Strelzoff

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The world's largest single train ammonia plant, with a design capacity in excess of 1700 tons a day, has gone on-stream in Chiba, Japan. The Nihon Ammonia Company facility was designed by The M. W. Kellogg Company, Houston, a division of Pullman Incorporated, and constructed by Sumitomo Chemical Engineering Company, Tokyo. Kellogg also provided basic engineering, while Sumitomo completed the design engineering on the plant. Kellogg Technical Services Company, Tokyo, an affiliate of M. W. Kellogg, provided liaison and advisory services throughout the life of the project, and startup assistance as the plant neared completion and acceptance.

Foreword

REVERSING A PRIMAL TREND

In 1898 Sir William Ramsey, discoverer of the inert gases, pointed out the depletion of the world supplies of fixed nitrogen. In view of the rapidly rising population and increasing intensity of agriculture, he predicted world disaster due to a fixed nitrogen famine by the middle of the twentieth century. That this had not occurred is due to the discovery by F. Haber of a method of fixing nitrogen by reacting it with hydrogen to give ammonia.*

Modern astronomers tell us that the quantity of fixed nitrogen in the world has been decreasing for a long time. They say that the primeval atmosphere was composed principally of hydrogen, ammonia, water vapor, and methane. There was little free nitrogen, and the atmospheric oxygen on which life now depends was tied up in metal oxides in the rocks and in the water. Gradually the free hydrogen, which is too light to be held in the atmosphere of a planet of the size of the Earth, was lost to space, while ammonia dissociated into nitrogen and hydrogen.

The oxygen of our present atmosphere has been produced by plant life, which is believed to have descended from initial life forms that were born in the less harsh, reducing atmospheres of those primeval times. After chlorophyll appeared in plants, the living plants gradually built up the concentration of oxygen in the atmosphere by consuming carbon dioxide, which they converted to oxygen and organic solids. Plants require combined or fixed nitrogen, which they extract from the soil. Animals also

*Reuben, B. G., and Burstall, M. L., *The Chemical Economy*, Longman Group, London, 1973. Other sources attribute this prediction to Sir William Crookes, discoverer of the cathode ray.

require fixed nitrogen; herbivores obtain it from eating plants and carnivores get it from eating animals. Since only a minor portion of the plants can fix nitrogen by converting it from a gaseous to a chemically reactive form, nitrogen is not returned to the soil at the rate at which plants and animals consume it; and it is the resultant gradual depletion that led to the 1898 prediction of nitrogen famine.

About 10 years later (in 1909) in Germany, Badische Anilin and Soda Fabrik (BASF) undertook to develop the Haber process for the direct synthesis of ammonia. If the needs for fixed nitrogen had not established the importance of ammonia, the commercial and technical concepts born of the Haber process would have done so. Through the Haber process, ammonia became the first substance to be synthesized in a specialized plant; and the overall process was the first to solve the now familiar problem of preparing a reaction mixture from a suitable feedstock.

Even the impending nitrogen famine might not have caused the production capacity of ammonia to grow so fast (it now exceeds all other chemical products) had not humanity's desire to eat been complemented by an urge toward self-destruction, which can be conveniently fulfilled by means of the powerful polynitro explosives derived from ammonia. The first Haber plant came on stream in 1913, just before World War I was declared. From an initial capacity of about 7500 long tons of nitrogen in 1913, Germany's ammonia capacity from the Haber process grew to 95,000 tons in 1918, at the end of the war, or from less than 1% to more than 50% of total production within five years. This is a remarkable growth rate for any new process. It is doubtful whether Germany could have survived in that war so long, under the naval blockades, had it not been for the Haber process.

The world was eager to acquire technology that had served Germany so well. By 1921, the first U.S. plant built after the Haber process was producing 3600 tons of ammonia per year. Elsewhere, analogous methods were applied in processes that have differed primarily in the synthesis pressure and the efforts to make most efficient use of manufactured hydrogen. By the dawn of World War II, the world ammonia capacity had grown nearly fortyfold, from Germany's 95,000 tons/year in 1918 to 3.7 million tons/year in 1939. Again war brought a spurt in production. During 1941–1945, the United States alone added 20% to world capacity with 10 new plants capable of producing 800,000 tons/year.

