

Chapter 2

Electric Arcs, Cyanamide, Carl Bosch and Fritz Haber

2.1 Electrochemistry

Concerns over depletion of reserves of caliche, and the Chilean hold on the saltpetre monopoly, led leading European scientists to encourage investigations into methods for the direct fixation of atmospheric nitrogen. In Britain they included Sir William Crookes (1832–1919), who in 1898, in his presidential address to the British Association for the Advancement of Science, at Bristol, spoke of a Malthusian threat represented by an impending fertilizer crisis once the Atacama Desert's deposits were spent. Crookes' speech on "The World's Wheat Supply," predicting certain doom unless the nitrogen problem was solved, was widely publicized. Not everyone however agreed with his prognosis. Some thought that he was given over to exaggeration [1, 2]. Estimates of reserves varied, from two decades to half a century, and in the case of the nitrate industry to over a century. During 1871–1880, Crookes had been a director of the Native Guano Company, founded in London in 1869 to convert human excrement into fertilizer. In his 1898 speech he alluded to investigations into the capture of atmospheric nitrogen with the aid of electricity.

By this time electrochemistry had become an established industrial field. Early processes, for aluminium and inorganic chemicals, were based on electrolysis. In 1886, Charles Martin Hall (1863–1914) in the United States and, independently, Paul L. V. Héroult (1863–1914) in France, reduced aluminium oxide (alumina) to the free metal, aluminium [3]. The process involved dissolving alumina in fused cryolite, a natural mineral containing aluminium. This was followed by a process for preparing magnesium. From 1884, Chemische Fabrik Griesheim in Germany began to develop electrochemical processes, in association with two other firms. This led to the foundation of Chemische Fabrik Elektron in 1892 to work a chlor-alkali (chlorine-alkali hydroxide) process based on electrolysis of a solution of potassium chloride. Elektron's factory, opened in 1895 at Bitterfeld, north-east of Halle, was powered by inexpensive local brown coal. The same process

was adopted by BASF at Ludwigshafen to manufacture the potassium hydroxide required in its synthetic indigo process. In the United States, Herbert H. Dow (1866–1930), at Midland, Michigan, during 1889–1890 developed a process for obtaining bromine by electrolysis and soon after adapted this to electrolysis of sodium chloride to give sodium hydroxide and chlorine.

Another approach used electrothermal reactions, those carried out at high temperatures in electrically heated furnaces. In 1891, the American Edward Goodrich Acheson (1856–1931), using such a furnace, discovered, by heating a mixture of coke and quartz, the refractory, abrasive material, silicon carbide, which from 1894 he marketed as Carborundum. In May 1892, the Canadian inventor Thomas Lovell Willson (1860–1915), then in Spray (later Eden), North Carolina, heated lime with tar in an electric arc furnace in an attempt to produce calcium metal from the lime. Instead, he obtained calcium carbide, which with water produced acetylene. Willson collaborated with James Turner Moorhead, who commenced carbide manufacture in 1894. By the end of the decade acetylene had become an important source of lighting—with a flame far brighter than that from coal gas—used in lamps for home and industrial purposes. In 1896, train lighting with acetylene lamps was introduced in Germany. Carbide, and the acetylene industry, was of interest to the young German engineer Walther Rathenau (1867–1922), whose father, Emil Rathenau (1838–1915), had founded the Allgemeine Elektrizitäts-Gesellschaft (AEG) electrical-engineering corporation [4, 5]. Walther Rathenau joined the board of AEG in 1899.

AEG saw acetylene lighting as a potential competitor to the electrical lighting system that was a mainstay of its business, and, not wishing to lose out to the rival form of illumination, established the Elektrochemische Werke GmbH in 1893 at Bitterfeld. However carbide for acetylene lighting was not the main product. Instead the factory produced chlorine and sodium hydroxide from electrolysis of salt. Five years later, AEG built a second electrochemical factory, with a carbide furnace designed by Walther Rathenau, at Rheinfelden, on the Lower Rhine, near Basel, Switzerland, but encountered technical difficulties, and leased the site to Elektron [6]. In 1898, Elektron merged with Griesheim to create Chemische Fabrik Griesheim-Elektron.

The Schuckertwerke electrical firm of Nuremburg opened carbide factories in Norway, under the ownership of a Swiss firm, and Bosnia. In Norway, Schuckert collaborated with engineer Knud Bruyn (1855–1941), founder in 1898 of the Hafslund company, that embarked on construction of the first large hydroelectric power station in the country. The availability of cheap hydroelectricity became a critical factor in the siting of many carbide factories. This is why the British Aluminium Company, on the west coast of Scotland, manufactured carbide for acetylene from 1896 until 1903. United Alkali in England took up small-scale manufacture during 1902–1904. In both cases, costs were high, and demand was restricted, in part because of the widespread use of electrical lighting. Newer uses for acetylene emerged, including in welding, and in the synthesis of chlorinated solvents and acetic acid. Carbide, moreover, was to become an important starting point for one of the main synthetic nitrogen fertilizers discussed here.

2.2 The Burning of Air

By the mid-1890s, scientific and technical interest in electrothermal processes was already aroused among inventors interested in fixing atmospheric nitrogen. The main limitation of thermal reactions carried out at elevated temperatures was the lack of reliable high voltage transmission systems, which restricted geographical distribution of technically viable processes to localities that offered generation of cheap hydroelectric power, or access to sources of low cost coal. Nevertheless by the turn of the century electricity generated at Niagara Falls was transmitted over 150 miles. In 1897, Lord Rayleigh (1842–1919), taking the basic idea from Henry Cavendish, suggested the industrial combination of nitrogen with oxygen in an electric arc, which directed a number of studies into gaseous electrothermics. This was not only a stimulus to further investigations in laboratories and workshops in Europe and the United States, but also an indication of frantic efforts being made to gain fame and fortune through capturing nitrogen. In all the electric arc methods, and there were many, though very few ready for industrial application, discharges arising from the application of mainly single phase alternating current were turned into flames when subjected to blasts of air. The general idea was to spread out and concentrate the discharge, increasing its contact with the air, and thereby form nitric oxide.

The work was daunting, and until the turn of the century invariably ended in failure. In Manchester, England, the electric arc of Arthur McDougall and Frederick Howles (1899) met with no success, at least on a technical scale. In the United States, the similar arc process of Charles Schenk Bradley and Robert D. Lovejoy was introduced in 1902 at Niagara Falls, New York State, by the Atmospheric Products Company. It was not viable commercially due to the complexity of the furnaces when scaled up; the factory was closed within two years [7].

Another electric arc method was devised during the first years of the 20th century by the Polish chemist and inventor Ignacy Mościcki (1867–1945), who moved back and forth between chemistry and politics. He studied chemistry at Riga Polytechnic, graduating in 1891 under organic chemist Karol A. Bischoff, and took up residence in Warsaw, then in the western part of the Russian Empire. However, he did not remain long in Warsaw. A Polish patriot and socialist, he plotted with others to assassinate the governor of the city. In 1892, sought by the Tsarist police, he moved to England, where he followed chemistry courses at Finsbury Technical College. In 1896 he was appointed assistant to physicist Józef Wierusz-Kowalski at the University of Freiburg. There he invented his electric arc method for fixing atmospheric nitrogen, and with the collaboration of Kowalski set up an experimental plant in the city around 1903. Shortly after they began manufacture of nitric acid, trading as Société de l'Acide Nitrique. However it was at the time no more efficient than the other early methods [8].

More success was achieved in 1903, after Norwegian physicist and inventor Kristian Olaf Bernhard Birkeland (1867–1917), at the University of Kristiania (Oslo), met engineer Samuel Eyde (1866–1940) during a dinner party at the home of Norwegian cabinet minister Gunnar Knudsen (1848–1928), who later served

Fig. 2.1 Kristian Birkeland.
(Yara International ASA)



twice as prime minister of Norway. Birkeland, born in Kristiania, had engaged in high-latitude Norwegian polar explorations to gather magnetic field data, from which global patterns of electric currents in the region were established; developed a theory of the Aurora Borealis, that was ridiculed, particularly by British scientists, though proved correct in the 1960s; and worked on electromagnetic devices, including a cannon, though without much success (Fig. 2.1) [9]. Invariably short of funding for his research, Birkeland received some assistance towards his expeditions from Knudsen, who had a financial interest in Birkeland's cannon. During a demonstration on 3 February 1903, the cannon failed due to a short circuit, causing massive flames to appear at the muzzle. Birkeland noticed that the flames were deflected by the electromagnetic field. It was just a week or so before Knudsen's dinner party.

Eyde, born in the port town of Arendal, north of Kristiansand, close to the extreme south of Norway, studied engineering in Berlin, then worked on railway construction projects, prior to forming the successful engineering firm of Gleim and Eyde [10]. By 1903, Eyde was interested in developing hydroelectric power generation. At Knudsen's party, Eyde, well aware of Birkeland's interest in electromagnetism, suggested the capture of atmospheric nitrogen by the most powerful flash of artificial lightning that could be achieved. Birkeland, apparently, used his observation of the deflection of flames from the mouth of the cannon to devise within days an electric arc incorporating an electromagnetic field that spread out and concentrated the discharge. This mode of producing continuous artificial lightning enabled capture of nitrogen by what appeared to be a technically viable method. The first patent application was filed on 20 February 1903.

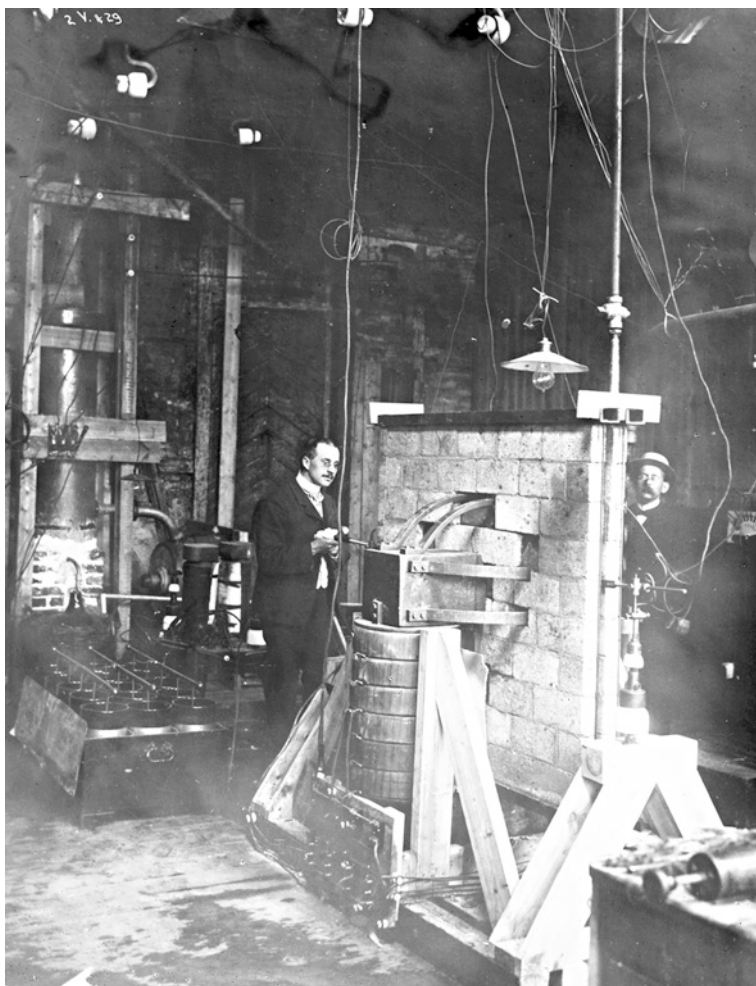


Fig. 2.2 Birkeland-Eyde experimental set up, Frognerkilen Fabrik, Kristiania, 1903. Christian Birkeland is standing *at right*, Samuel Eyde *at left*. (Yara International ASA)

Subsequently Birkeland and Eyde developed what became known as the Birkeland-Eyde electric arc process, with, in 1903, an experimental installation at the Frognerkilen Fabrik, of Kristiania (Figs. 2.2 and 2.3), and, in October, a pilot plant at Ankerløkken, where a 1-m diameter furnace was tested. In this, as in other arc processes, atmospheric nitrogen, introduced near the electrodes, was captured as nitric oxide. Birkeland's lightning, also called an electric sun, had the appearance of a circular sheet of flame, created when the arc between the two electrodes (supplied with alternating current), at right angles to a magnetic field, was rapidly deflected from one side to the other. It was this arrangement that concentrated the discharge, expanded the arc, and enabled the working of large furnaces (Figs. 2.4 and 2.5) [11].

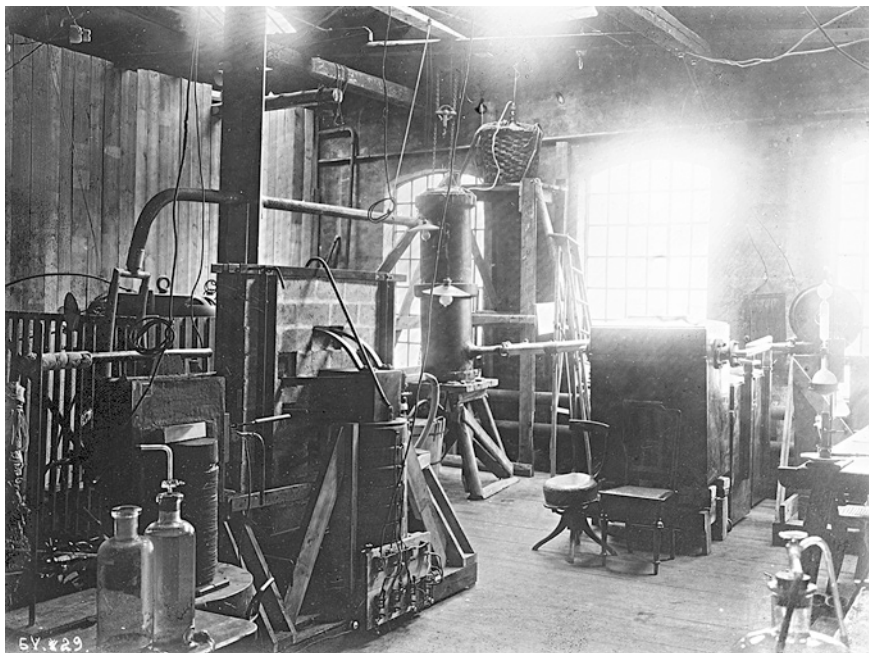
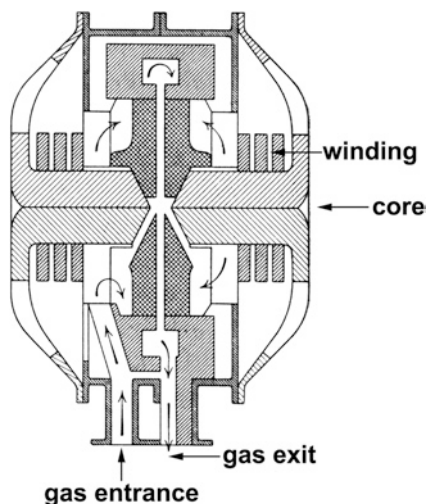


Fig. 2.3 The most prominent feature of the Birkeland-Eyde apparatus was the large electromagnet, here seen on the experimental version at Frognerkilen Fabrik, Kristiania, 1903. (Yara International ASA)

Fig. 2.4 Sectional elevation of Birkeland-Eyde electric arc apparatus for capture of atmospheric nitrogen, at right angles to arc disc. (Adapted from Georg Lunge, *Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige*, 2 vols. Braunschweig: Friedr. Vieweg & Sohn, 1916, vol. 1, p. 259)



At the end of 1903, Eyde and Birkeland, jointly with the Swedish bankers Knut Agathon Wallenberg (1853–1938) and Marcus Wallenberg (1864–1943), backed by Stockholms Enskilda Bank, set up the firm Elektrokemisk, followed by Notodden

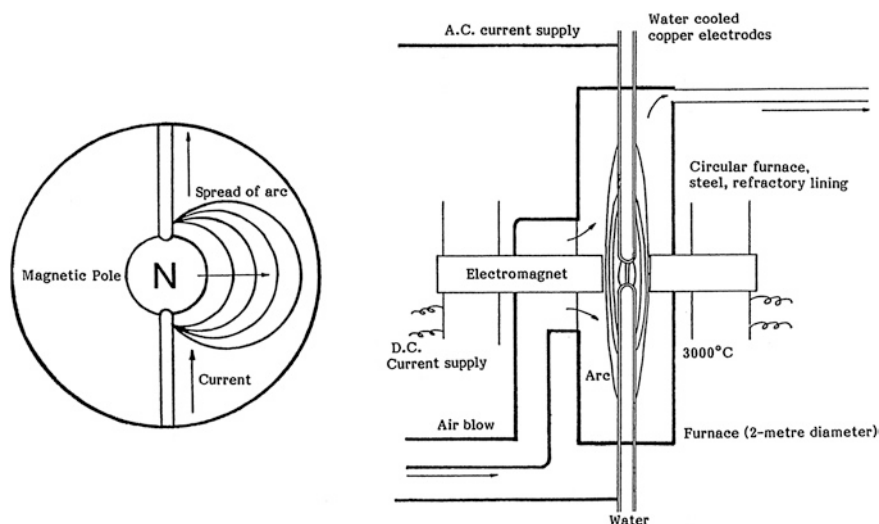


Fig. 2.5 General arrangement of Birkeland-Eyde electric arc apparatus. The rapid to-and-fro movement of the semi-circular arc created an apparent spherical shape

Saltpeterfabriker AG (1904) to undertake nitrogen fixation at Notodden (in Telemark). Towards the end of the year a prototype 2-m diameter iron electric arc apparatus was constructed in a new test facility, at Vassmoen, near Arendal. The nitric oxide product readily formed the dioxide which with water gave nitric acid. The acid was then converted into calcium nitrate. Trials of this product as fertilizer were undertaken at the Ås agricultural college; they indicated that calcium nitrate was as good a fertilizer as sodium nitrate. Work on a small factory began on 2 May 1905 at the Notodden site, with three 500-kW furnaces, working at an annual capacity of 2,000 tons of nitrate. Power was supplied by the Tinfos hydroelectric power station, opened in 1901 [12].

The gas leaving the furnace contained 2–3 % of nitric oxide. Rapid quenching in an aluminium vessel lowered the temperature to prevent decomposition of the oxide. The cooled nitric oxide gas was passed through oxidation chambers, vertical iron tanks lined with acid-proof stone, to form dioxide and other oxides, particularly nitrogen tetroxide, N_2O_4 (the main reacting species in the liquid phase; in the past it was often called, incorrectly, nitrogen peroxide). In the presence of water, dilute nitric acid was formed. This was the earliest type of nitric acid absorption plant. In the first factory, the dilute acid was passed through a series of four stone towers, each twenty metres in height, and filled with broken quartz, over which the acid trickled. The nitric acid was concentrated in the first tower to 50 %, and to progressively lower concentrations of acid in succeeding towers, such that in the fourth tower the concentration was just 5 %. The more dilute acids were then progressively recirculated to provide a greater volume of 50 % acid. In a fifth stone tower, filled with bricks, residual acid was reacted with limestone to give calcium nitrate. After further processing, concentrated calcium nitrate was run

into 200-l iron drums, ready for shipping. Later, wooden barrels, of 100 kg capacity, were introduced. Nitrous acid was also produced, for reaction with sodium carbonate (soda) in wooden towers to give sodium nitrite, exported to German dye firms for use in the manufacture of azo dyes.

