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Anthony S. Travis

The Synthetic Nitrogen Industry in World War I

Its Emergence and Expansion

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ISSN 2191-5407 ISSN 2191-5415 (electronic)
SpringerBriefs in Molecular Science
ISSN 2212-991X
SpringerBriefs in History of Chemistry
ISBN 978-3-319-19356-4 ISBN 978-3-319-19357-1 (eBook)
DOI 10.1007/978-3-319-19357-1

Library of Congress Control Number: 2015940967

Springer Cham Heidelberg New York Dordrecht London

Printed on acid-free paper

Springer International Publishing AG Switzerland is part of Springer Science+Business Media
(www.springer.com)

Preface

In 1909, the German physical chemist Fritz Haber devised an apparatus for the synthesis of ammonia from its elements, hydrogen and nitrogen, under conditions of very high pressure and temperature, in the presence of a catalyst, osmium in particular. Four years later, in September 1913, mainly thanks to the industrial chemist Carl Bosch at BASF, Haber's method was turned into a process for the manufacture of nitrogen fertilizer. It was, arguably, one of the greatest inventions of the twentieth century, and for many certainly the most beneficial. However, the inauguration less than a year before the outbreak of World War I of what became known as the Haber-Bosch process would mean that its earliest large-scale application was to be in the manufacture of explosives for the Kaiser's armed forces. Nevertheless, and despite much belief to the contrary, then and now, it was not the only important process employed in Germany for the manufacture of nitrogen products during the war.

My own interest in nitrogen products began in the early 1980s, when working with Brent Schools and Industry Project, a programme of the London Borough of Brent aimed at introducing the application of science into the classroom. At that time, the few studies of the history of the ammonia process and of related early twentieth-century nitrogen fixation processes were written for specialist audiences. The outcome of my research was the publication in 1984 of *The High Pressure Chemists*. Usefully, the project was aided by the presence in Brent, at North Wembley, of the research laboratories of the (British) General Electric Company (GEC), with which Haber's skilful coinventor Robert Le Rossignol was associated. It was through former GEC head chemist the late Dr. Ralph C. Chirnside, a close friend of Le Rossignol, that I learnt about some of the connections with Haber. No less important was the manufacturing and research facility of Johnson Matthey Metals Limited located on the site of the former Wembley Exhibition grounds. There I was able to view the weaving of platinum wire gauzes required in the oxidation of ammonia to nitric acid, a vital step in the munition manufacture that was brought to perfection under conditions of war after 1914. Johnson Matthey also operated a nitric acid pilot plant adjacent to the facility.

Since the 1980s, there have appeared several published accounts of the life and work of Fritz Haber, who also happens to be associated with the introduction of large-scale gas warfare in 1915. None of these accounts, however, deal in a balanced way with the technical story of both ammonia, with which Haber and Carl Bosch were so intimately associated, and the rival nitrogen processes, in particular the electric arc and Frank–Caro (cyanamide) processes. It is in order to make up for this lacuna that I here present the result of an extensive reworking of my earlier research, incorporating the studies of several colleagues, including participants in the European Science Foundation's Evolution of Chemistry in Europe, 1789–1939 programme. I would especially like to acknowledge the members of the committee of the Historical Group of the Royal Society of Chemistry who kindly invited me to give the 2014 Wheeler Award Lecture on the topics dealt with here. The staff of the Wellcome Collection, London, and the Sidney M. Edelstein Library for the History and Philosophy of Science, Technology and Medicine at the National Library of Israel, Jerusalem, are thanked for great assistance. Luca Bianchi of Casale SA kindly answered a number of questions and provided useful background information. A special thanks to Peter J. T. Morris, of the Science Museum, London, with whom I have shared an interest in the history of chemical technology for over two decades, and at whose suggestion I undertook the writing of this monograph. I am grateful to Dr. Morris for extensive review of an earlier version of the manuscript and for kindly providing information based on his own research. Finally, it is important to emphasize that the events described in Chaps. 1 and 2 are as much a prelude to World War I as were the stories of the build-up of fleets of battleships among the "Great Powers" in the decade or so prior to 1914. In Chaps. 4 and 5, this is reflected, at the climax of the war in November 1918, through the vast nitrogen factories undergoing expansion, under construction or planned in Germany, Britain, France, and the United States, and, in the aftermath, the struggles until the mid-1920s to develop rivals to the Haber-Bosch process mainly based on research started during 1916–1918.

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Units of measurement are as given in the original sources.

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About the Author

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He has edited and coedited several volumes and special issues of journals dealing with the history of chemical sciences, technology and the environment. Publications include *The Rainbow Makers: The Origins of the Synthetic Dyestuffs Industry in Western Europe* (Lehigh: Lehigh University Press, 1993); (with Carsten Reinhardt) *Heinrich Caro and the Creation of Modern Chemical Industry* (Dordrecht: Kluwer, 2000); *Dyes Made in America, 1915–1980: The Calco Chemical Company, American Cyanamid, and the Raritan River* (Jerusalem: Edelstein Center/Hexagon Press, 2004); and *On Chariots with Horses of Iron and Fire: The Excursionists and the Narrow Gauge Railroad from Jaffa to Jerusalem* (Jerusalem: Magnes Hebrew University Press/Shapell Manuscript Foundation, 2009).

Chapter 1
Introduction

1.1 War and Fixed Nitrogen

> The story still is told of a Minister, a member of the War Cabinet, who, finding the conversation at a certain dinner turning to the sinister menace of the submarine campaign, then at its height, and its effects especially on the Chile communications, turned to his neighbour with the enquiry: 'Tell me, what *is* this nitrate they are all making such a fuss about?'
>
> Stanley I. Levy, "The Status of Chemists and Chemistry," in *Chemistry and Industry*, no. 11, 14 March 1924, pp. 285–286.

Apocryphal or not, this extract from the correspondence columns of the then new British journal *Chemistry and Industry* in 1924 exposes the apparent general ignorance in Britain, and also for a time in Germany, of a crucial and often desperate episode in the conduct of World War I. "Nitrate," a commodity essential to the production of all modern explosives used in warfare, mainly the aromatic nitro compounds such as TNT (trinitrotoluene) and picric acid, was common currency to all belligerents. Nevertheless outside of scientific and industrial circles the critical roles of what was in fact Chilean nitrate (Chile saltpetre, or sodium nitrate; the term saltpetre refers to the potassium salt), and other nitrogen-containing chemicals of commerce, such calcium cyanamide and ammonia, as sources of vast destructive power, was generally given little, if any, prominence at the start of the war in early August 1914.

Within weeks the German Army, pursuing the campaign drawn up by Count Alfred von Schlieffen, had occupied Luxembourg, crossed neutral Belgium, and entered northern France, laying waste to towns and cities. Acts of aggression were reported, and sometimes greatly exaggerated. Belgian civilians were shot, including in groups, in response to trumped up charges of sabotage, and the ancient library at Louvain was reduced to ashes. In France, Lille and Douai were lost, the cathedral at Rheims damaged, and Arras almost destroyed. The French army was pushed back to within forty miles of Paris. It was only through a massive effort

A.S. Travis, *The Synthetic Nitrogen Industry in World War I*,
SpringerBriefs in History of Chemistry, DOI 10.1007/978-3-319-19357-1_1

during September 6–8 that the German advance was brought to a halt at the First Battle of the Marne by an Allied counter-attack on a front extending from Verdun to the Oise. The Germans retreated a short way to the north across the River Aisne. Both sides then raced north to the coast. The Kaiser's army gained the ridge that overlooked Flanders, at the First Battle of Ypres (October–November). The battlefront soon stretched four-hundred-and-forty miles, from Dunkirk, across Belgium and northern France, to the Swiss border. The subsequent stalemate on what became known as the Western Front would last almost four years.

All belligerents were unprepared for the prolonged war; hardly any effort had been made to mobilize industry in a support role. Only a few, and mainly chemists, had considered the critical role of chemical industry in the supply of modern explosives. In particular, the availability of nitrogen products was seriously underestimated by the over-optimistic German military. That changed with the stalemate that began on the banks of the River Marne, and ensuing systems of long, winding trenches excavated by both sides from early 1915. This stimulated new approaches to large-scale warfare based on nitrogen products, later capturing the public's attention in ways quite unlike that in which the very same or similar products, as fertilizers, would serve to sustain so much of the world's growing population. It represented a major step in the near-total reliance of warfare on science and technology, and brought on the rapid emergence of the first major modern military-academic-industrial complexes.

While the massive expansion of the nitrogen industry during World War I is a principal focus here, our historical understanding of how it was enabled to take place requires a thorough review of formative developments during the previous several decades. Here the story begins with the importation into Europe from the west coast of South America of naturally occurring nitrogen-containing products, guano (containing uric acid and other nitrogen compounds) and sodium nitrate, that enabled significant improvements in crop yields. This was a major enterprise from the 1840s, around which time agricultural science developed, with an emphasis on the role of fertilizers, and nitrogen-containing manures in particular. Over the following years, agriculture experiment stations opened, at first relying on the studies of one or two individuals, generally with training in chemistry. With the growing importance of the need to satisfy the food requirements of expanding populations, and the emergence of modern agricultural sectors, colleges of agriculture were established, in both Europe and the United States.

By 1880 the best quality guano had been consumed, and there were concerns in Europe over how long the supply of nitrates would last. This encouraged laboratory and industrial efforts to directly fix the unreactive gas nitrogen in the atmosphere as stable compounds that could be used as fertilizer. There were additional concerns, since from imported nitrate was obtained the nitric acid required in the manufacture of explosives, such as Alfred Nobel's dynamite. Meantime the production of illuminating gas, and later coke, from coal encouraged recovery of the byproduct ammonia for use as a fertilizer.

The widespread availability of electrical power during the 1890s directed the research effort towards fixing nitrogen, by its combination with oxygen, in the flame generated by an electric arc. This was useful in the manufacture of nitric acid required by the explosives industry, as well as of nitrate fertilizer. Another approach, also requiring electrical power, involved production of calcium cyanamide from calcium carbide. The solid cyanamide released ammonia when applied to the soil. These were the two main innovations of the first decade of the 20th century, and, provided that the supply of electrical power was cheap enough, offered some independence from the naturally occurring nitrates.

It was not only the finite reserves of Chilean nitrate that caused concern. The supply was controlled by commercial monopolies, which in turn also encouraged ongoing research into synthetic alternatives. This was particularly the case in Germany, a nation with limited natural resources, and dependent on the South American product to support its extensive agricultural industry. The research effort was further stimulated by the fact that the large German chemical corporations engaged in the manufacture of synthetic or coal tar dyes had begun to diversify, taking up interests in areas of chemistry other than those based on organic chemical products. Nitrogen fixation by its combination with hydrogen to give ammonia was attempted, in Germany and elsewhere, but each worker in turn abandoned the study when low yields, explosions, and other complications hindered the work. Then in 1909, at the Karlsruhe Technische Hochschule, a benchtop process was demonstrated in which nitrogen and hydrogen were combined at a high temperature and under pressure in the presence of a catalyst. By 1913 this had become the basis of an industrial process that was worked for production of the fertilizer ammonium sulphate. A novel process for manufacture of nitric acid was also taken up in Germany, the catalytic oxidation of ammonia from gas works, and increasingly from the new synthetic nitrogen processes. The nitric acid processes were not worked on a large scale before August 1914, and often in any case encountered technical difficulties in operation.

The military stalemate reached in September 1914 led to immediate and unprecedented demand for the nitrogen products ammonia and nitric acid, as well as for coal tar toluene and phenol (carbolic acid) that were nitrated, giving TNT (trinitrotoluene) and picric acid, respectively. That demand became even more urgent in Germany when at the end of the year, through the efforts of the British Royal Navy, German manufacturers of nitric acid and explosives were denied access to Chilean nitrate. From then on, the Kaiser's chemists and industrialists gave top priority to the capture of atmospheric nitrogen for both feeding the population of Germany and slaughtering the armies of the Entente Powers, the United Kingdom, France and Russia, generally referred to as the Allies (joined by Italy in 1915). This was the turning point in the modern manufacture of nitrogen products. State sponsorship of and industrial investment in essential nitrogen products enabled the construction of vast chemical works for purposes of war, but with the potential of no less vast markets after the war. German science and technology succeeded magnificently, something over which even the Allies were in agreement. Moreover, and as a measure of the complexities overcome by German scientists and technologists, their achievements could not be matched elsewhere. Fortunately for the Allied nations, they could continue to rely on the natural nitrates, despite submarine attacks on merchants shipping. In many respects, the impact during the years immediately following cessation of hostilities was no less great, as Germany's former enemies fought to catch up in nitrogen fixation processes and the development of high-pressure chemical technology that it spawned. No less than the synthetic dye industry, the synthetic nitrogen industry was seen as a key strategic sector that was essential to the survival of every industrialized, and industrializing, nation.

The main personality in this account of the success of large-scale fixation of atmospheric nitrogen is the German physical chemist Fritz Haber, who has been accorded the dubious honours of enabling Germany to conduct war after September 1914, and of introducing large-scale gas warfare in April 1915. Notwithstanding his ingenious solution to fixing atmospheric nitrogen, the former honour was, and is, based more on rhetoric and propaganda put out by industrialists and scientists to suit political masters in both England and Germany than was actually the case. More recently, and as the result of concerns of later generations, it has become the fashion to sensationalize Haber's role in these two chemistry-related sectors of modern warfare. Haber has come to personify the evil scientist who unquestionably places his personal interests and those of the state he serves above all else. For this reason, it is occasionally necessary here, for sake of completeness, to turn off the main route of the narrative to explore subsidiary themes related to Haber's activities.

Among other issues, I examine some purported, or at least "advertised," facts, including certain persistent myths concerning Haber's roles, and reinterpret the foundations of stories about the "Haber factories" that many believed almost alone enabled Germany to wage war from the autumn of 1914, or even earlier, right through to the Armistice on 11 November 1918. While these are shown to be erroneous, there is no denying that Haber's role as an outstanding administrator of war-related affairs during the "Chemist's War" were no less significant than his scientific and technical expertise.

1.2 Background to Fixed Nitrogen

The gas nitrogen constitutes about 80 % of our atmosphere. It is essential to plant growth, as fertilizer. There are few natural forms in which it is found in a combined state, for direct, or indirect, application. Formerly the principal supply was animal excrement, from which was obtained potassium nitrate (saltpetre, or nitre), also employed in gunpowder and the manufacture of nitric acid.

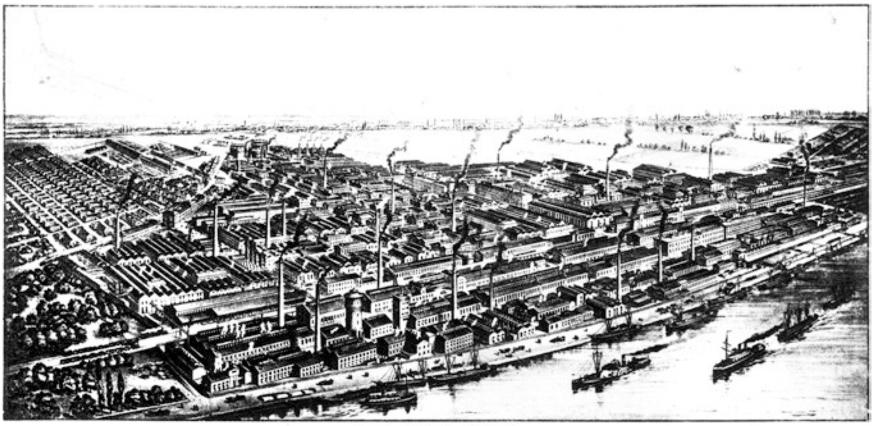
Attempts to combine atmospheric nitrogen with other elements, such as hydrogen to give ammonia, and oxygen to afford oxides which could be readily converted into nitric acid, reportedly formed the basis of 3,000 publications and patents by 1914. Mostly, they were unsuitable for commercial development, due to inefficiency of the methods, lack of scientific and technical knowhow, and high energy and installation costs.

Studies of nitrogen-containing gases go back to the last quarter of the 18th century. Joseph Priestley (1733–1804) was the first to examine the chemical composition of ammonia (NH_3), which in 1774 he decomposed with an electric spark. The colourless, alkaline gas, was known long before. Ammonia is named after the Temple of Jupiter Ammon in the oasis of Siwa in the western Egyptian desert [1]. It was there that, so the story goes, sal ammoniac (ammonium chloride) was found in camel dung and decomposing remains of animal sacrifices left out in the searing desert heat.

In 1772, Priestley established the composition of nitric oxide (NO, nitrogen monoxide), and also reported nitrous oxide (N_2O). In 1777 he prepared nitrogen dioxide (NO_2) [2]. Henry Cavendish (1731–1810) made nitric oxide using frictional electricity to spark together nitrogen and oxygen, and obtained what he called nitrous acid (nitric acid) [3]. Around the turn of the century Humphry Davy (1778–1829) prepared and analysed oxides of nitrogen [4]. The French chemist Frédéric Kuhlmann (1803–1881) in 1838 reacted nitric oxide with air to form nitrogen dioxide which with water afforded nitric acid [5]. This became the basis of a French patent filed early in 1859 by Madame Louise Lefêbvre. (Her English patent was dated 26 April 1859.) Unfortunately theories of physical chemistry were not advanced sufficiently to assist her, nor was there an economical source of electricity to bring about the continuous combination of oxygen with nitrogen.

An alternative approach used the combination of metals with nitrogen at elevated temperatures to form metal nitrides, which in turn yielded ammonia by reaction with steam. This was the approach taken in France during 1859 by Charles Tellier (1828–1913), who in 1880 formed a short-lived company to license this route. Ottokar Serpek in Norway worked with nitrides of aluminium, before devoting his firm's activities more profitably to extraction of aluminium.

The more viable processes for fixing atmospheric nitrogen, those described in this monograph, had to wait until the start of the 20th century. Of the three main rivals, it was the Haber-Bosch process, inaugurated in 1913 by the German dyemaking firm Badische Anilin- & Soda-Fabrik (BASF, also once known as the Badische) of Ludwigshafen, almost opposite Mannheim, on the west bank of the River Rhine, that would come to the fore by the end of World War I (Fig. 1.1).



Ludwigshafen Works.

Fig. 1.1 BASF factory, Ludwigshafen, 1890s. (Sidney M. Edelstein Library)

BASF and the other leading German dye firms were founded in the 1860s and 1870s. In 1904 they formed two groups of loose alliances: BASF, AGFA (Actien-Gesellschaft für Anilin-Fabrikation), and Bayer, together known as the Dreibund, or Triple Confederation; and Leopold Cassella & Co. and Hoechst, the Double Alliance, in 1907 joined by Kalle & Co., and from then on known as the Tripartite Association. In 1916, at the height of World War I, the two groups formed a community of interests, the Interessengemeinschaft der deutschen Teerfarbenindustrie, often called the I.G. In 1925, they merged to create the behemoth Interessengemeinschaft Farbenindustrie Aktiengesellschaft, better known as I.G. Farbenindustrie AG, or I.G. Farben.

1.3 Natural Nitrogen Fertilizers

For much of the 19th century, the principal source of fixed nitrogen for use in agriculture and the manufacture of nitric acid was the west coast of South America. First was a natural fertilizer, guano, found in great abundance mainly on the three Chincha Islands, off the coast of Peru, close to the town of Pisco (south of Lima). Its history, in Europe at least, began after the explorer and geographer Alexander Humboldt (1769–1859) and botanist Aimé Bonpland (1773–1858) visited Spain's American colonies. During five years, from 1799 to 1804, they gathered information on geology, botany, anthropology, and economics, as well as specimens of plants and minerals. One of the latter was a substance covering the three islands, with the power, as Humboldt was informed by the Spanish, who learned it from the Indians, of greatly aiding the growth of plants. This was guano. On return to Paris, where Humboldt was residing, he communicated with the chemists Antoine-François Fourcroy (1755–1809) and Louis-Nicolas Vauquelin (1763–1829), requesting an analysis of guano. They had just completed an analysis of bird excrement, which Humboldt believed, correctly, had a composition similar to that of guano. In 1805 the two chemists published their analysis of Humboldt's sample, demonstrating its nitrogen content: the Chincha Islands were comprised of vast amounts of fixed nitrogen (mainly uric acid) in the form of bird droppings. Guano had also accumulated in many places along the coastline of mainland Peru.

This was less than a decade after the English cleric Thomas Robert Malthus (1766–1834) in his *An Essay on the Principle of Population* warned that food supplies could not keep pace with population growth. The time was ripe for sending guano to Europe. Nevertheless, it took until 1840 before guano was first exported, to England, from where the European market was mainly financed and controlled. Less than 2,000 tons arrived in 1841, but within a decade this figure had risen to over 200,000 tons per year. The Caribbean Island of Rodonda was also a significant source of guano, from 1843 until just after the outbreak of World War I (from the mid-1860s it was the inspiration for a mythical kingdom). Americans also took a particular interest in guano. In 1856 Congress passed the Guano Islands Act that empowered US citizens to take possession of unoccupied islands containing guano.

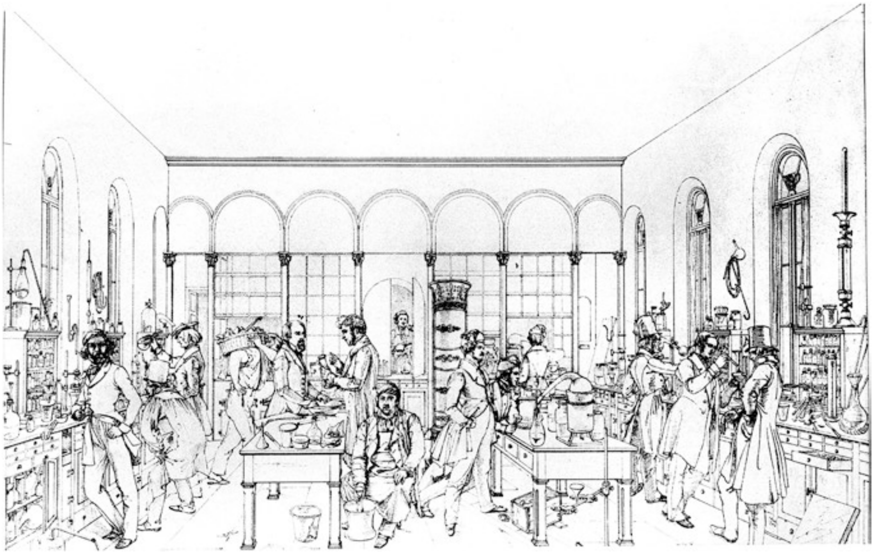


Fig. 1.2 Justus Liebig's laboratory at Giessen, around 1840. Liebig was ennobled in 1845. From J. Hofmann, *Acht Tafeln zur Beschreibung des chemischen Laboratoriums zu Geissen*. Heidelberg, 1842. Lithograph by Trautschold and Ritgen. (Sidney M. Edelstein Library)

The role of excrement, human and animal, as well as waste from crop production, rather than guano, as sources of fertilizer on arable land, was emphasized by various individuals, including John Mechi (1802–1880), in England in the 1840s, and the German chemist Justus Liebig (1803–1873), at Giessen (Fig. 1.2) [6]. Liebig, the leading promoter of agricultural chemistry, was for some time uncertain of the value of added nitrogen in the form of guano, at least until its phosphate content was established.

1.4 Fertilizers and Agriculture Experiment Stations

The scientific approach to agriculture, with a major input from chemistry, relied on agriculture experiment, or research, stations, dedicated colleges, and associations of agriculturalists. Their histories in Europe went back to the 1830s and early 1840s. In France during 1836, Jean-Baptiste Boussingault (1802–1887) opened a research station some 60 km north of Strasbourg, where his experiments included studies on the role of nitrogen in plant growth. Boussingault's work would be brought to an abrupt halt at the outbreak of the Franco-Prussian War of 1870–1871. In 1842, James F. W. Johnston founded the Agricultural Chemistry Association of Scotland. One year later John Bennett Lawes (1841–1900) began field experiments at Rothamsted, Harpenden, north of St. Albans, England, in partnership with the chemist Joseph Henry Gilbert (1817–1901) who emphasized the role of nitrogen as fertilizer. In 1851, the first German agriculture experiment station was established at Möcken, near Leipzig; in the 1860s a Union of Experiment Stations existed in Bavaria. The rapid growth in agricultural chemistry, with its focus on fertilizers, was demonstrated in 1862 at the International Exhibition in London. There, the "industry of manures" occupied a prominent place in "Section A, Chemical Products and Processes," with a "Tribute to Messers. Lawes and Gilbert," and a "Homage to Liebig" [7].

The academic study of agriculture and the soil expanded during the last three decades of the 19th century. By the early 1870s over twenty experiment stations existed in Germany, particularly in Saxony. Two decades later there were over seventy such stations in Germany [8–11]. In Holland an experiment station opened at Wageningen in 1877. Other important Dutch stations were at Gröningen and Delft. Notable also were Belgium's Institut agricole de Gembloux, and agricultural colleges and universities in Italy, Denmark, and the union of Sweden and Norway. In Sweden, agricultural institutes opened in 1848 at Ultuna and in 1862 at Alnarp. Norway's first agricultural college opened in 1859 at Ås, near Kristiania (now Oslo). By the 1880s these institutions, and their allied associations and unions, had facilitated the emergence of agricultural science as a profession in its own right.

The first two US state agriculture experiment stations opened in 1876, in Connecticut and California. The American Association of Official Agricultural Chemists was founded in 1884, and included chemists charged with enforcement of state fertilizer laws. The interest in fertilizers stimulated transmittal of information on analyses, use, and application through specialist technical and chemical journals.

The agricultural sector in Germany was highly dependent on imported nitrogen products, as a result of the limited natural resources and a growing population. It provides a useful example of how the demand for and application of nitrogen fertilizer (and German phosphate, mined at Stassfurt, near Magdeburg, since 1861) increased productivity of the soil, notably in potato and sugar cultivation [12]. By 1890, this enabled Germany to become, as it had been decades earlier, a net exporter of agricultural products.

1.5 Expansion of the Nitrogen Industry

The demand for the nitrogen-containing guano and other agricultural fertilizers, including phosphates, from just before the mid-19th century was driven by massive growth in populations among the rapidly industrializing European nations, the contribution of chemistry to agricultural science, and expansion of steam-driven transport networks on both land and sea. The trade in export of guano brought about a boom in the economies of Peru, Bolivia and Chile, encouraging Spain to regain control over its former colonies, Peru and Chile. The outcome was the Chincha Islands War (1864–1866). In this, the Spanish failed.

Guano created not only huge fortunes in South America, but also for the Englishman William Gibbs of Anthony Gibbs & Sons. By 1857, 2.4 million tons of guano had arrived in Britain, from where considerable amounts were sent to France, Prussia, and, later, the Netherlands [13, 14]. The peak of guano production was reached in 1870, when 280,000 tons were imported into Britain. In 1872, the Peruvian government placed restrictions on export because the quality of the remaining guano was less suited to use as a fertilizer. In 1880, for example, just 20,000 tons arrived in Britain [15]. Guano from other sources never matched that of Peru in terms of value as a fertilizer [16]. It was replaced by another local source of nitrogen, though found some distance inland.

This was the nitrate industry based on sodium nitrate—variously called Chile saltpetre, Chile nitre, Chile nitrate, nitrate of soda, and salitre; until early in the 20th century also Chili saltpeter—obtained from the mineral caliche found in abundance throughout parts of the dry, desolate Atacama Desert, a plateau, approximately 700 km long, lying between the South Pacific Ocean and the Andes. In July 1835, Charles Darwin had observed caliche in the north of the province of Tarapacá, then in Peru, and suggested that it might have once formed the coastline of the sea. The richest deposits, once containing up to 50 % or more of sodium nitrate, are in the northern part of present-day Chile in the provinces of Antofagasta and Tarapacá.

There was also the traditional saltpetre (potassium nitrate), which had long been employed in the manufacture of gunpowder in Europe. A principal source was India. Throughout Europe saltpetre was largely produced from animal excrement. Antoine Lavoisier (1743–1794) studied the manufacture and use of saltpetre, in both agriculture, as fertilizer, and gunpowder manufacture.

The South American saltpetre (sodium nitrate) industry served European manufacturers of gunpowder and nitric acid from around 1830; though for explosives the moderately deliquescent sodium nitrate was converted into potassium nitrate, known as artificial saltpetre. The sodium nitrate was first used directly by American manufacturers of gunpowder in the South during the Civil War years, when the Union blockade cut off supplies of Indian saltpetre from Confederate forces. Significantly, in 1857, Lamont du Pont (1831–1884) had substituted sodium nitrate from Chile for potassium nitrate in blasting powder. During the 1860s, South American saltpetre began to displace not only guano but also the Indian product, and facilitated the growth of mining industries and railway construction, paralleling the expansion in populations and spread of railway networks, in addition to enabling preparations for war. The industry grew under ownership of the Compañía de Salitres y Ferrocarriles de Antofagasta. Chilean, British, and other European interests invested in infrastructure during and after the 1870s, including a narrow gauge railway driven inland into the desert from the coast. For manufacture, the Shanks process was adopted. The caliche was crushed and placed in dissolving tanks. The mixture was steam heated, and on cooling withdrawn into settling tanks. After the suspended solids had settled, the liquid, saturated with nitrate, was drawn off, and crystalline sodium nitrate allowed to separate out and dried. The mother liquor was removed and transferred back to the dissolving tanks. Reuse of the liquor was important due to the scarcity of water supplies in the desert regions [17]. The processes, both in mining the caliche and in extracting the nitrate, were labour intensive, and wasteful in energy. The monopolistic control ensured such a high level of profit that this mattered little, especially now that fertilizer was added to the large-scale uses of the nitrate. In Britain, annual nitric acid production from imported sodium nitrate in the mid-1870s was around 10,000 tons.

