to API 620, states that risk assessment should be conducted by the purchaser of the tank to determine the tank configuration.

Tank design, installation, and operation should comply with the best available operating procedures based on hazard & operability (HAZOP) studies, bow-tie analysis, and/or similar process-risk evaluation tools. The design of individual storage tanks and their associated ancillary equipment can vary. Items that require systematic attention during a tank's lifetime include relief valves; nozzles; drainage systems; roof, wall, and bottom insulation; piles and foundation (elevation surveys); tank integrity inspection (especially weld joints); piping inspection; and fitness-for-service assessment.

11.2. Tank Design and Safety Aspects. The following design features are recommended for high integrity ammonia tanks:

- The atmospheric ammonia storage tank should be of DWDI type with insulation on the outer wall and be designed for 14-kPag internal pressure.
- The tank should be designed, fabricated, erected, and tested in accordance with the generally accepted standard, API 620, Appendix R. A new code API 625, published in 2010, describes the various tank systems (single, double, and full containment). It refers to the updated API 6202012 edition for steel tank construction and ACI 3762010 edition for concrete tank construction.
- The tank should be erected on an elevated piled concrete slab foundation to prevent the ground freezing below the tank, since this design will negate the potential damage of the foundations or the tank itself due to frost heave. The top of the concrete slab shall be at an elevation of about 2 m above the surrounding area.
- The foundation and tank should be designed to withstand a full hydrostatic test of the tank. Both inner and outer tanks should be hydrotested.
- The tank design should accommodate movements of the tank due to thermal changes and minimize induced bending stress in the shell.
- For installation in a region of seismic activity, a seismic analysis of the tank and associated pipe work should be carried out.
- The design should include the required allowances for cyclonic wind and earthquake conditions per country standards.
- The design should be suitable for a marine environment as many sites may be close to the sea.
- Drain lines are to be provided both for the inner and outer tanks.

Tank Materials. The inner and outer steel tanks should be of all welded construction and fabricated from normalized carbon–manganese steel. API 620 Appendix R lists acceptable materials for tank construction together with code designations and material properties. Materials for atmospheric ammonia tanks should be selected to satisfy the requirements specified in the design code. The standard type of material is low temperature certified carbon–manganese steel, impact tested at or below –40°C. Welding and any Charpy V-notch testing will be carried out to meet the quality requirement of the tank plate and the welding procedures at the tank design conditions.

The supporting/load bearing rings underneath the tank walls should be a treated wood (lignostone) or equivalent type of material. Treated wooden blocks are preferable to Perlite concrete blocks for insulation at the bottom of the tank. The outer tank anchoring material should be identifiable against mill certificates giving chemical analysis and mechanical properties. Any components welded directly to the tanks should be fabricated from the acceptable materials listed in API 620 Appendix R. All nozzle/manway welds in the lower strakes should be PWHT (post weld heat treated, stress relieved) to remove residual stresses from the welding process. No hard stamping of materials is allowed as this causes stress raisers.

Pressure Relief. As a minimum, at least two pressure relief valves and two vacuum relief valves are recommended for each atmospheric storage tank to protect against overpressuring or vacuum conditions that may occur. The design configuration of the relief valves should be such that any one valve can be removed for examination or maintenance without losing the tanks protection. An isolation valve between the tank and each relief valve and a mechanical linkage system should be incorporated so that only one valve can be isolated at any time (a Nederlock/Castel Key system can also be used). Relief valves and safety devices should be assessed (sized) according to the requirements of API 2000.

A permanent nitrogen connection to maintain tank pressure as one (additional) layer of protection is recommended in case of a low–low pressure scenario (nitrogen addition instead of air ingress avoids the potential for stress corrosion cracking). An emergency shut-off valve in the liquid supply line is needed to activate on high–high pressure in the tank.

Instrumentation. Tanks should be fitted with three independent level and pressure indicators. There should be an independently activated high level shut-off valve to close the feed to the tank at very high level in the tank (a 2 out of 3 level transmitter safety trip system).

Electrical. Tanks should be fitted with earthing bosses, and tanks over 30 m in diameter should have three earthing bosses. The earthing bosses should be constructed of austenitic steel for the studs and washers and protected copper conductor strips to prevent contact with ammonia. Earthing bosses need to be evenly spaced around the tank. Where personnel need access for maintenance, adequate lighting shall be provided.

Piping. All flanges should be of minimum 150# rating. Bottom liquid nozzle connections should be of minimum 300# rating. Screwed connections are not allowed.

Insulation. External insulation should be covered with a continuous flat aluminum vapor barrier. Single profiled sheets for the aluminum vapor barrier must not be used. External insulation procedure and design must be evaluated by a specialist insulation designer to insure nil water ingress, which would allow ice to form on the tank shell or the base, potentially causing heaving. The ambient temperature for design of the insulation system is a maximum temperature of 50°C and a minimum temperature of –40°C.

Tank Nondestructive Testing (NDT). The primary NDT used on the NH_3 tank throughout its life should be the acoustic emission (AE) testing method. The tank design should include all permanent fittings/modifications required to minimize time and disruption during setup and testing. The tank should be installed with waveguides for AE tests during initial fabrication. The initial AE test must be conducted at the hydrotest stage so that any construction defects can be fixed prior to placement of the tank into service. A second AE test also needs to be carried out during first fill of liquid ammonia into a new tank.