More recently, the strongest demands for ammonia have come from humanity's desire to eat better. Uses as agricultural fertilizers have expanded the world consumption of ammonia; by 1976, consumption approximated 68 million tons/year, divided according to area as follows:

Area	Consumption (1000 metric tons/year)
Africa	1,750
Asia	10,800
Oceania	800
Western Europe	19,000
Eastern Europe	12,000
North America	18,000
Central America	700
South America	5,000
Total	68,050

Today, ammonia has achieved the status of an international bulk commodity, like crude oil or iron ore, to be shipped by ocean-going vessels and cross-country pipelines. International commercial agreements involving ammonia can be as significant as diplomatic treaties.

Such contracts, with far-reaching effects extending over dozens of years, place an enormous burden on the reliability of the technology for manufacturing ammonia. Relatively inconsequential oversights in making or meeting specifications can cause repercussions far out of proportion to the scale of the equipment involved. Consequently, designers and operators of modern ammonia plants tend to be biased toward one or another system that has been shown reliable. There is need for a book, such as this one, to keep the discrete parts of ammonia technology continually in perspective, so that each variable or each possibility for improvement stands revealed for its liabilities and its advantages.

With a subject as complicated as the technology and manufacture of ammonia, a balanced perspective could be offered only by an exceptional individual, such as this book's author, Samuel Strelzoff. Born in Russia in 1901, he attended the Imperial University at Odessa from 1917 to 1920, when he fled the revolution and settled in Belgium. There he attended the Royal University at Liège, graduating cum laude in 1925. Immediately after graduation from the university, he went to work for the then young Société Belge de l'Azote (SBA), where he actively participated in research and development on various processes involved in the conversion of raw materials to ammonia. At the beginning of World War II, he emigrated to North America, where he worked for American Cyanamid in its Chemical Construction Division, which had inherited much of the technology for ammonia synthesis that the United States had obtained from Germany. He remained with the division until 1969; and as it became the independent

engineering company Chemical Construction Corp. (Chemico), he rose through such positions as Process Engineer, Chief Process Engineer, Assistant Chief Engineer, Vice President, and Senior Vice President. Since 1969, he has been active in a number of international ammonia projects as a consultant. Well known to hundreds of engineers, who have heard him at various meetings and read his papers, he remains one of the world's foremost authorities on ammonia and nitrogenous compounds.

RYLE L. MILLER, JR.

Preface

Elementary nitrogen is relatively inert and is responsible for the nonactive properties of air, of which it comprises about 78%. Combined with other elements, nitrogen is present in all living tissues; it is also present in natural and artificial textiles, in dyestuffs, in military and industrial explosives, in plastics, and so on. Most important for humans, it is a component of albumin, a basic nutrient found in vegetables, which have the ability to synthesize it directly from nitrates or ammonia-containing compounds.

Various leguminous plants incorporate atmospheric nitrogen into proteins, which appear as nodules on the plants' roots. When such plants die, the fixed nitrogen remains in the soil and thus becomes available as food for other plants. When ammonia, a combination of nitrogen and hydrogen, is injected into the soil, certain types of bacteria oxidize it into nitrites, which are in their turn oxidized into nitrates that are directly available as plant food. These nitrobacteria are able to assimilate about 220 pounds of nitrogen per acre per year.

The nitrogen fixation of leguminous plants has been recognized for 160–175 years and has been used in agricultural practices by means of a three-year rotation cycle. After two years of producing crops, the land is planted with leguminous plants, such as clover, and that crop is subsequently turned under. Also, naturally occurring nitrogenous chemicals, such as Chile saltpeter (sodium nitrate), have been put into soils as fertilizers for over 100 years. The relatively limited supply of such chemicals, combined with increased demand by a rapidly growing world population, has stimulated scientific efforts toward industrial methods of nitrogen fixation.