The emergence of Chile as a new economic power, through investments in Bolivian and Peruvian nitrate industries, created acute political tensions with its two northern neighbours. The great profits that accrued as a result of the export trade in South American nitrates, much of it controlled by British and Chilean interests—causing taxes to be imposed by Bolivia, and Peruvian nationalization of mines—and uncertainties over the national border between Bolivia and Chile, led to rivalry and eventually warfare in 1879 between Chile and Bolivia, the latter aided by Peru. This War of the Pacific ended when Bolivia and Peru capitulated in 1883 (though Bolivia did not sign a peace treaty until 1903). The borders between Chile and Bolivia, and between Chile and Peru, were changed to the benefit of Chile, which now became principal world supplier of sodium nitrate for agricultural and explosives industries. Chile saltpetre, as it was now called, was exported to London, Liverpool, and Hamburg, for distribution throughout Europe. Exports from the Tarapacá and Antofagasta regions quadrupled between 1880 and 1890, from 226,090 tons to 1,065,277 tons, respectively. The time taken for a ship loaded with nitrate (as well as guano) to reach Europe by sea was generally three months. Nitrate was shipped to both east and west coasts of the United States [18].

Another source of nitrogen was the ammonia obtained during the destructive distillation of coal at gas and coke works (Fig. 1.3). Generally, the ammoniacal liquors were concentrated and absorbed in sulphuric acid. The resulting ammonium sulphate was used as a fertilizer, and also in the manufacture of sodium carbonate (soda). By 1890, 140,000 tons of the ammonium sulphate were produced from European gas works ammonia each year. German-born Ludwig Mond (1839–1909)—who studied under Hermann Kolbe (1818–1884) at Marburg and Robert William Bunsen (1811–1899) at Heidelberg, prior to entering industry, first in Germany, then in The Netherlands, before settling in England—gained practical experience in ammonia production during the 1870s in connection with his working of the Solvay ammonia-soda process for sodium carbonate. This was in partnership with John Tomlinson Brunner at Winnington Hall, near Northwich, Cheshire. It represented the foundation period of the prominent British alkali manufacturer Brunner, Mond & Company.

Mond also became interested in fixation of atmospheric nitrogen, in particular an improved process for making ammonia. To achieve this he heated barium carbonate (as briquettes) with carbon (coke), bonded with pitch, to form barium cyanide. Treatment of the cyanide with superheated steam gave ammonia. In 1882, he filed a patent for the process, but it proved unworkable on a commercial scale because his apparatus was unable to withstand the high temperature requirement of the reaction [19].

Though Mond's main interest during the 1880s was in ensuring a reliable supply of ammonia for his factory, he increasingly realised the great potential for satisfying the market for artificial nitrogen fertilizer, writing in 1890 of "the

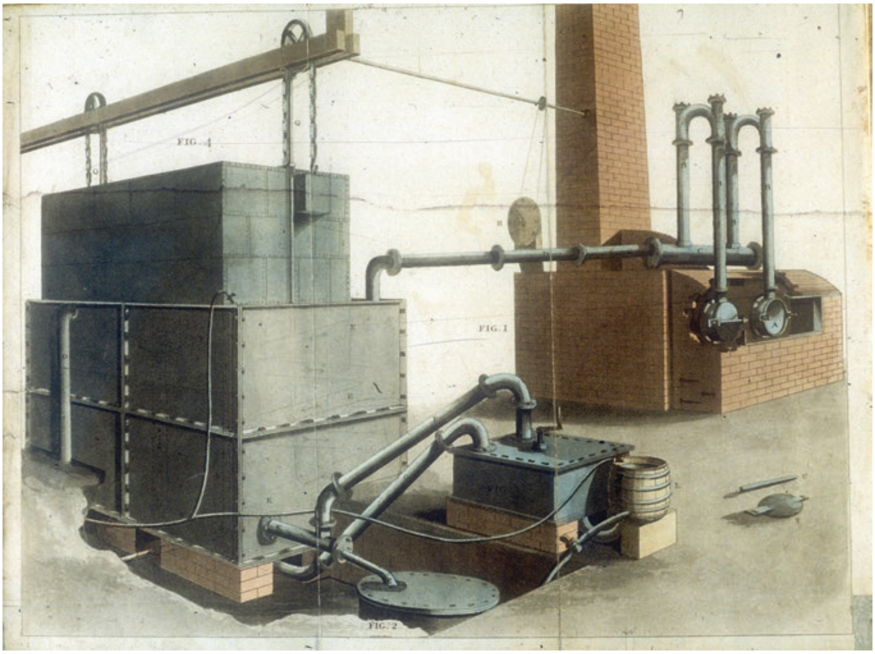


Fig. 1.3 Manufacture of coal gas by destructive distillation of coal. From Frederick Accum, *Description of the Process of Manufacturing Coal-Gas. For the lighting of streets, houses, and public buildings, with elevations, sections, and plans of the most improved sorts of apparatus. Now employed at the gas works in London*. London, 1819. (Sidney M. Edelstein Library)

immense importance of an abundant supply of ammonia, more particularly to the Old World, with its teeming population and worn-out soil." After referring to the vast sums paid for imported "ammonia in shape of guano, and more recently … sodium nitrate (from Chile)," he then drew attention to the problem "of making ourselves independent of a country so far away for the supply of a material upon which the prosperity of our agriculture—our most important industry—depends … (It) is certainly one of the most important which our science has to solve" [20].

According to Mond, in 1889, 750,000 tons of Chile saltpetre were exported, of which 650,000 tons arrived in Europe. Mond at that time was promoting his new process for coal gas production—an alternative to the Semet-Solvay coke ovens introduced in 1885—which afforded a cheap supply of ammonia. In Mond's process, combustion of low quality coal, rather than coke, with steam in a current of air gave what became known as Mond gas, or producer gas, a mixture of nitrogen and carbon monoxide (Fig. 1.4). As in the other coal gas processes, the byproduct ammonia was scrubbed out and converted to ammonium sulphate. Mond's process was worked at Brunner, Mond & Company's Winnington works from 1902. At that time, total British production of ammonium sulphate was 220,000 tons, of which 148,500 tons came from gas works, and 19,000 tons from coke and carbonizing works and Mond gas. Two-thirds of this ammonium sulphate was exported [21].

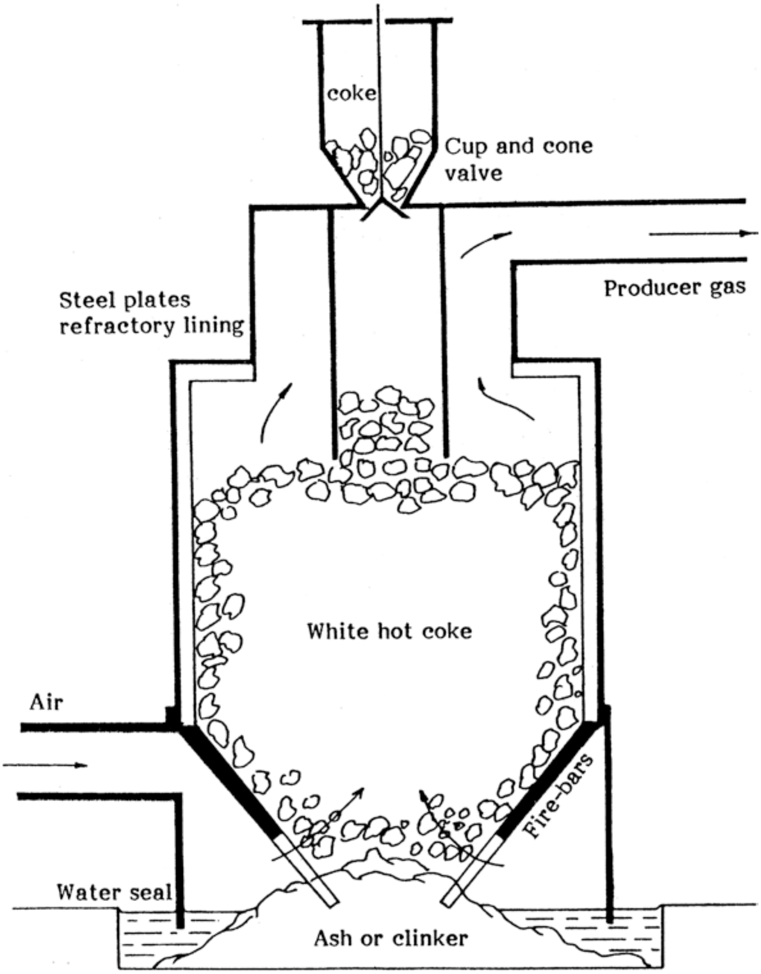


Fig. 1.4 Manufacture of producer gas (carbon monoxide and nitrogen)

In 1910, British production of ammonium sulphate from gas works, coke ovens and producer gas works amounted to 367,587 tons, and supplemented the supplies of fixed nitrogen, as sodium nitrate, from Chile [22].

From the 1880s, when demands on agricultural output accelerated, Chile saltpetre became the nitrogen fertilizer of choice, particularly in Belgium, France, Germany, Holland, Hungary, and Italy. Until 1914, it represented two-thirds of the world's supply of fixed nitrogen fertilizer. Three decades later, with the success of the industrial processes, mainly the Haber-Bosch synthesis of ammonia and oxidation of ammonia to nitric acid, both expanded during World War I, it represented no more than around 5 % of the world supply of fertilizer.

Fig. 1.5 Heinrich Caro. (Edelstein Center)

In 1914, Chile saltpetre was also the principal raw material employed in the manufacture of nitric acid. The acid was used to nitrate aromatic compounds, such as benzene and toluene, as well as phenol. The large-scale industrial manufacture of nitro compounds began at the end of the 1850s, and was pioneered by William Henry Perkin (1838–1907) at his dyestuff manufacturing factory, located at Greenford Green, northwest of London. Perkin's nitro compounds (and those of other dye-making firms that emerged from around 1860), after reduction to aromatic amines, such as aniline, were reacted with various reagents to afford synthetic dyes [23]. The German chemist-colorist Heinrich Caro (1834–1910) designed the first modern nitration and reduction equipment while working in Manchester around 1860 (Fig. 1.5). Later he would spearhead the massive scientific–technical endeavours that would bring BASF to the forefront of modern chemical industry by 1900.

In the manufacture of nitro compounds, a mixture of both nitric and sulphuric acids was required. Some of the nitro compounds were useful dyes, such as picric acid (trinitrophenol). There was also trinitrotoluene, discovered during 1863 in Germany by Julius Wilbrand (1838–1906) while investigating synthetic dyes. This was around the same time that Alfred Nobel (1833–1896) developed nitroglycerine as an explosive, followed in 1866 by dynamite [24]. Picric acid's use as a dye was no more than a few years. At the end of the century it became an important explosive. Trinitrotoluene, despite its explosive properties, was not adopted for military purposes until 1902, when it was used in artillery shells in

Germany. The aromatic nitro compounds used in explosives were manufactured in factories similar to those in which dye intermediates were synthesized. This meant that any nation with a well-established synthetic dye industry was well prepared for the contingencies brought on by armed conflict, as was the case in Germany during 1914, though not in Britain, which had lost most of its dye industry to German rivals by around 1880. However, German production of explosive nitro compounds relied on adequate supplies of raw materials for the manufacture of nitric acid, in particular Chilean nitrate. This would not be the case from late 1914.

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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 Multhusian 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

A.S. Travis, *The Synthetic Nitrogen Industry in World War I*,
SpringerBriefs in History of Chemistry, DOI 10.1007/978-3-319-19357-1_2

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-Geselleschaft (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 Jósef 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.

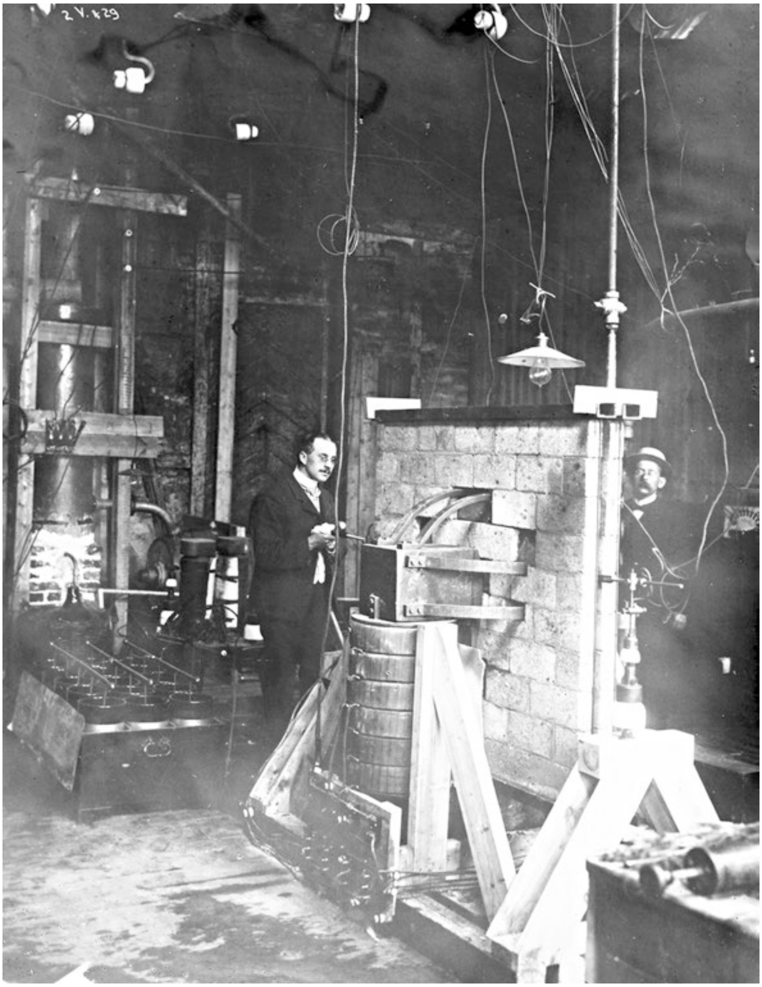


Fig. 2.2 Birkeland-Eyde experimental set up, Frognerkilen Fabrik, Kristiania, 1903. Christian Birkeland is standing *at right*, Samuel Eyde *at left*. (Yara International ASA)

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].

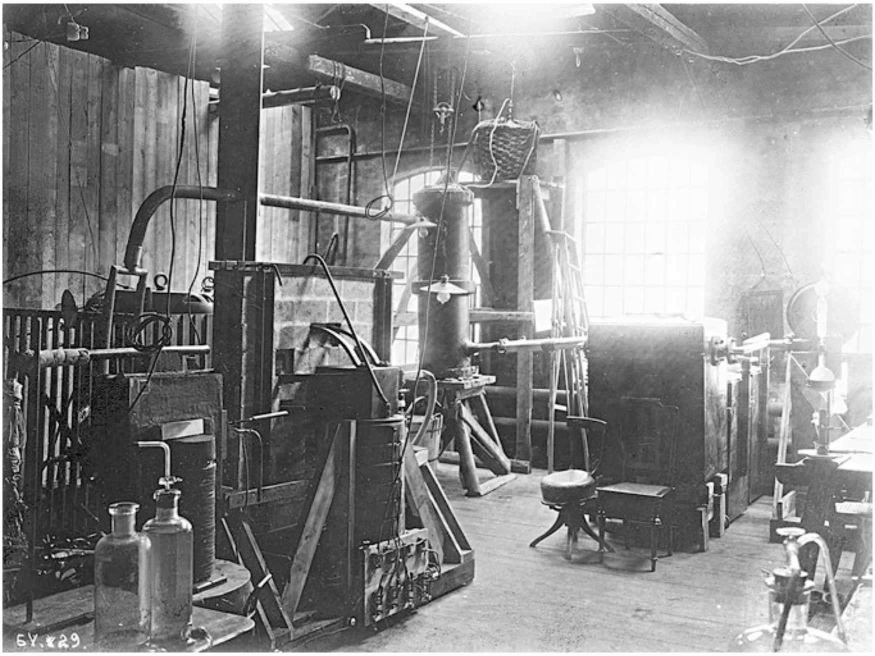


Fig. 2.3 The most prominent feature of the Birkeland-Eyde apparatus was the large electromagnet, here seen on the experimental version at Frognerkilen Fabrik, Kristiania, 1903. (Yara International ASA)

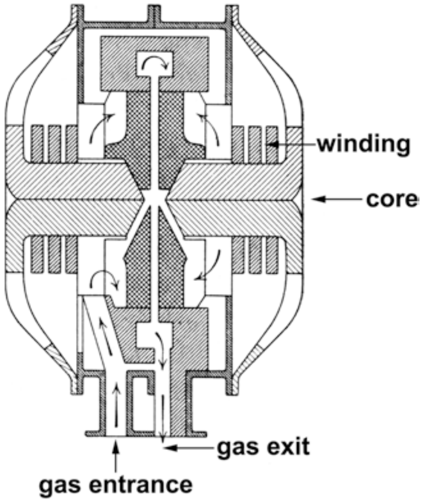


Fig. 2.4 Sectional elevation of Birkeland-Eyde electric arc apparatus for capture of atmospheric nitrogen, at right angles to arc disc. (Adapted from Georg Lunge, *Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige*, 2 vols. Braunschweig: Friedr. Vieweg & Sohn, 1916, vol. 1, p. 259)

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

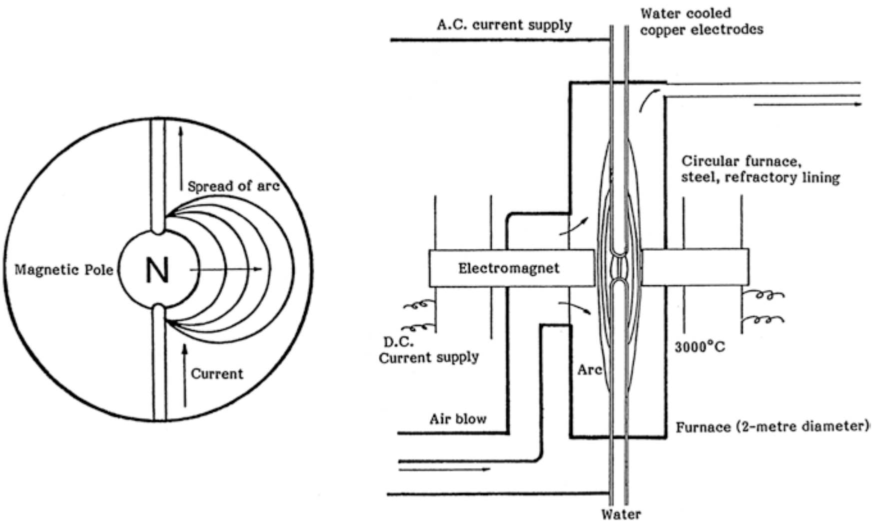


Fig. 2.5 General arrangement of Birkeland-Eyde electric arc apparatus. The rapid to-and-fro movement of the semi-circular arc created an apparent spherical shape

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-Eye 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 Svelgfoss 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 Svelgfoss 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 Såheim in Vestfjorddalen, some distance northwest of Nottoden, was inaugurated (Fig. 2.6). Electricity was generated nearby, at the Vemork power station, next to the

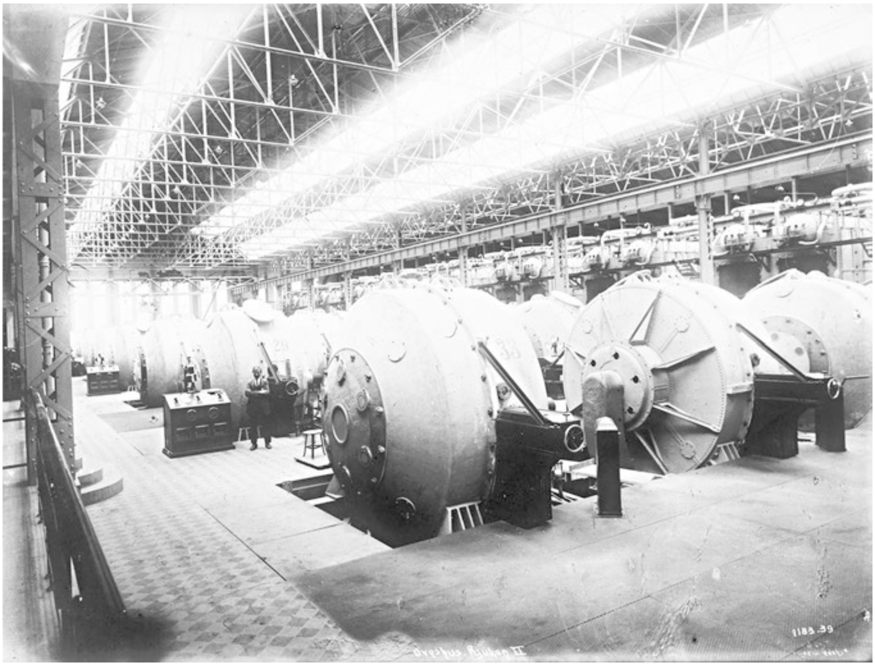


Fig. 2.6 Birkeland-Eyde furnaces, Rjukan factory, 1912. (Yara International ASA)

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 Såheim (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 Odda, 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.

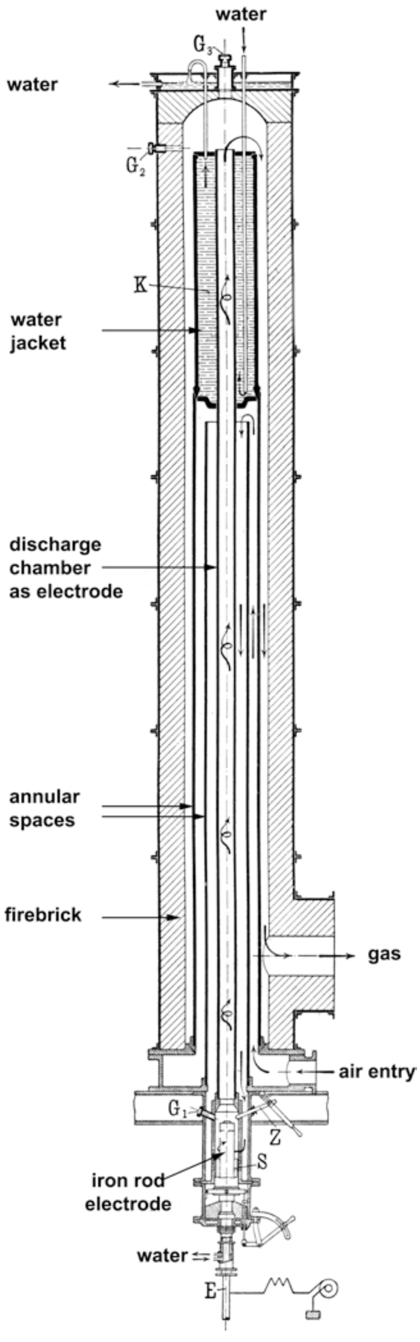
Also worked in Norway, jointly with Norsk Hydro, was the BASF electric arc process of Otto Schönherr. This came about following meetings between Birkeland, Eyde, Heinrich von Brunck, and Rudolf Kneitsch in 1905 on the occasion of Witt’s Berlin lecture. Otto Schönherr (1861–1926), born in Chemnitz, studied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



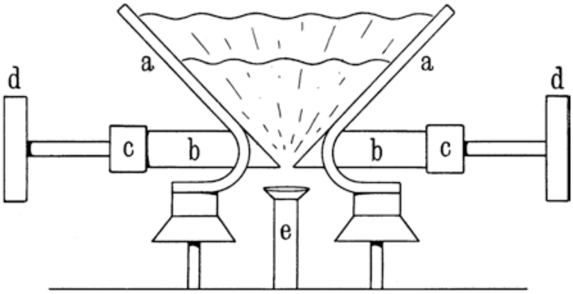


Fig. 2.11 Pauling electric arc apparatus for capture of atmospheric nitrogen: **a** electrodes; **b** iron knives; **c** insulation; **d** distance regulators; **e** air nozzle. (Georg Lunge, *Handbuch der Schwefelsäurefabrikation und ihrer Nebenzweige*, 2 vols. Braunschweig: Friedr. Vieweg & Sohn, 1916, 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 Sione, 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, $NC\text{-}NH_2$. 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.

$$\underset{\text{calcium carbonate}}{\mathrm{CaCO_3}} \rightarrow \mathrm{CaO} + \mathrm{CO_2}$$

$$\mathrm{CaO} + 3\,\mathrm{C} \rightarrow \underset{\text{calcium carbide}}{\mathrm{CaC_2}} + \mathrm{CO}$$

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.

$$CaC_2 + N_2 \rightarrow \underset{\text{calcium cyanamide}}{CaCN_2} + C$$

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 Johaness 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.

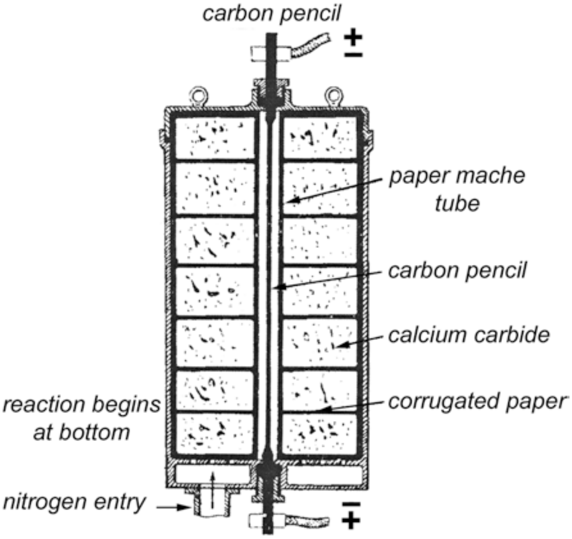
$$\mathrm{CaCN_2} \quad + \quad 3\,\mathrm{H_2O} \quad \rightarrow \quad \mathrm{CaCO_3} \quad + \quad 2\,\mathrm{NH_3}$$

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 Consolidierte 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 Eidgenössichen Polytechnikums (Eidgenossiche 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)

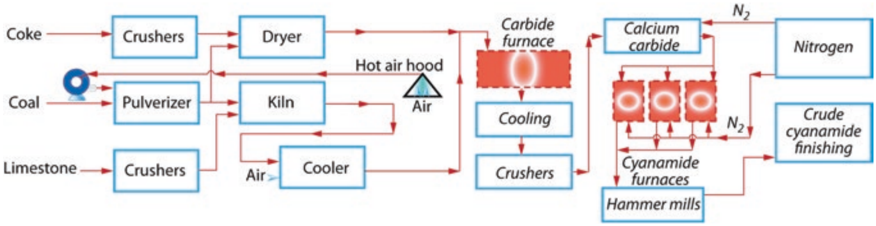


Fig. 2.16 Scheme for manufacture of calcium carbide and its conversion into calcium cyanamide, both by electrothermal processes. (Based on C. L. Mantell, *Industrial Electrochemistry*, 2nd edn. New York: McGraw-Hill, 1940, p. 521)

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:

> Theirs 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)

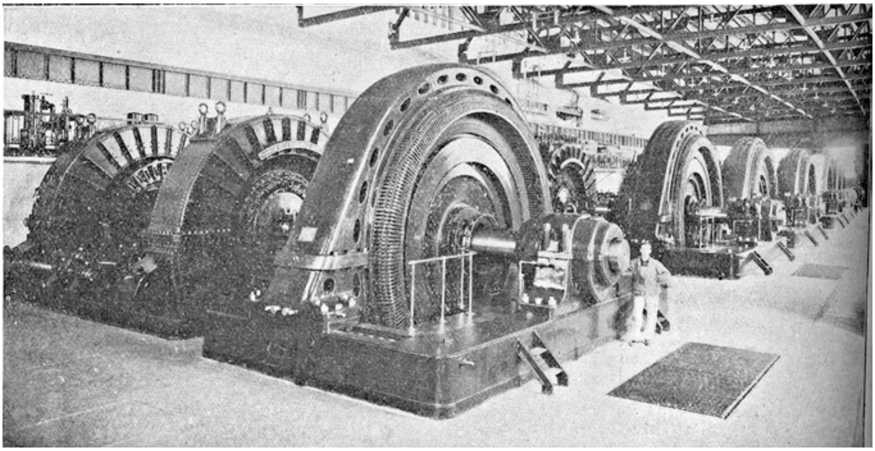


Fig. 2.18 Interior, electricity generating station of the Ontario Power Company, on the Niagara River, opened in 1905. The six generators shown here, each connected to two turbines, produced in total the equivalent of 60,000 horsepower. From 1909 the station provided power to American Cyanamid's Niagara 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 re-form 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 orginal 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 Nitrogeneous Fertilizer Company (Nippon Nitrogen Fertilizer, Nippon Chisso Hiryō Kabushki 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 Fredik 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 Schönherr 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. Chirnside (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 Wrocłow, 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.

$$\underbrace{N_2 \quad + \quad 3\,H_2}_{\text{4 volumes}} \quad \rightleftharpoons \quad \underbrace{2\,NH_3}_{\text{2 volumes}} \qquad \Delta H = -92\ \text{kJ mol}^{-1}$$

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, fomer 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 600º 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 Gerhardt 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-Oslight, 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 *Os*mium-Wolf*ram*.) 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,