Details of the Birkeland-Eyde process were described by the chemist Otto Nicolaus Witt (1853–1915) on 25 November 1905 at the inauguration of the new technical chemistry institute at the Royal Technical College Berlin (Königliche Technische Hochschule zu Berlin, also known as the Technische Hochschule Charlottenberg). Witt had made his name as a dye chemist while working in England, in particular with the development of azo dyes and a theory of colour and constitution. He was now a leading promoter of electrothermics, thoroughly familiar with the process after serving as one of twelve consultants to investors in the Birkeland-Eyde process who arrived at Notodden by continental train in the early hours of 14 July 1905 to evaluate the commercial viability of manufacturing nitric acid [13]. Following Crookes, Witt also warned of future shortages of Chile saltpetre, suggesting that the caliche would begin to run out by the mid-1920s. Witt saw the solution to the problem in the electric arc [14]. Birkeland and Eyde were in the audience, as were Heinrich von Brunck (1847–1911), managing director of BASF, and his colleague the chemist Rudolf Kneitsch (1854–1906), also at that time committed to capture of atmospheric nitrogen through electric arcs. Witt brought von Brunck and Eyde together for informal business discussions at his home.

One week later, on 2 December 1905, Norsk Hydro-Elektrisk Kvælstofaktieselskab (Norwegian Hydroelectric Nitrogen Company), better known as Norsk Hydro, was founded with mainly French capital (from Banque de Paris et des Pays-Bas, or Paribas). Marcus Wallenberg was first chairman of the board [15]. Trials with Norsk Hydro's nitrate were conducted in Sweden, France, Germany, Austria-Hungary, Italy and Great Britain. The Birkeland-Eyde process was at the heart of what was now to become Norway's first multinational corporation. Six months earlier, in June, Norway gained its independence from Sweden.

Another of the experts brought in by Birkeland and Eyde was the British physicist Silvanus P. Thomson (1851–1916), at London's Finsbury Technical College. Mościcki was probably among the students who followed Thomson's popular courses on electricity and electrical engineering at the college during the 1890s. On 2 February 1906, Thomson lectured on electrothermal capture of nitrogen as the oxide at London's Royal Institution. It was certainly a heady time for those following up the latest developments in electrothermal nitrogen fixation. Six months later, on 2 July 1906, Birkeland addressed the Faraday Society in London on nitrogen fixation with electric arcs, with special reference to the working of the then newly constructed Norsk Hydro factory at Notodden. The discussion revealed that Thomson and Witt had visited, in addition to Notodden, the test facility near Arendal, where, as Thomson pointed out [16]:

all manner of small variations in the conditions of manufacture were being carefully and thoroughly investigated, using the most modern scientific methods of recording, [and] making frequent analyses....Not satisfied with a few days' working of the process, Professor Otto Witt had the whole apparatus cleared out and a new test run started with perfectly

fresh raw materials. This test lasted for two weeks...The various results agreed sufficiently closely to enable the Commission to assert that an output of 500 kg of nitric acid, per kilowatt year, could be looked for with confidence in any new plant that might be laid down.

Thomson also suggested that it was Birkeland's work on the Aurora Borealis that led to his studies of the deflection of "electric flames in magnetic fields," though, as noted earlier, other sources state that it was the effect of electromagnetism on the flame exiting from Birkeland's cannon on the day it misfired that served as an inspiration.

Fifteen months later, in October 1907, the Notodden facility became engaged in full-scale commercial production of calcium nitrate (Norges-salpeter, Norwegian saltpetre, nitrate of lime, air-saltpetre). Electricity came from the new Svelgfooss power station, 5 km away, the largest in Europe, and second largest in the world after that of the Ontario Power Company, at Niagara Falls (opened in 1905) [17]. By 1909, thirty-six furnaces had been installed, thirty-two powered by Norsk Hydro's Svelgfooss station and four by the Tinfos power station. The total investment was the equivalent of six million US dollars. The annual production capacity was claimed to be of the order of 20,000 tons of calcium nitrate. Further expansion took place at Notodden in 1910.

In 1911, what became known as the Rjukan facility, situated at S  heim in Vestfjorddalen, some distance northwest of Nottoden, was inaugurated (Fig. 2.6). Electricity was generated nearby, at the Vemork power station, next to the

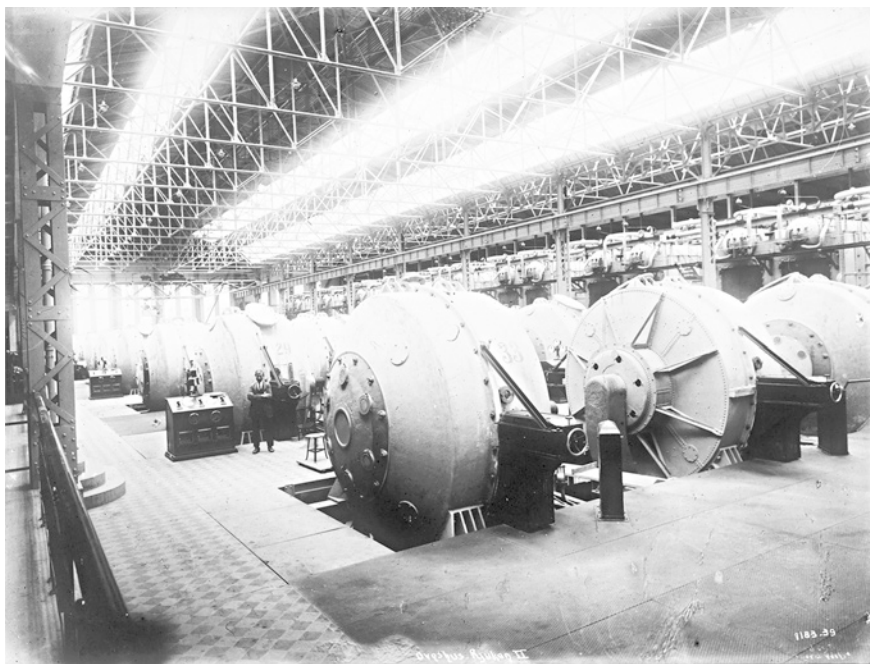


Fig. 2.6 Birkeland-Eyde furnaces, Rjukan factory, 1912. (Yara International ASA)

Rjukanfossen waterfall on the Måne (Maan) River. This hydroelectric plant, also, known as Rjukan I, was the largest power station in the world when built (1907–1911). It generated 140,000 horsepower from ten dynamos.

In November 1911, Norsk Hydro employed 143 officers and 1,340 workmen at its manufacturing sites. In 1912 a new factory was built at Glomfjord, in northern Norway. By 1913, at Rjukan alone, two thousand workmen and four hundred “engineers and officers” were employed [18]. During 1912–1913, demand for Norwegian nitrogen doubled. An even larger power station at Sâheim (Rjukan II) was brought into operation in 1916, with nine generators that supplied 167,000 horsepower to forty furnaces located in the same building [19].

Granite absorption towers, seventy feet high and twenty feet in diameter, were installed at Rjukan. Eventually, the introduction of earthenware filling, instead of quartz, enabled operations in smaller, and less expensive, towers. Dilute nitric acid was concentrated, it was claimed, to 98 % by making use of the hot gases leaving the furnaces. Additional acid towers were installed bringing the total to thirty-six. The remote location and the large number of workers required for the factory and power plant led to the founding of a company town, Rjukan, and the laying down of a 16 km railway line (during 1908–1909) for transport of nitric acid and other nitrogen products to Mael, on Lake Tinnsjø. There, the railway wagons were loaded onto a train ferry, which crossed the lake to Tinnoset, where they continued by another railway to Nottoden (Figs. 2.7 and 2.8). The nitrogen products were



Fig. 2.7 Location of the nitrogen industry in southern Norway, early 1900s. Norsk Hydro (Birkeland-Eyde) factories were located at Notodden and Rjukan. The North-Western Cyanamide Company’s factory was located at Odde, southeast of Bergen



Fig. 2.8 Nitrogen products from Norsk Hydro's remote Rjukan facility were carried by both rail and water transport to the port at Skien, including a railway ferry that plied the 30 km from Mael to Tinnoset across Lake Tinnsjø, and until 1919 a barge from Notodden, on a branch of the Telemark Canal, then on the main canal, to Skien, a distance of 54 km. This is the train ferry terminal at Tinnoset in 2009. (Photo by Nick Lera)

then taken by canal barge to Skien for export. The concentrated acid was safely transported in aluminium tanks. By 1914, designs had been drawn up for steamships to carry 600–700 tons of acid to Britain. In 1919, an extension of the railway south from Nottoden replaced the canal to Skien. The output of Norges-salpeter in 1906 was 1,200 tons, in 1911, 15,000 tons, in 1912, 71,000 tons, and in 1916, 110,000 tons. The other products were sodium nitrite and refined sodium nitrate. In 1908, the main export customer was Germany, which took 3,841 tons, out of a total production of 7,082 tons; in 1910, Germany and Britain each took just under 5,000 tons out of a total of 13,530 tons, as recorded by the Central Bureau for Statistics at Kristiania [20–22].

The production of ammonium nitrate for the British market by Norsk Hydro is not without interest. To satisfy demands from manufacturers of explosives, mainly used in mining, ammonia liquor from British gas works was sent by sea, canal, and train to Nottoden, where it was combined with nitric acid made by the electric arc process to afford ammonium nitrate, which was then sent to Britain, mainly to the Nobel factory at Ardeer, Ayrshire, on the west coast of Scotland.

Fig. 2.9 Portrait of Kristian Birkeland, from a painting by Asta Nørregaard, 1906. (Yara International ASA)



This somewhat long-winded procedure, and the fact that in one direction the liquid sent from gas works was mainly water, caused one British observer to comment somewhat wryly: “It is this kind of thing that has caused scientific and engineering circles in Germany to get the impression of us which they have” [23].

Birkeland continued with development of related processes, including production of concentrated nitric acid, until around 1910. However, this was far removed from his main interest (Fig. 2.9). He sold some of his shares in Norsk Hydro during 1906 and 1907, and the remainder in 1910. The wealth that he accrued from the electric arc process gave him the independence to conduct further expeditions and academic work of his own choice. He died in Tokyo in 1917, apparently after taking an overdose of Veronal, the first synthetic barbiturate, introduced by Bayer.

Also worked in Norway, jointly with Norsk Hydro, was the BASF electric arc process of Otto Schönher. This came about following meetings between Birkeland, Eyde, Heinrich von Brunck, and Rudolf Kneitsch in 1905 on the occasion of Witt’s Berlin lecture. Otto Schönher (1861–1926), born in Chemnitz, studied chemistry at the Technische Hochschule Dresden, then spent some years

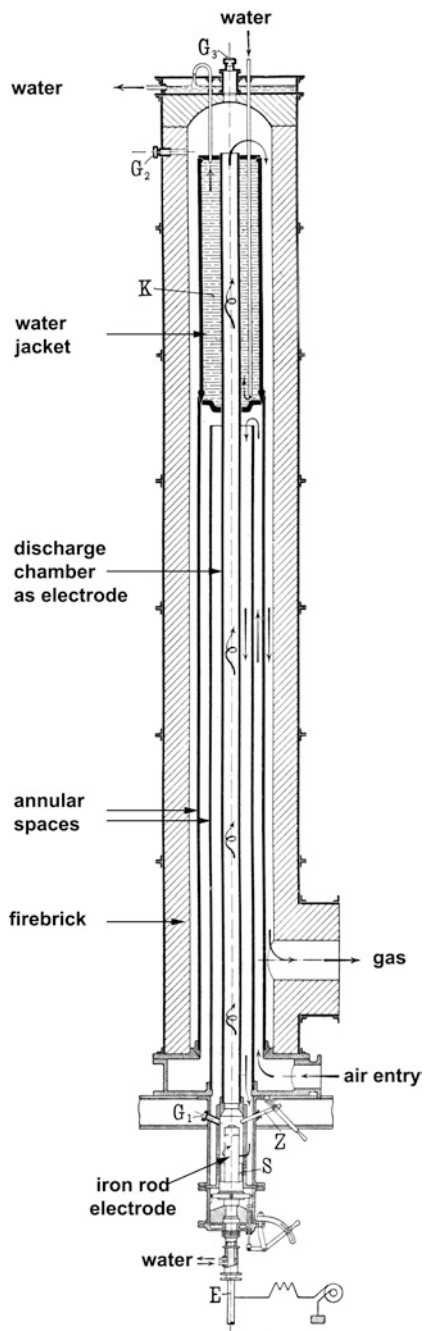
in industry, before joining Karl Elbs (1858–1933) at the University of Giessen in 1894 to undertake research in electrochemistry [24]. Schönherr received his doctorate in 1895, and in June 1896 joined BASF. From 1899, working under Kneitsch, and encouraged by von Brunck, he investigated electrothermal capture of atmospheric nitrogen [25]. In 1905, a long, slender discharge furnace, an iron pipe incorporating within concentric iron pipes surrounding an inner electrode, was developed in collaboration with the electrical engineer Johannes Hessberger (1871–1934). Unlike the Birkeland-Eyde process that spread the arc in a magnetic field, this process relied on a long, steady column of discharge.

The lower end of the furnace incorporated an insulated electrode, comprising an iron rod inserted into a water-cooled copper block, used to start the arc in the main, inner, electrode. Air introduced at the bottom of the furnace with a rotary motion moved up an intermediate pipe, and travelled down a second pipe that surrounded the inner electrode chamber, where it was preheated. The air then entered the discharge region, moving up in a whirling motion, and again down, this time within the outer annular ring, next to the firebrick lining of the furnace (Fig. 2.10). This arrangement ensured a longer contact with the arc and heated area than in rival processes. The gas mixture left the furnace near its lower end. The process consumed 14,800 kWh per metric ton of nitric acid, equivalent to just under 67,000 kWh per metric ton of nitrogen [26]. From the absorption towers, 40 % nitric acid was obtained. It was further concentrated, or reacted with limestone to give calcium nitrate.

On 11 September 1906, Norsk Hydro, and its Swedish and French investors, signed an agreement with BASF, in partnership with Bayer and AGFA, the Dreibund, for joint developments at Rjukan. Norsk Hydro took care of the hydroelectric plant; BASF was responsible for the chemical side, including production of nitric acid. This arrangement also affected Notodden. There were considerable polemics over the most suitable type, or the number of each type, of electric arc furnace, Birkeland-Eyde or Schönherr, to be installed. Relations quickly became strained. Eyde was opposed by the other partners, and forced to step down from involvement in the various concerns. In the autumn of 1907, the BASF electric arc furnace was tested at a site in Kristiansand. In 1909 ten such furnaces, each one twenty-three feet in height, were installed at Notodden [27]. A second group of taller furnaces, ninety-six in all, were installed at the Rjukan facility in 1911. The latter were worked alongside Birkeland-Eyde furnaces for comparative evaluations [28].

The yield of desired nitric oxide from the BASF process was higher than in the Birkeland-Eyde process. Also, the cost of the BASF furnace was lower, and repair and maintenance costs were not great. However, taller BASF furnaces were problematic in operation. BASF commissioned the academic physicist Jonathan Zenneck (1871–1959) of the Technische Hochschule Braunschweig to take up residence in Rjukan for some time in an effort to bring about improvements. In 1910, BASF consultant Fritz Haber was also called upon to assist. He and an assistant undertook experiments with a laboratory-size Schönherr furnace and found that an increase in pressure of the air blown into the tube had no advantage [29]. Little came out of these efforts. The Birkeland-Eyde furnaces were found to be more efficient than the newer BASF furnaces. BASF and Norsk Hydro parted company

Fig. 2.10 Schönherr (BASF) electric arc apparatus for capture of atmospheric nitrogen. (Adapted from Georg Lunge, *Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige*, 2 vols. Braunschweig: Friedr. Vieweg & Sohn, 1916, vol. 1, p. 266)



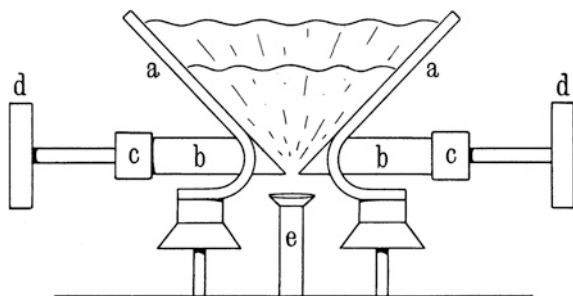


Fig. 2.11 Pauling electric arc apparatus for capture of atmospheric nitrogen: **a** electrodes; **b** iron knives; **c** insulation; **d** distance regulators; **e** air nozzle. (Georg Lunge, *Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige*, 2 vols. Braunschweig: Friedr. Vieweg & Sohn, 1916, vol. 1, p. 254)

after Eyde returned, through arranging a buyout of BASF shares, on 28 September 1911 [30]. Meantime, BASF had become involved in another, quite different, way of fixing nitrogen based on the work of Haber.

A few other electric arc processes were developed on an industrial scale, including, in 1902, one by Harry Pauling (1875–1956), citizen of Brandau, Bohemia, Austria-Hungary, in which a stream of fast moving air was blown against an arc struck between two diverging electrodes. This horn-arrester, based on the horn-break lightning arresting device, consisted of two hollow iron electrodes arranged to form a “V”. Charge was applied to thin horizontal knives at the base of the furnace to start the arc [31]. Air blown up through a nozzle into the lower part of the arc was deformed into a flame (Fig. 2.11). The process was used at Salpetersäure-Industriegesellschaft Gelsenkirchen, of Cologne, at Patsch, near Innsbruck, from 1904 (with 24 furnaces), at La Nitrogène Cie., Roche-de-Rame, Hautes-Alpes, France, from 1908 (18 furnaces were installed by the end of 1912), and at Legnano, near Milan, from 1911. All these factories relied upon hydroelectric power. Nitric acid of 35–40 % concentration was obtained from absorption towers; it was concentrated further by hot gases generated during the arc process. Harry Pauling guaranteed “60 g of 100 % HNO_3 per kW-hour of electrical energy, measured at the entrance of the electric transmission line into the factory” [32]. Pauling worked in partnership with his brother, G. Pauling. They employed the British research chemist Glyn William Arnold Foster, who shortly after 1900 had undertaken research with Fritz Haber. In the United States the Pauling process was investigated by James B. Duke (1856–1925) and the Du Pont company. Duke, who had made his fortune in tobacco, invested in hydroelectric power from 1904, and obtained US rights to the Pauling process. He set up the Southern Electrochemical Company, of Nitrolee, South Carolina, using hydroelectric power to produce nitric oxide, and in turn nitric acid. Production began in 1913. However, the high cost of the acid, 19,500 kWh per ton, caused closure of the plant in 1916.

During 1905–1908, the Swiss chemist Philippe-August Guye (1862–1922), at the University of Geneva, developed an electric arc process in collaboration with

his brother, the physicist and electrical engineer Charles-Eugene Guye (1866–1942), also at Geneva, and chemist and agronomist Aloys Adrien Naville (1853–1912). This emerged from an electric arc method they had investigated in the mid-1890s. It was similar to the Pauling process in that a horn arc, with cylindrical electrodes, was used. Any technical application, if at all, was limited [33].

By late 1907, Ignacy Mościcki had improved his arc process based on what was described as a rotating circular arc. It was adopted in Switzerland by Aluminium-Industriegesellschaft Neuhausen at Chippis, near Sion, on the River Rhône [34]. Concentrated nitric acid was produced there from 1910. In 1912, Mościcki moved to Lwów (Lvov) University of Science and Technology, where until 1925 he taught chemistry and technical electrochemistry.