The first successes in these efforts were obtained near the end of the nineteenth and the beginning of the twentieth century. According to studies by W. Nernst, reasonable amounts of nitric oxides were obtained by heating air above 3000°C, followed by rapid cooling and absorption

with water, when the oxides are converted to nitric acid. Birkeland and Eyde constructed an electric-arc furnace in which such high temperatures were obtained, and their development was commercialized by Norsk Hydro Co. in Norway, where resources for production of relatively low-cost hydroelectric power abound. Large amounts of calcium nitrate were produced by neutralizing the resulting nitric acid with calcium carbonate and were shipped from Norway to many other countries. However, it became more economical, even in Norway, to produce ammonia from air and hydrocarbons.

In 1898, Frank and Caro in Germany succeeded in fixing atmospheric nitrogen with calcium carbide to form calcium cyanamide containing about 20–21% fixed nitrogen. Cyanamide was used for fertilizer as well as raw material for production of several valuable chemicals, some of which were important industrial explosives. By hydrolysis, cyanamide was also converted to ammonia. The newly formed American Cyanamid Company built one of the first cyanamide production plants at Niagara Falls, Ontario, Canada, in 1909. The conversion of cyanamide to ammonia and further to nitric acid permitted U.S. industry to meet wartime demands for explosives when handicapped by shortages of Chile saltpeter during World War I.

In 1901, Le Chatelier in France demonstrated the possibility of synthesizing ammonia from a mixture of hydrogen and nitrogen under pressure. Industrial development of this synthesis took place in Germany, when in 1909 Fritz Haber, with the aid of studies made by Nernst, le Rossignol, and Van Oordt, made considerable progress by performing the synthesis of ammonia over a catalyst. BASF scientists Bosch and Mittash adopted the Haber process, and by September 1913, the first commercial plant was put into operation at Ludwigshafen-Opau, Germany, with a capacity of 7000 metric tons per year.

The first plant in the United States to synthesize ammonia from hydrogen and nitrogen was built in Syracuse, New York, in 1921. It was followed in 1928 by a much larger one in Hopewell, Virginia. Both plants were designed and engineered by Atmospheric Nitrogen Corporation. In the meantime, other ammonia plants were built in 1926 at Niagara Falls, New York, and at Belle, Virginia, and in 1929 a plant was built at Long Beach, California. The American technology, which was developed by Nitrogen Engineering Corp. (NEC), was also used to build an ammonia plant for Kuhlmann Co., in France, in 1928, and soon after that to build a plant in the U.S.S.R. The Soviet plant used wood as raw material and fuel for syngas generation. Later, the NEC process was adopted by Chemical Construction Corp. (Chemico).

Meanwhile, Claude in France, Casale and Fauser in Italy, and Mont Cenie in the United States created other versions of the ammonia synthesis process, all different from the original Haber–Bosch process. With air supplying the nitrogen, hydrogen was produced by treatment of by-product cokeoven gas, by electrolysis of water, and by gasification of solid carbonaceous materials, such as coke, coal, lignite, and wood.

Even before World War II, processes had been developed for producing hydrogen-rich synthesis gas via reforming methane over a catalyst in the presence of steam, by I. G. Farbenindustrie in Germany, by Imperial Chemical Industries (ICI) in England, and by Shell Chemical in the United States. Shell may have been the first to produce a hydrogen–nitrogen mixture through steam reforming of natural gas. During the second World War, several ammonia plants were built in Canada and the United States using mostly ICI steam-reforming technology. Natural gas was pipelined from gas fields to plants. With few exceptions, all ammonia plants built in the United States continue to use natural gas as raw material since World War II to the present. The same is true for most of the ammonia plants built over the last three decades in Europe, U.S.S.R., Pakistan, Mexico, Algeria, Indonesia, and Japan. Also, during the 1960s, several plants were built using a naphtha-reforming process developed by ICI and others in countries without supplies of natural gas. The naphtha was supplied from local refineries or imported from abroad.

The Texaco and Shell partial-oxidation processes have permitted generation of hydrogen-rich synthesis gas from heavy fuel oil, and they will eventually be of use for coal gasification in competition with older processes by Lurgi, Koppers-Topzek, and so on.