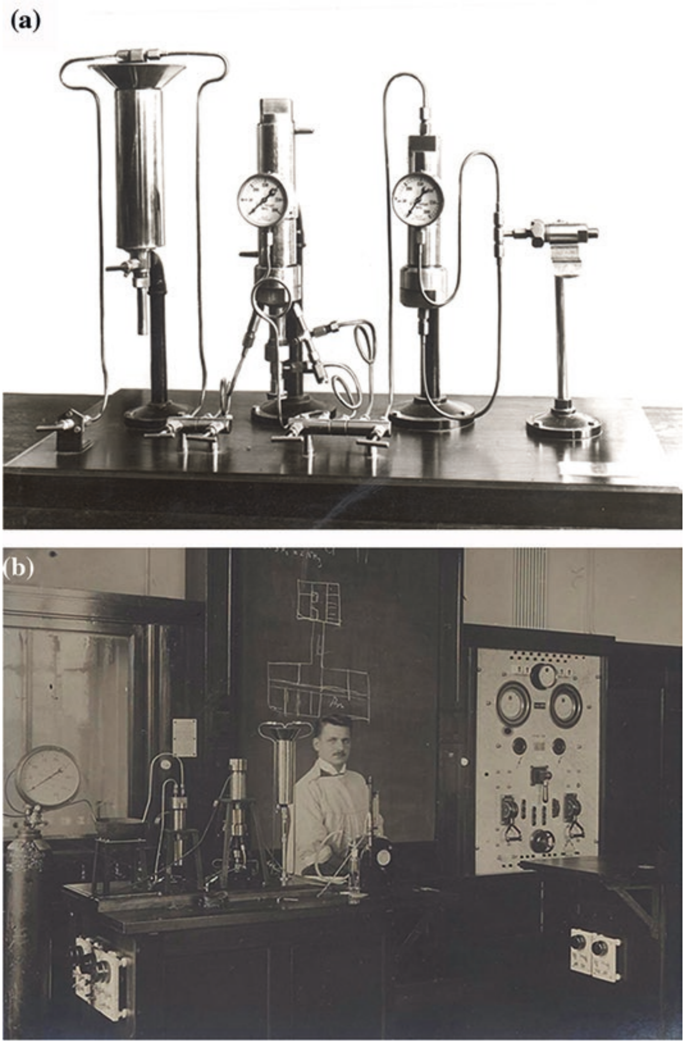


Fig. 2.21 **a** Haber-Le Rossignol 1909 benchtop apparatus for synthesis of ammonia, as originally designed and constructed by Robert Le Rossignol, with assistance from technician Friedrich Kirchenbauer, shown without the circulating pump. The mixture of hydrogen and nitrogen under pressure was delivered 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)

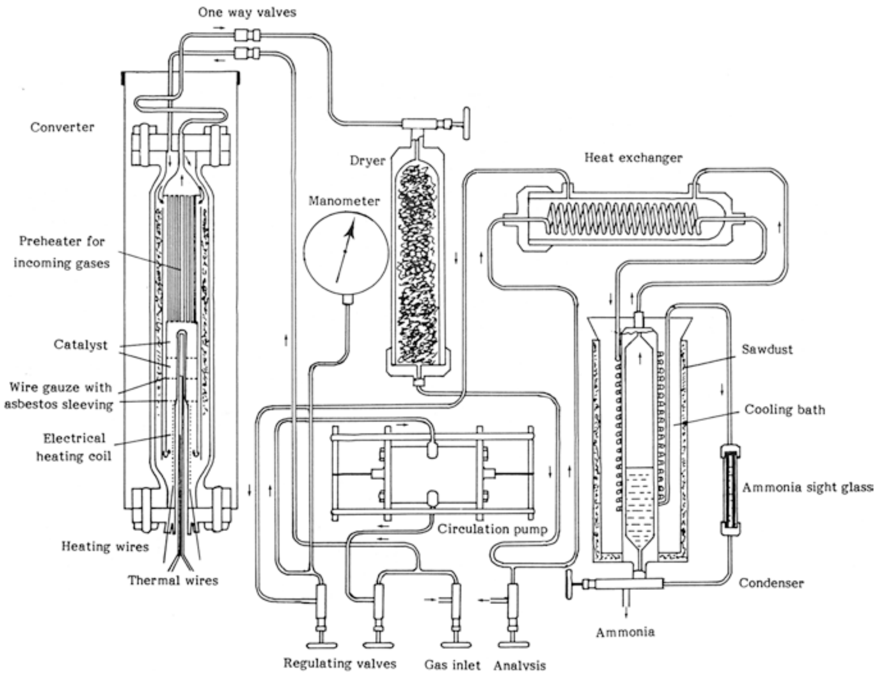


Fig. 2.22 Diagram of laboratory apparatus for continuous synthesis of ammonia from nitrogen and hydrogen, with complete loop, after Fritz Haber and Robert Le Rossignol

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 cm^3/min and it was possible to raise it to 2.5 cm^3/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 seemless 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

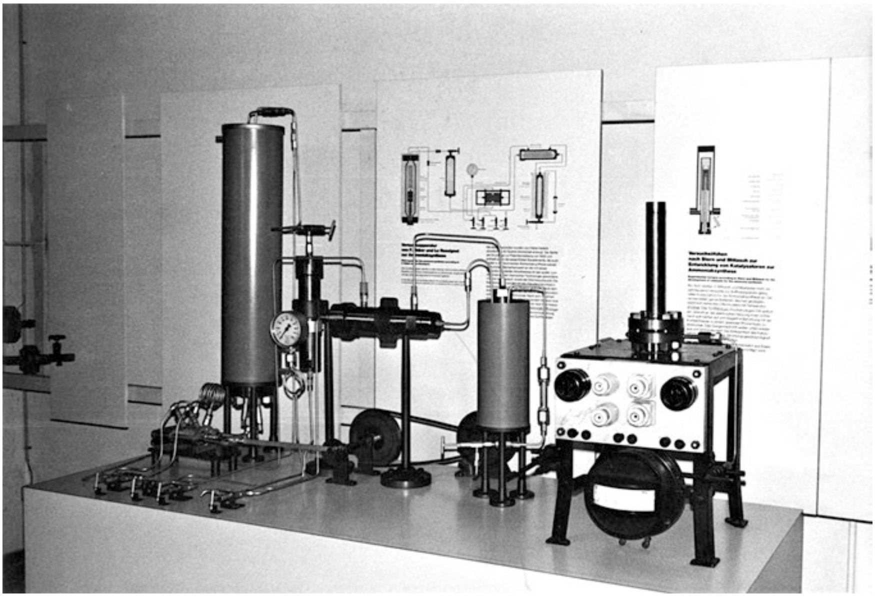


Fig. 2.23 At *right*: BASF catalyst test apparatus, with vertical pressure tube, as used by Alwin Mittasch. At *left*: replica Haber-Le Rossignol benchtop apparatus for synthesis of ammonia. (Photo by author, Deutsches Museum, Munich, 1982)

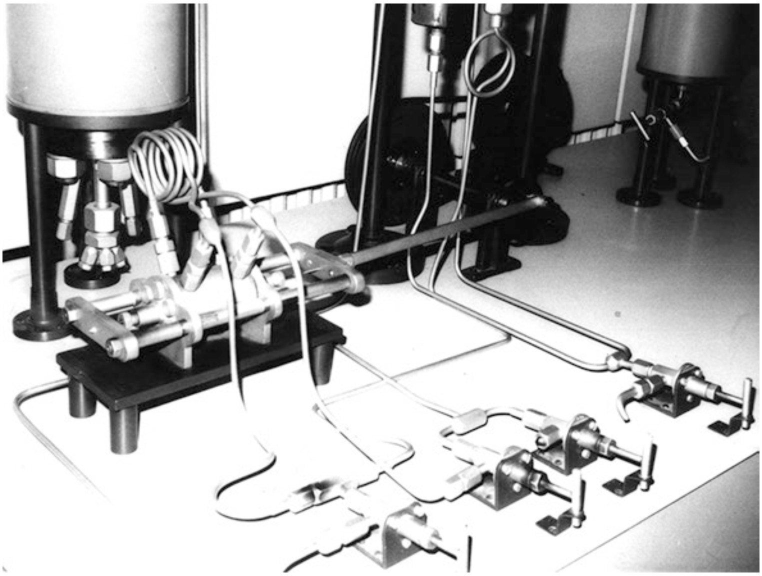
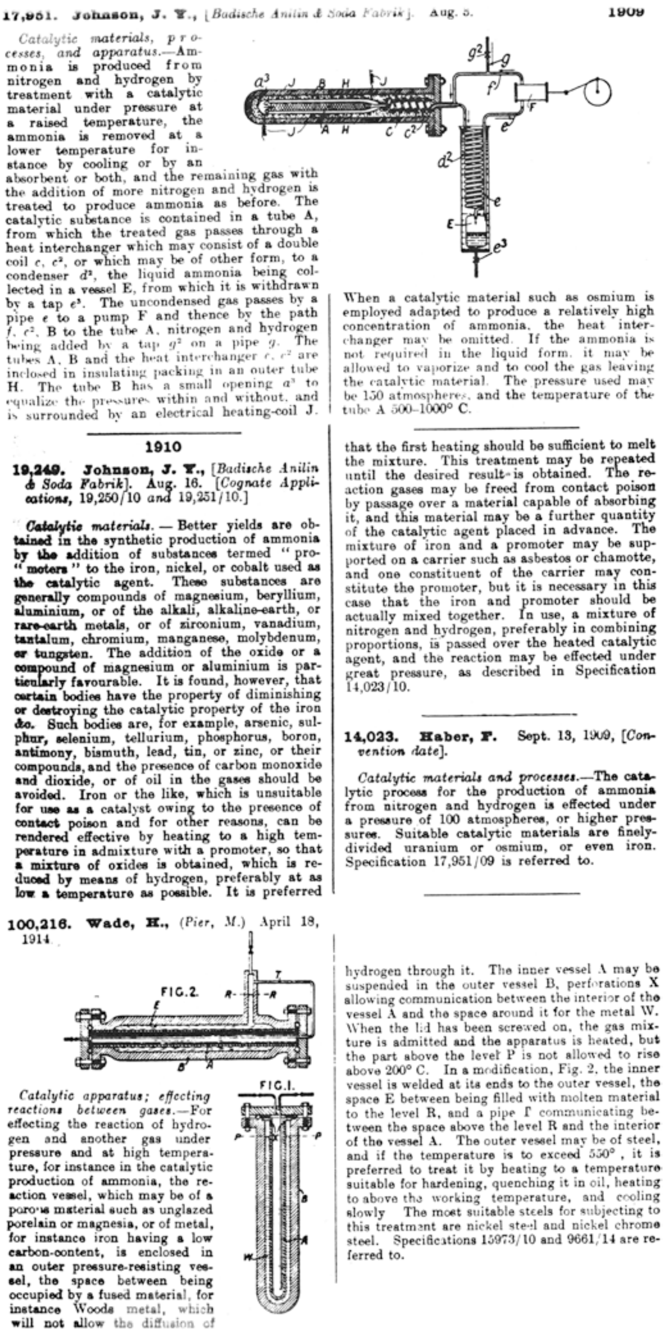


Fig. 2.24 Valves for control of gas flow and recirculating pump, on replica Haber-Le Rossignol benchtop apparatus

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. Y., [*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*², or which may be of other form, to a condenser *d*², the liquid ammonia being collected in a vessel E, from which it is withdrawn by a tap *e*³. The uncondensed gas passes by a pipe *e* to a pump F and thence by the path *f*, *c*², B to the tube A, nitrogen and hydrogen being added by a tap *g*² on a pipe *g*. The tubes A, B and the heat interchanger *c*, *c*² are inclosed in insulating packing in an outer tube H. The tube B has a small opening *a*³ to equalize the pressures 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. Y., [*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 pressures. 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 porelain or magnesia, 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 Γ 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°, 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)

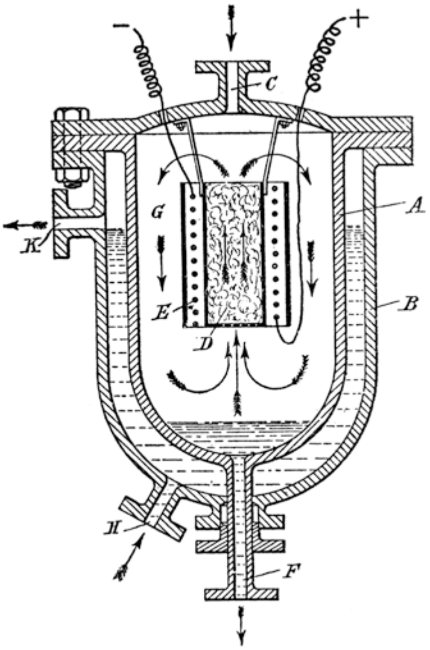


Fig. 2.26 Apparatus for synthesis of ammonia, as appearing in BASF British patent 13,097 of 30 May 1910. "… ammonia is condensed by abstracting heat from a surface in or forming part of the walls of a vessel in which the combination takes place…the reaction vessel *A*, capable of withstanding pressure, 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.

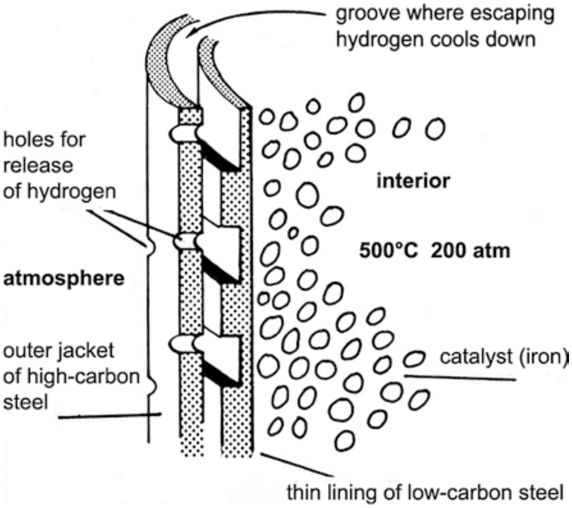
On 11 September 1912, Bernthsen, now no longer enamoured with electric arc fixation of nitrogen, and with great pride and confidence in Bosch's achievement, gave an outline of the new BASF synthetic ammonia process, with special reference to catalyst promoters and poisons, at the Eighth International 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



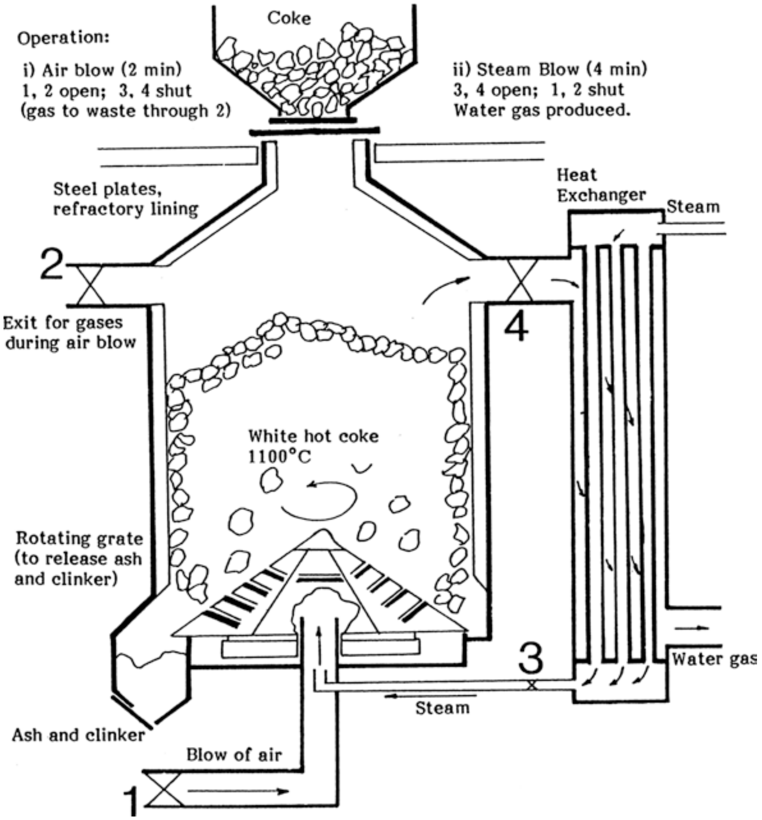


Fig. 2.29 Manufacture of water gas (carbon monoxide and hydrogen) from coke, steam and air, by the Bamag (Berlin-Anhaltische Maschinenbau AG) process

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.

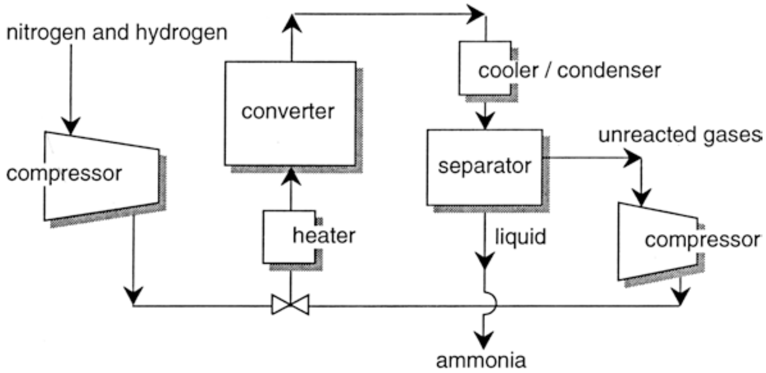


Fig. 2.30 Block diagram for synthesis of ammonia

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

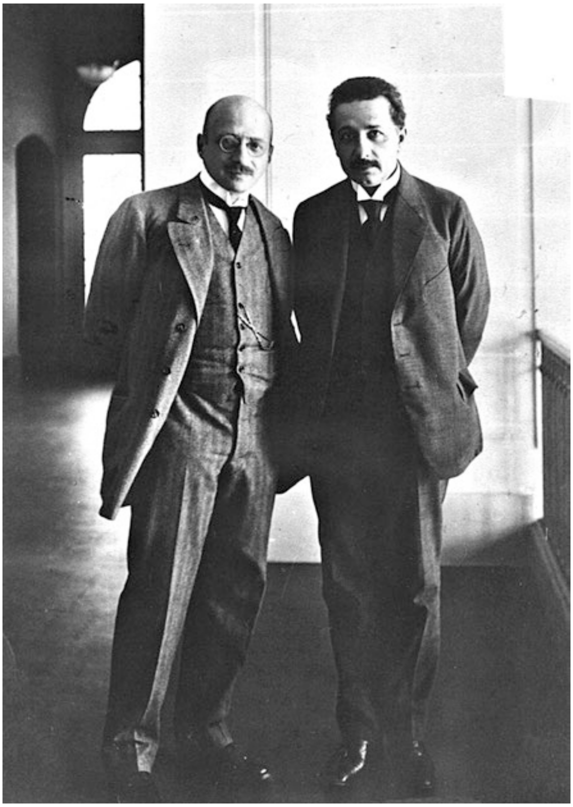


Fig. 2.32 Fritz Haber, at left, and Albert Einstein, at Haber’s Berlin institute in the summer of 1914. The photograph was taken by Haber’s Japanese colleague Setsuro Tamaru. (Tamaru Family Collection/The Albert Einstein Archives, The Hebrew University of Jerusalem, call no. 64-007). In 1905, his “year of miracles” (annus mirabilis), Albert Einstein, as a patent examiner in Bern, reviewed Ignacy Mośćicki’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. (Mośćicki 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 Steinkohlenbirgwerks 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.

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Chapter 3
The Great War

3.1 Chemistry at War

In August 1914, the German plan of attack, the Schlieffen plan, was aimed at the rapid surrender of Paris and capitulation of France, while Russia was held at bay by a small force. It included riding roughshod over neutral Belgium. Anticipating a rapid German victory, several leading scientists and scholars volunteered for service at the front, some well over conscription age. They included Walther Nernst and the sociologist Alfred Weber. Scientific prowess played no part at this stage. Reality soon set in. The Schlieffen plan failed during the first two weeks of September 1914 at the banks of the River Marne. Many intellectuals returned to their institutions; some would not return. This foreshadowed the four years of extended trench warfare along a front that extended from Dunkirk to the border with Switzerland.

The Kaiser's army, and navy, had now to grapple with the ramifications. To maintain military strength, new strategies had to be called into play, particularly for the supply of the matériel of war, not least of which were aromatic nitro compounds for explosives, and also for the intermediates from which dyes were synthesized, now mainly field grey and navy blue. The availability of nitro compounds in turn relied on adequate supplies of nitric acid, and expansion of science-based chemical industry. Nitrogen products came to the fore. The Germans were fortunate, for a while, in that a substantial amount of Chile saltpetre, in excess of 20,000 tons, had been abandoned by the retreating Belgian army at Antwerp, while stocks were held by various companies in Germany. But these were hardly adequate for meeting the demands of prolonged warfare. Synthetic nitrogen products were required for machine gun and rifle bullets, mines, mortars, shells and torpedoes. Meantime, there were already threats to the sea lanes that stretched across the Atlantic. The military leaders needed to be made aware of the situation.

On 13 August 1914, Walther Rathenau, of AEG, was placed in charge of the War Raw Materials Office (Kriegsrohstoffabteilung, KRA) by the Prussian War Minister

A.S. Travis, *The Synthetic Nitrogen Industry in World War I*,
SpringerBriefs in History of Chemistry, DOI 10.1007/978-3-319-19357-1_3

Erich von Falkenhayn, who one month later was appointed Chief of General Staff of the German Army, replacing Helmuth von Moltke. Rathenau was assisted by AEG engineer Wichard von Mollendörff (1881–1937), who had earlier drawn up the draft plan on which the KRA was based. In the first months of the war, and even until late in 1914, it was not just the German military that grossly underestimated the nitrogen requirements. The same was true of the chemical industry. Late in August, Bosch had advised Haber, who was working with Rathenau and the supplies section of the Prussian War Ministry, that he did not anticipate significant expansion of the Oppau plant, at least in the near future. This was apart from pre-war plans to increase Oppau's annual production to 130,000 tons of ammonium sulphate, for fertilizer, by the end of 1915.

The situation changed within weeks. On 30 September 1914, a Reich war chemicals corporation, the Kriegschemikalien AG (Kriegschemikalien AG zur Bewirtschaftung chemischer Rohstoffe), under the presidency of Gustav Aufschläger (1853–1934), for procurement of chemical raw materials and organization of their usage was created. It was one of several large government-supervised corporations established to ensure adequate supplies of war materials. Bosch, present at the inaugural meeting, was encouraged to increase the BASF output of ammonia. The challenge remained of conversion of ammonia to nitric acid suited to manufacture of explosives. Bosch, however, was not prepared at first to share details of progress at BASF into nitric acid work with other parties.

Organic chemist Emil Fischer (1852–1919) (Fig. 3.1) had just completed a review of the nitrogen situation for Rathenau's office. In his report of October 1, presented in Essen, Fischer recommended adoption on a large scale of the Haber-Bosch process, and conversion of the ammonia to nitric acid by a method that was far from technically perfect. Together with Haber he warned of the impending crisis in nitric acid supply [1, 2]. Rathenau, with the support of Haber, arranged for Carl Bosch to meet with representatives of the War Ministry in Berlin to discuss the nitrogen situation. Bosch was struck by the ignorance of basic scientific and technical knowledge among senior military personnel, and had to describe the various processes involved in production of conventional high explosives, the aromatic nitro compounds, in particular the need for nitric acid. That mainly relied upon the nitrates imported from distant Chile, the supply of which could not be guaranteed, and, in any case, took three months to arrive at Hamburg by sea. It was necessary to supplement this source of nitric acid with acid from the new nitrogen processes already worked in Germany and from the Norwegian electric arc factories.

The Antwerp supply, and other stocks in hand of Chilean nitrate, which Haber during late 1914 believed to be around 14,000 tons, would not last long. In November alone, the requirement of sodium nitrate for use in manufacture of explosives was 20,000 tons [3]. The military needs of finished explosives, per month, were calculated to be 12,000 tons, or more, a 20-fold increase on peacetime production. This relied on the arrival of nitrate from Chile.

However, the availability of nitrate from Chile depended on the tide of war at sea, which was about to change. In September, the Germans won advantages

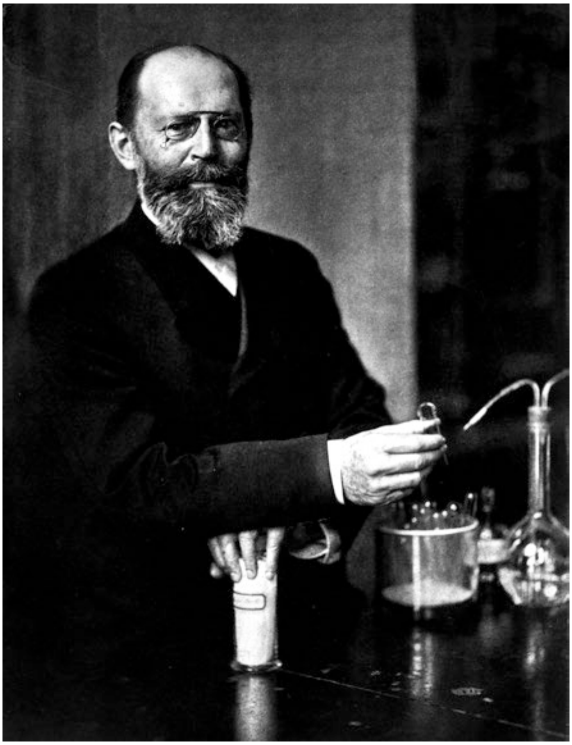

Fig. 3.1 Emil Fischer (Edelstein Center)

in commerce-raiding and submarine operations. On 1 November 1914, a British Royal Navy squadron in the South Pacific Ocean off the Chilean coastal city of Coronel suffered a major defeat in a duel with the German East Asia Squadron, commanded by Vice Admiral Maximilian Reichsgraf von Spee. Admiral Spee's squadron was now free to attack merchant ships loaded with consignments of nitrate destined for the Allies, and to help strategic supplies reach Germany. The situation was soon reversed, on December 8, at the Battle of the Falkland Islands, when Spee went down with his flagship, the *Scharnhorst*, and all but one of the German squadron (Fig. 3.2). From then until the end of the war Chilean nitrate was cut off from Germany by the British blockade. The export of nitrate, that had fallen considerably from August (Germany was a major customer), now recovered. Though the Allies continued to be hampered at sea, including by an intensive programme of submarine attacks between late February and mid-May 1915, and especially during 1916–1917, they were not denied access to nitrate.

For expansion of synthetic ammonia production, Haber, on behalf of the Reich, had already on October 24 drawn up a draft contract with BASF at Ludwigshafen. The final version was ready for signing in mid-November, but was then renegotiated to include further expansion, no doubt as a result of the loss of Chile saltpetre. The contract was made ready for signing in mid-January 1915. The total subsidy offered to BASF was raised from four to six million marks. For the

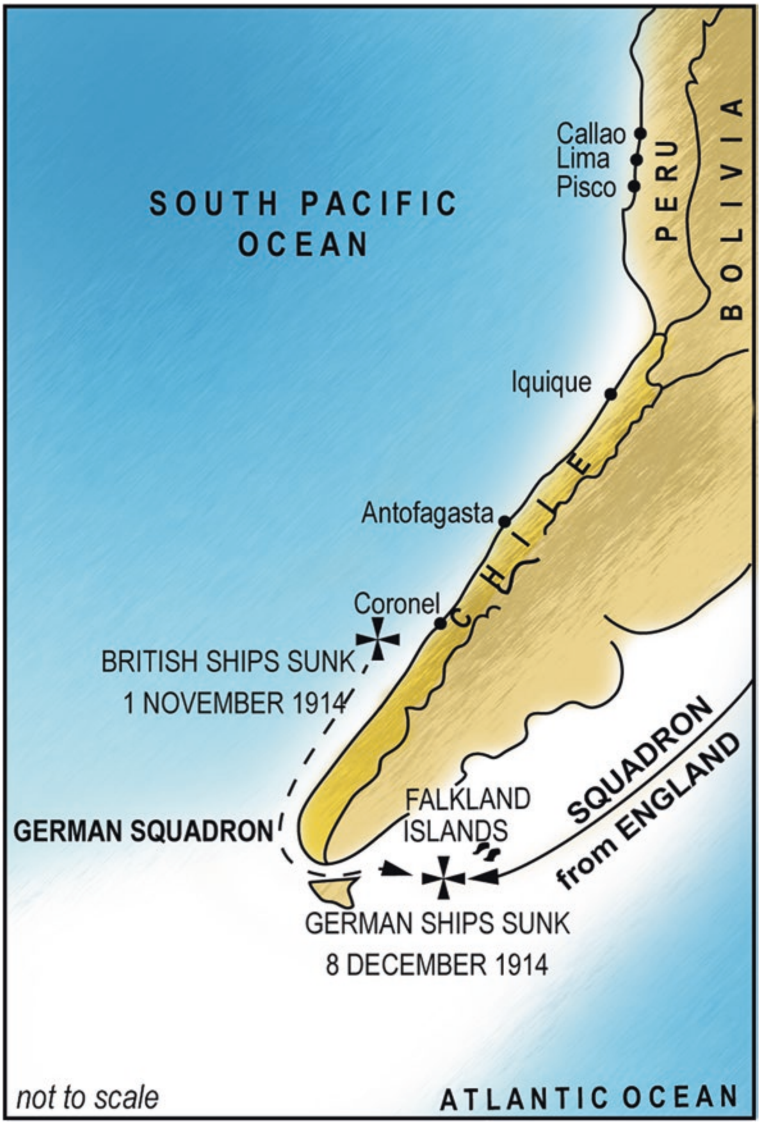

Fig. 3.2 The battles of Coronel and the Falkland Islands, 1914

concentrated nitric acid required by manufacturers of explosives, ammonia was at this time oxidized to dilute nitric acid, that was converted into sodium nitrate, from which concentrated acid was obtained [4].

Bosch was pushed by Fischer to start adding capacity to the Oppau facility even before contracts with the War Ministry had been finalized [5]. There was widespread and behind the scenes rivalry, as well as over-optimistic, if not downright exaggerated, claims by manufacturers anxious to participate in the expanding nitrogen business, not only during the war, but also in anticipation of peacetime conditions.[1] A great deal was at risk, and not just the German war effort. Great profits as well as royalties on inventions were to be had from wartime manufactures based on the latest chemical inventions. Then as now, shareholder value and dividends had to be maintained, which would certainly be enhanced if the government placed orders, made guarantees, and subsidized the building of factories for war production. This also held out possibilities of formerly unthinkable expansions, and profits that would continue to be generated long after cessation of hostilities.