At the time of the 1906 jubilee celebrations for the foundation of the synthetic dye industry by William Perkin, there was a further considerable emphasis on electrical methods for capturing nitrogen. And, it appeared, foremost among the international companies and inventors engaged in research towards their exploitation was, rather than Norsk Hydro, BASF that had made good progress with the Schönherr electric arc furnace. Celebrants at the New York event were informed by Hugo Schweitzer that [35]:

The experience gained in electric methods is being applied to the problem of using the nitrogen of the air, and to judge from past successes it will not be many years before the Badische Anilin- und Soda-Fabrik [BASF], in whose laboratories experiments in this direction are being conducted, will bring into the market nitrates, nitrites and nitric acid made from atmospheric nitrogen instead of Chile saltpetre, the supply of which is calculated to last no longer than about twenty years.

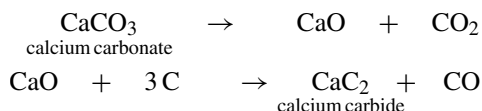
In November 1907, encouraged by results obtained from the Schönherr electric arc, BASF's von Brunck advised the Prussian Ministry of Trade and Business that the firm's "epoch-making" electric arc process offered an increase in yield over the Birkeland-Eyde process. Also, that the cyanamide process (see next section) was not suited to manufacture of nitric acid required for explosives and for use in chemical industry. BASF was planning to build a factory to work the Schönherr process in Bavaria next to the River Alz, a tributary of the River Inn, 7 km downstream of the small market village of Trostberg (population 174). The site was linked by a branch railway to Traustein. However, the Bavarian government was not keen on this, and as a result BASF continued its arrangements with Norsk Hydro.

2.3 Cyanamide

Another approach that relied on cheap electrical power involved the reaction in an electric furnace between calcium carbide, made from coal and lime, and atmospheric nitrogen to afford the calcium salt of the compound cyanamide, NC-NH_2 . The early commercial product (sometimes called lime nitrogen) reportedly contained 12–15 % of nitrogen, later increased to 23 % of nitrogen.

In the early 1890s Ferdinand Frédéric Henri Moissan (1852–1907), professor of toxicology at the School of Pharmacy in Paris, and an expert in carbides, reacted

coke and calcium carbonate (limestone) in an electric furnace in his laboratory to form, in two steps, calcium carbide.



Moissan conducted his experiments under more careful conditions than those used by Willson, and claimed to have obtained calcium carbide in a crystalline form. Intriguingly even in the 1950s, it was stated that “no one has been able to repeat his preparation of ‘pure’ calcium carbide” [36]. Moissan reported that the carbide did not react with nitrogen even at an elevated temperature. He was soon proved wrong.

In 1895, the study of the absorption of nitrogen by carbides was taken up in Germany by chemists Adolph Frank (1834–1916) (Fig. 2.12) and Nikodem Caro (1871–1935) (Fig. 2.13). Frank studied pharmacy, chemistry, and technology, and in 1863 received his doctorate in chemistry at Göttingen. It was for a treatise on production of sugar, an industry in which he was already involved. Later he worked on the application of potash from the important deposits at Stassfurt in agriculture, and then managed a glassworks in Berlin-Charlottenberg. In 1885 he became an independent consultant, with a special interest in the paper industry [37]. Nikodem Caro (a relative of Heinrich Caro, head of research and development at BASF), grew up in Lodz, Upper Silesia. He arrived in Berlin in 1888, where he studied chemistry at the Technische Hochschule Charlottenberg. Four years later, in 1892, he was awarded his doctorate from the University of Rostock [38]. Over the next three decades or so Caro published widely on a range of topics related to chemistry and chemical industry.

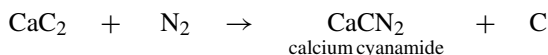
Fig. 2.12 Adolph Frank’s portrait on a commemorative medallion. (Evonik Industries)



Fig. 2.13 Nikodem Caro.
(Evonik Industries)



For Dynamit AG (formerly Alfred Nobel & Company), of Hamburg, Frank and Caro undertook research into a method for making sodium cyanide, used in recovery of precious metals, that did not infringe the Hamilton Y. Castner patent as used by the MacArthur-Forrest Company [39]. They heated barium or calcium carbide in a stream of nitrogen and found that both of these carbides absorbed nitrogen on heating. The first patent, filed on 31 March 1895, was for barium cyanide, obtained in around 30 % yield. And though it mentioned in passing that calcium carbide absorbed nitrogen, the main product was not identified. In 1898, following collaboration with Fritz Rothe (1867–1958), of Dynamit, it was found that the nitrogen product from calcium carbide was calcium cyanamide. The calcium carbide had to be heated at around 1,100–1,600 °C in order to take up the nitrogen. Patents were filed for the cyanamide process.

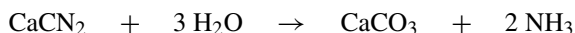


Together with the firms Deutsche Bank, Siemens and Halske, and Degussa (Deutsche Gold- und Silberscheideanstalt vormals Roessler), Frank, Caro and Rothe founded in 1899 the Cyanidgesellschaft mbH in Berlin. A factory was erected in Frankfurt. The first product was barium cyanide. Sodium cyanide was also manufactured, starting from calcium cyanamide, which was fused with

calcium carbide and sodium chloride in an arc furnace, followed by rapid chilling of the melt. The presence of carbide prevented loss of nitrogen at the high temperature required. The resulting sodium cyanide was used in gold extraction.

In 1901, Degussa chemist Johanness Pfleger (1867–1957) improved on the Castner cyanide process. At the same time the price of cyanide, mainly used in gold extraction in South Africa, fell sharply as a result of the slowdown in mining during the Boer War (1899–1902). Degussa withdrew from the partnership since the Frank-Caro cyanide product could no longer compete in the rare metals cyanide market.

The reorganized Cyanidgesellschaft was directed by Nikodem Caro and managed by Frank's son, Albert Rudolph Frank (1872–1965), jointly with chemist Hermann Freudenberg. Albert studied chemistry at the University of Munich, before moving on to the Technische Hochschule Charlottenberg where he received his Ph.D. in 1900 [40]. In the same year, Caro found that calcium cyanamide when heated with steam gave ammonia.

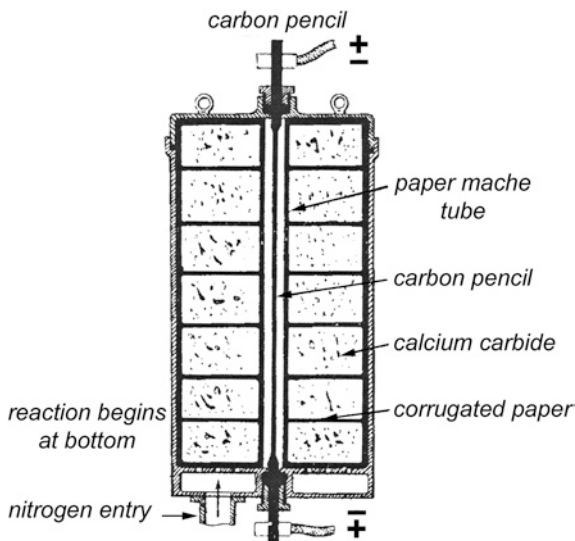


In 1901, Albert Frank and Freudenberg established that calcium cyanamide released ammonia when added to the soil. They filed patents for the application of cyanamide as a fertilizer in Germany, Britain, the United States and elsewhere [41]. Later, details appeared in the scientific literature [42, 43].

In 1905, a pilot plant for manufacture of cyanamide was set up at Westeregeln, near Magdeburg, Saxony-Anhalt. A factory with an intended initial capacity of 500 tons per year began operating in central Italy at Piano d'Orta, Abruzzo, making use of hydroelectric power from a generating station opened in 1904 [44]. These first attempts ended in failure because of the limited lifetime of the externally heated retorts. Usefully, Adolph Frank suggested that since the reaction converting carbide to cyanamide was exothermic the heat given out by the reaction, once started, could be used to help maintain the carbide at the reaction temperature. Accordingly, he developed an internally heated electric oven incorporating a carbon "pencil" electrode, inserted into the drum of carbide. Frank's thin electrode provided the heat to start the reaction (Fig. 2.14). The old retorts were abandoned, and in 1907 the Italian factory, now fitted with self-heating ovens, commenced production at the rate of 4,000 tons of calcium cyanamide per year. In the same year, La Società Generale per la Cianamide, backed by German and Italian investors, and with control over the Frank-Caro patents, was founded in Rome. Also in 1907, the improved Frank-Caro cyanamide process was adopted in France at Notre Dame de Briançon, Hautes-Alpes, by Le Société des Produits Azotés, associated with Henri Gall's carbide manufacturing installation, Société d'Electrochimie. The Westeregeln installation ceased working in 1912.

In early practice, the carbide was held within paper sections inside the furnace. Centrally placed was a vertical paper tube for the carbon "pencil" electrode. After the furnace was closed and made air tight, the pencil was inserted into the paper tube, and the alternating current switched on. Nitrogen under pressure was fed in at the bottom of the furnace. The heat destroyed the paper tube and partitions. The absorption of nitrogen took place at the point of contact of the pencil with carbide

Fig. 2.14 Early Frank-Caro furnace for production of calcium cyanamide.
(Redrawn from Ernest Kilburn Scott, "The Manufacture of Nitrates from the Atmosphere," *Nature*, 89, no. 2228 (11 July 1912): 492)



and continued gradually outward [45]. After around 25 h the current was switched off, and the furnaces left a further 10 h, by which time all the nitrogen had been absorbed. The cyanamide, appearing as a black-grey clinker, was turned out, crushed, ground, and packed in bags for shipping. Several innovations were later introduced, including spraying the cyanamide with water to remove free carbide that might otherwise form explosive acetylene. Despite improvements, the high operating temperature kept the power cost high.

That changed with the introduction of a rival calcium cyanamide process, developed in 1901 by Austro-Hungarian chemist Ferdinand Eduard Polzenius (1862–1918). He overcame the furnace difficulties, mainly the high temperature requirement, by introducing calcium chloride as catalyst. This enabled reduction of the operating temperature from 1,100 °C to 700–800 °C. With Constantin Krauss, Polzenius developed a cyanamide manufacturing process and obtained financial backing, mainly from Metallurgische Gesellschaft (Metallgesellschaft) of Frankfurt am Main. In 1904, the process was taken up, also at Westeregeln, but it proved uneconomic, perhaps due to problems with the furnaces. Following improvements to the process, the Deutsche Karbid Gesellschaft was founded on 31 May 1906 in Frankfurt am Main by Metallgesellschaft, whose Dr. Rudolf de Neufville was the first chairman. A new factory was erected, at Knapsack, south west of Cologne in the brown coal (lignite) district. It began operating, with three furnaces, in October 1907, using purchased carbide. A brown coal power plant and calcium carbide production facility were added in 1908. Several difficulties were encountered, including with the supply of labour. The conditions were hardly salubrious and the work arduous. "The furnaces were tapped with 6 m long rods as the carbide was discharged from the furnaces at a temperature of more than 2,000 °C. It was exhausting work that only a few could do for any length of time, in spite of the high wages offered... the company looked more like a camp of desperadoes than a factory" [46].

In 1909, Aktiengesellschaft für Stickstoffdünger was cofounded by Metallgesellschaft and Konsolidierte Alkali-Werke to take over the Knapsack factory and rights to the Polzenius process. In the following year Krauss was appointed manager. In 1911, Knapsack began the manufacture of ammonia and ammonium sulphate from cyanamide, which was made in a continuous process, using a horizontal cast iron cylinder, some 150 ft in length and 6 ft in diameter, through which a rail track was laid. Twenty-eight trucks loaded with carbide were pushed into the cylinder, which was then closed and made gas tight, and the reaction started.

In 1907, cyanamide manufacture by the Frank-Caro process was licensed to the British-controlled North-Western Cyanamide Company, Limited, which erected factories at Odda (Hordaland), Norway, some distance south east of Bergen, and at Alby, Sweden. The British connection followed the founding in 1904 by Alfred Ernst Barton of the Sun Gas Co., to manufacture acetylene. To ensure a supply of carbide, Barton took over Alby Carbid Fabrik, and soon after became interested in manufacture of cyanamide. With support from Samuel Eyde and the Wallenbergs, Barton set up North-Western Cyanamide in July 1906. In 1907, a manufacturing and market sharing arrangement was concluded with the assignee of Frank-Caro patents, La Società Generale per la Cianamide, whereby North-Western Cyanamide controlled markets in Britain, Norway, Sweden, Denmark, Belgium, and all British “colonies, protectorates, and dependencies, except Egypt and Canada.” This was followed, in 1912, with the setting up of the subsidiary Nitrogen Fertilizers, Limited, to which ownership of the Odda and Alby factories was assigned, and in 1913 of Nitrogen Products and Carbide Company (Limited). The technical director was Albert Johan Peterssen (1870–1914), who had studied at Zurich’s Eidgenössischen Polytechnikums (Eidgenössische Technische Hochschule, or ETH). He was responsible for all development work.

The Odda cyanamide facility, located at the south end of Sørfjorden, a branch of Hardanger Fjord, received hydroelectricity generated at Tyssedal, a few miles to the north, on the east side of the fjord. Carbide furnaces were installed, in addition to 196 cyanamide furnaces, from which, it was reported, thirty tons of cyanamide containing 18 % nitrogen were produced during every 24 h. Waterfalls in Norway and Iceland were acquired to enable further expansion. Unlike the arc processes, the cyanamide process required pure nitrogen. The Frank-Caro cyanamide works were the first bulk customers for nitrogen obtained by fractionation of air according to the 1908 process of former locomotive engineer and refrigeration inventor Carl von Linde (1842–1934). At Odda, some one-hundred tons of air were liquefied daily by the Linde liquid air installation.

In 1907, Cornell-trained American civil engineer and entrepreneur Frank Sherman Washburn (1839–1922), while in Europe with the intention of negotiating rights to the Birkeland-Eyde electric arc process, changed his mind, and travelled to Rome to secure US rights to the Frank-Caro calcium cyanamide process from La Società Generale per la Cianamide.

The American Cyanamid Company was formed by Washburn and partners in July 1907. The company planned to erect a factory at Muscle Shoals, Alabama. However, the Canadian side of the Niagara Falls, in Ontario, was chosen instead.

Fig. 2.15 Banks of Cyanamide furnaces, American Cyanamid Company, Niagara Falls. They are similar to the furnace invented in 1906 by Adolph Frank. (C. L. Mantell, *Industrial Electrochemistry*, 2nd edn. New York: McGraw-Hill, 1940, p. 520. American Cyanamid Company photograph)

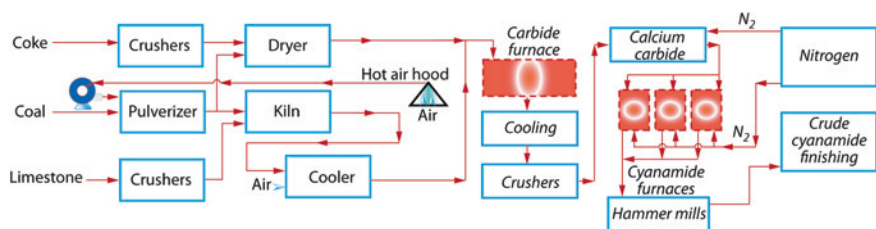
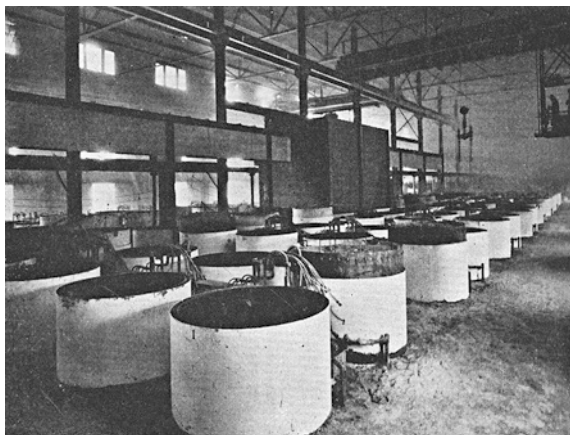


Fig. 2.16 Scheme for manufacture of calcium carbide and its conversion into calcium cyanamide, both by electrothermal processes. (Based on C. L. Mantell, *Industrial Electrochemistry*, 2nd edn. New York: McGraw-Hill, 1940, p. 521)

From late 1909 (officially 18 January 1910) the Frank-Caro process was worked at this site [47]. The initial capacity was 5,000 tons per annum, soon increased to 25,000 tons (Figs. 2.15, 2.16, 2.17 and 2.18).

Williams Haynes, historian of American chemical industry, in an incomplete (and sometimes whimsical) manuscript intended for publication to mark the hundredth anniversary of American Cyanamid, described the early construction work thus:

There was not a simple, easy job, for they were building a plant the like of which had never been seen on this continent to operate a process with which none of them had any experience. They were not even sure how to pronounce the name of their company and its sole product—*cy-an-amid*, with the accent on the second syllable. They had to work with foreign blueprints measured in meters, not inches and feet, whose instructions and specifications seemed curiously worded.... They built the first cyanamide plant in America in eleven months, thirty days ahead of schedule. The first shipment—52,240 pounds—rolled away from Niagara Falls, Ontario, bound for Baltimore, Maryland, on December 4, 1909.... Even within the American Cyanamid Company nobody really knew, firsthand, anything about the uses of cyanamide, and so while [Kenneth F.] Cooper [a Stanford trained engineer] and his gang were building the plant, a couple of boatloads of crude



Fig. 2.17 The Niagara Falls, around 1905. (From John G. Leigh, “The Water-Power Stations of Niagara Falls.” In Archibald Williams, ed., *Engineering Wonders of the World*. London: Thomas Nelson and Sons 1909, vol. 2, pp. 295–311, on p. 295. Ontario Power Company photograph)

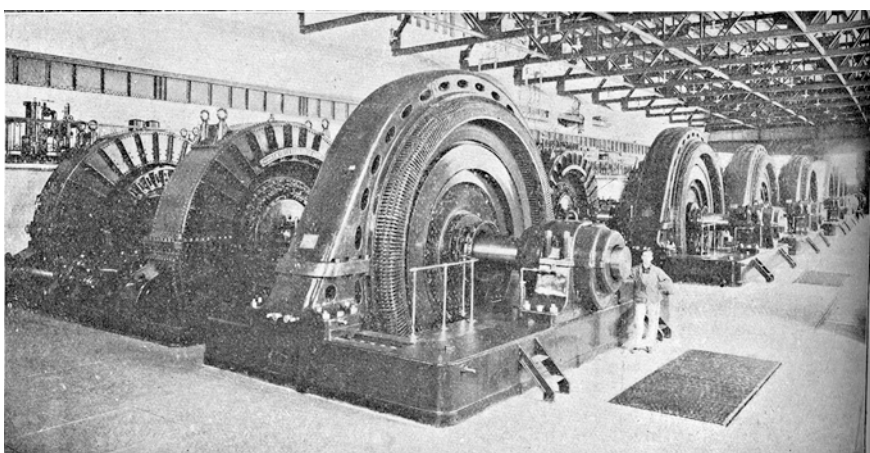


Fig. 2.18 Interior, electricity generating station of the Ontario Power Company, on the Niagara River, opened in 1905. The six generators shown here, each connected to two turbines, produced in total the equivalent of 60,000 horsepower. From 1909 the station provided power to American Cyanamid’s Niagara factory. (From John G. Leigh, “The Water-Power Stations of Niagara Falls.” In Archibald Williams, ed., *Engineering Wonders of the World*. London: Thomas Nelson and Sons 1909, vol. 2, pp. 295–311, on p. 308. Ontario Power Company photograph)

cyanamide, unhydrated, right out of the furnaces, were imported from the Odda works in Norway. It was landed at Baltimore.... Baltimore and Charleston were the then headquarters of the fertilizer trade.... That crude cyanamide from Norway had to be refined and even then was an exceptionally dusty fine powder, black as ink.