In the meantime, the direct application of liquid anhydrous ammonia to soils was widely adopted by agriculture; and liquified ammonia became available to nonproducing countries via shipment in ocean-going tankers. For example, liquid ammonia is shipped from Trinidad to Europe and the United States for conversion to solid fertilizers.

Before the second World War, production capacity of synthesis converters was in the range of 20–50 tons per day per converter. During the war, Chemico designed and built several plants with synthesis converters having a capacity of about 80 short tons/day of ammonia. During the Korean War (1950–1951), ammonia plants were built with the converter having daily production capacities of 150–200 short tons. In 1963, the first 600 ton/day converter was installed for Amoco in Texas City, Texas. Soon after, the capacity of single converters grew to 1000, 1200, and 1500 short tons/day. Such plants were built in the United States, Western Europe, and Japan. A 1700 short tons/day converter was supplied by Pullmann–

Kellogg for a plant in Japan. More recently, ICI has developed a design for a 2500 MTD converter. In 1974, a complex of four 1500 ton/day plants was ordered from Chemico to be erected at Togliatti in Soviet Russia. The ammonia produced by this complex is pipelined to Odessa on the Black Sea and to another port on the Baltic Sea, from which it is transported to the United States and other countries.

This growth in plant capacity has been due mostly to the development of large single-line centrifugal-compression systems for air, synthesis gas, and refrigeration, along with large-capacity reforming furnaces employing well-integrated heat recovery systems. High pressure steam produced by heat from the synthesis reaction, plus steam generated during synthesis gas production, is used for steam turbines driving the compressors.

THE CONTEMPORARY PROCESS

Contemporary ammonia plants typically use natural gas for generating synthesis gas. A mixture of the preheated natural gas and steam is delivered (see diagram opposite) at about 500–550 psig to the tubes of a primary reforming furnace, where the hydrocarbons (mostly methane) in the gas are converted over a nickel catalyst to a mixture of hydrogen, carbon monoxide, carbon dioxide, and unreacted methane (Table i.1). The tubes of the furnace are heated by burning natural gas or other fuels to supply heat for the endothermic reactions:

$$CH_4 + H_2O = CO + H_2$$
$$CH_4 + 2H_2O = CO_2 + 4H_2$$
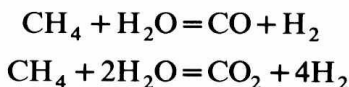
The heat remaining in the combustion gases leaving the furnace reaction section is used to preheat feed gas, air, steam, and boiler feedwater. The reaction effluent is conveyed to the secondary reformer, where more methane is made to react with steam over a nickel catalyst to produce more hydrogen, as heat is supplied by combustion of a certain part of the hydrogen with air that simultaneously introduces the nitrogen needed for ammonia synthesis. After being cooled in a waste heat boiler, the effluent from the secondary reformer enters a shift converter, where carbon monoxide reacts with steam over an iron oxide catalyst to produce still more hydrogen:

$$CO + H_2O = H_2 + CO_2$$
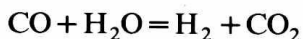
The resulting $H_2 - N_2 - CO_2$ mixture is passed through a heat recovery system, where it is cooled and most of the water vapor condensed, and then to a scrubbing column, where carbon dioxide is absorbed by a
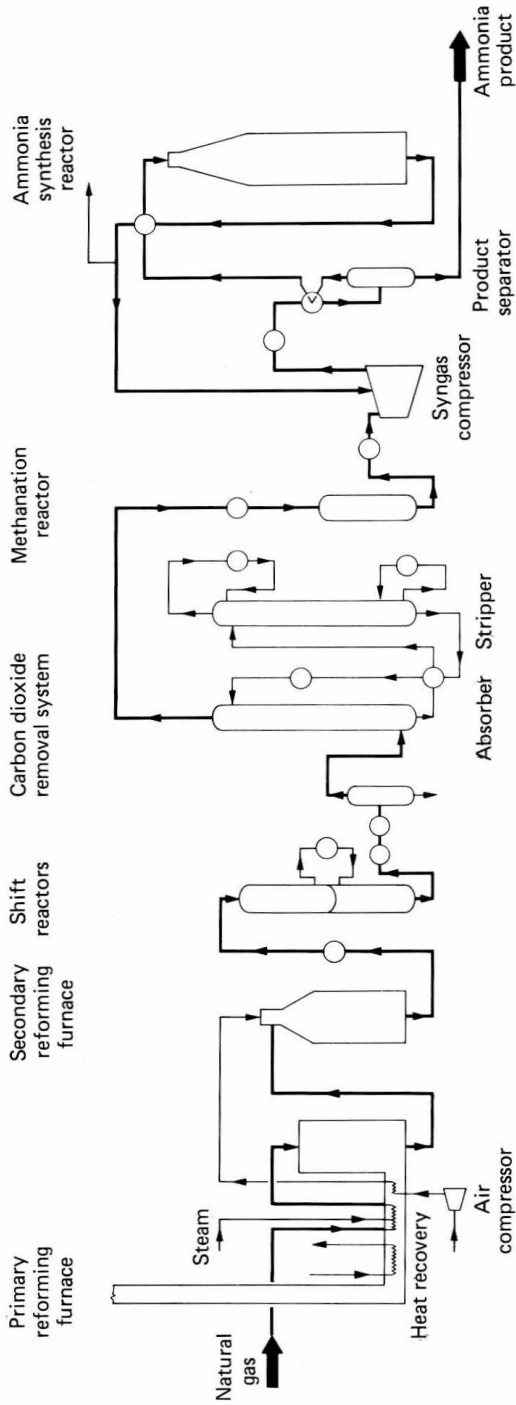
TABLE i.1 Compositions and Specific Heats of Streams in the Contemporary Ammonia Synthesis Process[a]

Location	Composition (%)								Specific Heat at $T°C$ (kcal/m^3·°C)									
	N_2	A	H_2	CO	CO_2	CH_4	NH_3	H_2O	20	100	200	300	400	500	600	700	800	900
Primary reformer exit	0.2	0	34.3	6.4	8.3	5.0	—	45.8	0.35	0.35	0.36	0.37	0.37	0.38	0.38	0.39	0.39	0.40
Secondary reformer exit	12.7	0.2	31.5	8.6	6.5	0.2	—	40.3	0.34	0.34	0.35	0.35	0.35	0.36	0.36	0.36	0.37	0.37
HT shift exit	12.7	0.2	37.9	2.2	12.9	0.2	—	33.9	0.34	0.35	0.35	0.36	0.36	0.37	0.37	0.37	0.38	0.38
LT shift exit	12.7	0.2	39.8	0.3	14.8	0.2	—	32.0	0.34	0.35	0.36	0.36	0.37	0.37	0.37	0.38	0.39	0.39
CO_2 absorber exit	23.6	0.3	73.9	0.6	0.3	0.3	—	1.0	0.31	0.31	0.32	0.32	0.32	0.32	0.33	0.33	0.34	0.34
Methanator exit	24.0	0.3	72.1	—	—	1.3	—	2.3	0.31	0.31	0.32	0.32	0.32	0.32	0.33	0.33	0.34	0.34
Synthesis loop feed	24.6	0.3	73.8	—	—	1.3	—	—	0.31	0.31	0.32	0.32	0.32	0.32	0.33	0.33	0.34	0.34
Recycle gas	19.6	3.2	59.0	—	—	12.8	5.4	—	0.32	0.33	0.34	0.35	0.36	0.37	0.39	0.40	0.41	0.41

[a]Source: ICI.