Wilhelm Ostwald and Eberhard Brauer, as well as the coal industry for which they acted as consultants, favoured the nitric acid process adopted at Gerthe. The owners of Gerthe promised Fischer that they were in a position to build twenty plants with an output of 6,000 tons of sodium nitrate from coal gas ammonia every month. Fischer also considered the electric arc method of the Pauling brothers, which though simple suffered from short electrode life (however, the Paulings claimed that they could produce concentrated acid), and the Birkeland-Eyde and Schönherr furnaces. BASF had already, in 1911, dropped its interest in the Schönherr furnace, convinced that the process based on Haber's work was superior to the electrothermal processes. Thereafter the Schönherr furnace was relegated to a topic of mainly academic interest [6, 7].

Though reliable quantitative figures for German nitrogen manufacturing capacities, according to products and processes, vary, they can be used to draw up a rough guide of overall production, and of the relative contributions, not long before the outbreak of war. Comparisons with the following years will demonstrate how the technology of nitrogen production changed rapidly. Until August 1914, Chile saltpetre and gas works ammonia were major sources of nitrogen by far. According to an account appearing in the *Frankfurter Zeitung* on 23 November 1919, nitrogen consumption by Germany in 1913 was made up as follows: Chile saltpetre, 750,000 tons (of which the nitrogen content was 116,000 tons); ammonium sulphate, from gas works, 460,000 tons (nitrogen, 92,000 tons); Norwegian nitrate, from the electric arc processes, 35,000 tons (nitrogen 4,500 tons); calcium cyanamide, 30,000 tons (nitrogen 6,000 tons); and Haber-Bosch derived ammonium sulphate, 20,000 tons (September to December; nitrogen 4,000 tons). The total, calculated as nitrogen, was 222,500 tons [8]. Fritz Haber, when addressing the Society of Chemical Industry in Liverpool during November 1913, indicated that 36,000 tons of cyanamide were manufactured annually (in Germany alone), for use directly as a fertilizer, or by conversion, with steam, to ammonia [9]. Haber was then of the opinion that the recently introduced Haber-Bosch process of BASF would have little impact on other producers of nitrogen products, since demand for nitrogen was so great.

The German press report certainly drew attention to the overriding importance of Chilean nitrate. Germany had since the turn of the century been the main

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[1] Historian Margit Szöllösi-Janze has undertaken an in-depth study of the politics and various personalities involved, including their affiliations [1]. See esp. pp. 100–103, and 106–118.

importer, mainly for the agricultural sector. The supply of nitrogen was under the remit of the Ministry of Agriculture, and mainly the concern of soil chemists. This was very much the situation in September 1914, by which time the Haber-Bosch process had been in operation for just one year. In 1913, the monthly output of the Haber-Bosch process at Oppau, according to BASF, and in contrast to the 1919 press report, was 600 tons of ammonia, converted into 3,000 tons of ammonium sulphate, a rate that was increased by the autumn of 1914.

3.2 Badische versus Bayrische

While soldiers of Germany and Austria-Hungary, the Central Powers (joined by the Ottoman Empire in October 1914), and the Allies, Britain, France and Russia, fought on battlefields with nitrogen products, men of science and industry fought in German boardrooms and government offices over contracts and subsidies for nitrogen products. Sometimes this fighting included vendettas going back over previous years, and efforts to exclude rivals through outrageous claims. At other times it involved struggles over available competing technologies. Adversaries included personalities as well as companies.

Shortly after the outbreak of war, Nikodem Caro negotiated with Emil Fischer for additional electrical power for the Bayrische Trostberg cyanamide works in order to meet the needs of the agricultural sector. Caro wanted sufficient power to increase production of cyanamide at Trostberg at least fourfold. Eberhard Ramm, of the Prussian Ministry of Agriculture, became engaged in discussions with Caro concerning expansion of the cyanamide process, towards which some preference was shown. The cyanamide factories were well established and the manufacturing process perfected. Moreover, not only had conversion of cyanamide to ammonia been achieved, but oxidation of the ammonia had been integrated into the Trostberg facility. In addition, the cyanamide process required much simpler equipment than the Haber-Bosch process, though the energy requirements were considerably greater.

BASF had already antagonized cyanamide manufacturers with public statements to the effect that the grey-black cake of calcium cyanamide was little more than intractable dark muck. The Ludwigshafen firm also claimed that the quality of its ammonia was superior to that obtained from calcium cyanamide. Probably that did not go down well with Karl Helfferich—a member of the board of Deutsche Bank which had invested heavily in cyanamide—who was appointed secretary of the Imperial Treasury Office in December 1914. Walther Rathenau, who had expended much effort into advancing nitrogen fixation as one of the most important strategic projects, favoured cyanamide and recommended construction of new facilities, particularly for supplying the agricultural sector. However, cyanamide was not then sufficiently widely used as fertilizer, and many farmers were not happy with the novel product, particularly when confronted with problems of application during the spring dressing. A competition was announced for the design of a suitable spreading device, which became available by the end of 1915 [10].

Norsk Hydro, incidentally, held contracts with both German and Allied firms, and was anxious to continue supplying all parties with nitric acid and ammonium nitrate. Though Eyde was perceived by French investors in Norsk Hydro to be pro-German, the French armed forces received over half the output, mainly as the nitrate, and the Germans just 13 %, and perhaps less after the German contracts were completed in 1915 [11]. In 1916, Rjukan produced 80,000 tons of ammonium nitrate for supply to the Allies.

Haber, as an important government officer engaged in procuring essential chemicals, and though obliged to deal with all the nitrogen firms, certainly favoured BASF, whose chemists and engineers were working on a commercially feasible means for oxidizing synthetic ammonia to nitric acid. No less important was their emphasis on concentrating the acid, for use in manufacture of explosives, without conversion first to sodium nitrate.

Rivalry for lucrative, long-term nitrogen contracts became increasingly aggressive, with Bosch and BASF pitched against Caro and the Bayrsiche Stickstoffwerke. A nitrogen commission, whose purpose was to draw up contracts with manufacturers, was established on 28 November 1914 (Commission for the Preparation of Contracts for the Purpose of Increasing Nitrogen Production; Kommission zu Vorbereitung der Verträge zwecks Steigerung der Stickstoffproduktion). The Ministry of Agriculture was closely involved in the work of the commission, whose policy was invariably formulated, understandably, by those with the greatest experience, and also the greatest vested interests.

Though Rathenau, as head of the KRA of the German War Ministry, oversaw the work of Haber as head of the Chemical Section, he had little time for academics, whether scientists or economists. As a result he had a falling out with Haber and Fischer, who favoured BASF ammonia (as well as with Richard Willstätter (1872–1942)) at the beginning of October 1914, from which time he took over total control of planning for war raw materials, in particular nitrogen products.[2]

Following Rathenau's considerable emphasis on cyanamide-derived ammonia, the Reich Treasury in early 1915 agreed to provide funds and guarantees that enabled an unprecedented programme of expansion and construction of new facilities. Trostberg underwent expansion from 1915, following agreements with Caro, and sales guarantees from the Reich. However, there was a limit to the facility's capacity, and new works elsewhere were essential. On 5 March 1915,

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[2] Robert Le Rossignol, while at Karlsruhe, married a local girl and in 1909 they moved to Berlin, where, on Haber's recommendation, in July he joined the laboratories of the Auer-Gesellschaft, manufacturer of the Osram lamp. For a time he continued with work on the ammonia process, but without making any further useful contributions. As an enemy alien living in Germany, Le Rossignol was interned at the outbreak of war. Haber intervened and arranged Le Rossignol's release in 1915. He then returned to the laboratories of the Auer-Gesellschaft. Le Rossignol left Germany for England on 6 December 1918. In 1919, he joined the Hammersmith (London) laboratories of the British Osram Company Ltd., a firm sequestered as enemy property, and which from 1916 was wholly owned by the General Electric Company. From 1923, General Electric research was carried out at purpose built laboratories in North Wembley (Fig. 2.20, p. 55). There, Le Rossignol developed large high-powered transmitting valves for radio communication.

the treasury, with Rathenau's backing, commissioned Bayrische Stickstoffwerke to erect and manage state-owned cyanamide production facilities at Piesteritz (Reichsstickstoffwerke Piesteritz; the Imperial Nitrate Works), on the River Elbe, near Wittenberg, and at Chorzów (German: Königshütte), near Katowice (German: Kattowitz), northwest of Cracow, with a plentiful supply of local coal, in Prussian Upper Silesia. Both were producing cyanamide by the end of 1915. Piesteritz began large-scale production in early 1916. Also commissioned was a large brown coal-fired electrical generation facility, from Braunkohlen Golpa-Jessnitz AG (BG-JAG), to serve the Piesteritz works. Brown coal was also the source of electrical power for the Chorzów facility. Even allowing for vested interests by those responsible for commissioning these works, their orders were hardly based on bad decisions. Haber-Bosch synthetic ammonia had yet to come to the fore.

After arranging the increases in cyanamide production with Bayrische, in March 1915, Rathenau resigned. He returned to the management of AEG.

Fischer and Haber enabled additional and very favourable financial arrangements to be made with BASF, particularly after the departure of Rathenau. Fischer believed early on that the Haber-Bosch process was superior to the other nitrogen fixation processes. The product was cleaner, certainly more so than the coal distillation processes, and the labour requirements were less. Once large-scale production by the various nitrogen-capture and nitric acid processes was successfully underway he began to favour the Haber-Bosch process, at least for military explosives. As a result, by January 1916, the output of Oppau had been increased fourfold to 80 tons of ammonia every day.

Electric arc methods also received some support. Fischer had considered the Pauling process in September 1914, when he was advised that it was capable of producing a concentrated nitric acid. The Pauling brothers' firm subsequently erected a new factory near Bitterfeld at Muldenstein, drawing power from a coal-fired generating station that served Germany's first long-distance electrified railway (from Bitterfeld to Dessau, opened in 1911; it reverted back to steam traction in August 1914, as a result of the war). The Pauling nitric acid plant ceased production early in 1917, mainly as the result of shortages of brown coal. In any case, its output was not great. Problems of electricity supply also reduced capacity at the cyanamide works.

Max Sering (1857–1939), of the University of Berlin, who headed the War Ministry's Scientific Commission (Wissenschaftliche Kommission), founded in 1915, wrote in that year, perhaps somewhat optimistically: "The complete cutting off of the supply of Chili saltpetre during the war has been made good by our now taking nitrogen directly out of the air in large factories built during and before the war. With extraordinary rapidity the question has been solved of how the enormous quantities of the needed ammunition were to be produced, a question which in England still meets with difficulties, in spite of the help from America" [12].

Much of this expansion in nitrogen was in fact then still at the planning stages, or at best about to be implemented. Certainly German synthetic ammonia, available from both the cyanamide and Haber-Bosch processes, was converted into nitric acid, required in the production of explosives, far more than into fertilizer. Overall control and production had become a state monopoly, directed by Julius Bueb (1865–1944), Reich Commissioner for the Nitrogen Economy (Reichcommissar für die Stickstoffwirtschaft).

3.3 The Explosives: Nitro Compounds

Throughout World War I, military shells containing high explosives were filled with aromatic nitro-compounds, of which 2,4,6-trinitrotoluene, TNT, or trotyl, was used more largely than any other. TNT was manufactured from toluene, an aromatic coal tar hydrocarbon closely related to benzene; both were obtained from the distillation of coal tar [13]. The wartime demand for toluene often exceeded the supply. As a result, in Germany ammonium nitrate was mixed with trotyl—as was the case in Britain—in order to conserve and extend the use of toluene. The German mixture known as Gestrecktes Füllpulver contained 40 % ammonium nitrate and 60 % trotyl [14]. In Britain, the similar product was called amatol, for which the Allies produced over a million tons of ammonium nitrate: from calcium nitrate (the Norsk Hydro product); by ammoniating Chilean nitrate; and by reacting the Chilean nitrate with ammonium sulphate and fractionally crystallizing the product from solution.

German nitro compounds employed in aerial bombs and torpedoes often contained such mixtures as trotyl and hexanitrodiphenylamine, on account of their great shattering power. There was also picryl sulphide, again a nitro compound, used for similar purposes by the Germans.

The French relied extensively on picric acid, made from phenol, another coal tar product, obtained by distillation of the “carbolic acid” fraction. The fraction was treated with sodium hydroxide, dissolved in soda solution, separated from oil, and the crude phenol was liberated with sulphuric acid or carbon dioxide. It was then fractionally distilled. Nitration of phenol commenced with sulphonation, in sulphuric acid, followed by addition, with stirring, to concentrated nitric acid, giving, in two steps, the picric acid, 2,4,6-trinitrophenol, which was melted and poured into shells. The nitro compound mixed with guncotton (nitrocellulose) was called melinite in France, and lyddite in Britain. At times the supply of phenol was scarce, and demand was such that picric acid was manufactured during the war from benzene, in five steps: conversion to nitrobenzene, then to chlorobenzene, dinitrochlorobenzene, dinitrophenol and finally the trinitrophenol, picric acid. The process was developed at the United Alkali Company in Britain [15]. An alternative process involved sulphonating benzene, followed by neutralization, as its sodium salt, and fusion with sodium hydroxide. The latter, the sulphonate melt, was dissolved in water, the phenol was liberated, and purified, as in the usual process.

Britain before the war and during the early stages had relied mainly on lyddite. The British subsequently developed the manufacture of TNT to a high standard, and replaced lyddite by TNT, and amatol. Much of this effort was due to American-born chemical engineer Kenneth Bingham Quinan (1878–1948), who was brought to England late in 1914 by the Committee on Supply of High Explosives from the Nobel explosives factory near Cape Town. He immediately implemented a programme of construction of new munitions factories. Among the innovations was a continuous process that employed toluene produced from petroleum, rather than coal tar [16].

Two important high explosives did not require the valuable toluene. Both were made from benzene. Tetryl, nitramine (tetranitromethylaniline, trinitrophenylmethylnitramine), a violent explosive, was used to transmit the explosion of the

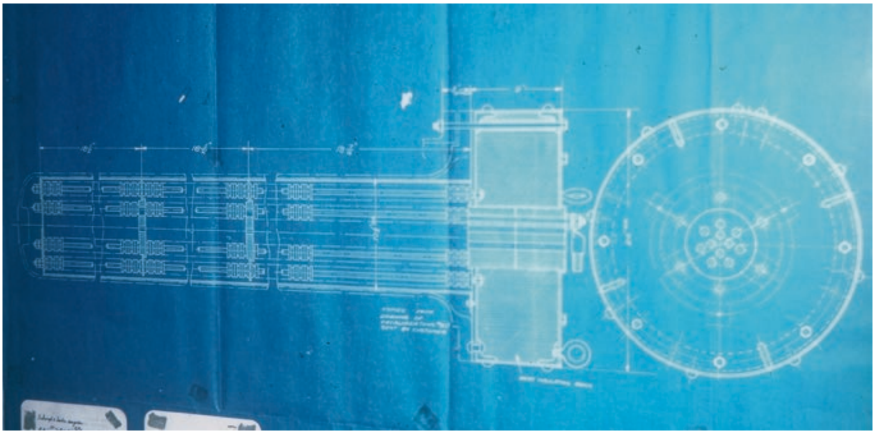

Fig. 3.3 Blueprint of vessel for Chaim Weizmann's fermentation process used in the production of acetone during World War I. (Photo by author, Weizmann Institute of Science, 1985)

detonator in a shell to the less sensitive TNT or picric acid. The high explosive TNA (tetranitroaniline) was made in Germany, and also in the United States by the Calco Chemical Company of New Jersey [17].

The concentration of nitric acid required to produce explosives varied. Nitration takes place in mixed acid, made up of nitric acid and sulphuric acid. As nitro groups are successively introduced into aromatic compounds, such as toluene, it becomes increasingly necessary to exclude water, and as a consequence to employ more concentrated acids.

In addition to high explosives, there were also the propellants, based on nitroglycerine and nitrocellulose, the main constituents of the smokeless powders, such as cordite. The nitration was also achieved with mixed acid. For nitroglycerine, nitric acid of 98–99 % concentration was required. In Germany during the war, wood cellulose was often used instead of cotton. Manufacture of tetryl and cordite required plentiful supplies of acetone, a solvent that was in short supply in Britain, until the novel fermentation process of chemist Chaim Weizmann (1874–1852) was introduced on a large scale from 1915 (Fig. 3.3). Maize, rice, various cereals, and, less successfully, horse chestnuts, were the starting materials [18, 19].

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Chapter 4
Concentrated Nitric Acid and Expansion of the Nitrogen Industry in Germany, France and Britain

4.1 Catalytic Oxidation and Cyanamide

Around 1912–1913, laboratory studies into the manufacture of nitric acid from synthetic ammonia had been taken up by both the Hoechst Dyeworks and BASF. The Bayrische factory at Trostberg, as noted, already produced nitric acid from cyanamide, while the coal industry used the Gerthe (Ostwald) process to make the acid from coal gas works and coke oven ammonia. Both used platinum as catalyst, as did the important contact process for sulphuric acid. The rare metal was in short supply after August 1914, since the main source was the Ural Mountains in Russia.

The main research into developing an alternative, low cost, readily available, catalyst for ammonia oxidation was done at BASF, whose first patent, in 1913, made claim to a catalyst that might be "one or more oxides of metals in the iron group." Alwin Mittasch worked on improvements from early in 1914; he aimed at efficient and economical production of nitric acid, and in turn of nitrates. In July, in collaboration with Christoph Beck, he came up with an iron oxide catalyst containing a promoter. An efficient iron-bismuth catalyst was also discovered. It was Mittasch's success which enabled Carl Bosch in October 1914 to promise that new enlarged plant at Oppau would meet much of the needs of the military by the following spring [1]. For the oxidation units, BASF scientists and engineers introduced acid-resistant alloys containing silicon.

To start the exothermic ammonia oxidation, the catalyst was heated. Oxidation of ammonia was rapid, giving 96 to 98 % nitric oxide. The temperature rose to around 900 °C. Excess air prevented explosions from unwanted reactions.

$$4\,NH_3 + 5\,O_2 \rightleftharpoons 4\,NO + 6\,H_2O \quad \Delta H = -909 \text{ kJ mol}^{-1}$$

A.S. Travis, *The Synthetic Nitrogen Industry in World War I*,
SpringerBriefs in History of Chemistry, DOI 10.1007/978-3-319-19357-1_4

The nitric oxide combined with oxygen to give nitrogen dioxide.

$$2\,NO + O_2 \rightleftharpoons 2\,NO_2 \quad \Delta H = -115\ kJ\ mol^{-1}$$

The dioxide, existing reversibly with its dimer, N_2O_4, was absorbed in water to afford dilute (“weak”) nitric acid, not unlike a similar step in the electric arc processes. Dilute acid could not be concentrated directly by distillation since it formed an azeotropic mixture with water (a constant boiling mixture containing 68.5 % acid by mass at 122 °C).

As a result, for obtaining concentrated acid, the pathway used until well into 1915 by those manufacturers starting with ammonia involved conversion of the dilute nitric acid into sodium nitrate (with sodium carbonate), evaporation to dryness, and reaction of the salt with oil of vitriol (concentrated sulphuric acid). This was similar to the process used with Chile saltpetre.

In May 1915, BASF began production at Ludwigshafen/Oppau of nitric acid from ammonia by its new catalytic oxidation process. Moreover, and no less important around this time, concentration of nitric acid obtained directly from oxidation of ammonia was achieved by the introduction of absorption towers not unlike those used in electric arc processes, and using a counter-current principle. A mixture of nitric acid, of 50–60 % concentration, and sulphuric acid, of 95–96 % concentration (to remove water), entered at the top of the tower, which was packed with rings. The mixture met an upward flow of steam injected at the base. Vapour of concentrated nitric acid exited from the top of the tower. Dilute sulphuric acid was collected at the bottom. This completely overcame the wasteful and long-winded process of first converting dilute nitric acid to nitrate. Also, overall, the consumption of sulphuric acid was less.

A similar ammonia oxidation process was used at Bayer’s Leverkusen factory in 1915. Bayer’s catalyst was described as made up of iron oxide with a heavy metal oxide, no doubt the work of Mittasch, after Bosch agreed to share the results of BASF catalyst studies with other firms. Acid of up to 47 % concentration was produced. Further concentration, of up to 94 %, was achieved by addition of oil of vitriol and steam and blowing into the mixture hot burner gases.

By the spring of 1915, Hoechst had also become engaged in the manufacture of nitric acid, starting with cyanamide. This followed the purchase during November and December 1914 of shares in Aktiengesellschaft für Stickstoffdünger, the Knapsack facility, from investors Berliner Handelsgesellschaft, Metallbank, and Metallgesellschaft. Hoechst thereby controlled almost half of this major cyanamide producer. In return, Hoechst had priority over the supply of cyanamide, for conversion into ammonia, and promoted the Knapsack products. Hoechst expanded the Knapsack ammonia plant in 1915. New carbide furnaces were installed. The workforce was increased from 60 to 400. An improved process for oxidation of ammonia was developed for the new Hoechst Nitrogen Department by a small group of chemists, headed by Martin Rohmer, at Gersthofen, near Augsberg, a site that Hoechst had purchased around 1900 in connection with one of the indigo processes [2, 3]. (Rohmer in 1913 invented an ammonia oxidation process which gave mixed oxides from ammonia that were converted into nitrate.) The Linde process for nitrogen was introduced at Knapsack in 1916.

Though calcium cyanamide was generally intended for agriculture, a considerable amount was diverted to munitions production. In 1916, the War Ministry authorized further expansion at Knapsack, resulting in a new facility capable of producing from cyanamide the ammonia that Hoechst converted into concentrated nitric acid on an increasing scale. Hoechst had already invested considerable effort into production of concentrated nitric acid from ammonia [4]. In 1916, also, Harry Pauling's electrolytic plant developed in 1908 for manufacture of concentrated nitric acid was installed by Hoechst.

As ammonia oxidation catalyst, Hoechst first used platinized asbestos, diaphragms of platinum, or a narrow tube of platinum, none of which were entirely successful. In February 1918, a new acid plant in which platinum gauzes were used was installed. This enabled Hoechst to manufacture 16,500 tons per month of nitric acid using ammonia from both Ludwigshafen and Knapsack. A Reich War Ministry report of a visit to the recently enlarged nitric acid facility in July 1918 observed: "…in its efforts to manufacture concentrated acid, Hoechst has been more successful than any other company. Hoechst has solved the problem of the nitric acid and sulphuric acid concentration in a manner that indicates that the required production output will be achieved also in future." By the war's end, Hoechst's ammonia oxidation plant had 252 converters, each fitted with a 20-in. gauze, supervised by one man per shift [5]. The output in 1918 was the equivalent of 375 tons of 100 % nitric acid a day, whereas BASF produced 140 tons a day of 100 % acid [6]. The Hoechst ammonia oxidation process, while important to the war effort, was far from economic, and much of it, including installations at Knapsack, was shut down after the cessation of hostilities. In 1923, a comparison of costs for production of nitrogen compounds among the "I.G." firms found that they were highest at Hoechst. The nitric acid equipment, in particular, was outmoded, much of it representing hasty wartime installations, and would remain so until well into the 1940s [7].

During the war there were significant improvements in the platinum catalyzed ammonia oxidation based on the investigations of Ostwald and Caro. Multiple platinum gauzes replaced single gauzes, and electrical heating was discontinued. "This type of plant supplied all the nitric acid required for explosives in Germany during the later years of the war…A much greater catalyst life was obtained in this design of plant, extending to six months, provided that conditions were uniform and that the gases were free from impurities that might have a poisoning effect" (Fig. 4.1) [8]. Shortages of platinum may in part have been restored after the armistice with Russia on 15 December 1917, following the Russian Revolution, and especially after the Treaty of Brest-Litovsk (3 March 1918).

The wartime emergency and organization of a new sector of chemical industry in Germany based on ammonia and nitric acid was the outcome of outstanding research efforts and commitment. It involved not only close integration between the activities of laboratory, pilot plant and construction departments, as well as

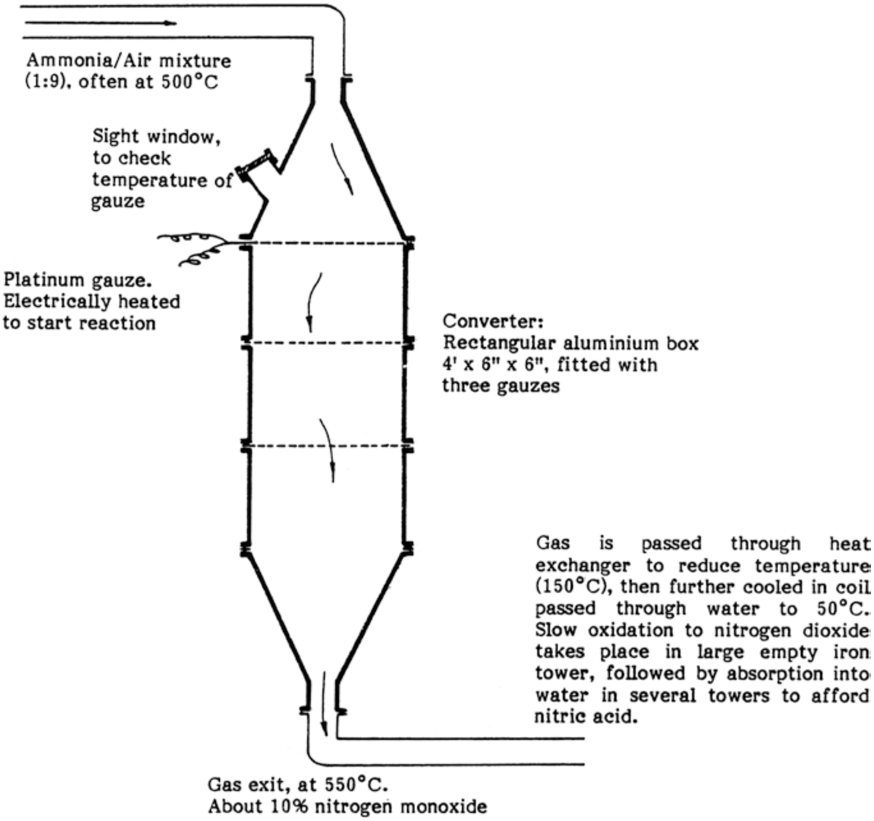

Fig. 4.1 Diagram of converter for oxidation of ammonia to nitric acid. Though based on an Imperial Chemical Industries (ICI) converter, it is essentially the same as that designed by Nikodem Caro and colleagues during World War I

manufacturers of specialized equipment, such as Krupp of Essen, and Bamag, but also on negotiations with the state and its military arm, and substantial support from the Reich Treasury [9].

The response in France to the nitrogen problem was not altogether different to the situation in Germany, apart from the absence of the Haber-Bosch process. In 1917, German submarine attacks on Allied shipping and the threat to supplies of Chilean nitrate encouraged the French to expand calcium cyanamide factories at Notre Dame de Briançon, Hautes-Alpes, and Bellegarde, Rhône-Alpes, both dependent on abundant hydroelectric power [10]. The platinum-catalyzed ammonia oxidation process was named by the French the Kuhlmann-Ostwald process in honour of the Frenchman Frédéric Kuhlmann, who had undertaken ammonia oxidation experiments in 1838 [11]. Problems similar to those encountered in Germany had to be overcome, particularly corrosion, until improved stainless steel was introduced for the reactors. Ammonia oxidation was in full production during 1917, at Angoulême, in the Poitou-Chantres region [12].

French cyanamide production was increased from an annual output of just 7,500 tons in 1913, to 100,000 tons in 1917 [13]. Licenses were issued to the French government for working the cyanamide process of Nitrogen Products and Carbide Company (Limited), of London, which had a major interest in the working of the Frank-Caro process in Scandinavia, and held a license for the Ostwald process for oxidation of ammonia. Among the new cyanamide works commissioned was Lannemezan, to be supplied with hydroelectricity from stations at Bordères-Louron and Lendenvielle. However, it was not complete at the Armistice (Table 4.1).

The French also relied on imported Chile saltpetre, ammonium sulphate made from British gas works ammonia, and ammonium nitrate from Norway, particularly from 1915 to 1916. In 1915, as a result of the French investment in Norsk Hydro, and agreement with the French War Ministry, the Norwegian firm became engaged in construction of an electric arc factory at Soulom, Hautes-Pyrénées. From 1916, the factory produced 300 tons of nitric acid per month, converted mainly into ammonium nitrate, but also sodium nitrate. This was the only Birkeland-Eyde facility ever worked outside of Norway. Hydroelectricity came from a Midi Railway power station on the River Gave de Luz.

Britain and its allies, now mainly ruling the waves of the South Pacific and Atlantic oceans, despite attacks on merchant shipping, continued to rely on Chilean nitrate and gas and coke works ammonia for nitric acid, and on Canada and the United States for explosives. From 1917, the French became increasingly reliant on explosives from the United States. There was also cyanamide from Odda and Alby, when the supply lines were not threatened.

Baron Moulton, director general of the British Explosives Supply Department (successor to the Committee on Supply of High Explosives), first at the War Office, and then at the Ministry of Munitions, formed on 9 June 1915 in response to the British "shell crisis," had brought together a group of capable scientists and administrators to maintain high production levels of explosives and shells. The effort was in many respects comparable in scale and scope to that of the German nitrogen programme, though it relied mainly on organizational ability rather than new technical innovations and novel chemistry. This is where Quinan's skills were so critical. Imports of nitrates, including potassium nitrate from India, grew from 199,000 tons in 1914 to 388,000 tons in 1916, and reached 526,000 tons in 1918 [14]. However, the supply of ammonium nitrate from Norsk Hydro almost ceased, as was also the case for cyanamide from both Norway and Sweden, as a result of the German threat at sea.

By 1916, the ongoing war effort, and losses to German submarine attacks during the early part of the year, stimulated efforts to introduce the new synthetic nitrogen processes. This was the remit of the Nitrogen Products Committee, of the Munitions Inventions Department, Ministry of Munitions, created in June 1916, following recommendations taken by the Council of the Faraday Society [15]. The main interest was in the Haber-Bosch process. But how to cope with its severe working conditions was a complete mystery.