Before the Linde process for nitrogen was introduced at the American Cyanamid factory, as Haynes tells us, the inert gas was obtained by a novel route [48]:

In the original plant, nitrogen was obtained by feeding natural gas into retorts filled with copper oxide. The gas took up the oxygen of the oxide leaving the copper in a metallic state. Air was then passed over the heated copper which took up the oxygen again to reform copper oxide, leaving...nitrogen of sufficient purity for use in the cyanamide ovens. The copper oxide was then again reduced to copper by re-introduction of natural gas and the process repeated over and over again. Since the oxidation of copper took up only oxygen the rare gases in the air were left with the nitrogen, and in 1913 [US] General Electric suggested that, if the argon could be stripped out of this gas mixture, they would buy it. Irving Langmuir [1881–1957] had just developed [at General Electric] his original idea that instead of striving to get a more perfect vacuum in electric light bulbs, their efficiency might be increased if they were filled with an inert gas. Cyanamid accepted what was the first industrial order for any of the rare gases and between December 1914 and May 1915 delivered 8,000 tons of argon.

Several difficulties were experienced in formulating a suitable cyanamide fertilizer product, until after chemist Walter Savage Landis (1881–1944), an expert in electrothermics at Lehigh University, was taken on. In around 1912, Landis steamed “out the nitrogen in cyanamide under pressure to produce ammonia,” which was reacted with phosphoric acid to give ammonium phosphate, a two-element fertilizer. Plans for a calcium cyanamide factory in the Cotton Belt, backed by British investors, were cancelled after Congress vetoed a Bill for authorization of construction of a dam on the Coosa River. Meantime the Niagara Falls plant capacity was raised to 32,000 tons.

To sell the nitrogen-phosphorus product the Ammo-Phos Corporation was founded after, in the late spring of 1914, “Frank Washburn and James Duke met by chance on The Strand in London. These hydro-electrical enthusiasts had known each other and they went off to lunch at the old Northumberland hotel on Trafalgar Square, famous for its whitebait and fillet of sole.” Washburn’s description over lunch of work on the new fertilizer certainly appealed to Duke, who, as we have seen, had at that time an interest in the Pauling process [49]. Moreover, Duke owned a phosphate mine in Florida, and apparently was also interested in producing a nitrogen-phosphorus fertilizer. As a result of the meeting, Duke’s Amalgamated Phosphate Company, of Brewster, Florida, became the Ammo-Phos Corporation, and eventually led to Duke becoming a major investor in the American Cyanamid Company. The site chosen for the Ammo-Phos factory was at Warners, New Jersey.

While the fertilizer did not generate great profits, its development gave American Cyanamid invaluable experience in converting cyanamide, via ammonia, into nitric acid, a process that would bring about much needed income during Word War I. Significantly, immediately after the outbreak of war in Europe in August 1914, Landis sailed for Germany to collect two autoclaves—ordered in the spring of that year—designed by Adolph Frank for converting cyanamide into ammonia. Landis was fortunate to get them out of Europe, just before Germany imposed an embargo on export of chemical manufacturing equipment. The autoclaves were installed at Warners, and, with the aid of blueprints, enabled design of home-built vessels. In the spring of 1916, work began on a pilot plant for oxidation of cyanamide-derived ammonia to nitric acid at Warners.

Another important Frank-Caro facility opened in 1909 was that of the Japan Nitrogenous Fertilizer Company (Nippon Nitrogen Fertilizer, Nippon Chisso Hiryō Kabushiki Kaisha, or Nichitsu), at Kinzei, near Osaka [50]. A second factory was opened at Minimata, Kumamoto Prefecture, around 1911. The company was headed by Shitagau Noguchi (1873–1944), who had studied electrical engineering at Tokyo Imperial University, opened a hydroelectric power station in 1906 (Sogi Electric Company), and a carbide factory, at Minimata, in 1908 (Japan Carbide Company). This represented an important phase in the early development of the modern Japanese chemical industry, leading later to other carbide-derived chemicals. Previously the main Japanese activity was manufacture of sulphuric acid by the Sumitomo company, for superphosphate production at Tokyo Fertilizer (later Nissan Chemical Industries), also serving the agricultural sector. The fertilizer businesses flourished due to the scarcity of arable land, and small size of farms, in Japan.

Frank-Caro operations in Germany had been delayed until late 1908, when Frank and Caro came to an arrangement with Polzenius over the latter's cyanamide patent. As a result, on 6 November 1908, Cyanidgesellschaft, with the backing of Deutsche Bank, created a subsidiary, Bayrische Stickstoffwerke AG, in Munich, for the manufacture of calcium cyanamide in Bavaria. A large factory was built at Trostberg, supplied with electricity from a hydroelectric power station on the River Alz, both inaugurated in 1910. Carbide was manufactured nearby at Schalchen, Upper Austria (and from 1919 at Hart, also on the Alz). In 1913, Trostberg began operating a tunnel (horizontal) furnace, with countercurrent flow of nitrogen and carbide, for calcium cyanamide manufacture. However such furnaces were costly, and yield and quality were not up to expectations, which did not justify their widespread installation. Following the agreement with Polzenius all calcium cyanamide furnaces were worked at the lower temperature. Adolph Frank and Nikodem Caro were the principals of Bayrische Stickstoffwerke. Albert Frank worked in administration until 1916, when following the death of his father he joined the board. The rulers of Bavaria, Prince Luitpold until 1912, then Prince Ludwig during 1912–1913, both on behalf of King Otto, and Ludwig III, 1913–1918, followed developments at the company, in which the Bavarian state held a substantial interest.

The hygroscopic flux calcium chloride was later replaced with, for example, calcium fluoride, as introduced by Oskar Fredrik Svante Carlson (1844–1916), founder of Stockholms Superfosfat Fabriks Aktiebolag (other alkali and alkaline earth salts were also specified as catalysts). Oskar was assisted by his son, Birger Carlson (1873–1928), who was educated at the Technische Hochschule Charlottenburg. They worked a small-scale cyanamide process at Mansbo, near Avesta, Sweden, around 1912, and constructed a large works shortly after, near Alby. The Carlson process was continuous, employing a tower, fitted with shelves, rather than a tunnel. Carbide was charged at the top, and pushed down mechanically from one shelf to the next. The process turned out to be problematic when, as a result of the mechanical action, the product caked up.

Fritz Rothe continued with his investigations into electrothermal fixation of atmospheric nitrogen and in 1911 filed an electric arc process patent with Elektrochemische Werke GmbH zu Berlin. In 1912, fourteen cyanamide factories were operating worldwide (Table 2.1).

Table 2.1 Manufacturers of calcium cyanamide, and reported annual capacities, in 1912

Company	Place	Capacities, annual in tons, approx.
Nitrogen Fertilizers (1912) (North-Western Cyanamide Co.)	Odda, Norway	15,000 (12,000 in 1909)
Nitrogen Fertilizers (1912) (North-Western Cyanamide Co.)	Alby, Sweden	15,000
Società Italiana di Prodotti Azotati	Piano d'Orta, Italy	4,000
Società Italiana per il Carburo di Calcio	Collestate, near Terni, Umbria, Italy	15,000
Società Piemontese per il Carburo di Calcio	San Marcel, Aosta Valley, Italy	3,000
Le Société des Produits Azotés	Martigny, Switzerland	7,500 (3,750)
Le Société des Produits Azotés	Notre Dame de Briançon, France	7,500
Bayrische Stickstoffwerke	Trostberg, Bavaria	15,000
Ost-Deutscher Stickstoffcalc und Chemische Werke	Bromberg, Province of Posen, Prussia	2,500 (2,500)
AG für Stickstoffdünger	Knapsack, near Cologne, Westphalia	18,000 (5,000)
Società per l'Utilizzazione delle Forze Idrauliche della Dalmazia	Cernica, near Sebenico, Dalmatia, Austria-Hungary	4,000
Società per l'Utilizzazione delle Forze Idrauliche della Dalmazia	Dugirat, near Almissa, Dalmatia, Austria-Hungary	80,000
Japan Nitrogenous Fertilizer Co. (Nichitsu)	Kinzei, near Osaka	4,000
American Cyanamid Company	Nashville, Tennessee	4,000 planned only
American Cyanamid Company	Niagara, Ontario	25,000 (5,000, in 1910)

From Ernest Kilburn Scott, "The Manufacture of Nitrates from the Atmosphere," *Nature*, 89, no. 2227 (4 July 1912): 463–465, on 463, etc. Capacities in 1909 are shown within brackets. Most of the companies in the table worked the Frank-Caro process under license

Manufacturers and users of novel agricultural products were alerted to the need for careful testing on the soil following studies of the efficacy of Chile saltpetre in the 1890s. These revealed the adverse impact of perchlorate contamination [51]. Adolph Frank, around 1905, asked chemist Paul Wagner, head of Darmstadt Agriculture Experiment Station, who had investigated perchlorate in saltpetre, to identify any toxic action arising from use of calcium cyanamide. Wagner's report was favourable, suggesting conditions for optimal application, though drawing

attention to problems arising from certain soil types and concentrations [52]. In actual practice, the crude cyanamide was generally applied direct to the soil as fertilizer. However, not every farmer was made familiar with the product and methods of dispersal. This was also a problem in the United States. Improvements in the manufacturing process and application were made during World War I.

By 1914, annual production of calcium cyanamide was 220,000 tons, one-quarter of which was manufactured in Germany, mainly at Trostberg and Knapsack. Production would increase considerably from 1915.

All electrothermal processes continued to be located close to sources of cheap electricity, mainly hydroelectricity. This situation would change only in the 1920s, when large-scale electrical transmission networks, capable of handling thousands of kilowatts, were introduced. Nevertheless the vast capital investments in generating and chemical plant and laying down branch railways and sidings made before 1920 meant that the existing factories would remain in their original sites even when process changes, requiring less power, were introduced.

The significance of the various developments in electrothermic chemistry as related to nitrogen fixation was not lost on the Nobel Prize committee at the Swedish Academy of Sciences [53]. The committee considered fixation of atmospheric nitrogen from around 1909, when Peter Klason, of the Stockholm Institute of Technology, guided members in their deliberations. Klason initially favoured Adolph Frank, alone or possibly with Caro, but later expressed more interest in Birkeland. Difficult relations between Sweden and Norway at the time, the fact that Birkeland had formed a commercial partnership with Eyde, and more, that Eyde wanted to be a co-nominee, may have militated against Birkeland being awarded the prize. The committee, unable to reach a consensus, dropped nitrogen fixation from its agenda, at least for the time being. In 1912, both Birkeland and Otto Schönher were nominees. For his several achievements in physics and chemistry, between 1907 and 1917, Birkeland was nominated for the Nobel Prize seven times in all [54].

2.4 BASF

The market for fertilizers in the western hemisphere expanded greatly after 1900. Artificial nitrogen products, if they could be manufactured at the right cost, offered the potential for substantial profits from the agricultural sector. The interest in nitrogen was especially strong at BASF, the leading dye manufacturer at the turn of the century. In part this interest had to do with overcoming Germany's shortage of resources and its considerable dependence on other countries. In the case of fixed nitrogen, there were concerns over not just British participation in the Chile saltpetre monopoly, and how long the supply of natural nitrate would last, but also external shocks such as economic and political events, including the outbreak of war. Moreover, nitrogen offered an opportunity for diversification at German firms away from dyes. To provide a clear picture of how BASF came to lead in nitrogen

fixation developments in the early 1900s it is necessary to review the firm's rise to leading place in the realm of science-based industry.

BASF was founded in 1865, at Mannheim, but soon after moved to nearby Ludwigshafen, on the west bank of the River Rhine, in Bavaria. Much of its early success was due to Heinrich Caro, who developed a process for manufacture of synthetic alizarin (1869–1870), the important red dye previously obtained from the root of the madder plant, based on academic-industrial collaboration in Germany, and exchange of technical information with William Perkin's firm in England. Perkin, founder of the synthetic dyestuffs industry through his 1856 discovery of aniline purple (Tyrian purple; from 1859 known as mauve) relied mainly on his own research effort, unlike the Germans who built up teams of researchers. This is why after 1872 German firms led in production of synthetic alizarin, and prospered. These circumstances led Perkin to sell his business in 1873. Similar inadequate methods of conducting science-based research and development aimed at novel chemical inventions brought about the decline of much of the British synthetic dye industry during the following decade. This also impacted on other sectors in the British chemical industry.

Synthetic alizarin caused the collapse of the massive trade in the natural dye, and placed the German dye industry on a secure footing. Elsewhere, a crisis unfolded in the market structure of natural dyestuffs. Caro and others at BASF, as well as chemists at Hoechst, Bayer, and AGFA, invented several processes for manufacture of intermediates and novel synthetic dyes, and inaugurated widespread research into synthetic colorants, as well as contributing to a patent system in Germany that was without equal when it came to protecting chemical inventions. In the case of Heinrich Caro, his diverse talents brought together expertise in chemistry, dyes and dyeing, and control of patents into a single work space that enabled the rapid growth of BASF. Exploiting new theories and methods of synthesis in chemistry, with the aid of academic and industrial chemists, he created a revolution in the production of novel materials, based on discovery and invention [55]. In 1874, Adolf Baeyer (1835–1917; ennobled 1885), at the then new German University of Strasbourg (Kaiser-Wilhelm-Universität), and Caro together published the modern structural formula of alizarin. It was Caro who inaugurated an industrial programme for synthetic indigo, working closely with Baeyer, following his move to Munich. In 1883 Baeyer sketched, in a private letter to Caro, the almost correct chemical structure of the natural blue colouring matter, mainly available from India and over which Britain held the monopoly. This opened the way to the synthetic product. In the late 1880s, Caro was responsible for the design and construction of the Central Research Laboratory at the BASF Ludwigshafen factory. Its activities encompassed not only research and development projects, but also the critically important support service required in patent litigation.

Mainly as a result of Caro's research, BASF was adept at undertaking risky and expensive ventures based on close collaboration with academic inventors. The success of BASF, and of the Hoechst Dyeworks, with the manufacture of synthetic indigo from 1897—following the research of Baeyer and Caro, and a synthetic

route devised by Karl Heumann (1850–1914), at Zurich's ETH, in 1890—was a source of considerable concern among British importers of the blue dye.

By 1900, the major German dye firms, bolstered by strong reserves and with the confidence of the banking industry behind them, were engaged in diversification, including, at Bayer, into pharmaceuticals and, at AGFA, photo products. The most difficult challenge was fixation of atmospheric nitrogen. In this endeavour, academic chemists and inventors were encouraged to collaborate with dye firms, especially BASF. By 1907, the firm expressed considerable optimism in its Schönherr furnace. Apart from electric arc and cyanamide processes, some interest was shown in the combination of hydrogen and nitrogen to produce ammonia. This was taken up at Leipzig by the leading physical chemist Wilhelm Ostwald (1853–1932) [56].

On 12 March 1900, Ostwald advised the BASF management that he had devised a method for preparing ammonia directly from its elements by applying a high temperature in the presence of an iron wire catalyst [57]. Ostwald filed a patent, confident that his process worked and could be exploited industrially. However, when the method was tried at BASF it was found that ammonia was formed not directly, from nitrogen and hydrogen, but from an iron-nitrogen compound. The scientist in charge of the evaluation and who exposed the failure of Ostwald's method was Carl Bosch. Little wonder then, that for the next few years so much faith was placed in the electric arc.

2.5 Carl Bosch

Carl Bosch (1874–1940) grew up in Cologne, where his father owned a metalworking business that served the needs of local coal gas suppliers. His uncle, Robert Bosch, founded the Bosch electrical engineering firm in 1886, in Stuttgart. In the Cologne workshop, Carl made his own equipment, with the assistance of a foreman. In 1893, he undertook an apprenticeship in a metallurgical factory, and during 1894–1896 studied metallurgy and mechanical engineering at the Technische Hochschule Charlottenberg. In 1896, he undertook research in chemistry at the University of Leipzig. Among the topics that attracted his attention was spectral analysis, which later, usefully, aided his understanding of the structures of metals and probably led to an interest in astronomy. In 1898, he received his doctorate in organic chemistry under Johannes Wislicenus (1835–1902) [58, 59].

Bosch joined BASF in April 1899, working in the Indigo Department with Rudolf Knietsch (1854–1906), who came to Ludwigshafen in 1884 from the dye firm Bindschedler & Busch of Basel. Around 1900, Bosch was assigned to the problem of nitrogen fixation; it was here that he quickly showed why Ostwald's ammonia process was flawed. From 1902, Bosch investigated metal cyanides and nitrides as possible sources of stable nitrogen products. The indirect cyanide method involved the high temperature reaction of barium oxide from barytes with carbon (from coal) and nitrogen to give barium cyanide. With steam, the cyanide

decomposed to ammonia and barium hydroxide. It was not altogether different from Mond's method of the early 1880s, and even showed some similarities with the early carbide work of Frank and Caro. A pilot plant for barium cyanide was erected in 1907, but it was not viable as a technical route, and was abandoned in 1908. The failure of Ostwald's method and huge energy requirements of the cyanide method certainly emphasized the great challenges posed to academic and industrial chemists, and inventors, in their attempts to fix atmospheric nitrogen. The complexities and technical difficulties pushed the boundaries of scientific and technical knowledge and expertise to the limits for those who sought both prestige and profit.

The challenges of nitrogen fixation, and their implications, were expressed in no uncertain terms during the summer of 1903 by Ostwald, writing in the *Schwäbische Merkur*. "The significance of bound nitrogen...is especially high for both war and peace...Without saltpetre the best military is almost helpless...Were a war to break out today between two great powers, one of which was able to prevent the export of saltpetre from Chile's few harbours, that ability alone would allow it to render its opponent almost incapable of fighting" [60]. Therein lay the nitrate problem. Its solution was a strategic necessity, quite apart from the critical importance to agriculture.

This was also recognized in Britain, where electrical engineer Ernest Kilburn Scott (1868–1941) advised the British Association for the Advancement of Science in 1911 and the Royal Society of Arts in 1912 of the strategic need for developing technical methods of nitrogen fixation. In 1912, he pointed out that "Nitric acid is, of course, the main constituent of gun-cotton, dynamite and smokeless powders, etc., and at the present time we are mainly dependent on overseas supplies of raw material from which to make the acid. In case of war we should undoubtedly be in a very serious position, for whereas most Continental countries have plants for the fixation of nitrogen from the air, this country does not make a single ounce" [61]. Such a situation, he reminded his audience, had strong parallels with the Napoleonic wars, when the French faced shortages of saltpetre. Kilburn Scott believed that electrochemical and electrothermal industries would in time become more significant than electric traction, which had made great strides in the early 1900s, with electrification of street tramways, underground railways and tunnels, long distance main lines, and power generation and distribution.

In 1915, Kilburn Scott repeated his earlier calls for action, this time reminding members of the Society of Chemical Industry, that "I urged the necessity of starting the production in this country of nitrates from air by electricity" [62]. Kilburn Scott was promoting his three-phase electric arc process for capturing nitrogen as nitric oxide, for which, by 1915, a laboratory scale apparatus had been assembled at Northampton Polytechnic Institute, Clerkenwell, London, where he was a lecturer [63]. A three-phase arc process for capturing nitrogen was worked in Zurich by the Nitrum firm, at least until the 1920s. The main inventor was Werner Siebert, who later collaborated with Nikodem Caro and Albert Frank in development of improved processes for manufacture of concentrated nitric acid.