Following the hydrostatic and AE tests, water should be held in the inner tank at the height equivalent to the maximum operating level for a period of seven days to ensure that future foundation settlement does not occur. The constructor inspection test plan (ITP) should also allow for witness points during construction.

11.3. General Requirements. The stairway to the top of the tank should be a spiral type, with the separate stand-alone access tower for its access. Platforms with access from the main stairway should be provided to ensure necessary maintenance access. The design and coverage of this platform should consider the safety of personnel working in the platform area.

11.4. Ammonia Storage Facility. When designing and building the ammonia storage system, a layer of protection analysis (LOPA) study should be conducted to determine the following safety instrumented functions:

- Remote shut-off valves are provided on the liquid ammonia main inlet and outlet line to/from ammonia storage tank.
- The refrigeration system should be based on recognized and proven industrial compressors.
- There must be an auto compressor loading/unloading facility for tank pressure control.
- A review of stand-by equipment for critical duties and utilities is required.
- The design should consider a closed vent and drain system for ammonia.
- Redundancy in critical instrumentation and control is required.
- Thermal relief valves must be installed on the ammonia lines where there is a possibility of blockage or heat ingress.
- Any fugitive ammonia emission should be minimized. Where ammonia venting is needed from relief valves or from maintenance activities, these must be piped back to the ammonia storage tank.
- Any venting of ammonia to the flare shall be avoided or minimized.
- An ammonia leak detection system in the storage area is necessary.
- Lightning protection and earthing protection for the tank is mandatory.
- Emergency power to one of the refrigeration holding compressors to maintain tank pressure during power failure is required in the design package.
- A flare is needed for controlled venting under extreme emergency situations.
- A wind direction indicator is suggested.
- Emergency plant lighting is necessary.

11.5. Commissioning. The commissioning procedure is as follows: purge the tank with nitrogen until the measured oxygen in the discharge gas is less than 4% (vol). Purge with ammonia vapor until the oxygen in the tank is <0.5% (vol). Cool the tank down to as low as possible with injection of liquid ammonia at a cooling rate lower than 2°C/h, preferably using a spray system. Measure the temperature in the tank away from the gas inlet. Take samples from the ammonia liquid in the tank and analyze them for water and oxygen.

11.6. Decommissioning. For decommissioning, empty the tank to the absolute minimum liquid level. Evaporate the remaining ammonia in a way that ensures uniform and slow heating, not exceeding 2°C/h. Purge with warm ammonia until all liquid ammonia is removed. Remove the ammonia gas in the tank by purging with nitrogen and not with air, to prevent the formation of an explosive mixture. To prevent environmental issues, flare all the ammonia-vapor-containing streams. Remove the nitrogen atmosphere by purging with air until the oxygen content is >19%. If ammonia is still measured in the gas phase due to residual oil, breathing equipment must be used when entering the tank. Residual oil remnants may require additional clean methods and additional personnel safety requirements and equipment.

12. Safety in Ammonia Industry

The chemical industry has a general practice of maintaining secrecy regarding the technical aspects of its plants, and there are several good reasons for this. In the ammonia sector, the practice of exchanging information had been going on for some time. In 1956, because of a series of explosions in air separation plants associated with partial oxidation ammonia plants of that era, a group of very concerned plant engineers from several companies formed a technical assessment committee. They reviewed and discussed the nature of the accidents, the probable causes, and corrective actions that could be taken. This network eventually transformed to AIChE symposium known as “Safety in Air and Ammonia Plants.”

The AIChE organization has played an important role in providing the platform, which has no doubt improved the safety of ammonia plants and saved lives and expense. The information shared at the symposiums also prevented many similar incidents from ever happening because people are aware of what has happened elsewhere.

The annual ammonia safety symposium is organized by AIChE’s Ammonia Safety Committee and is dedicated to improving the safety of plants that manufacture ammonia and related chemicals, such as urea, nitric acid, ammonia nitrate, and methanol. Attendees including plant safety personnel, plant managers, and process engineers representing a spectrum of nitrogen fertilizer-based industries do participate in the symposium, where they share technological advances and discuss strategies for improving plant safety, maintenance, and management. Ammonia industry leaders and practitioners describe how their organizations avoid or manage potential plant accidents and present solutions to a variety of safety engineering problems.

Knowledge of the bad experiences has helped others to avoid them. Knowledge of the positive experiences and design improvements has contributed to a more efficient industry.

13. Closing Thoughts

The production of ammonia has changed over the past 100+ year. Some of these changes have been dramatic, such as the production of synthesis gas. Yet, in all these developments, the ammonia synthesis loop has essentially remained the same as Haber-Bosch developed it. From humble beginnings, the production of ammonia has grown from very low production rates to more than 200 million tons per annum in more than 70 countries. This growth would not have been possible without the development efforts over the years by many process technology licensors.

Since BASF started producing 30 MTPD of NH_3 using the Haber-Bosch process 106 years ago, technology developments in all aspects of the NH_3 production process have been realized so that plants producing more than 3000 MTPD are operating today. Advances in process design, equipment, safety, and catalysts have all contributed to the current state of NH_3 production.

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