Table 4.1 Calcium cyanamide factories at the close of 1917

Original affiliation, or licensing arrangement with:	Company	Place	Notes
Cyanidgesellschaft (1899); La Società Generale per la Cianamide (1907)	Bayrische Stickstoffwerke (1908)	Trostberg, Bavaria	
La Società Generale per la Cianamide	Nitrogen Products and Carbide Company (Limited), London	Odda, Norway	Successor, with Alby United Carbide Company, to North-Western Cyanamide Company
	Nitrogen Products and Carbide Company (Limited), London	Meraker, Norway	Carbide manufacture
	Nitrogen Products and Carbide Company (Limited), London	Alby, Sweden	
	Società Italiana di Prodotti Azotati	Piano d'Orta, Italy	
	Società Italiana per il Carburo di Calcio	Collestate, near Terni, Umbria, Italy	
	Società Piemontese per il Carburo di Calcio	San Marcel, Aosta Valley, Italy	
	La Société des Produits Azotés	Martigny, Switzerland	
	Gotthardwerke	Bodia, Switzerland	
	Le Société des Produits Azotés	Notre Dame de Briançon, Hautes-Alpes, France	
	Le Société des Produits Azotés	Bellegarde, Rhône-Alpes, France	
	Ost-Deutscher Stickstoffcalc und Chemische Werke	Bromberg, Province of Posen, Prussia (today Bydgoszcz, Republic of Poland)	
	Reichsstickstoffwerke	Piesteritz, near Wittenberg, Saxony	Managed by Bayrische Stickstoffwerke
		Chorzów/Königshutte, Upper Silesia (today Chorzów, Republic of Poland)	Managed by Bayrische Stickstoffwerke

(continued)

Table 4.1 (continued)

Original affiliation, or licensing arrangement with:	Company	Place	Notes
	Außiger Verein	Falkenau, Bohemia, Austria-Hungary (today Sokolov, Czech Republic)	
	Società per l'Utilizzazione delle Forze Idrauliche della Dalmazia	Cernica, near Selenico, Dalmatia, Austria-Hungary (today Croatia)	
	Società per l'Utilizzazione delle Forze Idrauliche della Dalmazia	Dugirat, near Almissa, Dalmatia, Austria-Hungary (today Dugi Rat, Croatia)	
	Japan Nitrogenous Fertilizer Co. (Nippon Nitrogen Fertilizer Co., Nichitsu)	Kinzei, near Osaka; Minimata	
	Nitrogen Products and Carbide Company (Limited)	Dagenham Docks, near London	Ammonia from Odda cyanamide; then gasworks liquor. Late in the war joined with Alby United Carbide Company to enlarge the Odda works. Some work at Trafford Park, Manchester. Licensee of Ostwald process for oxidation of ammonia
	American Cyanamid Company	Niagara, Ontario	
Deutsche Karbid Gesellschaft (1906); AG für Stickstoffdünger (1909)	AG Stickstoffdünger	Knapsack, Westphalia	
	Electrizitätwerk Lonza	Visp (Viège), Switzerland	
	Österreichische Stickstoffwerke	Maria Rast, Steiermark (Lower Styria), Austria-Hungary (today Slovenia)	
	Ungarische Stickstoffdünger AG	Dicsöszentrmárton, Austria-Hungary (today Tirnaveni, Romania)	
	Mitteldeutsche Stickstoffwerke	Groß-Kayna, near Merseburg, Saxony	Subsidiary of AG für Stickstoffdünger. Limited production due to technical difficulties
	Lonzawerke	Waldshut, Baden-Württemberg	

(continued)

Table 4.1 (continued)

Original affiliation, or licensing arrangement with:	Company	Place	Notes
Other			
Oscar Fredrik Svante Carlson's process	Stockholms Superfosfat Fabriks Aktiebolag/Nitrogenium	Near Alby, Sweden	
	Bjølvefossen AS (1905); Elektrochemisk AS (1913)	Indre Ålvik, Norway	Production of carbide commenced 1919, then abandoned
Air Nitrates Corporation (American Cyanamide Company)	United States government	Muscle Shoals, Alabama	"U.S. Nitrate Plant No. 2." Construction commenced December 1917
Air Nitrates Corporation (American Cyanamide Company)	United States government	Toledo, Ohio and Cincinnati, Ohio	Authorised, work started, not completed
Frank-Caro; under license from Nitrogen Products and Carbide Company (Limited)	French government	Minor factories	
	French government	Lannemezan, Hautes-Pyrénées	Not operational at Armistice

Sources include Adolf Bräuer and J. D'Ans (editors) *Fortschritte in der anorganisch-chemischen Industrie an Hand der Deutschen Reichs-Patente*, Erster Band *1877–1917*, Zweiter Teil. Berlin: Verlag von Julius Springer, 1922, p. 2103.

Note The Piano d'Orta, Terni and San Marcel facilities merged their interests through Società Italiana per la Fabbricazione di Prodotti Azotati ed altre sostanze per l'Agricoltura (SIPA), founded in Rome in 1904. Production of calcium cyanamide increased from 114,000 Italian quintals in 1913 to 289,000 Italian quintals in 1915. SIPA ceased operating in 1924, at the time when cyanamide manufacture was being displaced by high-pressure synthetic ammonia processes, including the Italian Casale and Fauser processes. Cyanamide marketing agreements existed among British, French and German manufacturers, sometimes based on arrangements with the Italian patent holder for the Frank-Caro process. Italian architect-chemist Carlo Rossi (1877–1924), in 1916 initiated calcium cyanamide manufacture at Domodossola, northern Italy, at the foot of the Alps. He had earlier been responsible for introduction of the Pauling electric arc process in Italy, at the Legnano site (worked from 1911), and investigated improvements in the process.

4.2 Let's Mention the War…and Fritz Haber

Interest in Haber's novel ammonia synthesis outside of Germany was considerable even before its introduction in 1913, and would continue to grow, particularly during the war years. However much they tried, Allied scientists on both sides of the Atlantic were unable to replicate the high-pressure catalytic process. An ingenious, elegant example of chemical engineering, and of the application of science to industry, it is still viewed in awe today, even if not as much as in the past. It is perhaps that awe and the remarkable and unprecedented success of the industrial synthesis that exaggerated the role of the Haber-Bosch process, and in turn the role of Haber, in enabling Germany to wage war for at least three years, as observed in the British parliament on 28 June 1917 by Liberal politician and chemical manufacturer Sir William Pearce [16]. One thing however was clear: the mystique associated with the Haber-Bosch process abroad contributed to BASF's unrivalled prestige, which it would retain for decades.

Not untypical of responses to the vital role played by the Haber-Bosch process in the German war effort was that of Victor Lefebure (1891–1947), who had studied chemistry at University College London and during 1915–1919 served with the British army in France, specializing in gas warfare work [17].[1] In 1921 he published *The Riddle of the Rhine: Chemical Strategy in Peace and War*, subsequently reworked for the United States Chemical Foundation, which lobbied for a powerful and strategic dye industry [18, 19]. The book was both widely read and influential. Lefebure criticized the Treaty of Versailles for not giving adequate attention to German restrictions on use of the Haber-Bosch process [20].[2]

Then there was British physical chemist Brigadier-General Harold Brewer Hartley (1878–1972), an important postwar investigator of German developments, who before the war taught at the University of Oxford. As a member of the "British Mission Appointed to Visit Enemy Chemical Factories in the Occupied Zone Engaged in the Production of Munitions of War," sent out under the auspices of the Explosives Supply Department in February 1919, he reported with the usual somewhat exaggerated reference to the role of the Haber-Bosch process, as well as with more than a hint of admiration.[3]

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[1] Lefebure led a successful gas cylinder attack near Nieuport in 1916, and was subsequently rewarded with the rank of major. In 1917, he co-organized an inter-allied gas conference to which American observers were invited. He joined the British Dyestuffs Corporation at Blackley near Manchester, in 1919.

[2] Victor Lefebure opined, in connection with Article 172 of the Treaty of Versailles, that: "probably the most important point in the clause is its interpretations with regard to the Haber process. Its critical importance in the manufacture of explosives is so great that our neglect to use the Treaty to remove the monopoly is a direct menace to peace. This process undoubtedly saved Germany in 1915 and is largely responsible for the three years of war agony which followed." Lefebure [18], p. 24.

[3] "[T]he key to Germany's war production of explosives was the Haber process for the production of ammonia from atmospheric nitrogen. It is significant that large scale production by this process only began at the end of 191[3], and that [late in] 1914 great pressure was put on the

Much in the same way that Ostwald had drawn attention in 1903 to the critical role of Chilean nitrate, Hartley also opined: “In the event of another war we might be cut off from supplies of saltpeter.” The strategic implications were far reaching. Blocking the export of Chile saltpetre, as the recent war had demonstrated, threatened the ability to maintain a modern army. It was the German chemical industry’s tradition of focusing on priority projects, and their successful outcomes, as recently applied to nitrogen products, that emphasized the need to ensure independence in strategic nitrogen products. During Hartley’s on-site survey of German chemical industry, he was accompanied by seven British colleagues, in addition to delegates from the United States (seven), France (four), Italy (five), and Belgium (one). The secretary of the mission was chemist Stanley Isaac Levy (1890–1968), whose letter drawing attention to the purported ignorance shown by a minister in the British war cabinet of the nitrate problem was published in *Chemistry and Industry* during March 1924. Levy had served as research assistant at the Ministry of Munitions during the war, which perhaps suggests that he had reasonable evidence of such ignorance.

Just over a year earlier, in February 1923, *Chemistry and Industry*, emphasizing the role of synthetic ammonia in agriculture rather than in war following a survey solicited among readers, could only add to the praises for this remarkable achievement [21]:

> THE FIXATION OF ATMOSPHERIC NITROGEN receives the first place in this week’s letters….Pre-eminent, … [among chemical innovations], stands the synthetic ammonia process for the brilliance of the application of physical chemistry to its solution, and for the wonderful engineering skill displayed. But greatest of all we must recognize the profound influence which a cheap source of ammonia will exert on the most vital problem of the feeding of the rapidly growing population of the world by the intensive cultivation of the land with the aid of fertilizers.

That observation, however, only served to press home the importance of the Haber synthesis in both peace and war. Other observations, however, singled out, erroneously, the role of the Haber-Bosch process in enabling Germany to conduct the war from almost the first months. British chemist and industrialist Herbert Levinstein, who had managed to replicate the German synthetic indigo process during the war, had this to say of the ammonia synthesis: “Germany must have collapsed after the Marne but for Oppau. We [Britain] could not have carried on if the German blockade had cut off our Chile saltpetre” [22].[4]

Footnote 3 (continued)

Badische Co., to increase its output….Without such a process Germany could not have made the nitric acid required for her explosives programme, nor obtained fertilizers for food production after the supply of Chile saltpeter had been stopped by our blockade, and it is probable that she could not have continued the war after 1916.” Hartley [6], p. 214.

[4] In a similar vein, Victor Lefebure observed [18], p. 205: “It must be remembered that, after the first Battle of the Marne, the German Government turned to the I.G. [the community of interests of 1916] for a large part of its explosives and practically all its poison gas, and, as has been stated on many occasions, and with reason, Germany would not have been able to continue the war after the summer of 1915 but for the commercial development of the Haber process by the I.G.”

Baron Moulton, of the Explosives Supply Department, drew attention to the purported vital role of the "Haber factories" in Germany's preparations for war prior to 1914. Moulton went so far as to claim that the Germans had deliberately waited for the Haber factories to be got ready prior to embarking on war [23].

The myth was also perpetuated in Germany. In 1960, Nobel laureate Otto Hahn apparently remembered that on 29 January 1935, at a Kaiser Wilhelm Institute gathering honouring the late Fritz Haber, a meeting from which Civil Servants were excluded by the National Socialists, the society's president, Max Planck, in the opening address pointed out that "had not Haber made his magnificent discovery, Germany would have collapsed, economically and militarily, in the first three months of World War I" [24].

These and similar statements continue to provide the basis for unsubstantiated claims that the Haber-Bosch process sustained the German munitions industry throughout the war, at least from 1915. Less controversial is the role of Fritz Haber in leading Germany's chemical warfare effort. This was a response to the stalemate from the latter part of 1914, and the shortage of nitrogen products for filling shells, both then and later. Toxic gases acted as both substitutes and supplements for conventional nitrogen explosives. Moreover, no account of Fritz Haber's life, particularly during 1914–1918, can omit a summary of this episode in "The Chemist's War."

4.3 Chemical Warfare

Haber and Fischer, notwithstanding the falling out with Rathenau, and inter service and other rivalries, were not deterred from serving as loyal patriots of the Fatherland. The two academic chemists had made this clear when on 4 October 1914 they were among 93 signatories, men of arts and science, including Carl Engler, Walther Nernst, Wilhelm Ostwald, Richard Willstätter, Max Planck, and Philip Lenard, of Ludwig Fulda's "Der Aufruf der 93: 'An die Kulturwelt'" (Manifesto of the 93: To the Civilized World) that appeared in German newspapers rejecting claims of German aggression and barbarism against Belgium and its citizens and affirming loyalty to the German Reich [25]. Poets and writers rallied to the call. Britain, they proclaimed, was the evil aggressor, far more than France or Russia. It was time, German historians agreed, for Germany through war to gain equality with Britain. To attempt this, over the next four years Germany would mobilize eleven million men.

Haber's falling out with Rathenau provided an opportunity to follow agendas of his own making, including promotion of the Haber-Bosch process, and a growing role in the application of science to the needs of the military [26, 27]. His organizational skills would be harnessed in the services of the war economy and his own institute, quite apart from close and confidential co-operation with BASF that would enhance his royalty payments from the ammonia process.

By October 1914, the German military had been made aware of the danger posed by diminishing supplies of nitrogen products. A not altogether new method of warfare was suggested, one that did not rely on nitrogen, but other products made by the synthetic dye industry. The new strategy might even break the stalemate. Carl Duisberg (1861–1935), head of Bayer, at Leverkusen, was encouraged by the high command to test toxic chemicals, particularly dye intermediates, in shells. One such product tried late in 1914 was the irritant dianisidine-chlorosulphonate, a lachrymatory agent. Around 3,000 shells were fired at British and Indian troops near Neuve Chapelle on 27 October 1914. There was hardly any effect on the enemy.

The next chemical weapon to be used was the T-shell, filled with xylyl bromide and explosive; when tried against Russian troops in January 1915 it also had little impact, due to the cold weather. The French had employed the same organo-bromine compound as early as August 1914 in tear-gas grenades, also with little effect against their adversary.

Fritz Haber suggested firing shells filled with chemical agents from mortars. However, in the deployment of toxic chemicals, something simpler was needed to suit the growing urgency of the situation. By March 1915, there were shortages of explosives for shells on both sides, which made use of toxic chemicals, as some believed, a viable solution to the problem. But who would make the "first-strike" attack on a large scale and with any chance of success? The answer was found in Germany through the use of steel cylinders, filled with liquefied chlorine, supplied by the dye factories. This was Haber's idea. He was placed in charge of the installation and use on the Western Front of thousands of cylinders. Success relied on the wind being in the right direction to carry the gas against the enemy lines. The toxic gas was intended to drive the enemy soldiers from their trenches and dugouts. By mid-April 1915, almost 6,000 cylinders were lined up along a mile-and-a-half of trenches at Langemarck, near the Flemish town of Ypres. On 22 April 1915, the direction of the wind was in favour of the Germans and the valves of the cylinders were opened. The French thought at first that the cloud was a smokescreen, and ordered troops, including Algerians, to prepare for an attack of infantry. The yellow-green chlorine gas terrified soldiers who were witness to, and suffered the effects of, the first large-scale release of an effective war gas. There were around 5,000 casualties, with 1,000 dead, including a few Germans who found themselves in the way of the gas in this Second Battle of Ypres. Two days later a similar attack caused 10,000 casualties, with 4,000 dead [28–30].

On May 2, Haber's wife, Clara, committed suicide, though probably not in protest at her husband's new role in the killing machine (depression and suicidal tendencies were not unknown in her family; Hermann took his life in 1946, as did, later on, the oldest of his three daughters). Two-and-a-half years later Haber remarried, to Charlotte Nathan.

Bayer's Carl Duisberg was placed on the advisory committee of Haber's Kaiser Wilhelm Institute, now devoted entirely to war related work. Haber's colleagues in gas warfare research included Otto Hahn, James Frank, and Hans Geiger. Studies included the development of gas masks and suitable fillers, in which work organic chemist Richard Willstätter was involved. From February 1916 the institute's role as a servant of the state and military was formalized. A coordinating body was established, at the suggestion of Haber, who was backed by Koppel and Friedrich Schmidt-Ott (1860–1956) of the Prussian Ministry of Education. This Kaiser

Wilhelm Foundation for Military and Technical Sciences (Kaiser-Wilhelm-Stiftung für kriegstechnische Wissenschaften) became part of the Ministry of War in 1917. The ministry's Department 8 was devoted to chemical warfare under the management of Haber's institute, now the Kaiser Wilhelm Military Institute.

Moral distinctions had become blurred, and for some the limits of chivalry had come into question, and not just in relation to the use of toxic gas. Notwithstanding the 1899 Hague Convention, in which the signatories agreed to refrain from using projectiles to disperse asphyxiating or deleterious gases in warfare, as ratified in 1907, retribution to the use of chlorine in war was axiomatic. The British were not slow in responding, even if on the first occasion somewhat clumsily, or by unhappy accident [31]. A consignment of gas cylinders filled with chlorine was on the way to France by early July 1915. At Loos, the "cylinders were brought into a section of the British front line and embedded in the parapet. The instructions issued were of the vaguest character'—'Ere you are, Jock, 'ere's the key!'—a spanner with which to loosen the valve" [32]. It was 25 September 1915. The retaliation did not go well. The wind shifted direction, "and the gas blew back into our front and support lines and hung heavily in shell holes, inflicting considerable casualties." There were both Allied and German gas casualties on that day.

Laws and customs of war on the land, as defined by the Hague Convention, had been broken. The armies of the Allies and Central Powers developed ever more toxic and debilitating chemicals. The French called on the services of Victor Grignard, the British on Harold Hartley, and William J. Pope at the University of Cambridge. Captain Hartley in 1915 joined the Royal Engineers to work on gas warfare, taking on the role of chemical adviser to the Third Army in France. In 1917, as lieutenant-colonel, he was assistant director of Gas Services, General Head Quarters, France, and late in 1918, as brigadier-general, Controller of the Chemical Warfare Department, Ministry of Munitions. New developments followed, particularly phosgene, noted for its delayed effect, and mustard gas (yperite, summer 1917), as well as theories of meteorology to guide the attacker. An attempt to fill a shell with arsine and high explosive failed, since the toxic gas was destroyed at the point of explosion. Apart from the initial shock attack in April 1915, which the German military failed to use to advantage, the artillery barrages of toxic chemicals and irritants in fact played hardly any role in determining the outcome of the war. They did however leave many casualties, suffering the long-term effects. Conventional wisdom is that chemical warfare was not a major factor in the war effort.[5] There were also laboratory

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[5] After the first German gas attack with chlorine, the Allies condemned the Germans for acting in what in war was still expected to be "sportsmanlike" conduct. Apart from the element of surprise, it was the lack of preparation on the part of the Allies that caused the greatest alarm and provoked panic and hysteria. Nevertheless, for all the tales of horror, chemical warfare was certainly not necessarily as contentious as it was to become in later decades. Despite the condemnation of gas warfare, in public at least, and misgivings concerning its employment among some chemists, there were those in the military, as well as scientists, who believed in its potential for bringing about a quick end to battles. Moreover, the morality of war in general, whether by projecting nitro compound or toxic gases, was often called into question, and even used to argue in defence of gas weapons, including by Victor Lefebure, Harold Hartley, and Major General Amos Fries of the US Chemical Warfare Service.

causalties among those engaged in gas warfare work. Haber's assistant Gerhardt Just lost a hand, and a colleague was killed, during an explosion when working with a bromine compound.

Surplus war gases created problems of disposal, and even a few benefits. Disposal of mustard gas polluted French soil. Chloropicrin, known as a tear gas, when applied to the soil was used for effective control of nematodes and wireworms for as long as supplies lasted.

4.4 War Work: Ammonia Converters and Merseburg

According to an American report following the visit by a delegation to Lugwigshafen-Oppau in June 1919, the wartime Haber-Bosch facility was "the last word on the subject." The visitors were advised that "the German Government advanced something over 200,000,000 marks" towards its construction [33]. Another figure was 20 million pounds. This was the plant that, including oxidation of ammonia to nitric acid, Carl Bosch had promised would be in operation by the spring of 1915, and had subsequently been much enlarged. Bosch had kept to his word. A superb organizer, in 1916, as a result of his nitrogen work, he was appointed a director of BASF.

That work, spread over half a decade, had led to the introduction of a highly efficient, robust manufacturing plant. Inner diameters of ammonia converters were increased from an initial 500 mm to 800 mm. Rapid-response magnetic shut-off valves, instruments for controlling gas flows and compositions at high pressures, and various special valves and other instruments were devised. In order to maintain high production levels, of the order of 120 tons of ammonia every day, changes were made in the production of reactant gases. In 1915, an improved process for preparing hydrogen from water gas, as developed by Wilhelm Wild (1872–1952) during 1910–1912, was introduced into the Oppau factory, in collaboration with Bosch [34]. First, steam was blown over red hot coke to afford water gas, comprising equal volumes of hydrogen and carbon monoxide. The Bosch-Wild modification involved a further steam treatment at 350–450 °C over an iron-chromium catalyst to afford a mixture of carbon dioxide and extra hydrogen. This is the called the "shift reaction."

$$H_2O + CO \rightarrow CO_2 + H_2 \quad \Delta H = -41 \text{ kJ mol}^{-1}$$

Carbon dioxide was absorbed, and subsequently recovered, by physical solution, or scrubbing, in water.

The Bosch-Wild shift reaction was also called the Bamag process after the engineering firm responsible for the special equipment. The nitrogen-hydrogen mixture was made up from producer gas and water gas. Sulphur compounds were then removed (originally over activated carbon). The carbon monoxide was oxidized with steam by the shift reaction. (At one stage, the mixed gases were temporarily freed of nitrogen prior to the oxidation.) After removal of carbon dioxide, at 25 atmospheres, the mixed gases were compressed to 200 atmospheres, final traces of carbon monoxide were removed, and the hydrogen-nitrogen mixture was made up in the correct stoichiometric proportions, 75 % hydrogen and 25 % nitrogen, known as synthesis gas. This synthesis gas was introduced into the converter

From late 1914, Oppau ceased manufacture of ammonium sulphate fertilizer, and instead produced ammonia for munitions manufacture. By September 1916, expansion at Oppau enabled the production of ammonia in ten 12-metre high converters. The factory's output, as ammonium nitrate, was 60,000 tons a year. Technical limitations on size at the time required that these reactors consisted of two six-metre sections bolted together. Internal heat exchange was another innovation, closely following the reactors devised by Rudolph Knietsch for the contact process (for sulphuric acid). The Ammonia Laboratory continued to deal with design problems, including investigation of novel alloys. Bamag, as it had done with other firms, collaborated closely with Bosch in the development of ammonia oxidation plant [35].

Notwithstanding these tremendous developments, the Haber-Bosch process would come well to the fore only in 1917, with the opening of a new works in central Germany. Bosch, based on the success of Oppau, at the end of 1915 lobbied the German government to provide funding for the construction of a new Haber-Bosch facility. The site chosen was at Leuna, near Merseburg, southeast of Halle. Not only would it be safe from the frequent Allied bombing (the French had first bombed Oppau on 27 May 1915, in what was the first ever strategic air raid), but nearby were sources of water, brown coal and gypsum. During this period Bosch had to deal with the AEG engineer Wichard von Möllendorff, then director of Kriegschemikalien AG, and subsequently head of the Reichsstickstoffwerke (August 1915 to April 1916). An important factor in the decision-making process was the preferred location, in common with all major German nitrogen works constructed during World War I, in Prussia, rather than Bavaria (apart from Trostberg), that played a relatively small role in the war [36]. The Merseburg facility, ultimately covering thirteen square kilometres, was later known as the Leunawerke (Figs. 4.2, 4.3, 4.4, 4.5, 4.6, 4.7 and 4.8).

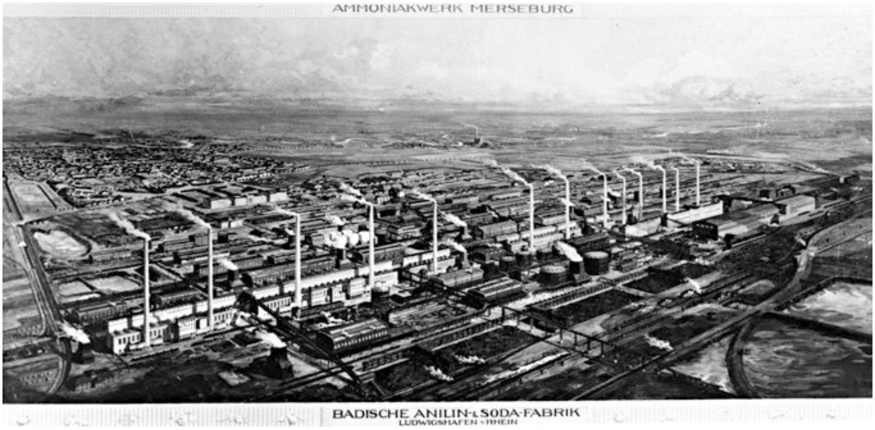


Fig. 4.2 The BASF Merseburg factory. From a painting by Otto Bollhagen. (Bild-Nr XIV/3 Haber, Archiv der Max-Planck-Gesellschaft, Berlin-Dahlem)

Fig. 4.3 Germany, including the Provinces of Posen and Silesia, showing locations of Haber-Bosch BASF ammonia and cyanamide factories, in 1917

Fig. 4.4 The Merseburg factory, showing the gas plant, with the capacity for producing up to 80 million cubic feet every day. (Bild-Nr XIV/3 Haber, Archiv der Max-Planck-Gesellschaft, Berlin-Dahlem)

Karl Helfferich at the Reich Treasury wished to control ownership of the new ammonia facility with an arrangement similar to that already in operation for the Reichsstickstoffwerke. Effectively he planned to create a state monopoly on nitrogen production. This was rejected by BASF. Agreement was finally reached

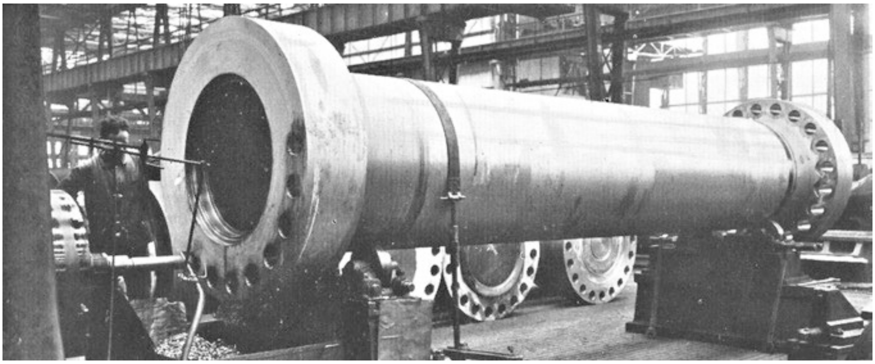


Fig. 4.5 Machining a hollow forged ammonia converter at the Fried. Krupp AG works, Essen. The holes in the flanges enabled connections between vessels to be made with bolts and studs. (Edelstein Center)

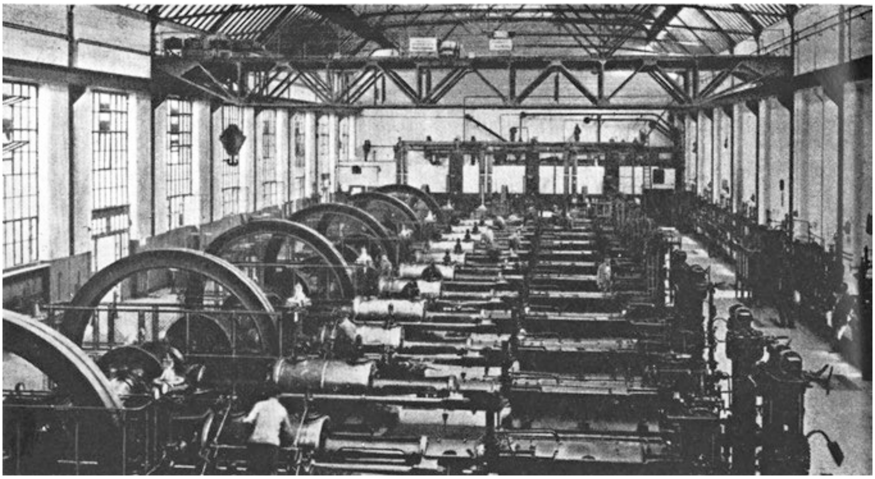


Fig. 4.6 Compressor room, BASF Merseburg/Leuna. Several reciprocating compressors were required since each one accommodated only a small volume of gas. (Edelstein Center)

on 10 April 1916. BASF accepted the cost of construction, with subsidies for the war work from the Reich, which pledged to purchase the entire output. Construction at Merseburg was directed by Carl Krauch and commenced on 19 May 1916. The factory was managed by Ammoniakwerk Merseburg, a subsidiary of BASF. It was said that an Allied spy, after observing the growing technological marvel, reported that the vast factory was something to behold, completely awe inspiring.