2.6 Fritz Haber

Haber was later accused by the cynics of having provided Germany with ammonium nitrate for explosives and making the war inevitable. He was later accused of providing poison gas to the army. This takes no account of what men, including chemists, [do] in the name of patriotism for the Country to which they belong, especially when both combatants are sure they have God on their side!

Ralph C. Chimside (colleague of Robert Le Rossignol), 1980.

Though several studies and numerous texts, as well as plays, novels, films, biographical articles, and more, have appeared on the life and times of Fritz Haber (1868–1934), the central figure here, it is worth recording the salient facts of his early life [64–76]. Haber was born into a secular Jewish family on 9 December 1868, at Breslau, in the Prussian Province of Silesia (Breslau is now Wrocław, western Poland). His father owned a business that traded in chemicals, including dyes, and intended that Fritz would eventually take over the day-to-day running. In 1886, at age 18, Fritz entered Friedrich-Wilhelms-Universität, Berlin (later Humboldt Universität), to attend the lectures of the ageing organic chemist August Wilhelm von Hofmann (1818–1892) and physicist-philosopher Hermann von Helmholtz (1821–1894). This was followed by studies at Heidelberg, under Bunsen. After returning to Berlin he embarked on research at the Technische Hochschule Charlottenberg under organic chemist Carl Liebermann (1842–1914), co-inventor with Carl Graebe (1841–1927) of the original method for synthetic alizarin. Haber graduated *cum laude* in 1891 with a doctoral thesis on an indigo derivative. Through exposure to Hofmann and Liebermann, who had both made massive contributions to science-based industrial organic chemistry, Haber would have received a thorough grounding in the role played by aromatic chemistry in Germany's emergence as a leading industrial power.

However, aromatic organic chemistry was a little too much like cookery for the ambitious Haber: His thesis was “miserable. One and a half years of new substances prepared like a baker's bread roll” [77]. Following his doctoral studies, there were short sojourns in industry at a Hungarian alcohol distillery, an Austrian Solvay factory, and a Polish salt mine.

Perhaps of more interest was a semester during 1892 at the chemical institute of Zurich's ETH, under the German-born Georg Lunge (1839–1923), former industrial chemist and a leading expert on gas analysis, which was critical to several areas of industrial application, including the products of coal gas works. By the 1890s, the manufacture, storage, transportation and analysis of gases were important for the chemical industry, including the dye-making firms. In 1888, Knietsch at BASF developed chlorine liquefaction, enabling the corrosive liquid to be stored and transported in steel cylinders. In 1901, of 25,000 tons of chlorine produced in Germany, 17,000 tons came from the electrolysis of sodium chloride, the chlor-alkali process [78].

After the short stay in Zurich, Haber joined his father's business, but not for long. The reason was timing of the purchase of a large amount of chloride of lime

(calcium chloride, CaCl_2) intended to prevent the spread of a cholera epidemic in Hamburg which in 1892—as a result of poor hygiene and contaminated water—took the lives of almost nine thousand people. The lime arrived too late to be of any use—the selling price fell as the outbreak subsided—and the large amount of unsold stock brought Fritz's commercial career to a quick end.

Through physicist Siegfried Czapski (1861–1907), a friend later associated with the Carl Zeiss Works, at Jena, Haber was enabled to join the university in that city as an assistant under the youthful organic chemist Ludwig Knorr (1859–1920). Fritz's interests were now moving towards the emerging field of physical chemistry, stimulated in part by attending lectures of the theoretical physicist Rudolf Straube (1858–1935), designer of the first anastigmatic lens for Carl Zeiss. It was Haber's intention to work with physical chemist Wilhelm Ostwald, though this did not work out. Meantime, in his mid-twenties, Haber underwent conversion to Christianity, an act, he hoped, that would improve his career prospects in the German Reich.

In 1894, Knorr gave Haber a letter of recommendation to another organic chemist, Carl Engler (1842–1925), at the Karlsruhe Technische Hochschule [79]. The attraction was probably Engler's involvement from the mid-1880s in petroleum technology, and the general interest in applied chemistry at Karlsruhe. Haber joined Engler's institute as a research assistant, and taught textile dyeing and printing. His research increasingly involved thermodynamics and reactions in the gaseous phase, particularly fuel technology, working with fuel technologist Hans Bunte (1848–1925). There was also an interest in the new field of electrochemistry, including experiments on reduction of nitrobenzene, the hydroquinone/quinone equilibrium, and on electrodes, probably encouraged by Austrian electrochemist Hans Luggin (1863–1899), who had previously worked with physical chemist Svante Arrhenius (1859–1927).

In 1896 Haber received his *Habilitation* working under Bunte, on “Experimentelle Untersuchungen über Zersetzung und Verbrennung von Kohlenwasserstoffen” (“Experimental Studies of the Decomposition and Combustion of Hydrocarbons”), and became a Privatdozent. In 1898, he published *Grundriss der Technischen Elektrochemie auf theoretischer Grundlage* (“Outline of Technical Electrochemistry on a Theoretical Basis”), and was appointed professor extraordinarius. In 1901, Fritz met fellow-chemist Clara Immerwahr (1870–1915) at a conference; they were married in August of the same year [80, 81]. A son, Hermann, was born on 1 June 1902, by which time Fritz Haber was an acknowledged expert in electrochemistry. In mid-August he departed on a four-month trip to the United States, first to represent the German Electrochemical Society (the Bunsen Society), at a conference of the American Electrochemical Society held at Niagara. This provided an opportunity to inspect the various manufacturing concerns that relied on hydroelectric power from the Niagara River, including the Bradley and Lovejoy electric arc facility, where he met with Bradley. Afterwards Haber travelled around the United States gathering information on chemical industry and university teaching.

2.7 Nitrogen Fixation: Haber's Studies

Haber's entry into the field of nitrogen fixation began in 1904 when he was asked by the Margulies brothers, Otto and Robert, owner and managing director, respectively, of the Österreichische Chemische Werke, based in Vienna, to investigate conditions for direct combination of atmospheric nitrogen with oxygen or hydrogen. Relevant here was the action of heat on ammonia and its decomposition into nitrogen and hydrogen, as studied in the 1880s by William Ramsay (1852–1916) and Sydney Young (1857–1937) [82]. This work, drawing attention to the equilibrium concentration of ammonia, was further studied at University College Cardiff in 1904 by Edgar Philip Perman (1866–1947), who, following earlier researchers, including Marcellin Bertholet (1827–1907), used a high potential electric discharge [83]. Also in 1904, Haber and his assistant Gabriel van Oordt studied the equilibrium at temperatures of around 1,000 °C. The percentage of ammonia was in the region of 0.102–0.024, depending on the temperature. It was apparent that since ammonia decomposed on heating, starting at around 500 °C, the synthesis from its elements had to be conducted below that temperature. At normal pressure in the presence of catalyst the yield of ammonia was just a trace, certainly far too low to suit industrial application [84, 85]. Haber concluded that the temperature should not be allowed to rise much above 300 °C; the equilibrium under these conditions would favour formation of ammonia only if a suitable catalyst could be found. In 1904, this was unlikely. The work was abandoned in 1905.

In 1905, Haber published *Thermodynamik technischer Gasreaktionen*, which included details of ammonia experiments undertaken for the Margulies brothers. Clara Haber assisted Fritz's chemical work by translating articles appearing in English-language journals. An English version of the book, *Thermodynamics of Technical Gas Reactions*, appeared in 1908. Haber drew attention to the problems associated with fixing nitrogen according to the synthetic methods devised over the previous years [86]:

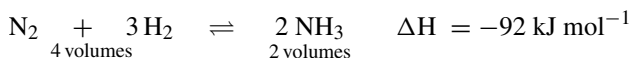
We may here appropriately discuss the preparation of nitric oxide from the air on a technical scale. This process, which we may call the "burning of air," is of the very greatest technical importance, because from nitric oxide, air and water we can make nitric acid, and from this the nitrates which are of such fundamental importance in agriculture and the manufacture of explosives. It is estimated that the saltpetre beds of Chile will be exhausted by 1940. No other natural deposits of importance are known. Attempts to fix the atmospheric nitrogen by heating calcium carbide and to then obtain a fertilizer [calcium cyanamide] which could take the place of saltpetre have been successful so far as the process itself is concerned, but it is doubtful how far this fertilizer can be substituted for saltpetre, and its transformation, first into ammonia salt and further into nitrates, does not stand perhaps on so favourable an economic basis as does the burning of air. It is possible to get nitric acid by the oxidation of ammonia with oxygen, and ammonia may be obtained in great quantities from the distillation (Mond) of coal. But it seems that this change is always connected with an appreciable loss of ammonia transformed into nitrogen, so that here too the economic basis is less favourable than in the burning of air, where all that is needed to produce nitric acid is air, water and power.

Around 1905, as noted earlier, and indeed for a few more years, the electric arc methods, outcomes of an ambitious collective research effort, now including by Haber, held out the greatest hope for capturing nitrogen. Among other industrial activities, Haber's new interest in nitrogen capture led him to collaborate with the Pauling brothers.

In 1906, Fritz Haber, then aged 38, was appointed professor at Karlsruhe and head of the Institute for Physical Chemistry and Electrochemistry. His interest in electrochemistry and his book on the thermodynamics of gas reactions, with a special emphasis on technical uses, had made his reputation. As a result, over the following years his laboratory would attract an international group of researchers whose main interests were in gas reactions and their practical applications.

Also in 1906, physical chemist Walther Nernst (1864–1941), who had left Göttingen for Berlin one year earlier, developed his heat theorem (later known as the third law of thermodynamics), which enabled calculation of yield from thermochemical data. He claimed that Haber's reported 0.005 % yield of ammonia, at 1,000 °C with an iron catalyst at atmospheric pressure, was larger than that predicted by the heat theorem. Nernst began an attack on Haber's findings related to the ammonia synthesis. Unlike Haber, Nernst had applied pressure in his experiments and managed to synthesize ammonia from its elements in a ceramic apparatus. The seemingly fractious debate soon spurred Haber to resort to experiments under pressure, starting at around 30 atmospheres, and in so doing he confirmed that his earlier results were correct [87].

The application of pressure to gas reactions was, however, quite novel. Theoretical developments followed the work of Henri Le Chatelier (1850–1936) in France who at the end of the 1880s formulated the principle that chemical changes take place in directions which tend to counteract the physical changes used to bring them about. The gas phase reaction between nitrogen and hydrogen in the synthesis of ammonia is a good example of this principle.



With application of pressure the equilibrium moves in the direction which reduces the effect of the pressure, that is, to the ammonia side of the equation.

Here, the effect of temperature is also important. Because the reaction is exothermic, lowering the temperature might appear to be an important factor in encouraging formation of product ammonia. However, at low temperatures the rate at which the reaction takes place is extremely slow. To activate the reactants and bring about the rapid formation of ammonia a high temperature is required, though as earlier studies had shown this in turn causes decomposition of the ammonia to the starting hydrogen and nitrogen. Haber had to confront the fact that high pressure and elevated temperature act in opposition in this particular situation. The way to reduce the barrier to reaction was to introduce a catalyst. Also, the decomposition of ammonia was minimized by its rapid withdrawal.

Le Chatelier, aware that a compromise between the rate of reaction and yield of ammonia could be obtained by adjusting the pressure and temperature and

introducing a catalyst, in 1900 investigated the synthesis of ammonia under such conditions. In 1901 he filed a patent for the method. Further development was brought to an abrupt halt when his apparatus blew up, caused by the presence of oxygen in the gas mixture. It was Perman who confirmed the validity of Le Chatelier's work. However, it was left to Fritz Haber to take up the ammonia story where Le Chatelier and Ostwald had left off.

Haber's work was followed closely by his superior at Karlsruhe, Carl Engler, who had joined the board of BASF in 1903, at the time when Schönherr was developing his electric arc and Carl Bosch was investigating fixation of atmospheric nitrogen by the indirect cyanide and metal nitride routes. The latter work was carried out in the Inorganic Department by Alwin Mittasch (1869–1953), who joined the firm in 1904. Mittasch received his doctorate in 1901, at Wilhelm Ostwald's institute in Leipzig, under the supervision of Max Bodenstein (1871–1942) [88].

On 16 February 1908, Engler recommended Haber to BASF as an expert in nitrogen fixation, particularly for his work on formation of nitric oxide using electrical discharges [89]. Shortly after, BASF Central Research Laboratory director August Bernthsen (1855–1931) visited Haber at Karlsruhe, as a result of which two research contracts were drawn up on March 6. One contract was between Haber, his colleague Adolf König, and BASF, for synthesis of nitric oxide. This was still Haber's favoured method, carried out jointly with König. The other was between Haber and BASF, allocating 6,000 marks a year until 1911 towards his research. Later it was extended to 1914. Details of methods and patents were to be assigned to BASF [90, 91]. König joined BASF, where he continued to investigate the electric arc method for nitric oxide, and collaborated with Haber who in 1909 filed his first patent for direct fixation of nitrogen, based on a cool electric arc.

The fact that until the summer of 1909 the electric arc remained the most viable route to nitrogen fixation in the opinion of most scientists was made clear in London at the Seventh International Congress of Applied Chemistry, formally opened on May 27 by the Prince of Wales (Later King George V) at the Royal Albert Hall. The sessions were held at University College London. The papers on electrothermal methods dealing with capture of nitrogen, and chaired by the then Sir William Ramsay, attracted good audiences. Present were Kristian Birkeland, Samuel Eyde, Nikodem Caro, BASF research leader August Bernthsen, Otto N. Witt, former consultant to Birkeland and Eyde, and Russian high-pressure chemist Vladimir Nikolayevich Ipatieff (1867–1952) [92]. Certainly this was the largest ever gathering of inventors and representatives of major electrothermal processes then in use for capturing nitrogen, including the cyanamide route. Birkeland reviewed progress in the application of his furnace. Bernthsen described the long tubular Schönherr furnace in which BASF held high hopes. At the same time he disparaged the calcium cyanamide product.

By then, however, Haber was on the point of achieving success in another direction, the high-pressure synthesis of ammonia from its elements.

2.8 “Es Tropft, Herr Geheimrat!” The Direct Synthesis of Ammonia

The second 1908 agreement between BASF and Haber included further investigation of the direct combination of nitrogen with hydrogen. It was perhaps fortunate that Nernst's attack on Haber's earlier results had provoked Haber to take a completely new approach, based on the application of pressure. Unlike Nernst, Haber opted for an apparatus made of steel.

Haber's response to Nernst's objections relied on the dexterity of his young English research assistant, Robert Le Rossignol (1884–1976), recently arrived from William Ramsay's laboratory at University College London. Le Rossignol, the son of a physician at St. Helier, on the Isle of Jersey, had achieved excellent results in the basement laboratories at University College, a far cry from the great comforts and conveniences of a modern German research institute. In 1907, Ramsay had recommended research under Richard Abegg (1869–1910) at Breslau, but Le Rossignol opted for Haber's laboratory because he had heard that there were already “too many Englishmen” at Breslau. Also arriving from Ramsay's laboratory was Joseph E. Coates. Together they worked at Karlsruhe on a pressure flame for fixation of atmospheric nitrogen (Fig. 2.19).

Le Rossignol was soon after assigned to a reinvestigation of the synthesis of ammonia. Haber was greatly impressed by the newcomer's efforts, especially after Le Rossignol confirmed the results of earlier work on ammonia. Haber at that time calculated that an estimated 8 % equilibrium yield of ammonia could be achieved at 600 °C and 200 atmospheres.

The application of pressure to bring about chemical reactions was not without dangers. There had been occasional explosions, and fatalities, in factories of the French and English manufacturers of intermediates for synthetic dyestuffs when they resorted to pressures of 50 atmospheres, or more. That was in the late 19th century. More recently, higher pressures had been applied. The use of very high pressures, as was now considered by Haber, was first introduced in the laboratory by Ipatieff, at St. Petersburg, in 1903. Ipatieff, who had received experience of materials and explosives in the military academy, was interested in applying high pressures in part to test the activity of catalysts under varying conditions. His “chief difficulty,” he recalled in this early work [93],

consisted in the construction of an apparatus which could be heated to 600 °C while under several hundred atmospheres pressure. Also, the apparatus had to be constructed in such a way that the pressure developed within could be measured continuously throughout the experiment....After many trials, I finally succeeded in constructing a high pressure apparatus which enabled me to perform thousands of experiments. The temperature in this apparatus sometimes reached 600° and the pressure at this temperature was about 400 atmospheres....Such an apparatus (bomb) was first constructed according to my drawings in the private workshop of Malwistrem, a mechanical engineer.

Ipatieff, unlike Fritz Haber, was mainly interested in organic reactions, such as the catalytic decomposition (dehydrogenation) of alcohols. But they both faced similar problems in their chosen pioneering areas of study.



Fig. 2.19 Fritz Haber (*front row, seated at centre*), colleagues, and guests from overseas, at Karlsruhe, 1909. Included in this group of forty are: technician Friedrich Kirchenbauer, *seated, cross-legged, on the ground*; in the *first, seated, row*, Robert Le Rossignol, *second from left*, and Adolf König, *second from right*; in the *second row*, Friedrich Bergius, *at extreme left*, Joseph E. Coates, *third from left*, and Setsuro Tamaru from Tokyo, *fourth from the left*. Also from Japan is Fusajiro Kotera, *in the fourth row, third from left*. The lady is a Ms Unkowskaja, perhaps a departmental secretary. *Seated to the right of Haber* are his assistants Gerhard Just (*with beard*), and Alfred Leiser. (Bild-Nr VII/3 Haber, Archiv der Max-Planck-Gesellschaft, Berlin-Dahlem)

In 1908, Haber, on the basis of his calculations, decided to resort to a high pressure, at an elevated temperature, in the presence of a catalyst, in an effort to improve the combination of hydrogen with nitrogen beyond trace levels. This was Le Rossignol's assignment, to make up steel apparatus of his own design, incorporating a novel compressor newly acquired by Haber that was capable of achieving a pressure of 200 atmospheres. Critical to the enterprise was the help of the laboratory technician Friedrich Kirchenbauer (1876–[1936]). In the machine shop, Le Rossignol, with the help of Kirchenbauer, fashioned an ultra-strong reaction vessel capable of withstanding both high pressures and high temperatures [94].

Le Rossignol succeeded in introducing several novel innovations. His first major contribution was a special valve, made in the Karlsruhe workshop with the help of Kirchenbauer. Later called the Le Rossignol valve, it withstood the high pressure and controlled the flow of hot gases. He registered a patent-like document that protected such inventions, a Gebrauchsmuster, or utility model. He

was rewarded with the equivalent of five hundred pounds sterling and promoted to Haber's private assistant at an annual salary the equivalent of fifty pounds. Publication in the German journal of electrochemistry revealed the direction of Le Rossignol's work with Haber [95].

By introducing a manganese catalyst, and carrying out the reaction at 200 atmospheres and in excess of 700 °C, an increase in conversion was observed. However, conversion at a lower temperature, 500–600 °C, was desirable. Catalysts based on iron, chromium and nickel were also tried. There was little enhancement until osmium, and uranium, as uranium carbide, were introduced as catalysts. In March 1909, finely divided osmium was found to be the most effective [96, 97]. This rare and valuable metal was received with the help of the banker and industrialist Leopold Koppel (1843–1943), for whom Haber acted as a scientific consultant. Koppel, whose brother Arthur co-founded the Orenstein & Koppel engineering firm, had taken over the troubled enterprises built up by Austrian chemist Carl Auer von Welsbach (1858–1929) after 1885. These concerns specialized in lamps, gas mantles (the main invention), and rare earth alloys. Welsbach achieved an early success with his electric light using metal ribbons based on osmium, the Auer-Oslicht, and also established the wolfram (tungsten) light. Haber's services were mainly to Auer-Gesellschaft, successor to Deutsche Gaslicht Glühlicht AG, founded in 1892 by Koppel and Welsbach. At Auer, a novel electric lamp, known as the Osram, a contraction of osmium and wolfram, the metals used in the filament, was developed. The name was registered in 1906. Soon after, the British General Electric Company joined with German partners, mainly Auer-Gesellschaft, to establish the Osram-Robertson Co. for manufacture of Osram lamps in England (Fig. 2.20).