solvent, which is regenerated by heating and pressure release. The gas leaving this absorber (see flowsheet, p. xiii) still contains small amounts of carbon dioxide (Table i.1) as well as carbon monoxide, and it is treated to remove these impurities by reaction with hydrogen to form methane in the presence of a nickel catalyst:

$$CO + H_2 = CH_4 + H_2O$$
$$CO_2 + 4H_2 = CH_4 + 2H_2O$$
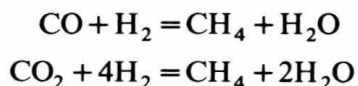
The resulting methane is inert, and the water is condensed. Thus purified, the hydrogen–nitrogen mixture with a ratio of $3H_2 : 1N_2$ is compressed to the pressure selected for ammonia synthesis, 2100–4250 psig, and is mixed with unreacted gas recycled from the synthesis reactor after this gas has been separated from ammonia in ammonia condensers. The combined feed and recycle gases are cooled by a heat exchanger and fed into the synthesis reactor, where ammonia is formed as the gases pass through beds of iron catalyst. About 10–20% of the hydrogen–nitrogen mixture reacts per pass, depending on the pressure, so that the unreacted gas is 5–10 times as much as the feed gas. The catalyst temperature is maintained at a level not exceeding 500°C either by quenching with cold feed gas or by indirect cooling. The heat of reaction is recovered by generating high pressure steam, which, together with steam produced in other sections of the plant, is used in turbines driving the compressors. The liquid anhydrous ammonia is conveyed to storage.

With the rapid growth since the 1970s in the cost of energy, the cost of feed and fuel has come to represent more than 75% of the cost of contemporary ammonia production. Thus ammonia plant designers have continued their innovative efforts toward reducing energy consumption. Two processes appearing at the end of the 1970s, for example (U.S. Pat. No. 4,148,866 and *Nitrogen*, Nov.-Dec., 1979), have reintroduced 100 atm. synthesis pressures, such as were employed in several plants using the Mont Cenis process over 40 years ago. In such processes, ammonia is recovered from the synthesis-reactor effluent through absorption with water and subsequent distillation. While its relatively higher investment costs discouraged its use when energy was less expensive, the Mont Cenis process may have come to be widely represented in analogous process schemes during the 1980s.

THE PURPOSE OF THIS BOOK

The world's production capacity for ammonia was 93 million tons in 1977 and is expected to grow to 137 million tons by 1985. An enormous expenditure of capital is required to provide this expected increase in

capacity, and, more importantly, a large corps of engineers with training and experience is required both now and in the future for the design, erection, and operation of the ammonia industry.

This book represents a humble though aggressive effort toward surmounting that more important problem. It is intended to supply all the necessary information and data needed by a qualified engineer to choose an optimum system and design large-capacity production facilities for ammonia synthesis. It aims to be a working tool that engineers can use to carry on their work without wasting time searching elsewhere for information pertinent to the process. The text consists of four sections: Section 1, Ammonia Synthesis; Section 2, Syngas Generation; Section 3, Carbon Dioxide Removal; and Section 4, Final Purification. Each of these sections contains descriptions with data in tables and charts to serve the needs of design engineers and operators. Descriptions of the more important items of equipment specific to ammonia production are accompanied with illustrations supplied by world-renowned engineering companies and equipment manufacturers.

In addition to relying on my own 55 years of experience with ammonia production, I have gratefully accepted help, both technically and through encouragement, from many friends in the industry. Among my many sources of information, the following were particularly applicable to this text:

- *Catalyst Handbook*, by authors from the Agricultural Div. of Imperial Chemical Industries, Ltd., Springer-Verlag, London, 1970.
- *An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia*, 3rd ed., by Dr. Anders Nielson, Jul. Gjellerups Forlag, Copenhagen, 1968.
- *Measurement and Calculation of Temperature and Conversion in Fixed-Bed Catalytic Reactors*, by Dr. Jergen Kjer, Jul. Gjellerups Forlag, Copenhagen, 1958.
- *Gas Purification*, by A. J. Kohl and F. C. Riesenfeld, Gulf Publishing Co., Houston, 1974.

While the text of this book is directed primarily to the needs of engineers and operators involved in the design engineering, construction, and operation of ammonia manufacturing facilities, it should also have value for chemical engineering students and their teachers. Practically every unit operation is examined in this book in terms of practical applications that supplement the general theory.