On August 18, the two groups of major German dye-making firms created the I.G. (Interessengemeinschaft der deutschen Teerfarbenindustrie) that included

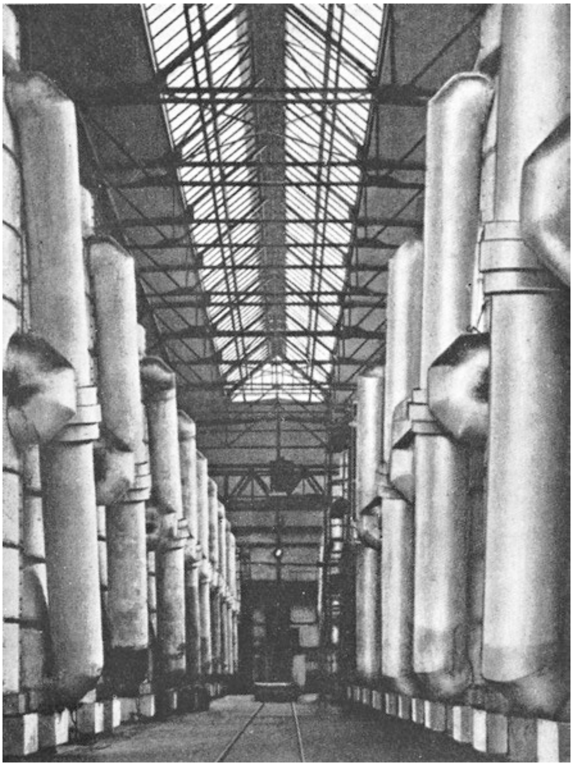


Fig. 4.7 Ammonia synthesis, BASF Merseburg/Leuna. (Tongue [43], Fig. 221. I.G. Farben photograph)

Weiler-ter Meer and Griesheim-Elektron. Three areas excluded from their joint interests were BASF synthetic ammonia, the Hoechst interest in acetylene chemistry, and the Griesheim-Elektron light metals business [37].

The year 1916 was critical in the conduct of the war. The German army launched the Verdun offensive against the French army in February, leading to a series of attacks and counter attacks, with losses of around 70,000 or more men every month (by December the French managed to recover their lost ground). On 1 July 1916, the British began their massive Somme attack, a major setback for the Germans, who were forced to move men and equipment from the Verdun sector (and also in response to a Russian offensive). At the end of August, Paul von Hindenburg and Erich Ludendorff, following their military successes on the Eastern Front since 1914, were appointed joint chiefs of staff, replacing von Falkenhayn, whose Verdun offensive, increasingly repelled, with continuing great loss of life, and suffering from the transfer of resources, was falling apart. The Somme and Verdun offensives cost Germany, France and Britain dearly in terms of dead, wounded and captured.

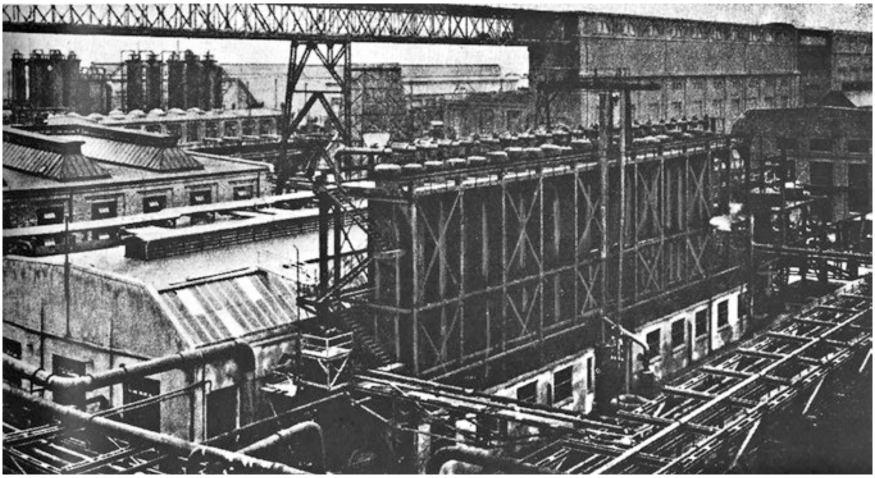


Fig. 4.8 Catalytic hydrogen plant at Merseburg/Leuna. This process was based on the Bosch-Wild modification in which steam treatment of water gas at 350–450 °C over an iron-chromium catalyst converted carbon monoxide into carbon dioxide and increased the hydrogen content (the "shift reaction"). (Tongue [43], Fig. 73. I.G. Farben photograph)

In August, the Hindenburg programme, for industrial reorganization, named after the elderly new chief of staff, and in which Carl Duisberg of Bayer played a prominent role, was brought into operation. The programme involved an industrialized war economy carried out on an unprecedented scale, with in particular centralized control of production of armaments, particularly shells and explosives. It called for urgent doubling and even tripling of war production [38]. This meant increased outputs of ammonia, cyanamide, nitric acid and nitrates, toluene and other aromatics, as well as the war gases. As a result, in 1916, Germany produced 36 million shells, a fourfold increase on 1915. It was not long before the Germans were firing 300 million rounds of ammunition every month.

On 15 September 1916, during the Battle of the Somme the British introduced the tank in an effort to clear the German trenches. A few days later, on 20 September 1916, Hindenburg's office wrote to the Reich Chancellor demanding that the Reich reduce the amount of nitrogen allocated to agriculture. The release of nitrogen would contribute towards the 20,000 tons per month required for 14,000 tons of propellant powder (Treibpulver), as required by the military. The letter revealed that monthly production of ammonia at that time amounted to: 8,000 tons from coke ovens, 5,000 tons from Oppau, and 4,700 tons from the cyanamide factories. This included a facility at Waldshut (Lonzawerke), south-western Baden-Württemberg, with an annual capacity of 60,000 tons of cyanamide. No further increase in coke oven ammonia was anticipated, the planned Merseburg works would initially provide an additional 2,500 tons, and ammonia output from cyanamide would be increased to 6,500 tons. Hindenburg strongly recommended that the Reich Chancellor work with the Ministry of Agriculture, the KRA, and the treasury, to deal with what was a matter of the utmost importance.

On the same day a meeting was held in Berlin to discuss the nitrogen situation. Present were Fritz Haber and Major Charles Garke (1860–1936), as representatives of the Prussian War Ministry, Nikodem Caro, representing the Reichsstickstoffwerke, Julius Bueb, commissioner for the nitrogen economy, Eberhard Ramm, of the Prussian Ministry of Agriculture, and representatives of the treasury, the War Food Office, the KRA, the Reich Interior Ministry, and the Bavarian Interior Ministry. The itinerary made clear that the meeting was charged with a sense of considerable urgency. Allowing for the additional needs of the military, shortfalls in the agricultural sector were anticipated for the autumn of 1917 and spring of 1918, unless (and probably even if) the new capacities became available. Agriculture required 50,000 tons of nitrogen per year, whereas only 30,000 tons were possible under the new arrangement. There was, overall, the need for an additional 6,000 tons per month, and, it was observed, "This cannot be achieved by *one* process alone" [39]. Options for making up the shortfall included the enlarged cyanamide capacity, by 1,500 tons per month through a new facility near Trostberg, and 800 tons per month by expanding Chozrów from 25,000 to 75,000 tons per year. Haber anticipated that a further 2,000 tons a month would be available from BASF by the end of 1917. This was to come from Merseburg, since, as the representatives of the Royal Bavarian government pointed out, additional ammonia capacity could not be achieved at Ludwigshafen/Oppau. They did however encourage the increased cyanamide capacity at Trostberg.

The figures given in Hindenburg's letter clearly demonstrate the extent to which even late in 1916 the Haber-Bosch process was by no means an overriding factor in production of essential nitrogen products required for both the military and agriculture. Nevertheless, while cyanamide ammonia was still important, with plans to build a new factory near Trostberg, and the threefold expansion of production at Chrozów, in the long term preference was to be given to the Haber-Bosch process. The latter, it was argued, required less labour for construction and operation, its power requirements were lower than for the cyanamide process, a particularly critical aspect when there was reliance on coal-fired power stations, and operation was less complicated than for cyanamide. Though this militated against cyanamide, production of the latter had one advantage: it required less sophisticated equipment. However, considerable manual work was involved, including the sizing of lime and coke with sledge hammers, and breaking up by hand of carbide pigs and cyanamide ingots (until mechanical hammers were introduced). As for coke oven ammonia, the greater part was assigned to agriculture.

While the new Merseburg ammonia facility was well suited to the demands of the Hindenburg programme, delays in construction were caused by the general war situation, including shortages of coal, and an unusually cold winter. The severity of the weather greatly affected the whole chemical industry, as well as society in general. For example, on 27 January 1917, with the temperature at −21 °C, the Bayer Flittard TNT plant was completely wrecked by an explosion when a foreman attempted to free a frozen pipe from ice [40]. The situation throughout Germany was aggravated by shortages of food, particularly potatoes and meat, arising from a poor harvest. The turnip became a substitute for other staple foods during what was long remembered as the Turnip Winter of 1916–1917.

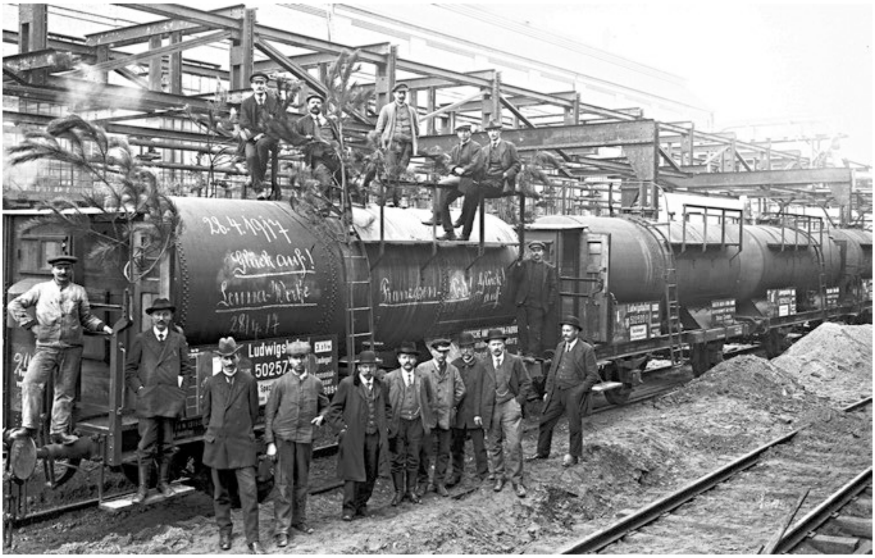
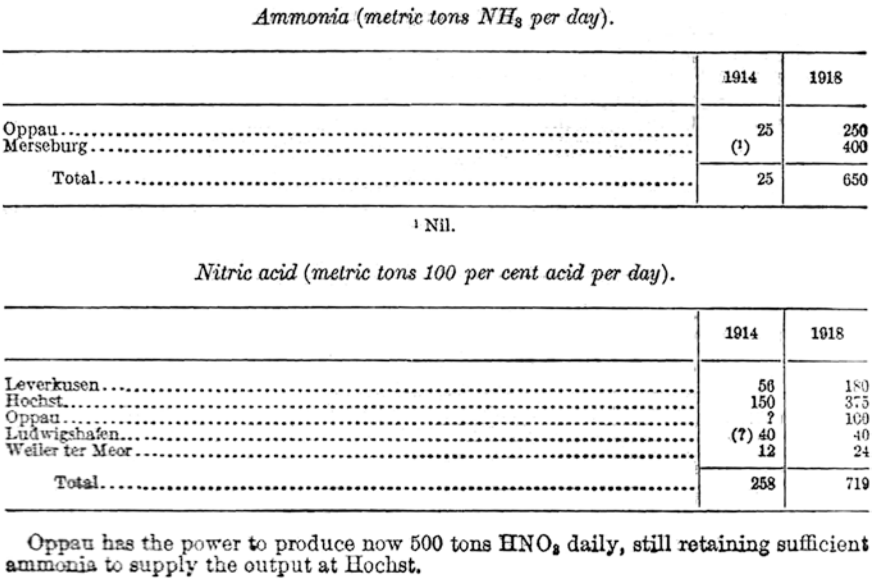


Fig. 4.9 The first trainload of ammonia awaiting departure from the BASF Merseburg works on 28 April 1917, bound for Ludwigshafen, where ammonia was converted into nitric acid. Written by workers in chalk on the tank of the first wagon are the date, “Good Luck,” and “Death to the French.” Tree branches serve as decoration. (LHSA, MER, 1 525, Fotosammlung, Nr. 786. Landeshauptarchiv Sachsen-Anhalt, Abteilung Merseburg)

On 28 April 1917, the Merseburg facility dispatched its first train of railway wagons containing ammonia to Ludwigshafen for conversion into nitric acid and ammonium nitrate. Chalked on the tank of the first wagon were the words “Death to the French” (Fig. 4.9). It was just three weeks after the United States declared war on Germany.

The initial planned plant capacity at Merseburg I was 30,000 tons per year, soon increased to 75,000 tons, then, in December 1916, in line with the demands of the Hindenburg programme to 160,000 tons (Merseburg II, but not in service at the Armistice). An Imperial trade inspection of the Merseburg facility on 15 December 1917 noted that: “The ammonia water is 20–22 %. It is of purity suitable for nitric acid production” [41]. Not long before cessation of hostilities there was a planned expansion to 240,000 tons per year (Merseburg III, July 1918). In 1917, German ammonium nitrate production, described by one source as “sulphate of ammonia (really ammonium nitrate),” was 700,000 tons, equal to that of Great Britain and the United States combined [42]. In January 1918, in response to the extreme food shortages experienced in Germany, and considerable social unrest, the Prussian Minister of Trade and Business was advised that some Haber-Bosch synthetic ammonia could be diverted to agriculture. This was made possible by the growing outputs at Merseburg and Oppau; the latter had increased production of what was later stated to be ammonium sulphate but more likely was ammonium nitrate from approximately 300,000 tons in 1916 to 500,000 tons in 1917 [43]. Some of this output relied on



Ammonia (metric tons NH_3 per day).

	1914	1918
Oppau	25	250
Merseburg	(1)	400
Total	25	650

[1] Nil.

Nitric acid (metric tons 100 per cent acid per day).

	1914	1918
Leverkusen	56	180
Hochst	150	375
Oppau	?	100
Ludwigshafen	(?) 40	40
Weiler ter Meor	12	24
Total	258	719

Oppau has the power to produce now 500 tons HNO_3 daily, still retaining sufficient ammonia to supply the output at Hochst.

Fig. 4.10 Tables of German production of ammonia and nitric acid, 1914 and 1918 (*Dyestuffs: Hearings before the Committee on Ways and Means, House of Representatives, on H.R. 2706 and H.R. 6495, June 18–20 and July 14–18, 1919* [66th Cong., 1st Sess., 1919]. Washington: Government Printing Office, 1919, p. 211)

ammonia from Merseburg. Expansion in Haber-Bosch ammonia enabled additional cyanamide to be applied to agriculture. In the long term, though, shortages of cyanamide (since carbide was also required for other purposes) and other fertilizers did little to stop the erosion of confidence among Germans in the war effort.

Limited statistical data for nitrogen production can be gleaned from Hartley's February 1919 report of visits to chemical factories in the occupied zone engaged in production of munitions. In 1918, it was estimated, Germany was producing 650 imperial tons of synthetic ammonia per day: 250 tons at Oppau, and 400 tons at Merseburg (Fig. 4.10). Significantly, and again despite later views to the contrary, Hartley noted in his report (ref [6], p. 212), that:

> No arrangements appear to have been made prior to the outbreak of war to utilize the resources of any of the dye factories for war purposes, and on mobilization their chemists were called up for military service. After the battle of the Marne the Government realized the need for expanding the output of explosives and most of the chemical works were producing small quantities by the end of 1914. The demands made on them increased during 1915, but it was not until 1916 that plant [at Merseburg] was laid down to assist in the enormous production of explosives required by the Hindenburg plan. Most of the big extensions of the synthetic ammonia and of the nitric and sulphuric acid plants date from this time, many chemists being released from the army and the scientific staff of some of the works being augmented.

From April 1918, Ludendorff, Supreme Commander of the German Army in Flanders, failed to hold back Allied forces along the coast of Belgium and northern

France. Apart from military failures, particularly in early August, followed by the Allied push in September, there were ever growing shortages of food, resulting in considerable part from the diversion of nitrogen products away from agriculture, as demanded by Hindenberg on 20 September 1916, and slowdown in manufacture. This extended the hardships of the general population as well as of soldiers. Other factors affecting agriculture and food supplies were the British blockade, shortages of horses, farm labour, and coal, worn out machinery, and transport difficulties. The outcomes were strikes, social unrest, and riots.

Shortly after the United States declared war in April 1917, German chemist Hermann Staudinger (1881–1965), at ETH, Zurich, predicted, on the basis of his study of available raw materials, including coal and iron ore, between 1860 and 1912, that Germany would be defeated. Staudinger opined that modern war was a question of technology rather than manpower [44]. However much German manufacturing technology had advanced, it would inevitably face a crisis brought on by severe shortages of essential raw materials. The nitrogen industry was no exception.

Yet notwithstanding the military failure, lack of food, and poor organization of factories and railways, the German nitrogen industry had expanded tremendously. In the final stages of the war, German calcium cyanamide production capacity, if not actual output, was close to an annual rate of 600,000 tons: at Reichsstickstoffwerke Piesteritz, the facility operated by the Bayrische, 175,000 tons; at Chorzów, likewise operated by the Bayrische, 150,000 tons; at the Hoechst-controlled Knapsack, enlarged considerably during the war, 140,000 tons; at Trostberg, aided by the associated Margarethenberg power plant, 75,000 tons; and at Waldshut (Lonzawerke), unchanged at 60,000 tons [45].

Immediately after the war the estimated potential in Germany for manufacture of nitrogen products was 500,000 tons, all as fertilizer: 60 % from the Haber-Bosch process, and 20 % each from the gas works and cyanamide factories [46]. By 1923, Merseburg's annual production of fixed nitrogen amounted to 220,000 tons. The factory employed 11,000 labourers, 2,500 craftsmen, and 150 chemists and engineers.

Manufacture of cyanamide in Germany was cut back considerably in the early post-war period due to lack of coal, which was exported in settlement of reparations claims. Piesteritz remained important to Germany, along with Trostberg and Knapsack [47]. There was loss of cyanamide capacity when Chorzów, located in Upper Silesia, was assigned to Poland, under Article 256 of the Treaty of Versailles. Meantime the German government sold the factory to a new company, Oberschlesische Stickstoffwerke AG, registered at Königshütte, and then in Berlin, early in 1920. On 15 May 1922, the convention regarding Upper Silesia was signed between Germany and Poland. On July 1, the local Polish court declared the original registration null and void, and assigned ownership of the factory to the Polish treasury. Two days later, under the direction of Ignacy Mościcki, work began on putting the German-built cyanamide factory back into operation. It was renamed the Polish State Factory of Nitrogen Compounds. The Germans claimed compensation. The matter dragged on for several years, beyond the mid-1920s, at various tribunals, until a compromise was reached. In 1926, Mościcki was elected president of the Republic of Poland, a position he held until 1939 [48, 49].

No less problematic was the cyanamide works at Dicsöszentrmárton in the Kingdom of Hungary. Until 1918 it served the needs of the Austro-Hungarian War Ministry. After the June 1920 Treaty of Trianon, the factory was in Romanian territory (at what is today Tirnaveni), and in a bad way. From March 1921, it was managed by the engineer and town planner Imre Forbáth (1875–1944), citizen of Hungary (born in Czechoslovakia), who had to ward off attempts by the Romanian War Ministry to take over the facility. Claims and counter claims lasted until the mid-1930s. Meantime cyanamide sales to Hungary had fallen off due to restrictions on imports of nitrogen fertilizer, in order to protect the new Hungarian synthetic ammonia factory (Magyar Ammóniágyar Rt) at Pétfürdő (authorized in 1928 by the Minister of Defence), which opened in 1932. Protectionism was also introduced elsewhere in order to support manufacturers of synthetic ammonia, particularly during the Great Depression. There were also controls arising from the international nitrogen cartel, formed in 1929 [50].

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Chapter 5
Nobel Prizes and New Technologies

5.1 Haber and the Nobel Prize: Don't Mention the War

Following the signing of the Armistice on 11 November 1918, Fritz Haber sent his family to Switzerland. Fearing that he would be charged as a war criminal, in particular for his involvement with gas warfare, Haber destroyed sensitive documents, grew a beard, and in disguise travelled to Switzerland to join his family. Though there were claims of charges made against Haber, they were not substantiated. Meantime the Swedish Royal Academy, in its deliberations related to the Nobel Prize for Chemistry, had from 1912 returned to an interest in nitrogen fixation, considering Haber, whose name was brought up in 1912, 1913, 1915, and 1916, including jointly with Carl Bosch in 1915 and 1916, as a strong candidate. One difficulty that the committee had to take into account was the lack of full published details of the Haber-Bosch process [1, 2].

In 1919, the academy announced recipients of the 1914–1919 Nobel Prizes. There were five Germans, including Fritz Haber, who was awarded the 1918 chemistry prize for his ammonia synthesis. The award ceremony and the presentation speech in 1920 related strictly to the production of stable nitrogen compounds as artificial fertilizers. There was hardly any hint of the production of explosives, even for peaceful purposes, just a single sentence indicating that the recent war had emphasized the importance of synthetic nitrogen. Haber in his speech observed that synthetic nitrogen processes, "relieve us of future worries caused by the exhaustion of the saltpeter deposits, which has threatened us these twenty years…. It may be that this solution is not the final one. Nitrogen bacteria teach us that nature, with her sophisticated forms of the chemistry of living matter, will understand and utilize methods that we do not as yet know how to imitate" [3]. The official Nobel biography was, however, a little more revealing of Haber's wartime activities. Elsewhere, responses to Haber receiving the Nobel Prize included the claim that without the "Haber" process, "it is doubtful if Germany would have started the war" [4].

A.S. Travis, *The Synthetic Nitrogen Industry in World War I*,
SpringerBriefs in History of Chemistry, DOI 10.1007/978-3-319-19357-1_5

In the light of such claims, many that persist, the question arises as to whether or not it is possible to arrive at even a rough estimate of the extent to which the Haber-Bosch ammonia synthesis kept Germany at war from early 1915, when synthetic ammonia production was first expanded, until November 1918. There is no direct or easy answer. The ability of Germany to keep going depended on the total supply of nitrogen products needed to both feed its army and citizens and satisfy demand from manufacturers of the explosive nitro compounds. Examining the evidence suggests that much of the supply of nitrogen, in the absence of Chile saltpetre, was derived from calcium cyanamide and the ammonia from coal gas and coke oven works, in fact almost exclusively until well into 1915. Though it was claimed that cyanamide-derived ammonia was inferior to that obtained from the Haber-Bosch converters, the former was certainly no less suitable for munitions manufacture. Thus outside of Germany, particularly in France, there was considerable reliance on cyanamide as a source of ammonia for explosives production. The same must have been true of Germany. Though Oppau was expanded considerably by late 1916, this was still not sufficient to make Germany dependent on the Haber-Bosch process. Nor did it help to stave off serious famine during the winter of 1916–1917. The change came only from April 1917 with the departure from Merseburg of trains of tanks wagons whose cargoes of ammonia would be transformed into nitro compounds and ammonium nitrate, and even eventually a little fertilizer. That is as close as we can get to a decisive factor in claiming support for dependence on the Haber-Bosch process; just the last eighteen months of the war. Before then it was one of the main contributors, but not the only one. But still a wonder of science and technology.

5.2 Gold from the Sea, and After

According to Article 231 of the Treaty of Versailles, Germany carried the full blame for the start of World War I. A 132 million mark indemnity, the equivalent of 50,000 tons of gold, was imposed on the nation. The conditions were ruinous. Ammonium sulphate, coal, coal tar, synthetic dyes and drugs, locomotives, etc., had to be handed over to the Allied nations, particularly France and Belgium, as reparations. Meantime Germany in 1919 was racked by chaos, revolutionary movements, and devaluation of the mark. In order to restore order, the new Weimar Republic was forced to call in the army against its own citizens. Haber, based in part on calculations of Svante Arrhenius, who in 1903 estimated that some eight million tons of gold existed in seawater, decided, in the hope of paying off Germany's debts, to extract gold from sea water. It was not altogether a new idea. In England during 1905, the Engineering and Industrial Trust, Limited, claimed to have similar intentions, though its real motives were unclear. Haber's project began in 1920, managed by Johannes Jänicke, but was abandoned in 1927 when it was found that the work was based on erroneous calculations, as evidenced by microanalysis [5].

From 1919, German scientists returned to research into war gases, under the direction of Haber, but, in order to circumvent the conditions of the Treaty of Versailles, the work was carried out in other countries, including the Soviet Union. In 1920, Haber cofounded the Emergency Fund for German Science (Notgemeinschaft der Deutschen Wissenschaft; later Deutsche Forschungsgemeinschaft). He supported bilateral exchanges with Japan. Throughout the 1920s, his institute was associated with outstanding young chemists engaged in a wide range of mainly theoretical studies, including structural chemistry, and free radicals.

This situation changed almost immediately after the National Socialists came to power in January 1933. The Law for the Restoration of the Civil Service, of 7 April 1933, required that Haber dismiss workers of Jewish descent. After doing so, he handed in his resignation on April 30. Support for Haber came from Harold Hartley, Sir William Pope, and others in Britain and elsewhere. In the autumn of 1933, Haber joined Pope at Cambridge. Chaim Weizmann, the chemist and Zionist leader, who had visited Haber in 1932, and modelled the Daniel Sieff Research Institute, at Rehovot, in mandate Palestine on Haber's institute, invited Haber to join the new desert institute, at least during the winter months. Haber intended to visit Palestine, but was suffering from heart problems, which would have made the long journey difficult. He died in Basel, Switzerland, on 29 January 1934. In April 1937, Joseph E. Coates, then Professor of Chemistry at University College, Swansea, gave the first Haber Memorial Lecture, before the Chemical Society in London. It was a detailed description of Haber's scientific achievements. By then Haber had been erased from accounts of the history of chemistry in Germany.

Nikodem Caro, also an ethnic Jew, emigrated from Germany in 1933. He died in Rome two years later. Albert Frank, whose family was also Jewish, left for the United States in 1938, during 1942–1945 worked with the Office of War Information, and after the war with American Cyanamid [6]. In 1939, the successor to Bayrische Stickstoffwerke AG became part of Süddeutsche Kalkstickstoff-Werke AG (from 1978, SKW Trostberg AG; AlzChem AG since 2011).

5.3 Non-BASF Ammonia Technology and Ammonia Oxidation

During the last phase of World War I, as discussed in the foregoing, the Haber-Bosch process became critical to the supply of nitrogen products in Germany. In contrast, the Allied nations continued to import and rely on Chilean nitrate; two million tons in 1915, and around three million tons in each of 1916 and 1917. The nitrate was employed in the manufacture of nitric acid, and ammonium nitrate, for amatol. By 1916, however, German submarines were causing considerable losses among Allied merchant ships, raising concerns over the reliability of Chilean supplies, quite apart from Scandinavian nitrogen products. One in four merchant ships that left Britain never returned.

Synthetic nitrogen processes had by then attracted considerable attention outside of Germany. The high-pressure ammonia technology was certainly realized to be a key to a new industrial sector, if not a key to a new industry, both in war and, especially, in peace. Therein lay its great significance. From 1916, considerable effort among Allied nations was invested into research aimed at replicating the Haber-Bosch process. The difficulties, and there were many, had been anticipated, for example, from the absence of detailed specifications for the converters; patent information was, invariably, insufficient. The challenges were enormous, which alone attested to the level of sophistication achieved by BASF, which jealously guarded its hard-won advantage. Perhaps no other major area of Allied wartime research was bedevilled by so many drawbacks. Meantime geography, through availability of water and topographies that favoured hydroelectric power, terrain suited to railway construction, and threats to sea routes, determined regional responses as much as willingness to tackle a new technology.

5.3.1 Britain

> The President of the British Nitrogen and Carbide Company expressed the opinion that it was hardly probable that the Haber-Bosch process could be extended much outside Germany because the operation of its costly and complicated plants presumes a high technical capacity.
>
> From Arturo Miolati, *Synthetic Ammonia* and the Casale Process. *Amplified edition of a lecture delivered the 27th February 1927 at the Institute of Chemistry of the Polytechnic School of Prague*. Rome: Ammonia Casale SA, 1927, p. 13.

Without exception, the Allies made little if any headway in their attempts to imitate the Haber-Bosch process before the end of 1918. Interest in Britain, certainly more than in France, was no doubt stimulated by the fact that hydroelectricity was not available, excepting limited facilities in Scotland associated with production of aluminium. Unlike the situation in France, with its hydroelectric power stations in the Pyrenees and Alps, cyanamide production had not been taken up in Britain. In addition, in France there was the Birkeland-Eyde electric arc process worked at Soulom. After the war Soulom manufactured calcium nitrate, until closure around 1925 [7]. In general, however, and apart from in Norway, the electric arc processes were hardly viable. BASF, confident over the success of Haber's method, had in 1911 extricated itself from the Norwegian electric arc industry.

Studies relevant to the synthesis of ammonia were certainly of interest in Britain. In Liverpool on 24 November 1915, members of the Society of Chemical Industry were treated to a long, detailed lecture by Setsuro Tamaru (1879–1944) on calorimetric measurements pertaining to ammonia that he had undertaken during his seven-year stay (1908–1914) with Haber's group. Tamaru, a graduate of the Imperial University of Tokyo, undertook experiments on the synthesis of ammonia with osmium as catalyst in order to gather precise data used to calculate the equilibrium constant for the reaction. He had pursued this work, successively, at Karlsruhe, the Auer-Gesellschaft and Haber's Kaiser Wilhelm Institute, where he was one of the first three researchers [8, 9]. At the outbreak of war, Tamaru, an enemy alien (Japan sided with the Allies), escaped to England, where he was at first a guest of Sir William Ramsay. In 1915, he joined Theodore W. Richards (1868–1928), recipient of the 1914 Nobel Prize in Chemistry, at Harvard. (In 1933, Tamaru, then at the Tokyo Institute of Technology, and Japanese industrialist Hajme Shoshi (1873–1951), were prominent among those who offered to assist Haber, inviting him and his assistants to Japan.)