At Karlsruhe, Le Rossignol put together the complete ammonia apparatus, in which the compressed mixture of reactant gases was, successively, dried, directed through the steel converter, and then cooled. The liquefied ammonia was separated from unreacted gases. During assembly every joint had to be made gas tight, otherwise the experiment would fail. With osmium from Koppel's Auer firm the yield was increased to around 5 %. After observing a successful run, Haber advised Engler: "Es tropft, Herr Geheimrat!" [98]. On 23 March 1909, Haber advised the BASF management of the results.

This was enough to encourage further investigation aimed at technical application. Haber and Le Rossignol had devised an apparatus capable of not only withstanding the high pressure but also of continuous operation. Elegant innovations included pre-heating of reactant gases by the outgoing reaction mixture while still in the converter, and recirculation of unreacted gases, which in turn were warmed up in a heat exchanger. The low yield required a closed, continuous process from which product ammonia could be separated, by liquefaction, and into which fresh charges of preheated hydrogen and nitrogen could be introduced (Fig. 2.21). Hydrogen was obtained by electrolysis. Le Rossignol arranged for a reciprocating pump to recirculate, under pressure, the nitrogen-hydrogen mixture. The small-scale benchtop demonstration apparatus was less than one metre high. In one configuration, platinum asbestos (platinized asbestos) was used to catalyze the reaction between hydrogen and any oxygen that might have entered the system; the gases were then thoroughly dried of resulting water before entry into the converter (Fig. 2.22).



Fig. 2.20 Osram Lamp Division, General Electric Company (from April 1962 Osram (GEC) Ltd), on the GEC North Wembley estate, northwest of London, in the early 1980s. (Osram is derived from *Osmium-Wolfram*.) From 1923, Robert Le Rossignol worked at the adjacent research laboratories

The heat removed from the exiting gases, it was realised, could be used to maintain the continuous operation. There was a further advantage; the process, if viable on a manufacturing scale, and unlike the electric arc and cyanamide processes, did not require a cheap source of electricity. It also provided a cleaner product than the cyanamide and coal gas processes [99–101].

In summary, optimum conditions were established at around 175 atmospheres with compressed gases (a 3:1 mixture of hydrogen and nitrogen) introduced into the electrically heated converter that contained the catalyst, at around 550 °C. It was a major breakthrough, since the process was entirely continuous with rapid withdrawal of product ammonia and recirculation of unreacted hydrogen and nitrogen.

2.8.1 *Bosch and Haber*

August Bernthsen at BASF was not particularly impressed with Haber’s ingenious, and certainly unconventional, if not overly complex, setup, and remained committed to the electric arc. Engler, however, on behalf of Haber, wrote to BASF suggesting that the experimental work was worth following up. As a result, Carl Bosch, as BASF nitrogen-fixation specialist, was instructed to observe Haber’s apparatus in operation at Karlsruhe. According to the reminiscences of one participant, on 1 July 1909, Bosch, Alwin Mittasch, and BASF chief mechanic Kranz,

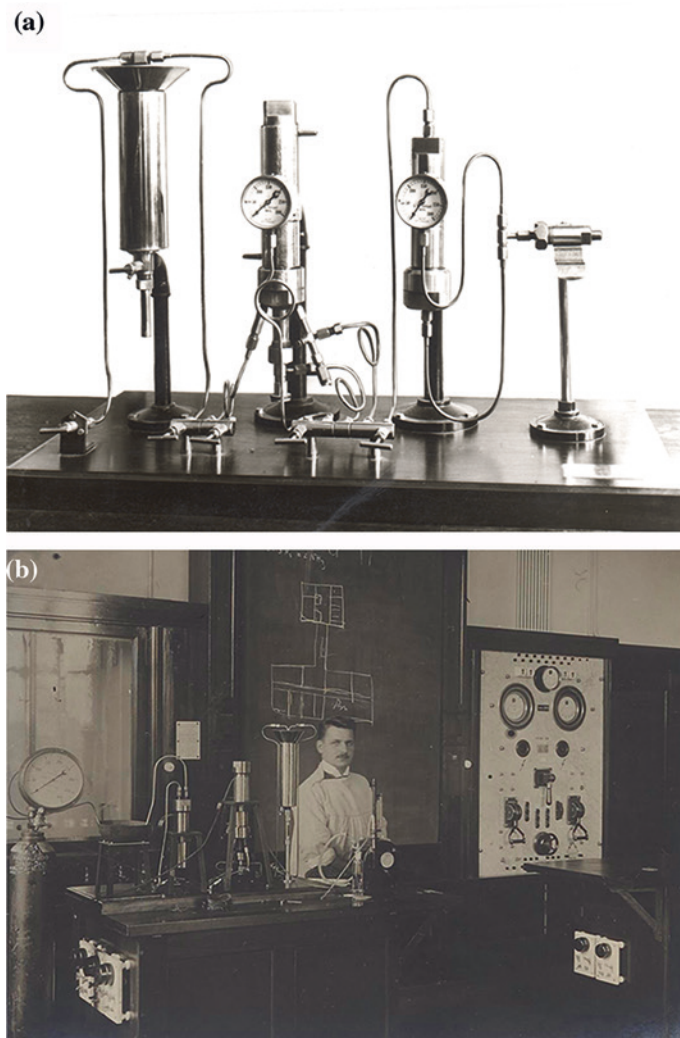


Fig. 2.21 **a** Haber-Le Rossignol 1909 benchtop apparatus for synthesis of ammonia, as originally designed and constructed by Robert Le Rossignol, with assistance from technician Friedrich Kirchenbauer, shown without the circulating pump. The mixture of hydrogen and nitrogen under pressure was delivered into the horizontal tube at right, where a heated platinum catalyst removed traces of oxygen, and then into the drying chamber (the first vertical column). The gas then entered the electrically heated converter, the second, central, column, where in the presence of catalyst the ammonia was formed. The mixed gases were cooled in the third column. There, unreacted nitrogen and hydrogen were separated from ammonia, and directed via the pipe at extreme left back to the converter (piping connection not shown). **b** An almost identical apparatus used for demonstration purposes at Haber's Kaiser-Wilhelm-Institut für physikalische Chemie und Electrochemie in Berlin, around 1914. Liquid ammonia was collected in the cylindrical glass container at the front of the bench. Note the electrical switchgear. Next to the apparatus is Gerhardt Just, Haber's first scientific assistant at Karlsruhe, who, along with Richard Leiser and Setsuro Tamaru, moved from Karlsruhe to Berlin in 1912. (**a**: Robert Le Rossignol/Ralph C. Chirnside/Edelstein Center; **b**: Setsuro Tamaru photograph/Tamaru Family Collection)

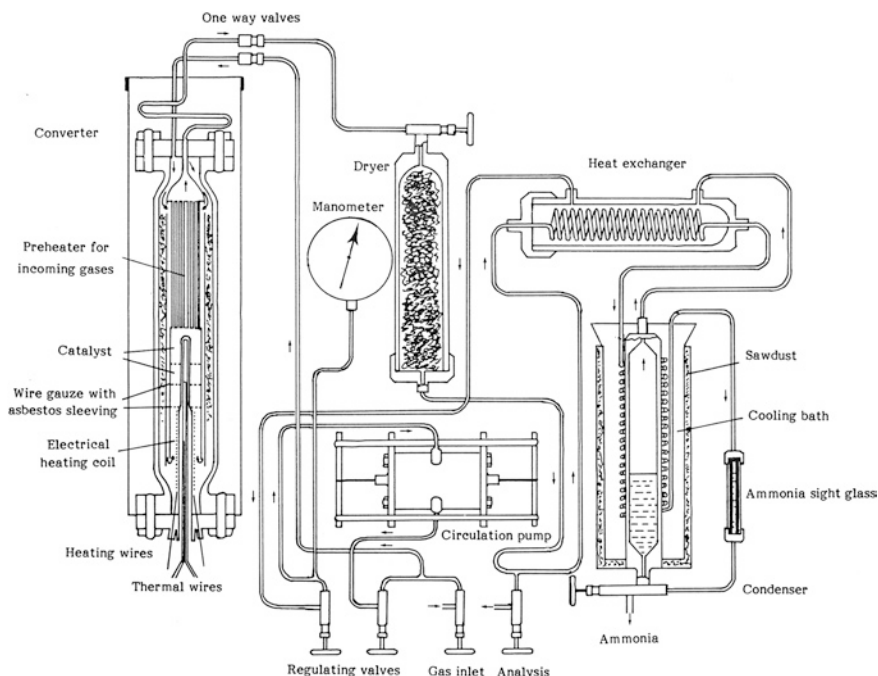


Fig. 2.22 Diagram of laboratory apparatus for continuous synthesis of ammonia from nitrogen and hydrogen, with complete loop, after Fritz Haber and Robert Le Rossignol

turned up at Haber’s laboratory. The first run of the apparatus was hardly auspicious. A bolt of one of Le Rossignol’s carefully made seals sprang under the great pressure. The circulation pump was shut down, and repairs put in hand. Bosch was unable to wait and returned to Ludwigshafen. Mittasch and Kranz remained, until the seal was put right; the next day they saw the liquefied ammonia appear. On July 3, Haber advised BASF [102]:

Yesterday we began operating the large ammonia apparatus with gas circulation in the presence of Dr. Mittasch and were able to keep its uninterrupted production for about five hours. During this whole time it had functioned correctly and it produced continuously liquid ammonia. Because of the lateness of the hour, as we were all tired, we had stopped the production because nothing new could be learned from the continuing experiment. All parts of the apparatus were tight and functioned well, so it was easy to conclude that the experiment could be repeated.... The steady yield was $2\text{ cm}^3/\text{min}$ and it was possible to raise it to $2.5\text{ cm}^3/\text{min}$. This yield remains considerably below the capacity for which the apparatus has been constructed because we have used the catalyst space very insufficiently.

Heinrich von Brunck and colleagues were impressed.

After much discussion in the boardroom, BASF agreed to invest in further studies based on Haber’s method. For the early experimental work at Ludwigshafen, around 100 g of osmium was purchased, probably at the time most of the world supply of the hard, bluish-white metal. Mittasch was assigned the challenge of developing an

inexpensive and equally effective catalyst, one that might make the method commercially viable [103]. In the works laboratory of the BASF Acid Department, his colleague George Stern devised an air-cooled, internally heated, laboratory apparatus for screening catalysts. Each test sample, of two grams, was introduced in small cartridges. Thirty identical experimental units were manufactured. One is preserved at the Deutsches Museum, Munich, as is a replica Haber-Le Rossignol apparatus (Figs. 2.23 and 2.24).

Bosch recognized that the complicated emission spectrum of iron suggested that the metal might be a good candidate as catalyst. This aided the investigations. After over six-and-a-half thousand screening experiments, involving 2,500 mixtures of metals, it was found that iron, activated by the presence of a promoter, and as first examined in 1910, was an ideal catalyst. The study of ammonia catalysts continued until 1922, by which time some 20,000 experiments had been undertaken (Figs. 2.25 and 2.26) [104, 105].

No less problematic were the metallurgical and engineering challenges. Carl Bosch worked on the design of a pilot plant, aided by chief engineer Franz Lappe. They had to construct a converter suited to continuous operation at the high pressure and high temperature. The special Mannesmann hot rolled seamless steel tubes acquired for this work burst under the forcing conditions, at first believed to be the result of embrittlement caused by nitrogen. Bosch (Fig. 2.27) used his training in metallographic research to establish the cause. At the high pressure, it was found that hydrogen diffused into the iron of the steel wall, reacting with carbon in its crystal

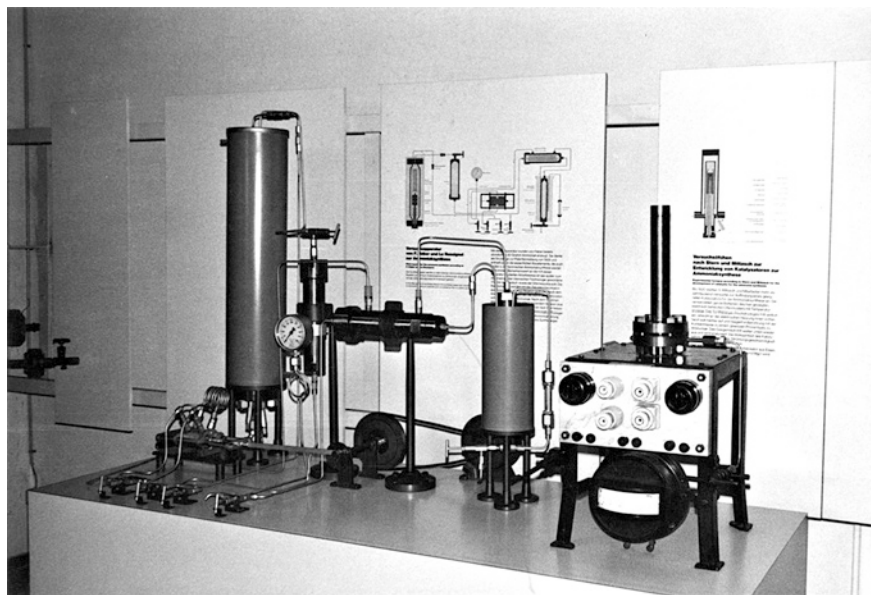


Fig. 2.23 At right: BASF catalyst test apparatus, with vertical pressure tube, as used by Alwin Mittasch. At left: replica Haber-Le Rossignol benchtop apparatus for synthesis of ammonia. (Photo by author, Deutsches Museum, Munich, 1982)

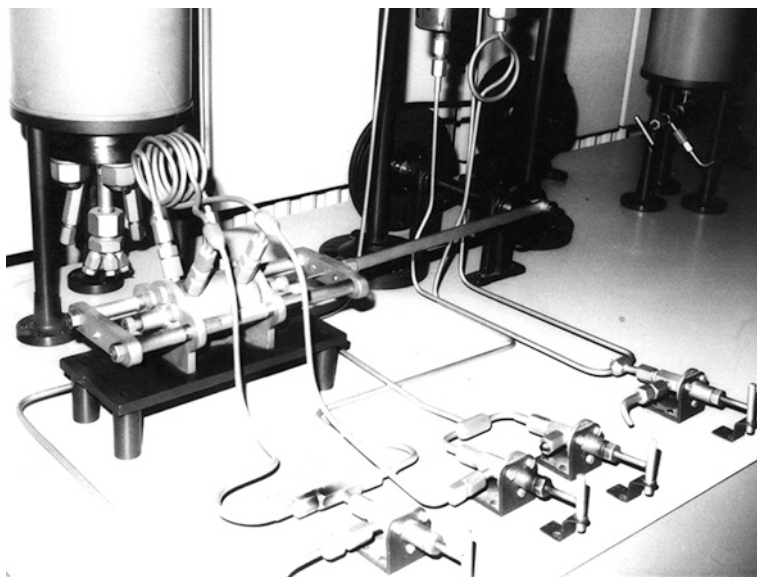


Fig. 2.24 Valves for control of gas flow and recirculating pump, on replica Haber-Le Rossignol benchtop apparatus

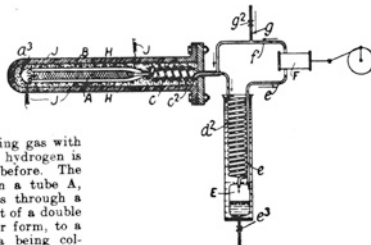
structure to form methane, causing the steel to blister, as a result of decarbonization. At high temperature and pressure the steel became brittle; explosions were inevitable. The converter was re-designed to prevent, or at least minimize, this difficulty. The development work continued with experimental and pilot-plant scale converters encased in concrete, minimizing damage to the surroundings from explosions. In February 1911, Bosch, aided by Lappe, overcame the problem by developing a double-wall converter. The inner wall, of soft iron, or low-carbon steel, which did not undergo decarbonization, allowed hydrogen to diffuse through it, with rapid loss of pressure, under which conditions the outer wall, of ordinary steel, did not become brittle. This was aided by narrow grooves machined on the outside of the inner wall as the tube was turned. Small holes in the outer wall enabled release of some hydrogen to the surroundings (Fig. 2.28). Early on, when the converters were externally heated, there was also the problem of large temperature gradients. This was overcome by burning inside the converter some of the reaction gas mixture with air, the so-called “reverse” flame [106]. One important advantage of increasing the dimensions of converters was that external heating was no longer required.

Gas compressors capable of providing the very high synthesis pressure—not previously used in chemical industry—had to be designed. These were of the reciprocating type, using pistons driven by a crankshaft to deliver reactant gases at 200 atmospheres. Tests carried out on 5 March 1911 with a 4-m high converter were considered sufficiently successful for the commissioning of a

17,951. Johnson, J. W., [Badische Anilin & Soda Fabrik]. Aug. 5.

1909

Catalytic materials, processes, and apparatus.—Ammonia is produced from nitrogen and hydrogen by treatment with a catalytic material under pressure at a raised temperature, the ammonia is removed at a lower temperature for instance by cooling or by an absorbent or both, and the remaining gas with the addition of more nitrogen and hydrogen is treated to produce ammonia as before. The catalytic substance is contained in a tube A, from which the treated gas passes through a heat interchanger which may consist of a double coil c, c', or which may be of other form, to a condenser d', the liquid ammonia being collected in a vessel E, from which it is withdrawn by a tap e'. The uncondensed gas passes by the path f, c' to a pump F and thence by the path g, c' to the tube A; nitrogen and hydrogen being added by a tap g' on a pipe g. The tubes A, B and the heat interchanger c, c' are inclosed in insulating packing in an outer tube H. The tube B has a small opening a' to equalize the pressure within and without, and is surrounded by an electrical heating-coil J.



When a catalytic material such as osmium is employed adapted to produce a relatively high concentration of ammonia, the heat interchanger may be omitted. If the ammonia is not required in the liquid form, it may be allowed to vaporize and to cool the gas leaving the catalytic material. The pressure used may be 150 atmospheres, and the temperature of the tube A 500–1000° C.

1910

19,249. Johnson, J. W., [Badische Anilin & Soda Fabrik]. Aug. 16. [Cognate Applications, 19,250/10 and 19,251/10.]

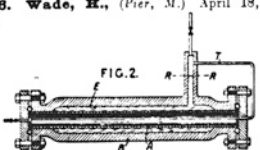
Catalytic materials.—Better yields are obtained in the synthetic production of ammonia by the addition of substances termed "promoters" to the iron, nickel, or cobalt used as the catalytic agent. These substances are generally compounds of magnesium, beryllium, aluminium, or of the alkali, alkaline-earth, or rare-earth metals, or of zirconium, vanadium, tantalum, chromium, manganese, molybdenum, or tungsten. The addition of the oxide or a compound of magnesium or aluminium is particularly favourable. It is found, however, that certain bodies have the property of diminishing or destroying the catalytic property of the iron &c. Such bodies are, for example, arsenic, sulphur, selenium, tellurium, phosphorus, boron, antimony, bismuth, lead, tin, or zinc, or their compounds, and the presence of carbon monoxide and dioxide, or of oil in the gases should be avoided. Iron or the like, which is unsuitable for use as a catalyst owing to the presence of contact poison and for other reasons, can be rendered effective by heating to a high temperature in admixture with a promoter, so that a mixture of oxides is obtained, which is reduced by means of hydrogen, preferably at as low a temperature as possible. It is preferred

that the first heating should be sufficient to melt the mixture. This treatment may be repeated until the desired result is obtained. The reaction gases may be freed from contact poison by passage over a material capable of absorbing it, and this material may be a further quantity of the catalytic agent placed in advance. The mixture of iron and a promoter may be supported on a carrier such as asbestos or chamotte, and one constituent of the carrier may constitute the promoter, but it is necessary in this case that the iron and promoter should be actually mixed together. In use, a mixture of nitrogen and hydrogen, preferably in combining proportions, is passed over the heated catalytic agent, and the reaction may be effected under great pressure, as described in Specification 14,023/10.