Solving the ammonia and nitric acid problem in Britain became the remit of the Munitions Inventions Department's Nitrogen Products Committee [10]. The committee, appointed in June 1916, was directed by the statistician John Allen Harker (1870–1923). He also directed the research effort, which for the high-pressure ammonia process and nitric acid production was carried out in three sections led by Frederick G. Donnan (1870–1956), who had received his Ph.D. under Ostwald. Each section included men who, in common with Donnan, had received training in Germany, and were well matched with their tasks:

- Ammonia synthesis, under Lieut. Harold C. Greenwood, who had worked with Haber on a uranium-based catalyst just before the war;
- Ammonia oxidation, under James Riddick Partington (1886–1965), later a noted historian of chemistry, who had worked with Nernst in Berlin during 1911–1913 on the specific heats of gases. While there, Partington prepared a draft for his *A Text-Book of Thermodynamics with Special Reference to Chemistry*, published in 1913 [11]; and
- Supply of gases, particularly pure hydrogen for ammonia production, under physical chemist Captain (later Sir) Eric Keightley Rideal (1890–1974), who received his Ph.D. under Richard Anschütz in Bonn (1912), and catalyst expert Hugh Stott Taylor (1870–1974), who had worked with pioneer electrochemist, and sometime assistant of Ostwald, Max Bodenstein, at the Technische Hochschule Hanover (and Berlin, from 1906).

Most of the British research was undertaken at University College London, with some conducted at King's College. Chemical engineer Kenneth Quinan, who as director of factories in the Explosives Supply Department oversaw construction of new factories for the Ministry of Munitions, assisted Donnan with the ammonia work. Sir William Ramsay, who retired from University College in 1913, had studied Haber's method and oxidation of ammonia—and no doubt gained much useful information from discussions with Tamaru—provided valuable assistance to the Munitions Inventions Department, though for only a short time. He died in July 1916 [12].

Following unrestricted submarine attacks on Allied shipping from 1 February 1917, which threatened to cut off the supply of Chilean nitrates, the Nitrogen Products Committee recommended construction of cyanamide and Haber-type plants. A small cyanamide facility was erected by Nitrogen Products and Carbide Company (Limited), British licensee of Ostwald's ammonia oxidation process, at Dagenham Docks, Essex (another facility was installed at Trafford Park, Manchester). Nitrogen Products and Carbide relied on Odda and Alby, which it controlled through affiliated British companies, for cyanamide as the source of ammonia. When the supply of cyanamide became severely restricted, in part due to shortages of coal and raw materials, as well as demand for carbide from other industries, ammonia was obtained from gas works liquor. However, oxidation of ammonia to nitric acid met with difficulties. Despite the close working with Scandinavian factories, and licenses issued to the French, calcium cyanamide was never produced on an industrial scale in Britain. Experiments on the impact of cyanamide on different soil types were conducted at Rothamsted and Odda, and the quality of the granulated product was improved. Nitrogen Products and Carbide had anticipated strong, and more profitable, sales, far more so than from supplying the needs of the military, after the war. However, as soon as the war was over the demand for cyanamide collapsed. The firm also collapsed, in 1922. Operations at Odda started again in 1924, as part of the Hafslund-Meraker combine, founder of Odda Smelteverk, specialising in carbide manufacture [13].

Introduction of high-pressure ammonia technology in Britain was hampered by the inability to develop equipment capable of withstanding the brute-force conditions. Details of the BASF process were still masked behind a veil of secrecy. Notwithstanding the difficulties with synthesis of ammonia, by mid-1917, considerable success had been achieved with oxidation of ammonia to nitric acid, using platinum or platinum-rhodium gauze catalysts. Partington took a prominent role in this work. The Munitions Inventions Department's apparatus, based on Partington's research, was not unlike that devised by Kaiser, and Frank and Caro. Heat exchangers preheated air entering the converter, which minimized energy consumption. Instructions for assembly of the apparatus were published for the benefit of manufacturers, who were left to make do and improvise as best they could, working with ammonia from gas works and coke ovens. "At some small acid plants in England the necessary parts have been purchased here and there and put together by the plant superintendent…. All of these home-made outfits use ammonia liquor as the raw material, and include a 'stripping column' for stripping the ammonia gas from the liquor by means of steam or hot air. They also use a multi-layer flat platinum gauze" [14]. A major user of the process was the United Alkali Company, in 1918, at its Widnes, Newcastle and Bristol facilities [15]. As elsewhere, there were difficulties with the absorption towers that were not overcome until well into the 1920s with the introduction of stainless steel.

As for the high-pressure ammonia synthesis, Moulton, it appeared, had "reluctantly decided that our scientific arrears of knowledge in this respect were too great to enable us to rely on such manufacture during the war" [16]. Moreover, there was another factor that held back progress: researchers were frustrated in their efforts by frequent changes of management at the Munitions Inventions Department [17]. Meantime Kilburn Scott continued to promote his three-phase electric arc process, drawing favourable comparisons with the other arc processes and discussing perceived advantages of arc processes over the cyanamide process [18]. Where they could not compete, however, was in relative energy costs; electric arc processes consumed four to five times more power than the cyanamide process.

Despite many difficulties, by March 1918 research into the Haber-Bosch process had reached the stage at which, it was believed, though with some hesitation, commercial plant could be erected. The Department of Explosives Supply authorized acquisition of land at Billingham, County Durham, for working the process. Prior to the Armistice, the plant did not supply nitrogen products; chemists at University College London managed to produce no more than a small amount in their laboratories.

Investigations did not cease following the end of hostilities. Synthetic nitrogen had become a strategic industry. Significantly, of the 1919 "Report of the Nitrogen Products Committee," it was said that a "No more important scientific report has ever been published by the Government than that of the over 350 pages presented in May [1919] last to the Minister of Munitions by the Nitrogen Products Committee of the Munitions Inventions Department" [19].

However, even if, like the dye industry, synthetic nitrogen was a key industry, no statistics of nitrogen output and use in Britain had been kept before 1914. Information was certainly wanting. Within twenty-four hours of the signing of the Armistice, Brunner, Mond & Co. proposed to Baron Moulton that a commission be sent out at the earliest opportunity to examine the ammonia works at Oppau.

Greenwood accompanied Hartley's mission to Germany in February 1919, but it took over two months before a group from Brunner, Mond & Co. undertook a thorough examination of the Oppau factory, starting at the end of April and continuing until June 5. Five individuals were involved: Herbert Alfred Humphrey (1868–1951), former assistant director of the Department of Explosives Supply, Greenwood, Colonel George Paton Pollitt (1878–1964), Captain A. H. Cowap, a Brunner, Mond engineer, and chemist Frank Fox. At the end of the trip, the notes and drawing made by the visitors disappeared from a railway wagon at Oppau in which they had been locked ready for onward movement (the intruders had sawn through the wooden floorboards). Observations had however revealed that earlier Allied wartime estimates of Haber-Bosch production costs were far too high.

On 24 April 1920, Brunner, Mond purchased the government's 266-acre Billingham site. Though the Atmospheric Nitrogen Corporation (see later) in the United States provided Brunner, Mond (as shareholder in the former Solvay Process Company) with details of its ammonia research, this was not enough to design a high-pressure converter. The British firm overcame shortcomings in bringing the ammonia synthesis on line partly through industrial espionage. In the autumn of 1920, two Alsatian engineers approached the company claiming to have received working experience with high-pressure plant at Oppau and Merseburg. They offered detailed drawings of Merseburg as well as suggestions for improvement. On December 20, Brunner, Mond paid August Koebele and René Adler for the information (Koebele and Adler had come to a similar arrangement with Establissements Kuhlmann SA in France). In 1921, an experimental plant was set up in Runcorn. This enabled manufacture of ammonia to commence in 1923 at Billingham, with plant closely modelled on Merseburg [20]. Despite a public outcry in 1925 that the British government had sold secret information concerning the process to Brunner, Mond, this was far from the case. In 1926, Brunner, Mond merged with Nobel Industries, United Alkali, and the British Dyestuffs Corporation to form Imperial Chemical Industries (ICI). This was mainly a response to the formation of I.G. Farben in Germany during 1925, which followed the wartime merger of interests among dye firms almost a decade earlier.

Following the success of ICI's ammonia, the British gas-making industry began to suffer losses on ammonium sulphate manufacture. Thus, for example, the Gas Light and Coke Company, Ltd., in 1932 lost four thousand pounds sterling on this business, in contrast to 200,000–300,000 pounds profit made in previous years.

5.3.2 *Italy: Casale and Fauser*

> Professor Haber, a distinguished German chemist, said, on the occasion of a reception given in New York [1924] in his and Dr. Casale's honour, that Dr. Casale was the man who had found the best way to apply the principles which he, Professor Haber, had established.
>
> From Arturo Miolati, *Synthetic Ammonia and the Casale Process. Amplified edition of a lecture delivered the 27th February 1927 at the Institute of Chemistry of the Polytechnic School of Prague*. Rome: Ammonia Casale SA, 1927, p. 34.[1]

Prior to around 1920, other former Allied nations attempted, with various degrees of success, to catch up with the Haber-Bosch process. Often it was the reticence of BASF to license its ammonia process, or release details, except in the case of France, and then under duress, that led to the development of significant alternative high-pressure ammonia processes—in France, Italy and the United States—and competition from engineering and chemical companies eager to export their new technologies. This spur to inventors and entrepreneurs to devise synthetic ammonia processes is particularly associated with Luigi Casale and Giacomo Fauser in Italy, and Georges Claude in France [21]. Their processes, though using the same basic chemistry as the Haber-Bosch process, incorporated a number of novel differences, as well as different catalysts. Luigi Casale's process offered greater simplicity as well as reliability and was ultimately the most successful. Apart from being the first original synthetic ammonia process to be fully commercialised after the Haber-Bosch process, it represents the best example of the rapid geographical spread of a rival technology, one that offered a number of novel features, and indeed, certain important advantages over the BASF process. The outcome was that by the mid-1930s the output of ammonia from Casale and other novel converters far exceeded that from BASF Haber-Bosch converters (BASF produced 90 % of synthetic ammonia in 1928, and less than 50 % in 1931).

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[1] Miolati was probably referring to an event related to the September 1924 centennial of the Franklin Institute, Philadelphia. See Fritz Haber, *Practical Results of the Theoretical Development of Chemistry; an address by Professor F. Haber, on the occasion of the centenary celebration of the founding of the Franklin Institute and the inauguration exercises of the Bartol Research Foundation, September 17, 18, 19, 1924*. Philadelphia: Franklin Institute, 1924.

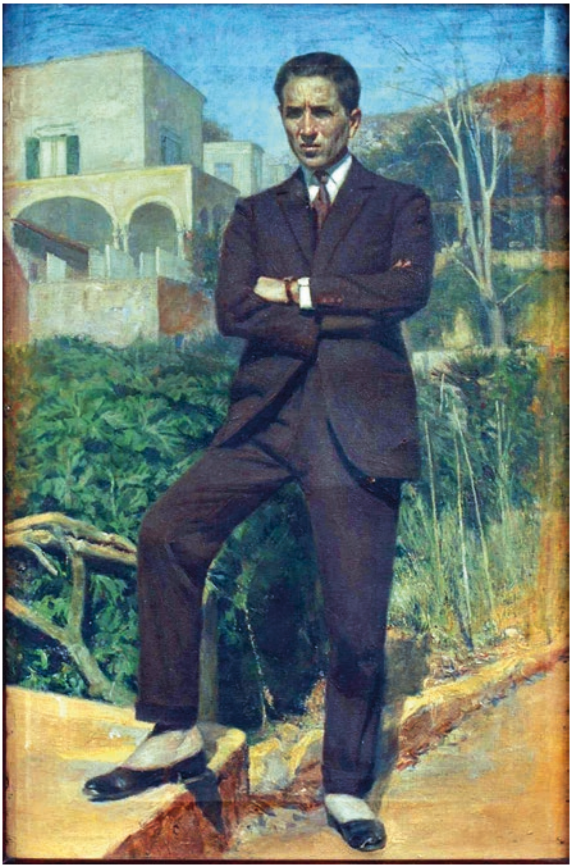

Fig. 5.1 Luigi Casale (Casali SA)

Luigi Casale (1882–1927) (Fig. 5.1), born in Longosco on 22 November 1882, studied chemistry under Arturo Miolati (1869–1956), professor of electrochemistry in charge of physical chemistry at the Reale Politecnico di Torino [22]. Casale graduated in 1908, and assisted Michel Fileti at the Torino Institute of Chemistry and Electrochemistry. During 1912–1913, he undertook research under Walther Nernst in Berlin, which brought him in touch with the latest developments in thermodynamics and stimulated an interest in ammonia. After returning to Italy he investigated the synthesis of ammonia as assistant of Miolati [23]. In May 1915, Italy joined the Allies, and Casale was assigned to chemical studies related to the war effort at the University of Napoli, including on asphyxiating gases and protective measures. Following a laboratory accident, he was forced to abandon this work, and again took up the study of ammonia, encouraged by Miolati, a prominent member of supply committees set up by the Ministry of Arms and Munitions. Synthetic ammonia was a no less strategic matter, since Italy suffered shortages of grain formerly obtained from Russia and Romania as a result of closure of the Dardanelles and was in dire need of fertilizer.

By 1919, Casale had invented a novel high-pressure process which, working at around 800 atmospheres, was even more efficient than the Haber-Bosch process; product ammonia was obtained in the anhydrous form simply by cooling. Casale filed patents for his ammonia synthesis, and received backing from a metallurgical company in Terni, where also in 1919 he set up a pilot plant. His experimental converter, in the best tradition of converting "Swords into Ploughshares," was based on the barrel of a gun from the armaments of the battleship *Dante Alighieri*. Casale placed inside the barrel concentric tubes. The converter was designed so that the barrel acted as the outer pressure tube; it did not attain a high temperature, and had only to withstand the high working pressure. The tubes were closed at their ends. The electrical heating element was placed within the innermost tube, and the catalyst in the annular space between the outer wall of the inner tube and the wall of the next, or second, tube (Fig. 5.2). Fixed between the second tube and third tube (in the case of the cannon the inner wall) was an undulated metal surface, the heat exchanger, thereby creating two annular spaces. Here, gases entering and moving up the vessel were preheated by the outgoing gas mixture, travelling in the opposite direction. Unlike the Haber-Bosch and other lower pressure processes, Casale's process did not require an absorption system to separate out the ammonia (as aqueous ammonia).

Hydrogen was generated by electrolysis at the Terni company. Mixed gases in the required proportions were made up in a furnace where oxygen was removed from air in an atmosphere of hydrogen to give steam. In the early trials a gas recirculation pump was incorporated into the synthesis loop.

In this work, Casale was assisted by his wife, Maria Sacchi-Casale (1889–1950), who held a degree in chemistry, and was an expert in analysis. In 1921 at Terni, Casale built a full-scale installation. On 21 April 1921, he set up the firm Ammonia Casale SA in Lugano, Switzerland, in partnership with a banker, to license the process. In the autumn, a converter with a daily capacity of two tons of ammonia began operating at Terni. It was later set to work by Cie d'Alais, Froges et Camargue, at Saint-Aubin, France.

Ammonia in the liquid state—rather than as ammonia liquor—was obtained by simply cooling the product gas, without the need for expensive refrigeration equipment. However the high pressure created a difficulty: great heat was generated during the reaction, which tended to overheat the catalyst. This was overcome by adding ammonia to the synthesis gas. Since Casale's iron catalyst, made from recycled catalyst or scrap iron, was inexpensive, it could be changed more often than the costly material used in the Haber-Bosch process. It also suffered less from poisoning caused by carbon monoxide.

Terni subsequently became the location of the Casale experimental and manufacturing facilities, operated, respectively, by Società Italiana Ricerche Industriali (SIRI), and Società Italiana dell'Ammonica Sintetica (SIAS). By 1923, borrowing from steam locomotive technology, Casale usefully introduced an ejector (injector) to replace the recirculation pump used in earlier work. In the early days, this static piece of equipment, with few moving parts, certainly offered advantages over reciprocating pumps then available, which were both costly and difficult to maintain. It avoided contamination of the reactant gases with lubricating oil used in reciprocating devices, and enabled the synthesis to take place at a lower pressure.

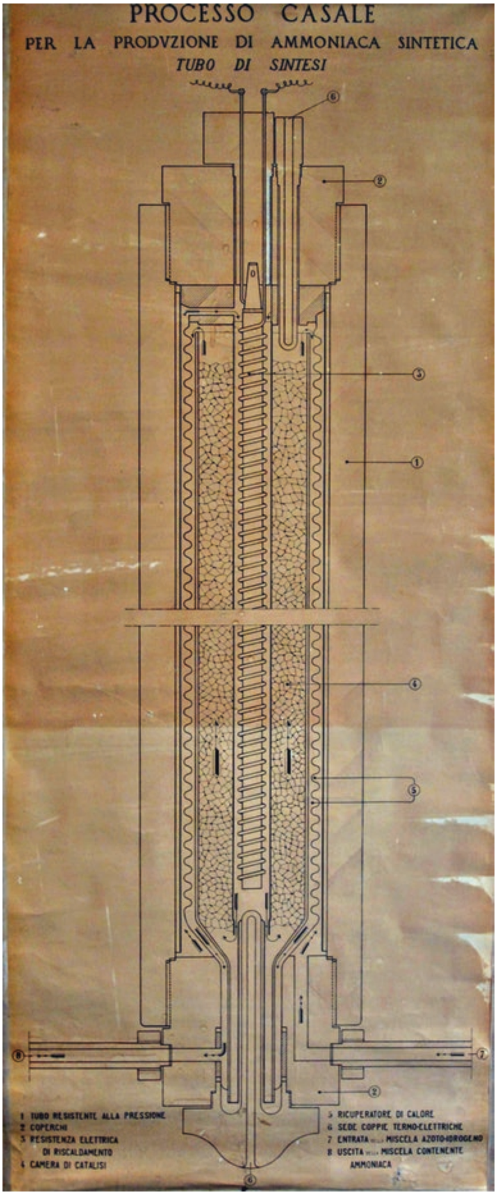

Fig. 5.2 Early Casale ammonia converter (Casale SA)

In addition, by flushing the pressure withstanding outer tube with synthesis gas it was kept at a lower temperature (Figs. 5.3 and 5.4). The Casale process was adopted by Union Chimique Belge at Ostend, using hydrogen from coke oven gas. It was installed during 1923–1924 at Néra Montoro (Italy), Sabiňánigo (Aragón, Spain), Saint-Aubin (France), Nobeoka (Japan), Visp (Switzerland), and Niagara (United States) (Figs. 5.5, 5.6, 5.7 and 5.8). Nobeoka was the first large Casale ammonia facility to open. At the end of 1924, there were fifteen factories using the Casale process, producing 80,000 tons of ammonia each year.

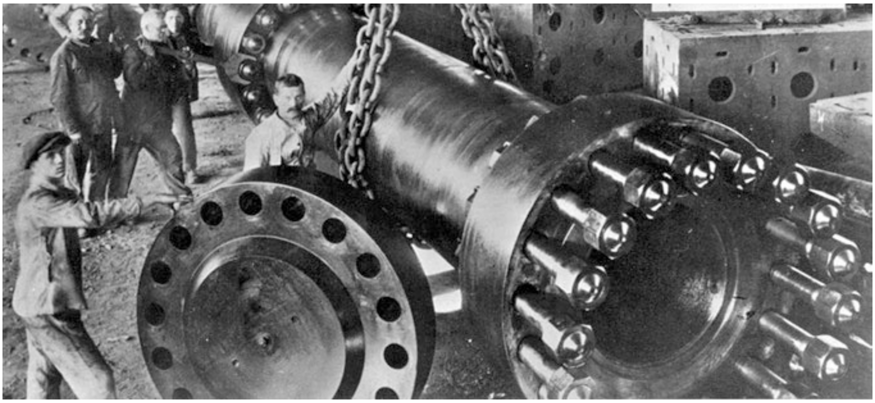

Fig. 5.3 Assembling a Casale ammonia converter, 1923. The lid is open, showing the massive bolts and studs required to maintain the high pressure, of approximately 800 atmospheres. (Casale SA)

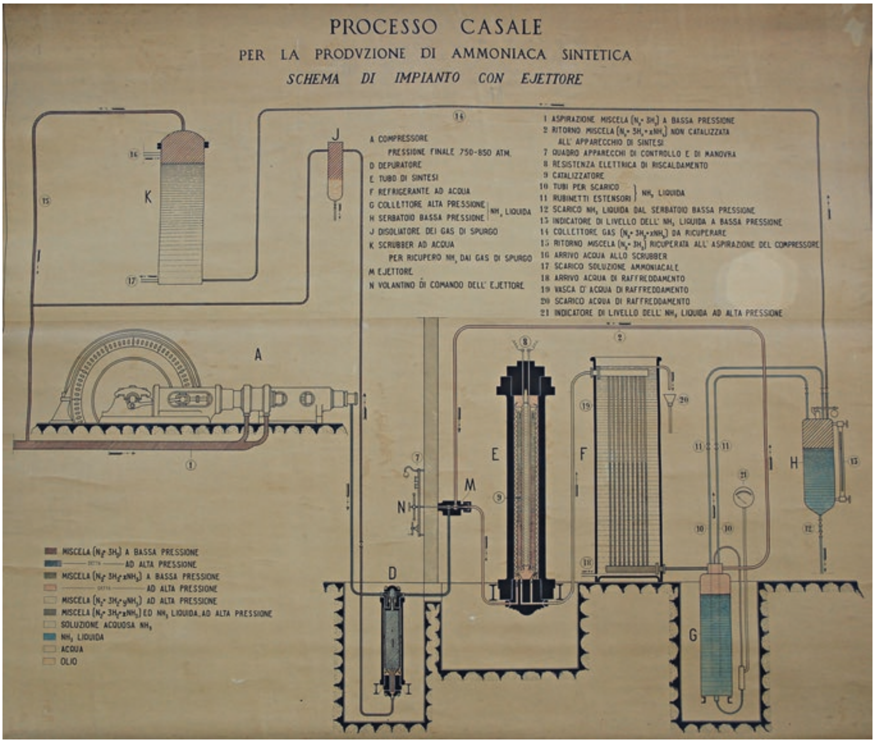

Fig. 5.4 Scheme for Casale synthetic ammonia process, incorporating ejector (injector), M. The product was anhydrous ammonia, unlike the Haber-Bosch process in which the ammonia was absorbed in water. (Casale SA)

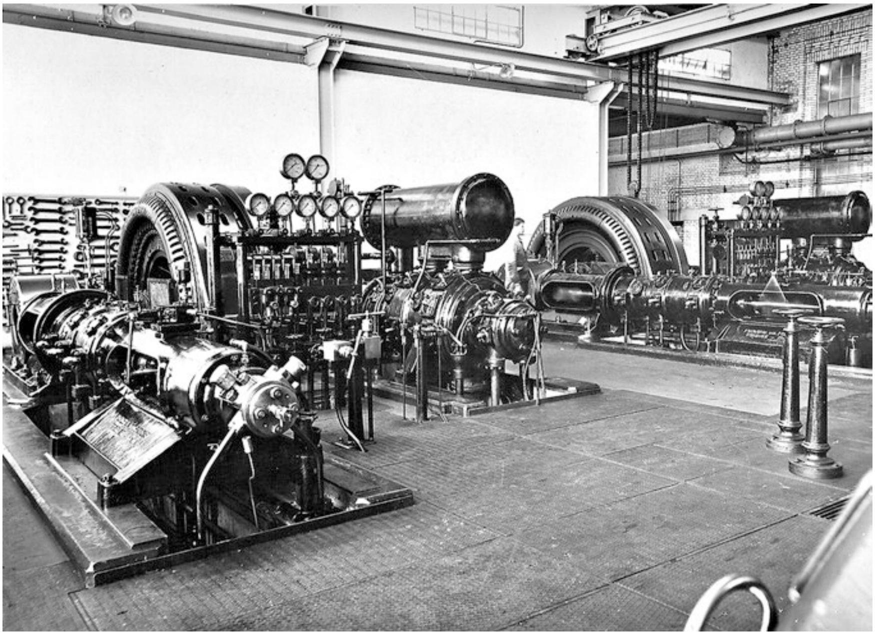

Fig. 5.5 Compressor room, Casale process, Union Chimique Belge, at Ostend, Belgium. (Casale SA)

Fig. 5.6 Electrolysis plant for hydrogen used in the Casale ammonia process, at Sabiñángo, Spain. (Casale SA)

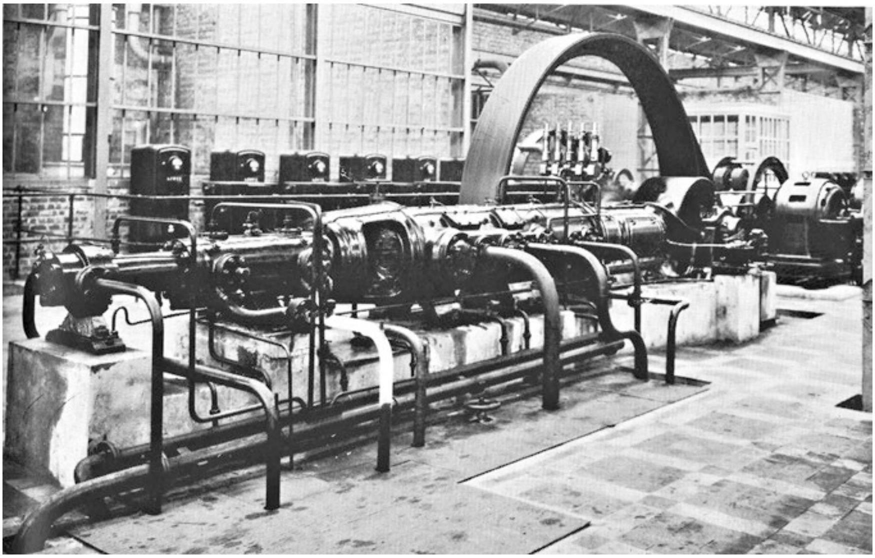

Fig. 5.7 Synthesis gas compressors, Casale process, at Visp (Viège), Switzerland. (Casale SA)

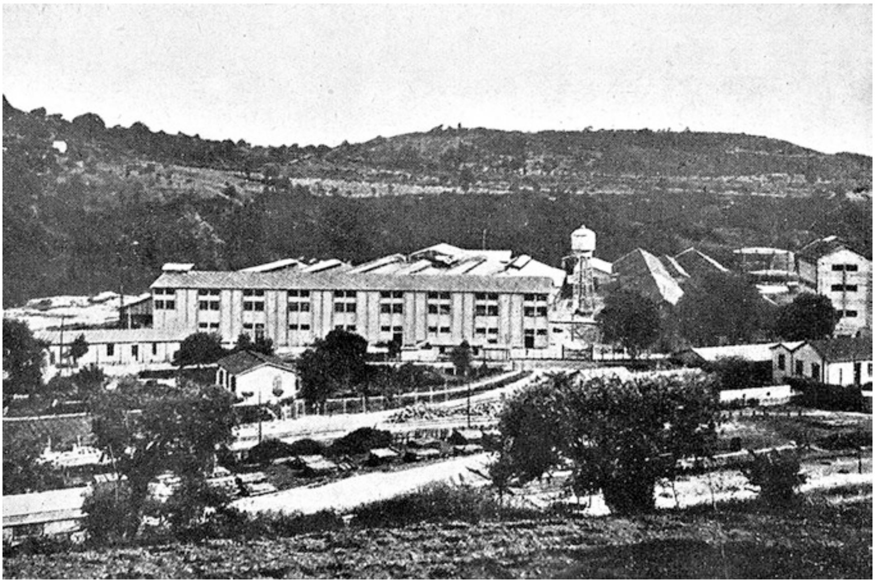

Fig. 5.8 Ammonia factory, Casale process, at Néra Montoro, Italy. (Casale SA)

By the end of 1926, the process had been licensed for use in England and Russia (Table 5.1). With its rugged simplicity, reliability and high yield, the Casale process was rightly seen as a major threat by the management at BASF (and later I.G. Farben); particularly in 1927, when three Casale plants were ordered for use in Germany. By then the capacity of twenty-four Casale-based factories (at work or under construction) was 160,000 tons, with the expectation that this would be more than doubled within a few years [24, 25].

Also in 1927, the Casale, and very high-pressure processes in general, as well as the proliferation of nitrogen factories outside Germany, came under attack from Nikodem Caro in a public lecture given on January 24. This lecture, when published, appears to have been drawn up, in part at least, to support the litigation over compensation demanded by the Germans for loss of the Chorzów factory, then in Poland. Caro not only criticized the smaller scale of working of rivals to the BASF process, but opined that in comparison with the German (BASF) synthesis tubes, “there is no form of construction which can be considered as an essentially economic innovation.” Further, he argued, synthetic ammonia should be manufactured only in factories located within the borders of Germany, since “their existence can only be justified by national considerations, or nationalistic to be more accurate, but not by economic reasons” [26].

Casale had already proved Caro’s remarks on the technology incorrect, as evidenced by Miolati in a detailed scientific and technical lecture he gave in Prague one month later, on February 27 [27]. Theory, experiment and large-scale application paid off handsomely. By the early 1930s, Casale ammonia converters were producing around 60 % of total world production of ammonia. Miolati would continue to emphasize the superiority of the process developed by his former student. Around two hundred factories eventually worked first-generation Casale Ammonia technology. Casale Ammonia also developed processes for preparation of hydrogen and nitrogen (the latter with the Casale burner). Many of Miolati’s students undertook research in the Casale research institute (SIRI). Of passing interest is the fact that closely involved with Casale Ammonia from the late 1920s until 1940 was engineer Carlo Emilio Gadda (1893–1973), who had studied at the Politecnico di Milano. He is best known as a leading Italian writer and poet [28].

In 1935, Ammonia Casale filed a patent for an internal combustion engine powered by ammonia, and undertook road trials around Italy with FIAT 509 and 527 Ardit vehicles. Later, ammonia was replaced by synthetic methanol, another of Casale’s high-pressure products.