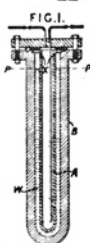
14,023. Haber, F. Sept. 13, 1909, [Convention date].

Catalytic materials and processes.—The catalytic process for the production of ammonia from nitrogen and hydrogen is effected under a pressure of 100 atmospheres, or higher pressure. Suitable catalytic materials are finely-divided uranium or osmium, or even iron. Specification 17,951/09 is referred to.

100,216. Wade, H., (Pier, M.) April 18, 1914.



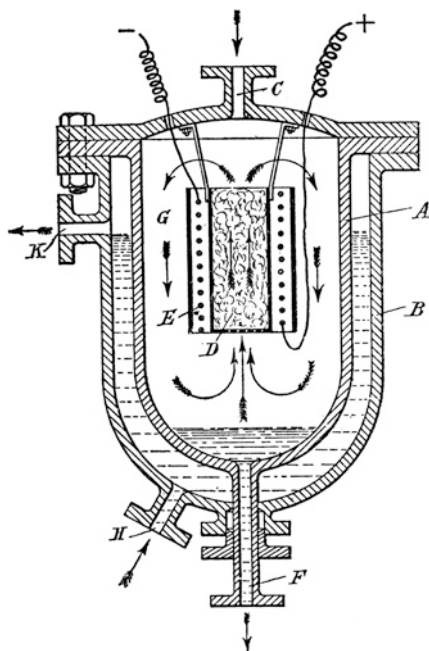
Catalytic apparatus; effecting reactions between gases.—For effecting the reaction of hydrogen and another gas under pressure and at high temperature, for instance in the catalytic production of ammonia, the reaction vessel, which may be of a porous material such as unglazed porcelain or magnesite, or of metal, for instance iron having a low carbon content, is enclosed in an outer pressure-resisting vessel, the space between being occupied by a fused material, for instance Woods metal, which will not allow the diffusion of



hydrogen through it. The inner vessel A may be suspended in the outer vessel B, perforations X allowing communication between the interior of the vessel A and the space around it for the metal W. When the lid has been screwed on, the gas mixture is admitted and the apparatus is heated, but the part above the level P is not allowed to rise above 200° C. In a modification, Fig. 2, the inner vessel is welded at its ends to the outer vessel, the space E between being filled with molten material to the level R, and a pipe F communicating between the space above the level R and the interior of the vessel A. The outer vessel may be of steel, and if the temperature is to exceed 550° C., it is preferred to treat it by heating to a temperature suitable for hardening, quenching it in oil, heating to above the working temperature, and cooling slowly. The most suitable steels for subjecting to this treatment are nickel steel and nickel chrome steel. Specifications 15973/10 and 9661/14 are referred to.

Fig. 2.25 British patent abstracts for synthetic ammonia, filed by Fritz Haber, BASF, and, below, Mathias Pier (who joined BASF in 1920)

Fig. 2.26 Apparatus for synthesis of ammonia, as appearing in BASF British patent 13,097 of 30 May 1910. “... ammonia is condensed by abstracting heat from a surface in or forming part of the walls of a vessel in which the combination takes place...the reaction vessel *A*, capable of withstanding pressure, is surrounded by a cooling jacket *B*. The reacting gases enter the apparatus at *C*, pass up through the catalyst *D*, which is electrically heated and the condensed ammonia collects at the bottom and is withdrawn through pipe *F*.” Such patents revealed sufficient to provide protection to the patentee, but not enough to enable technical working of the method. (Figure from patent abstract)



full-size manufacturing plant. What might have been a setback was an attempt by Hoechst—like other rival dye firms also interested in nitrogen fixation—to disallow the ammonia patents. Fortunately for BASF, the claim made by Hoechst, whose expert witnesses included Ostwald, was rejected in March 1912.

On 11 September 1912, Bernthsen, now no longer enamoured with electric arc fixation of nitrogen, and with great pride and confidence in Bosch's achievement, gave an outline of the new BASF synthetic ammonia process, with special reference to catalyst promoters and poisons, at the Eighth International Congress of Applied Chemistry, held in New York. On the same occasion, Samuel Eyde described the latest developments in the Birkeland-Eyde process.

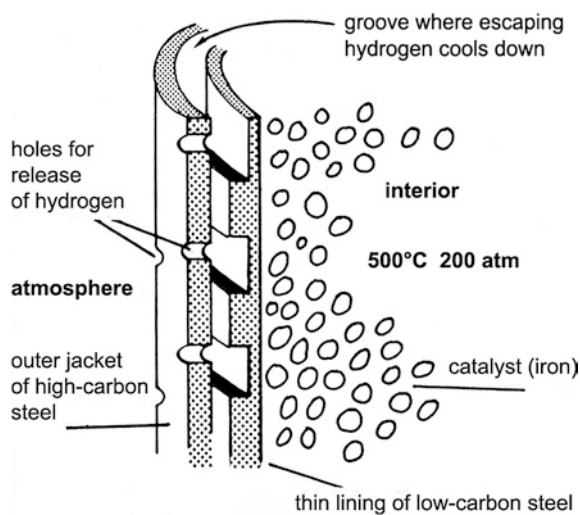
For the pilot plant, nitrogen was at first obtained by Carl von Linde's process for liquefaction and distillation of air, though it was restricted in output and expensive. Hydrogen came from electrolysis of brine. For full-scale production, the supply of large amounts of extremely pure nitrogen and hydrogen gases required improvement of existing coal-based processes, as well as methods of cleaning gases. Nitrogen was obtained by blowing air over coke to form producer gas, the mixture of carbon monoxide and nitrogen, in a process similar to that introduced by Ludwig Mond. Hydrogen was obtained from water gas, that is the mixture of carbon monoxide and hydrogen resulting from the action of steam on incandescent coke (Fig. 2.29).

Carbon monoxide was a known catalyst poison. At BASF it was removed from both producer gas and water gas by conversion to carbon dioxide. Removal of final traces of monoxide was achieved with a suitable copper solution that did

Fig. 2.27 Carl Bosch.
(*Erzeugnisse unserer Arbeit.*
Frankfurt am Main: I.G.
Farbenindustrie, 1938, p. 17)



Fig. 2.28 Simplified diagram of double wall converter, as invented by Carl Bosch for the synthesis of ammonia from nitrogen and hydrogen. The Bosch holes were used on early converters, before improved steels became available



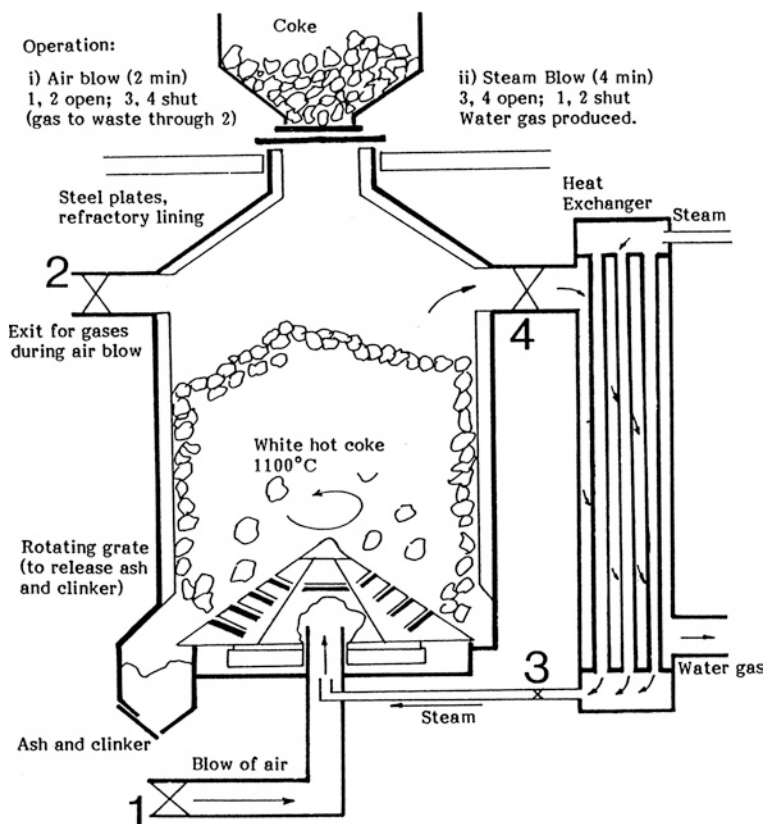


Fig. 2.29 Manufacture of water gas (carbon monoxide and hydrogen) from coke, steam and air, by the Bamag (Berlin-Anhaltische Maschinenbau AG) process

not corrode iron, as worked out by Carl Krauch (1887–1968), a former student of Nernst. This was adopted in the early stage of ammonia production. Significantly, Albert Frank, in collaboration with Caro and Linde, around 1909 developed a process for separating carbon monoxide and other unwanted constituents from hydrogen by liquefaction [107].

The new equipment, including compressors, 8-m high-pressure converters, each weighing eight-and-a-half tons, storage tanks, steel piping, recirculation pumps, with gas flow controlled by novel valves, was put together 3 km north of the Ludwigshafen factory at the new Oppau facility, starting in September 1912 (Figs. 2.30 and 2.31) [108, 109]. A dedicated Ammonia Laboratory, with a staff of around ten academically trained chemists, headed by Mittasch, served the new Nitrogen Department [110]. Production of synthetic ammonia began on 9 September 1913 at the rate of 20 tons per day. The ammonia was converted into ammonium sulphate for sale as fertilizer.

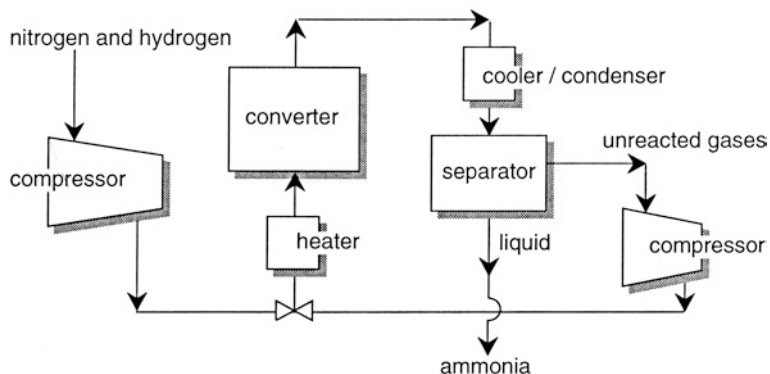


Fig. 2.30 Block diagram for synthesis of ammonia



Fig. 2.31 Early BASF Haber-Bosch converter, showing massive bolts and studs required to secure the cover plate. This converter is now preserved at the Wroughton outstation of the Science Museum London

Now a new source of stable synthetic nitrogen product was added to cyanamide, nitric acid from electric arc processes, gas works and coke oven ammonia, and, most importantly, imported Chile saltpetre. The latter was still the principal raw material for nitric acid production. Nevertheless, German hopes for self-sufficiency in nitrogen fertilizer had come a giant step closer. Carl Bosch had



Fig. 2.32 Fritz Haber, at left, and Albert Einstein, at Haber’s Berlin institute in the summer of 1914. The photograph was taken by Haber’s Japanese colleague Setsuro Tamaru. (Tamaru Family Collection/The Albert Einstein Archives, The Hebrew University of Jerusalem, call no. 64-007). In 1905, his “year of miracles” (*annus mirabilis*), Albert Einstein, as a patent examiner in Bern, reviewed Ignacy Mościcki’s Swiss patent application for an electric arc apparatus designed to capture atmospheric nitrogen. This led to meetings between the two men in Bern and at the University of Fribourg. (Mościcki to Einstein, 27 September 1932, The Albert Einstein Archives, The Hebrew University of Jerusalem, AE 71-782)

stretched available technology to the limit and succeeded. In 1914, BASF opened an Agriculture Experiment Station at Limburgerhof, near Ludwigshafen, to engage in fertilizer and agrochemical studies.

Meantime, in 1911, Haber, now a leading physical chemist, noted for his ingenuity and organizational skills, and supported by Koppel, was appointed head of the new Kaiser-Wilhelm-Institut für physikalische Chemie und Electrochemie, in Berlin, which opened in 1912 [111]. From 1914, the institute hosted Albert Einstein (1879–1955), while waiting for his institute of physics to be established (which took until 1917), and developing his field equations (1915) (Fig. 2.32). The Habers had acted as mediators during the separation of Einstein from his first wife, in July 1913 [112].

2.9 Nitric Acid

Production of synthetic ammonia by direct fixation of nitrogen was a triumph. For the agricultural sector the ammonia was available as ammonium sulphate, a product already produced from gas works ammonia. For many purposes, however, the ammonia needed to be converted into nitric acid. During the 19th century, nitric acid was manufactured by the reaction between Chile saltpetre and sulphuric acid in cast iron pots and passing the resulting nitrous fumes through a series of absorption towers. For the manufacture of nitrates and aromatic nitro compounds, particularly for use in high explosives, including nitroglycerine, in many cases nitric acid of medium to high (“strong”) concentration was essential.

Factories that used the electric arc processes incorporated tall absorption towers for producing and concentrating nitric acid. This stimulated development of processes not only for oxidation of ammonia to nitric acid, but also for its concentration, two difficult technical challenges that had to be overcome. Newly available were ammonia oxidation processes, used on a limited scale for conversion of cyanamide and gas works ammonia. In 1908 the first large plant for catalyzed air oxidation of ammonia to nitric acid was constructed by the *Gewerkschaft des Steinkohlenbergwerks Lothringen*. The ammonia came from a coke-oven plant at Gerthe, Westphalia, near Bochum in the Ruhr. This relied on Wilhelm Ostwald’s method, developed at Leipzig with Eberhard Brauer, his future son-in-law, during 1900–1901, using platinum, solid or spongy, as a foil or wire netting, as catalyst, for which a patent application was filed in 1902. Ostwald’s first apparatus was a vertical nickel tube into which was inserted a roll of platinum. A mixture of ammonia and air was introduced at the bottom and preheated by the outgoing gas mixture. For large-scale production, other firms among the consortium of local coal producers were involved. Brauer and *Köln-Rottweiler Sprengstoff-Gesellschaft* cooperated with *Kohlenzeche Lothringen*, also in Gerthe, in making improvements. Working closely with Ostwald in design of plant during 1906 was German engineer Friedrich Uhde (1880–1966), at *Kohlenzeche Lothringen*, where he was employed from 1905 to 1914. In 1921 he set up as an engineering contractor.

Though difficulties were encountered due to the impermeability of the platinum, the output of nitric acid from the ammonia process at Gerthe, based on Ostwald’s work, in 1911 reached 1,495 tons [113].

Because of prior publication by Kuhlmann and others, Ostwald’s main patent application in Germany was rejected (though it was accepted in other countries). This enabled researchers in Germany to investigate not only the action of platinum but also of other catalysts. Conveniently for later historians, Georg Lunge in 1916 drew up what was probably the most comprehensive overview of the existing nitrogen industry until 1914, including Chilean nitrate, and the many processes invented for capturing nitrogen, as well as methods for oxidation of ammonia to nitric acid, and concentrating the acid [114].

Nikodem Caro worked on the catalytic conversion of cyanamide-derived ammonia to nitric acid, using thorium compounds as catalysts at atmospheric pressure. In 1907,

Caro and Albert Frank collaborated with the engineering firm Berlin-Anhaltische Maschinenbau AG (Bamag), on developing ammonia oxidation in the presence of air using platinum as catalyst. Special tanks were designed for bulk transportation of the acid. Two years later, Karl Kaiser of the Technische Hochschule Charlottenberg proposed that the air be preheated prior to mixing with ammonia. Significantly in 1911 he suggested the use of platinum gauze. A pilot plant was erected at Spandau, Berlin, around 1912. It attracted little interest, apart from a single use at Kharkov, Russia. Nevertheless, Kaiser's gauze became a later standard [115]. Kaiser subsequently advised Bamag on plant design. In early 1914, probably to avoid reliance on platinum, a process employing Caro's thorium oxide catalyst was scheduled to be introduced on a manufacturing scale at Bayrische Stickstoffwerke. For Caro, H. Hackl and H. Bunzel investigated catalysts based on barium nitrate [116–118].

During 1914, Caro and Frank filed patents for oxidation of ammonia with an electrically heated platinum gauze catalyst. They also developed a much improved apparatus for the oxidation. This was a water-cooled aluminum box fitted with a conelike hood of aluminum incorporating a mica sight glass. Baffles distributed the incoming gases that were directed over an electrically heated single layer of platinum gauze. The nitrogen oxides arising from oxidation of ammonia were then absorbed in a stream of water, to give nitric acid. This work, also carried out with Bamag, offered a considerable improvement over Ostwald's corrugated platinum strip that had a lifetime of four to six weeks [119, 120]. When, shortly after the outbreak of war in 1914, Landis managed to ship to the United States ammonia oxidation converters they were no doubt of the Bamag type.

Despite considerable success, severe corrosion problems in absorption areas still had to be overcome. Under normal economic conditions this process could not provide the basis for replacing even in a small way the manufacture of nitric acid from Chilean nitrate. But this was not the case in a situation of war emergency. By 1916, Bamag had supplied more than seventy units for oxidation of ammonia, incorporating platinum gauzes, and as a result of war-related demand were called upon to manufacture several more.

Synthetic ammonia, and oxidation of ammonia to nitric acid, might well have remained no more important than many other novel industrial processes that were appearing during the first decade or so of the 20th century but for a world-shattering event: the assassination of Archduke Franz Ferdinand of Austria-Este, eldest son of Archduke Karl Ludwig, and heir presumptive to Franz Josef and the Austro-Hungarian Empire, and his wife, at Sarajevo on 28 June 1914. On 28 July there was the first declaration of what was to become the "All-Europe Conflict," or Great War. Until then there had been no general mobilization of industry for war. Oppau was producing (according to mainly post-war figures) around thirty tons of synthetic ammonia every day, by the Haber-Bosch process, for conversion to the fertilizer ammonium sulphate. Hugo Wolff at BASF had examined metals of the platinum group as catalysts for oxidation of ammonia. Studies on nitrogen fixation and oxidation of ammonia to nitric acid were conducted at Bayer, and at the Hoechst Dyeworks (Meister, Lucius & Brüning). They were about to receive priority.

References

1. Crookes W (1898) The world's wheat supply. Reports of the British Association for the Advancement of Science, London, p 4
2. Crookes W (1900) The wheat problem. GP Putnam's Sons, New York
3. Stock JT, Orna MV (1989) Electrochemistry: past and present. ACS Symposium Series 390. American Chemical Society, Washington
4. Mader U (2001) Emil und Walther Rathenau in der elektrochemischen Industrie, 1888–1907: eine historische Studie. Gesellschaft, Geschichte, Gegenwart, vol 20. Trafo Verlag, Berlin
5. Volkov S (2012) Walther Rathenau: Weimar's fallen statesman. Yale University Press, Yale
6. Bäumlér E (English version) (1968) A century of chemistry. Econ Verlag, Düsseldorf, pp 49–52
7. Trescott M (1989) The rise of the American electrochemicals industry, 1880–1910. Contributions in economics and economic history. Greenwood Press, Westport
8. Mierzecki R (1998) The Polish chemical industry: isolated developments in a divided country. In: Homburg E, Travis AS, Schröter HG (eds) The chemical industry in Europe, 1850–1914: industrial growth, pollution, and professionalization. Kluwer, Dordrecht, pp 59–71, on 70
9. Egeland A, Leer F (1986) Professor Kr. Birkeland: his life and work. IEEE T Plasma Sci PS-14(6):666–677
10. Grimnes OK (2001) Sam Eyde: Den grenseløse gründer. Aschehoug, Oslo (in Norwegian)
11. Kilburn Scott E (1912) The manufacture of nitrates from the atmosphere. Nature 89(2227) (4 July):463–465, and 89(2228) (11 July):490–492, on 463–464
12. <http://www.hydro.com/en/About-Hydro/Our-history/1900–1917/1905-Three-remarkable-men>. Accessed 12 Aug 2014
13. Sagatos OJ (2005) Progress of a different nature: Hydro 1905–2005. Pax Forlag, Oslo, pp 43–44
14. Witt ON (1905) Das neue Technisch-Chemische Institut der Königlich-Technischen Hochschule zu Berlin und die Feier seiner Eröffnung am 25. Nov. 1905. Weidmann, Berlin
15. Sagatos OJ (2005) Progress of a different nature: Hydro 1905–2005. Oslo, Pax Forlag, p 45
16. Birkeland K (1906) On the oxidation of atmospheric nitrogen in electric arcs. Discussion. T Faraday Soc 2:116–119, on 116–117
17. Taugbøl T, Andersen EM, Grønn U, Moen BF (2014) Nomination dossier: Rjukan-Notodden industrial heritage site. Nomination to the UNESCO World Heritage List, Norway, pp 44–46
18. Lunge G (1916) Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige, 2 vols. Friedr. Vieweg & Sohn, Braunschweig, vol. 1, pp 261
19. Eyde S (1912) Oxidation of atmospheric nitrogen and development of resulting industries in Norway. Ind Eng Chem 4:771–774
20. Crookes W (1914) Presidential address. J Soc Chem Ind 33(14):720–722, on 720
21. Lunge G (1916) Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige, 2 vols. Friedr. Vieweg & Sohn, Braunschweig, vol. 1, pp 261, 262
22. Taugbøl T, Andersen EM, Grønn U, Moen BF (2014) Nomination dossier: Rjukan-Notodden industrial heritage site. Nomination to the UNESCO World Heritage List, Norway, pp 31–42
23. Kilburn Scott E (1915) Production of nitrates from air, with special reference to a new electric furnace. J Soc Chem Ind 34(3):113–126, on 121
24. Behrman EJ (2005) Karl Elbs, 1858–1933. Bull Hist Chem 30(1):19–22
25. Scharff M (1927) Dr. Otto Schönherr zum Gedächtnis. 1861–1926. Z Angew Chem 40(14):393–394
26. Mantell CL (1940) Industrial electrochemistry, 2nd edn. McGraw-Hill, New York, p 576
27. Lunge G (1916) Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige, 2 vols. Friedr. Vieweg & Sohn, Braunschweig, vol. 1, pp 263–269
28. Kilburn Scott E (1912) The manufacture of nitrates from the atmosphere. Nature 89(2227) (4 July):463–465, and 89(2228) (11 July):490–492, on 465

29. Reinhardt C (1993) Ueber Wissenschaft und Wirtschaft: Fritz Habers Zusammenarbeit mit der BASF 1908–1911. In: Albrecht H (ed) *Naturwissenschaft und Technik in der Geschichte. 25 Jahre Lehrstuhl für Geschichte der Naturwissenschaft und Technik am Historischen Institut der Universität Stuttgart*. Universität Stuttgart, Stuttgart, pp 287–315
30. Johnson JA (2003) The power of synthesis, 1900–1925. In: Abelhauser W, von Hippel W, Johnson JA, Stokes RG, *German industry and global enterprise. BASF: the history of a company*. Cambridge University Press: New York, pp 115–206, on 144
31. Lunge G (1916) *Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige*, 2 vols. Friedr. Vieweg & Sohn, Braunschweig, vol. 1, pp 253–256
32. Kilburn Scott E (1912) The manufacture of nitrates from the atmosphere. *Nature* 89(2227) (4 July):463–465, and 89(2228) (11 July):490–492, on 491
33. Wisniak J (2007) Phillipe-August Guye. *Revista CENIC Ciencias Químicas* 38(3):415–422
34. Lunge G (1916) *Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige*, 2 vols. Friedr. Vieweg & Sohn, Braunschweig, vol. 1, pp 246–247
35. Schweitzer H (1907) In: Jubilee of the discovery of mauve and of the foundation of the coal-tar colour industry by Sir WH Perkin, F.R.S., D.Sc., LL.D., Ph.D., Dr.Ing. Meldola R, Green AG, Cain JC (eds). *Perkin Memorial Committee*, London, p 62
36. Kastens ML, McBurney WG (1952) Calcium cyanamide. *Modern chemical processes*. 3 vols (1950, 1952, 1954), vol 2. Reinhold Publishing, New York, pp 97–110, on 100
37. Evonik Industries (2014) Adolph Frank, chemist and entrepreneur. <http://history.evonik.com/sites/geschichte/en/predecessor-companies/skw-trostberg/frank>. Accessed 19 Aug 2014
38. Evonik Industries (2014) Nikodem Caro, chemist and entrepreneur. <http://history.evonik.com/sites/geschichte/en/predecessor-companies/skw-trostberg/car0>. Accessed 19 Aug 2014
39. Eissler M (1902) The cyanide process for the extraction of gold and its practical application on the Witwatersrand goldfields & elsewhere. Crosby Lockwood & Son, London
40. Evonik Industries (2014) Albert R Frank, chemist and businessman. <http://history.evonik.com/sites/geschichte/en/predecessor-companies/skw-trostberg/frank>. Accessed 19 Aug 2014
41. Cyanidgesellschaft, German patents nos 152,260 (1901), and 154,505 (1902)
42. Frank A[dolph] (1906) Über die direkte Verwertung des Stickstoffes der Atmosphäre zur Gewinnung von Düngemitteln und anderen chemischen Produkten. *Z Angew Chem* 19:835–840
43. Caro N (1906) Über einheimische Stickstoffquellen. *Z Angew Chem* 19:1569–1581
44. di San Filippo PA (1998) The Italian chemical industry from 1861 to 1918. In: Homburg E, Travis AS, Schröter HG (eds) *The chemical industry in Europe, 1850–1914: industrial growth, pollution, and professionalization*. Kluwer, Dordrecht, pp 45–57, on 49
45. Kilburn Scott E (1912) The manufacture of nitrates from the atmosphere. *Nature* 89(2227) (4 July):463–465, and 89(2228) (11 July 12):491–492
46. Bäumlér E (English version) (1968) A century of chemistry. Econ Verlag, Düsseldorf, p 61
47. Kastens ML, McBurney WG (1952) Calcium cyanamide. *Modern chemical processes*. 3 vols (1950, 1952, 1954), vol 2. Reinhold Publishing, New York, pp 97–110
48. Haynes W (1957) On the chemical frontier: the Cyanamid story. Copy held at Sidney M. Edelstein Library for the History and Philosophy of Science, Technology and Medicine, National Library of Israel, pp 22–24, 25–26, 48–49
49. Massell DP (2000) Amassing power: J. B. Duke and the Saguenay River, 1897–1927. McGill-Queens University Press, Montreal, pp 114–119
50. Moloney B (1990) Technology and investment: the prewar Japanese chemical industry. Harvard University Press, Harvard, pp 71–84
51. Travis AS (2014) The emerging role of titrimetry in late nineteenth-century industrial problem solving: the example of trace analysis for perchlorate in Chile saltpetre. *Ambix* 61(1):67–94
52. Pranke EJ (1913) Cyanamide: manufacture, chemistry and uses. Williams & Norgate, London
53. Crawford E (1987) The beginnings of the Nobel Institution: the science prizes, 1901–1915. Cambridge University Press, Cambridge, pp 181–183

54. Egeland A, Burke WJ (2005) Kristian Birkeland: the first space scientist. *Astrophysics and Space Library*. Springer, Dordrecht, pp 139–141
55. Reinhardt C, Travis AS (2000) Heinrich Caro and the creation of modern chemical industry. Kluwer, Dordrecht
56. Felck G (1993) Wilhelm Ostwald. 1853–1932. In: James LK (ed) Nobel laureates in chemistry 1901–1992, History of modern chemical sciences. American Chemical Society, Washington DC, pp 61–68
57. Stoltzenberg D (1994) Fritz Haber: Chemiker, Nobelpreisträger, Deutscher, Jude. VCH, Weinheim, pp 141–143. Abridged edition in English: Stoltzenberg D (2004) Fritz Haber: chemist, Nobel laureate, German, Jew. Chemical Heritage Foundation, Philadelphia, pp 80–81
58. Holdermann K (1949) Carl Bosch und die Naturwissenschaft. *Naturwiss* 36(6):161–165
59. Krauch C (1940) Carl Bosch zum Gedächtnis. *Angew Chem* 53:285–288
60. Stoltzenberg D (2004) Fritz Haber: chemist, Nobel laureate, German, Jew. Chemical Heritage Foundation, Philadelphia, quoted from p 130
61. Kilburn Scott E (1912) The manufacture of nitrates from the atmosphere. *Nature* 89(2227) (4 July):463–465, and 89(2228) (11 July 12):490–492, on 492
62. Kilburn Scott E (1915) Production of nitrates from air, with special reference to a new electric furnace. *J Soc Chem Ind* 34(3):113–126, on 113
63. Kilburn Scott E (obituary) (1941) *Engineer*, London 172(4462):41
64. Goran MH (1967) The story of Fritz Haber. University of Oklahoma Press, Norman
65. Wille HH (1969) Der Januskopf: Leben und Wirken des Physikochemikers und Nobelpreisträgers Fritz Haber. Verlag Neues Leben, Berlin
66. Harris H (1992) To serve mankind in peace and the Fatherland in war: the case of Fritz Haber. *Ger Hist* 10(1):24–38
67. Stoltzenberg D (1994) Fritz Haber: Chemiker, Nobelpreisträger, Deutscher, Jude. VCH, Weinheim
68. Szöllösi-Janze M (1998) Fritz Haber 1868–1934: eine biographie. VCH-Beck, Munich
69. Dunikowska M, Turko L (2011) Fritz Haber, the damned scientist. *Angew Chem Int Edit* 50:10050–10062
70. Hoffman R, Lazlow P (2001) Coping with Fritz Haber's somber literary shadow. *Angew Chem Int Edit* 40:4599–4604
71. Smil V (2001) Enriching the earth: Fritz Haber, Carl Bosch, and the transformation of world food production. MIT Press, Cambridge, pp 41–48
72. Gal J (2015) Remembering Fritz Haber in the year 2015. *L'Actualité chimique*, nos 397–398 (June–July), pp. 114–121
73. Charles D (2005) Master mind: the rise and fall of Fritz Haber, the Nobel laureate who launched the age of chemical warfare. Harper Collins, New York. In the UK: Between genius and genocide: the tragedy of Fritz Haber, father of chemical warfare. Cape, London
74. Bretislav F (2005/2006) Fritz Haber (1868–1934). *Angew Chem Int Edit* 44:3957–3961, and 45:4053–4055
75. Thomas H (2008) The alchemy of air: a Jewish genius, a doomed tycoon, and a scientific discovery that fed the world but fueled the rise of Hitler. Harmony Books/Crown Publishing Group/Random House, New York
76. Ragussis D (2008) Haber: the father of gas warfare. Film directed by Ragussis (United States)
77. Stoltzenberg D (2004) Fritz Haber: chemist, Nobel laureate, German, Jew. Chemical Heritage Foundation, Philadelphia, quoted from p 22
78. Müller G (1909) Die Chemische Industrie. B. G Teubner, Leipzig, p 199
79. Schuster C (1976) Wissenschaft und Technik. BASF, Ludwigshafen, pp 108–127
80. von Leitner G (1993) Der Fall Clara Immerwahr: Leben für eine humane Wissenschaft. C. H. Beck, Munich
81. Sicheritz H (2014) Die Hälfte des Lebens. Femina doctissima. Clara Immerwahr. Television film, directed by Sicheritz (Austria)
82. Ramsay W, Young S (1884) The decomposition of ammonia by heat. *J Chem Soc* 45:88–93
83. Perman EP (1905) The direct synthesis of ammonia. *Proc R Soc Lond* 76:167–174

84. Haber F, van Oordt G (1905) Über Bildung von Ammoniak aus den Elementen. *Z Anorg Chem* 43:111–115; 44: 341–378; 47:42–44
85. Dronsfield AT, Morris PJT (2007) Who really discovered the Haber process? <http://www.rsc.org/Education/Eic/issues/2007May/WhoReallyDiscoveredHaberProcess.asp>. Accessed 19 Aug 2014
86. Travis AS (1984) The high pressure chemists. Brent Schools and Industry Project, Wembley, p 15, quoting Haber
87. Barkan DK (1999) Walther Nernst and the transition to modern physical science. Cambridge University Press, Cambridge, pp 129–131
88. Holdermann K (1957) Alwin Mittasch, 1869–1953, in *Memoriam*. *Chem Ber* 90:xli–liv
89. Schuster C (1976) Wissenschaft und Technik. BASF, Ludwigshafen, pp 124–125
90. Smil V (2001) Enriching the earth: Fritz Haber, Carl Bosch, and the transformation of world food production. MIT Press, Cambridge, pp 75–82
91. Stoltzenberg D (2004) Fritz Haber: chemist, Nobel laureate, German, Jew. Chemical Heritage Foundation, Philadelphia, p 89
92. Ipatieff VN (1946) In: Ipatieff J et al. (eds) *The life of a chemist: memoirs of Vladimir N. Ipatieff* (trans. Haensel V, Lusher RH). Stanford University Press, Stanford, pp 154–155, 327–328
93. Ipatieff VN (1936) *Catalytic reactions at high pressures and temperatures*. Macmillan, New York, p 31
94. Stoltzenberg D (1994) Fritz Haber: Chemiker, Nobelpreisträger, Deutscher, Jude. VCH, Weinheim, pp 154–160
95. Haber F, Le Rossignol R (1908) Bestimmung des Ammoniakgleichgewichtes unter Druck. *Z Elektrochem* 14:181–196
96. Topham SA (1985) The history of the catalytic synthesis of ammonia. In: Anderson JR, Boudart M (eds) *Catalysis: science and technology*, vol 7. Springer, Berlin, pp 1–50
97. Tamaru K (1991) The history of the development of the ammonia synthesis. In: Jennings JR (ed) *Ammonia synthesis: fundamentals and practice*. Plenum, New York, pp 1–18
98. Schuster C (1976) Wissenschaft und Technik. Ludwigshafen, BASF, p 126
99. Haber F, Le Rossignol R (1913) Ammonia; technical preparation of...from its elements. *J Soc Chem Ind* 32(3):134–138
100. Le Rossignol R (1928) Zur Geschichte der Herstellung des synthetischen Ammoniaks. *Naturwiss* 186:1070–1071
101. Haber F (1920) The synthesis of ammonia from its elements, Nobel lecture, June 2, 1920. Nobel lectures including presentation speeches and laureates biographies, chemistry, 1901–1921. Nobel Foundation/Elsevier Publishing, Amsterdam, pp 326–340
102. Translation of Fritz Haber to BASF, 3 July 1909, in Zardi U, Zardi F (2009) 100 Not out. History of the birth of the modern synthetic ammonia industry. Paper presented at the Nitrogen & Syngas International Conference and Exhibition, Rome, Italy (22–25 February 2009)
103. Mittasch A (1951) *Geschichte der Ammoniak-synthese*. Verlag Chemie, Weinheim
104. Mittasch A (1950) Early studies of multi component catalysts. In: Frankenberg WG, Komarewsky VI, Rideal EK (eds) *Advances in catalysis*, vol 2. Academic Press, New York, pp 81–104
105. Appl M (1982) The Haber-Bosch process and the development of chemical engineering. In: Furter WF (ed) *A century of chemical engineering*. Plenum, New York, pp 29–53, on 39–40
106. Appl M (1982) The Haber-Bosch process and the development of chemical engineering. In: Furter WF (ed) *A century of chemical engineering*. Plenum, New York, pp 29–53, on 40–43
107. Teed PL (1919) *The chemistry and manufacture of hydrogen*. Longmans, Green & Co., New York, pp 113–125
108. Travis AS (1998) High pressure industrial chemistry: the first steps, 1909–1913, and the impact. In: Travis AS, Homburg E, Schröter H, Morris, PJT (eds) *Determinants in the evolution of the European chemical industry, 1900–1939: new technologies, political frameworks, markets and companies*. Kluwer, Dordrecht, pp 3–21, on 11–12, also p 1
109. Appl M (1982) The Haber-Bosch process and the development of chemical engineering. In: Furter WF (ed) *A century of chemical engineering*. Plenum, New York, pp 29–53

110. Reinhardt C (1998). Basic research in industry: two case studies at I.G. Farbenindustrie AG in the 1920's and 1930's. In: Travis AS, Homburg E, Schröter HG, Morris, PJT (eds) *Determinants in the evolution of the European chemical industry, 1900–1939: new technologies, political frameworks, markets and companies*. Kluwer, Dordrecht, pp 67–88, on 81
111. James J, Steinhäuser T, Hoffman D, Friedrich B (2011) *One hundred years at the intersection of chemistry and physics: The Fritz Haber Institute of the Max Planck Society, 1911–2011*. Walter de Gruyter, Berlin/Boston
112. Stern F (1991). *Together and apart: Fritz Haber and Albert Einstein*. In: *Einstein's German world: essays in European history*. Princeton University Press, Princeton
113. Travis AS (1984) *The high pressure chemists*. Wembley, Brent Schools and Industry Project, p 50
114. Lunge G (1916) *Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige*, 2 vols. Friedr. Vieweg & Sohn, Braunschweig, vol. 1, pp 138–295
115. McDonald D, Hunt LB (1982) *A history of platinum and its allied metals*. Johnson Matthey, London, pp 387–389
116. Lunge G (1916) *Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige*, 2 vols. Friedr. Vieweg & Sohn, Braunschweig, vol. 1, pp 282–287
117. Hunt LB (1958) The ammonia oxidation process for nitric acid manufacture. *Platin Met Rev* 2(4):129–134, on 133
118. Inskeep GC, Henry TH (1954) Nitric acid in Great Britain: oxidation of ammonia. *Modern chemical processes: a series of articles describing chemical manufacturing plants*, 3 vols (1952, 1953, 1954). Reinhold, New York, 1954, vol 3, pp 218–227, on 218
119. Hunt LB (1958) The ammonia oxidation process for nitric acid manufacture. *Platin Met Rev* 2(4):129–134, on 133
120. Miles FD (1961) *Nitric acid: manufacture and uses*. Oxford University Press, London

<http://www.springer.com/978-3-319-19356-4>

The Synthetic Nitrogen Industry in World War I
Its Emergence and Expansion

Travis, A.S.

2015, IX, 163 p. 66 illus., 16 illus. in color., Softcover

ISBN: 978-3-319-19356-4