Like Casale, Giacomao Fauser (1892–1971), a consulting engineer, had at first worked independently, using a 250 mm cannon as a converter in his garden, at Novara, and, apparently, without any of the information about the Haber-Bosch process that was obtained by other investigators [29]. From 1925, his studies were backed by Società Generale per l’Industria Menerarai ed Agricola Montecatini, and a viable ammonia process worked at 300 atmospheres was devised. Montecatini, at least at its Merano factory, in the north of Italy and close to hydroelectric power, relied on hydrogen obtained from electrolysis of water. The gas was quite pure, and traces of oxygen were removed by reaction with

Table 5.1 Licensees of the Casale process for synthetic ammonia, early 1927

Country	Licensee	Location
Italy	SIRI	Terni
	Società per l'Industria e Elettricità Terni	Néra Montoro
Belgium	SA des Fours à coke Semet-Solvay & Piette	Ostend
	Etablissements Kuhlmann	Selzaete[a]
Dalmatia	Società Italiana Forze idrauliche della Dalmazia	Dugirat[a]
England	United Alkali Company Limited	Widnes[a]
France	Cie d'Alai, Froges et Carmargue	Saint-Auban
	Société des Mines de Dourges	Hénin Liétard
	Société des Mines de Lens	Pont à Vendin
	Société des Mines de Viçoigne Noeux & Drocourt	Hénin Liétard
	Compagnie de Produits Chimiques Anzin, Kuhlmann	Anzin
	Société Houillère de Sarre & Moselle	Carling[a]
	Société des Engrais Azotés & Composés	Soulom
	French government	Toulouse (opened fully 1927)
	Société Marles Kuhlmann	Chocques[a]
	Compagnie de Roche la Molière	Firminy
Germany	Kohlechemie Akt-Ges	Duisberg[a]
Japan	Japan Nitrogenous Fertilizer Co. (Nippon Nitrogen Fertilizer Co., Nippon Chisso Hiryō Kabushki Kaisha, Nichitsu)	Nobeoka, Minamata, Korea[a]
Russia (Soviet Union)	Severny Chimichesky Trest (Northern Chemical Trust)	Ninjninovgorod (Nizhny Novgorod). Construction commenced 1926[a]
Switzerland	Usines Electriques de la Lonza SA	Visp (Viège)
United States	Ammonia Corporation	Niagara Falls
Joint development		
Russia (Soviet Union)	Government of Soviet Union (USSR)	Dzerzhinsk, near Gorky. Construction commenced 1926, opened 1928. Included Du Pont contribution. Also manufactured calcium cyanamide

Sources include Arturo Miolati, *Synthetic Ammonia and the Casale Process. Amplified edition of a lecture delivered the 27th February 1927 at the Institute of Chemistry of the Polytechnic School of Prague*. Rome: Ammonia Casale SA, 1927, pp. 42–43; and Mirko Lamer, *The World Fertilizer Economy*, issue 10. Stanford: The Food Research Institute of Stanford University, 1957, pp. 397–399

[a] Under construction

Note Hydrogen was prepared in 12 cases by electrolysis, in 10 cases from coke oven gas, and in two cases from water gas (by a modified BASF process). Nitrogen in 12 facilities was produced by liquefaction of air; two of these facilities also employed the Casale burner (burning hydrogen with atmospheric oxygen). Four facilities relied on the Casale burner alone. In five cases the source of nitrogen was not specified hydrogen over a platinized asbestos catalyst, as used by Haber in early experiments at Karlsruhe. Later, a copper deoxidiser was employed. As a low pressure process, the product ammonia, as in the Haber-Bosch process, had to be absorbed in water to enable its separation (or liquefied by external refrigeration). The Fauser process was worked by Montecatini, as the operating company, at various sites in Italy for production of fertilizer. In 1925, Montecatini began to license the process outside Italy, and in 1926 jointly with Evence Coppée, a specialist in coke ovens, set up SA Ammoniaque Synthétique et Dérivés (ASED) in Brussels to manufacture ammonia products and construct Fauser equipment. The Fauser process was adopted during 1929 in Belgium and Holland, and soon after in British Columbia, Poland, Czechoslovakia, Japan, and France. Around 1930, Fauser invented a process for oxidising ammonia into liquid nitrogen tetroxide, which was then converted into nitric acid. This was developed by Bamag-Meguin and used in many countries.

5.3.3 France

> If you wanted this type of plant you would not be able to build it and, even if you could build it, you would not be able to make it work.
>
> BASF to a French commission at Oppau. From Arturo Miolati, *Synthetic Ammonia and the Casale Process. Amplified edition of a lecture delivered the 27th February 1927 at the Institute of Chemistry of the Polytechnic School of Prague*. Rome: Ammonia Casale SA, 1927, p. 13.

The BASF management was within a few years proved completely wrong, thanks to Georges Claude (1870–1960). His work on liquefaction at the turn of the century had improved the fortunes of Société L'Air Liquide. Subsequently he developed neon lighting. From 1917, he investigated high-pressure ammonia synthesis using pressures of around 1,000 atmospheres at 500 °C or over. Tested at the Monterau plant of L'Air Liquide, its success enabled the firm to participate in formation of Société Belge de l'Azote in 1923. The ammonia process was worked such that the gases were passed through a series of converters, made of nickel-chromium steel, without recirculation. Because of the very high pressure the yield was high, and only 10 % of unreacted nitrogen and hydrogen remained after passage through four converters. By 1929, five French factories employed the Claude process. Hydrogen for the Claude process mainly came from coke oven gas. BASF and a few others relied on water gas, while Montecatini and several Casale licensees generated hydrogen by electrolysis. However, in terms of volume produced, water gas was the main source of hydrogen. According to Colonel Pollitt, during 1926–1927, 89 % of hydrogen used in manufacture of ammonia came from water gas, 3 % from coke oven gas, 6.4 % from electrolysis, and 1.6 % from other processes. By 1930, the amount of hydrogen from water gas declined to around 70 %, while coke oven gas and electrolysis each represented around 15 %. The main disadvantage of the water gas process was in the handling of solids, in particular brown coal, and purifying of gases. The process required very large, costly plant, including reciprocating compressors for stepwise increase of pressure, typically to 10, 50, and then 200 atmospheres.

After the war the Ludwigshafen-Oppau complex, situated on the west bank of the Rhine, was occupied by the French, who were anxious to gain access to details of the Haber-Bosch process. They were in a far better position to do so than the British. On 11 November 1919, a contract was signed between French representatives and the BASF management whereby in return for technical assistance the French agreed not to permit destruction of the Oppau works, which several Allied observers had (in addition to Merseburg) associated with the production of armaments [30]. To protect French commercial interests, its military and officials at Oppau, mainly chemists, sometimes hindered too-close access by representatives of other Allied countries to the converters and related ammonia apparatus, as experienced by at least the British contingent from Brunner, Mond. The French prevented any dismantling of equipment for observations and measurements. However, it took some years before a French plant began operating, in Toulouse. Part of the reason was competition from the French Claude process for ammonia. In February 1921, the Académie des Sciences was directed by the government to form a commission to investigate the merits of the rival Claude and Haber-Bosch processes [31]. Such was the strategic importance of ammonia that in 1924 the French government established the Office National Industriel de l'Azote. When the Toulouse facility finally opened in 1927 it was based on Casale technology, with a capacity of 60 tons a day (subsequently expanded to 120 tons). By then the Casale process had been licensed to another nine French concerns.

Meantime the French War Ministry had disposed of its wartime cyanamide factory at Lannemazen in the Pyrenees to Le Société des Produits Azotés [32].

By 1929, two Italian factories used the Claude process, six the Fauser process, and one the Casale process, which was soon after taken up in Argentina. Of the three processes, the Claude seems to have been the least successful, no doubt as a result of the extreme working conditions.

5.3.4 Other Developments in Europe, and Japan

In 1925, Vladimir Ipatieff visited German and Italian facilities to investigate possibilities for licensing high-pressure ammonia processes for use in the Soviet Union. In the following year the USSR inaugurated a major programme for construction of ammonia factories, initially favouring Casale technology. Through Ipatieff, the first major Soviet synthetic ammonia plant, built under license from Casale, but with input from Du Pont, opened near Gorky in 1928. Others would follow by 1933. There was also the synthetic ammonia factory erected in Hungary during 1931–1932. The engineering firm Skoda in Czechoslovakia manufactured both ammonia converters and other high-pressure equipment for use in the chemical industry. In 1929, Norsk Hydro, through an arrangement with

Fig. 5.9 Rail tank wagons for transport of ammonia from Norsk Hydro's Haber-Bosch Rjukan facility, opened in 1929 and closed, along with the railway and ferry connections, around 1990. Here seen at Tinnoset in 2009. (Photo by Nick Lera)

I.G. Farben, changed over almost exclusively from the Birkeland-Eyde process to the Haber-Bosch process, which was worked at Rjukan until the late 1980s (Fig. 5.9). However, some electric arc furnaces continued in operation until 1934 at Notodden, and 1940 at Rjukan.

Norsk Hydro's adoption of Haber-Bosch technology was conditional on I.G. Farben having control over output (I.G. Farben also acquired a quarter of the shareholding of Nork Hydro). This situation, typical of the German behemoth, had already acted as a further encouragement to the invention of rival operating systems. When a consortium of German mining companies failed to come to an agreement over licensing of the Haber-Bosch process, it funded the development of what became known as the Mont Cenis process, named after Gewerkschaft der Steinkohlenzeche Mont Cenis, of Herne-Solingen, Westphalia, which in 1925 commissioned chemical engineering contractor Friedrich Uhde of Dortmund to undertake the design of a converter. Uhde's catalyst was provided by Ivar Cederberg, who had undertaken catalyst investigations at Norsk Hydro. The converter operated at just 100 atmospheres, not unlike the conditions Uhde had investigated during World War I for synthesis of liquid hydrocarbons (at 350–500 °C, over a nickel catalyst). The ammonia patents were held by Gasverarbeitungs-Gesellschaft mbH of Herne-Solingen, where the first facility, with four converters, each capable of producing 25 tons a day, began full-scale operation in 1928. The converters incorporated heat exchangers, and the system included a two-stage refrigeration unit.

In 1927, Royal Dutch/Shell, anxious to diversify into chemical production, and in particular fertilizers for agriculture in the Netherlands, investigated both Mont Cenis and Casale processes, and later in the year opted for the Mont Cenis process. Its Ijmuiden plant began operating in September 1929. Despite initial difficulties involving poisoned catalyst, and problems with compressors, heat exchangers, gas losses, and refrigeration units, several improvements were made, including an increase of working pressure to 150, and later 300, atmospheres. These higher pressures were introduced into the Mont Cenis process following expiration of certain BASF patents during 1926–1927. Royal Dutch/Shell's improvements enabled the firm to bring about a break with the German patent holder in February 1934 [33]. Dutch State Mines adopted a quite different strategy; outright purchase of knowhow and equipment from Belgian chemical engineering contractor ASED (1928–1929) [34–36].

Japanese industrialists dealt with all the major innovators in and producers of synthetic ammonia, and introduced a number of useful improvements and innovations. This was typical of the Japanese chemical industry in general. The first producer, in 1924 at Nobeoka, was Shitagau Noguchi's Nichitsu, under license from Casale. The sale of the ammonia license for Japan for the sum of ten million lire at the end of 1921 provided much needed capital for Casale. Nichitsu opened two more facilities, one at its Minimata (cyanamide) site, and another in Korea (Figs. 5.10 and 5.11) (see Table 5.1). In 1926, Nobeoka and Minimata were the largest working Casale factories, both with operating capacities of around 60 tons of ammonia per day.[2] The planned capacity of the Korean factory, then under construction, was 120 tons per day. From 1931, the forerunner of Asahi Chemical Company (Asahi Kasei) undertook manufacture of ammonia at Nobeoka using Casale converters.

The Claude ammonia process was licensed to Kaneko. Fauser and Mont-Cenis processes were also worked in Japan. In 1931, Japanese-designed ammonia technology was introduced by Tokyo Koggo Shikenjo. As usual, I.G. Farben laid down stringent conditions in the use of the Haber-Bosch process when it was adopted in Japan during the mid-1930s [37].

5.3.5 *United States*

In the United States, the synthesis of ammonia and other nitrogen fixation processes, as well as oxidation of ammonia to nitric acid, were taken up with a

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[2] The Minimata facility was later to gain considerable notoriety arising from poisoning of villagers due to releases of mercury sludge. Nippon Chisso Hiryō Kabushki Kaisha (Nichitsu), became Chisso in 1965, and Japan New Chisso in 2012.

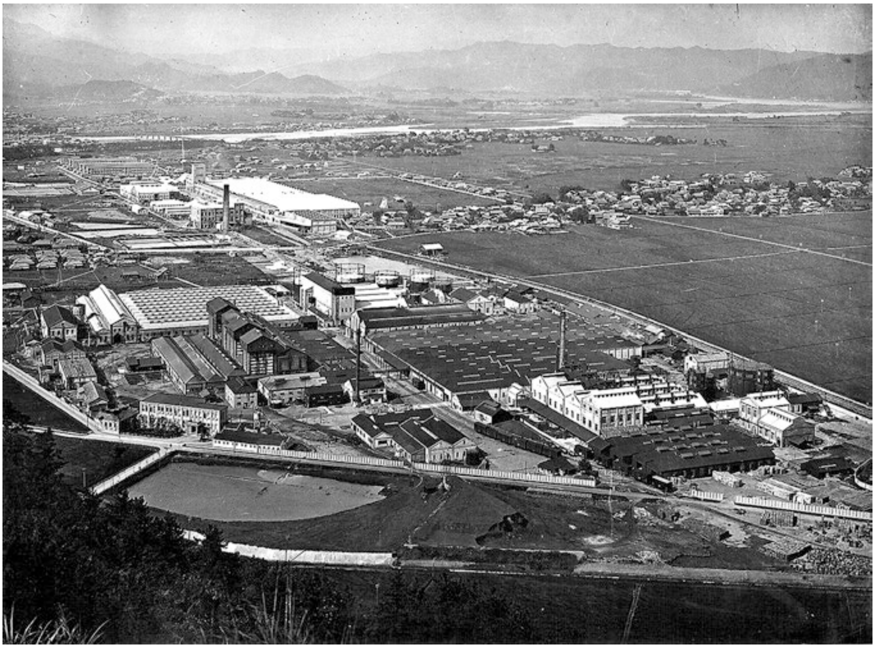


Fig. 5.10 Nobeoka ammonia factory (Casale process), Japan, around 1924. The capacity for ammonia production was 62 tons per day. (Casale SA)

sense of considerable urgency from 1916, following passage in June of the National Defence Act. In the same year, the Bureau of Soils at the Department of Agriculture began to study the ammonia synthesis. The American Cyanamid affiliate Ammo-Phos, at Warners, New Jersey, commenced the manufacture of nitric acid from cyanamide-derived ammonia, based on the equipment imported from Germany in 1914. This contributed considerably to the financial position of Ammo-Phos, which until then had struggled to find a good market for its fertilizer. During 1916–1919, the US Bureau of Mines investigated conditions for the catalytic oxidation of ammonia.

In 1917, the Americans decided to construct modified Haber-Bosch and cyanamide plants. The government instructed General Chemical Company, which had investigated high-pressure synthesis of ammonia since 1913, to build an ammonia plant at Sheffield, Alabama, based on the design of Frederick de Jahn. Though partly completed in September 1918, what was called the "U.S. Nitrate Plant No. 1," never became fully operational, and was abandoned; there were problems with the quality of the converters as well as with the catalyst.

In the autumn of 1917, the decision had been made to concentrate efforts on a new cyanamide facility at Muscle Shoals, near Sheffield, to be erected for the government by Air Nitrates Corporation, a subsidiary of American Cyanamid. The intention was to convert ammonia derived from cyanamide into ammonium

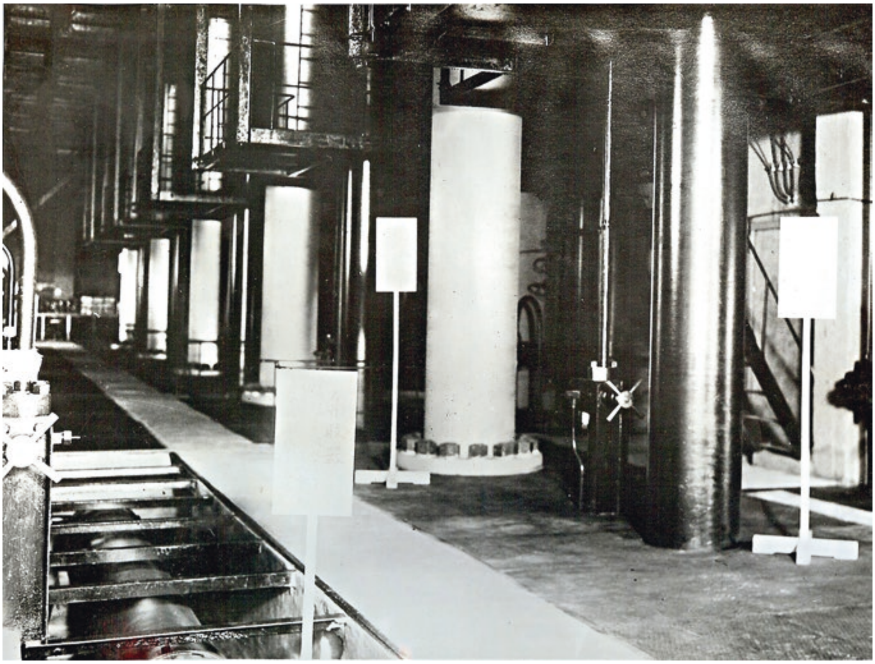


Fig. 5.11 Ammonia converters, Casale process, Minimata, Japan. The original capacity was 60 tons per day, expanded to 100 tons per day around 1927. The output of converters shown here was 40 tons per day, suggesting that they represent the enlarged section of the factory. (Casale SA)

nitrate, such that by 1919, producing ammonium nitrate at the rate of 110,000 tons per year, it would account for 13 % of all Allied explosives.

According to Williams Haynes, American Cyanamid was called upon to accelerate this work after difficulties were experienced with the synthetic ammonia factory at Sheffield. The Chief of Ordnance of the United States Army, General William Crozier (1855–1942), apparently “called Frank Washburn to Washington and said: ‘Unless the Cyanamid Company can and will provide the plants and produce the materials within twelve months, the plans for placing a great fighting force on the battlefields in France for the spring offensive of 1919 cannot be carried out’.”

For this enormous factory, American Cyanamid placed Walter Landis in charge of the design. Engineering work began on 17 December 1917. Ground was broken on 3 February 1918. The government constructed a “coal-powered electric generating plant to provide the electricity for the carbide furnaces. Twenty-five thousand men had been brought into the four-square mile area. And all the time the rain poured down…. After the influenza epidemic struck, man-power became critical” [38].

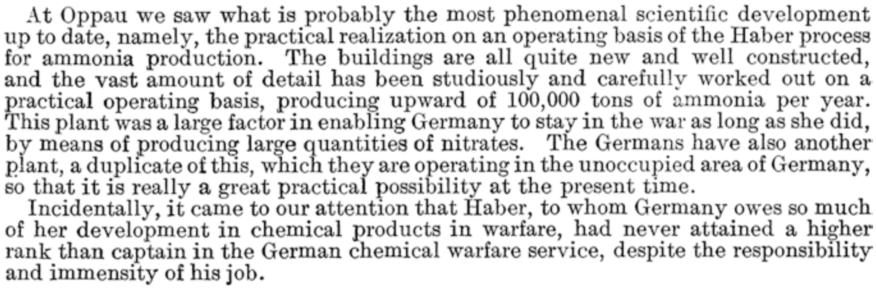
Notwithstanding labour and other difficulties, what was known as “U.S. Nitrate Plant No. 2” was completed just over eight months later, as the war came to an end. “The compressors in the liquid air unit [were] started up on October 23 and three days later the electric current was turned on the carbide furnaces.”

Fig. 5.12 Banks of cyanamide ovens, “U.S. Nitrate Plant No. 2,” Muscle Shoals, Alabama, 2 March 1919. (Library of Congress, Prints and Photographs Division, HAER ALA, 17-MUSHO, 1–65)

After break-in trials (with nitric acid produced on November 19, and ammonium nitrate on November 25), and some work early in 1919, the facility was promptly shut down through lack of demand (Fig. 5.12). During the war, plans had been drawn up for two other cyanamide factories on which, according to Haynes, work was started [39]. (In 1923, Landis, for his services to American Cyanamid, was appointed vice president of the corporation, a post he would occupy until his death in 1944.)

Also from 1917, the American Nitrogen Products Company of La Grande, Washington, worked the electric arc furnace developed in 1912 by the Norwegian inventor Franz Henrik Aubert Wielgolaski. He filed several patents, one in the United States jointly with Schönherr. The American Nitrogen Products process was not economically viable and was abandoned after a few years. American interest increasingly moved towards the high-pressure ammonia process.

American visitors to Germany in 1919, technical and non-technical, generally accompanied British and European experts on Allied missions, in part to acquiesce to German complaints about their engaging in industrial espionage [40]. Such was the case with the British mission in February 1919. A detailed American account of the state of German chemical industry supplemented those of the British and French. Major Theodore W. Sill, attached to the US Warfare Service, and though mainly interested in technical organic chemistry, in his report of the visit to Germany, declared “At Oppau we saw what is probably the most phenomenal scientific development up to date, namely, the practical realization on an operating



At Oppau we saw what is probably the most phenomenal scientific development up to date, namely, the practical realization on an operating basis of the Haber process for ammonia production. The buildings are all quite new and well constructed, and the vast amount of detail has been studiously and carefully worked out on a practical operating basis, producing upward of 100,000 tons of ammonia per year. This plant was a large factor in enabling Germany to stay in the war as long as she did, by means of producing large quantities of nitrates. The Germans have also another plant, a duplicate of this, which they are operating in the unoccupied area of Germany, so that it is really a great practical possibility at the present time.

Incidentally, it came to our attention that Haber, to whom Germany owes so much of her development in chemical products in warfare, had never attained a higher rank than captain in the German chemical warfare service, despite the responsibility and immensity of his job.

Fig. 5.13 Extract from the report of a visit to Oppau in February 1919 by Major Theodore W. Sill, US Warfare Service [41]

basis of the Haber process for ammonia production." Like his British colleagues, Sill was puzzled by the fact that "Haber, to whom Germany owes so much of her development in chemical products in warfare, had never attained a higher rank than captain in German chemical warfare service, despite the responsibility and immensity of his job" (Fig. 5.13) [41]. Sill, perhaps, had overlooked the fact that Haber's social origins precluded him from attaining a higher rank in the Kaiser's army.

Four months later, in June 1919, Philip Drinkner, lieutenant, US Army, Samuel Iserman, of The Chemical Company of America, and Edward C. Worden, a consulting chemist, surveyed operations at Knapsack, Oppau, and elsewhere. The visitors were impressed, not only with what had been achieved under wartime conditions, but by the fact that work was continuing on expanding the manufacturing facilities [42]:

> At Knapsack a large plant had been built during the war for the manufacture of calcium carbide, cyanamid, synthetic acetic acid, ammonia, etc.….At Ludwigshafen we saw the nitrogen fixation portion of the Badische Chemical Co. and were conducted through by a French officer thoroughly familiar with the plant and its technical operation. Conditions are best shown by the fact that at the time of our visit they were actually constructing important additions to the plant and this was before peace had been signed…The nitrogen fixation plant was entirely constructed during the war and is consequently the last word on the subject. … It is due mainly to the efforts of this concern that the German Government was enabled to carry out their program of powder manufacture. The size and importance of this plant [Oppau] was well known to the Allies during the war and it was consequently subject to numerous air raids.

In 1919, the Fixed Nitrogen Research Laboratory (FNRL), under the Nitrate Division of the Ordnance Department, was established, with facilities at the American University, in Washington, DC [43]. The War Department and Department of Agriculture undertook joint investigations at the FNRL into the use of munitions-grade ammonium nitrate as fertilizer. Though the solid nitrate was effective, it deliquesced and caked, and was expensive to produce. It would not enter the fertilizer market until around 1940, formulated at a lower concentration in nitrate.

The FNRL was taken over by the Department of Agriculture in 1921. By 1924, it had developed an ammonia process, though it was worked only on a small scale at two sites [44]. The United States continued to rely on imported Chilean nitrate (around half a million tons were imported into the United States in 1910), which until well into the 1920s was the most economical starting material for producing nitric acid. The export of Chilean nitrate peaked in 1928 [45].

In 1920, General Chemical Company, in cooperation with the Solvay Process Company, formed the Atmospheric Nitrogen Corporation, one of several US corporations, often representing European interests, whose titles proclaimed their close connections with nitrogen fixation. Allied Chemical (the 1920 merger of General Chemical, Solvay Process, and others), and E.I. Du Pont de Nemours & Co., at first adopted Claude technology. Work on Du Pont's facility at Belle West, Virginia, began in 1925 and was completed in 1927, but faced several difficulties. The promoters of the Claude process had promised lower working costs and the advantage of requiring smaller equipment, but, as Du Pont found to its great cost, this was not always realizable.

Du Pont soon moved over to the Casale process, and later developed an in-house process. Niagara Ammonia Corporation, a subsidiary of Ammonia Corporation, licensee of Casale's process, opened a synthetic ammonia factory at Niagara Falls in 1924. An American high-pressure process promoted by Nitrogen Engineering Corporation, founded by Louis L. Jones and Charles C. Brown, found application in Europe as well as in the United States. The process was adopted by Establissements Kuhlmann, in France, and orders were received from the Soviet Union and the Far East. This was especially the case after 1929, when Nitrogen Engineering was taken over by the American Cyanamid subsidiary Chemical Engineering Corporation, which offered design and construction services for high-pressure plant and equipment. It was American Cyanamid that ensured the future of cyanamide through successful diversification into novel products, including polymers [46].

5.4 Friedrich Bergius, Carl Bosch, and the I.G.

5.4.1 High-Pressure Catalytic Circulatory Plants

Several major developments in industrial chemistry after 1914 were conditional on the work achieved by Bosch and his team at BASF. Scientists and engineers at BASF continued to investigate high-pressure technology, mainly at first related to improvement of the Haber-Bosch process. In April 1918, the staff of the BASF Ammonia Laboratory moved to a new building on the Oppau site. A decade later it was the largest industrial research laboratory in Germany, and probably the largest in the world [47]. From 1927, there was massive international growth in output of synthetic ammonia, propelled by the perceived need to prove the worth of the new high-pressure technology, and also by over-optimistic forecasts of demand for fertilizers. This turned into a substantial glut by 1929. The situation did not improve for many years, notwithstanding formation of the international nitrogen cartel. As a result, by the early 1930s, many of the chemists at I.G. Farben's

Oppau Ammonia Laboratory had been transferred to other departments, including those dealing with new high-pressure processes.

Most relevant to the time period covered here was high-pressure research that had been conducted in Germany during the war aimed at conversion of coal to oil, and hydrogenation in general [48]. This was carried out by Friedrich Bergius (1884–1949), who received his doctorate at Leipzig in 1907, and then worked with physical chemists Nernst, Haber and Bodenstein, the latter at the Technische Hochschule Hanover, where in 1909 Bergius was appointed private lecturer and began his research into the application of high pressures. He produced hydrogen by reacting carbon and water at a reduced temperature under pressure; this gave a cleaner supply of the gas, and was carried out at Chemische Fabrik AG, of Posen. Bergius speculated that coal might combine with hydrogen under similar conditions to form oil, and was proved correct. He found metal oxide catalysts that improved the yield, and in 1913 patented his method for hydrogenation of coal. On 1 January 1914, at the instigation of chemical manufacturer Karl Goldschmidt (1857–1926), he joined Th. Goldschmidt AG, of Essen, in a newly constructed laboratory at Mannheim-Rheinau, where he was appointed research leader. The hydrogenation of coal to oil received priority once the war commenced, but it encountered major technical difficulties at the pilot plant stage and consumed considerable capital. Bergius joined the board of Goldschmidt in 1916, and in 1918 brought in partners when he attempted to establish a consortium for coal chemistry. In 1919, he left the firm, having lost the backing of Karl Goldschmidt. In 1922, Bergius operated a coal hydrogenation plant at Rheinau, operating at 100 atmospheres and 400 °C, which produced one ton of synthetic oil, containing 25 % motor fuel [49].

Carl Bosch, not long after he was appointed chairman of the BASF board in 1919, introduced a high-pressure process for methanol. The methanol reaction had been suggested in 1905 by Paul Sabatier (1854–1941), though he was unable to put it into practice through lack of a means for determining the equilibrium. The work at BASF began in 1914 when Mittsach and Christian Schneider attempted to obtain a single product from the reaction between carbon monoxide and hydrogen in the presence of a catalyst. As in the ammonia synthesis, thermodynamics and reaction kinetics showed that the reaction was encouraged by using a high pressure and low temperature.

$$2\,H_2 \quad + \quad CO \quad \rightarrow \quad CH_3OH \qquad \Delta H \quad = \quad -91 \text{ kJ mol}^{-1}$$

The two BASF chemists failed to obtain a satisfactory product, though they filed a patent for the method. The same reaction was investigated by the French Minister of Explosives, George Patart, who had been responsible for negotiations that led the French government to acquire rights to the Haber-Bosch process. Patart filed a patent in 1921, perhaps after learning of the studies by Mittasch and Schneider. To preempt rivals, Patart made claim to a wide range of metal catalysts, oxides and salts included, that might conceivably favour oxidation and hydrogenation. This stimulated a response from BASF, which in 1922 assigned the problem of high-pressure methanol synthesis to recently appointed chemist Matthias Pier (1882–1965); in 1914 he had filed patents for an ammonia converter with an inner lining of low-carbon iron. Pier achieved almost immediate success, working at 300 atmospheres and around 700 °C, using a chromium oxide-zinc oxide catalyst. A pilot plant began operating during May 1922. On 26 September 1923, the first railway tank wagon of synthetic methanol left the Merseburg (Leuna) works. In 1927, the output was 18,000 tons. The process would remain in use for four decades, after which it was superseded by a low temperature, low-pressure reaction. In common with the ammonia synthesis, on which they were closely based, and even made in the same converters, synthetic methanol, urea, and gasoline had become available as the result of developments in high-pressure catalytic circulatory plants (Figs. 5.14 and 5.15) [50].

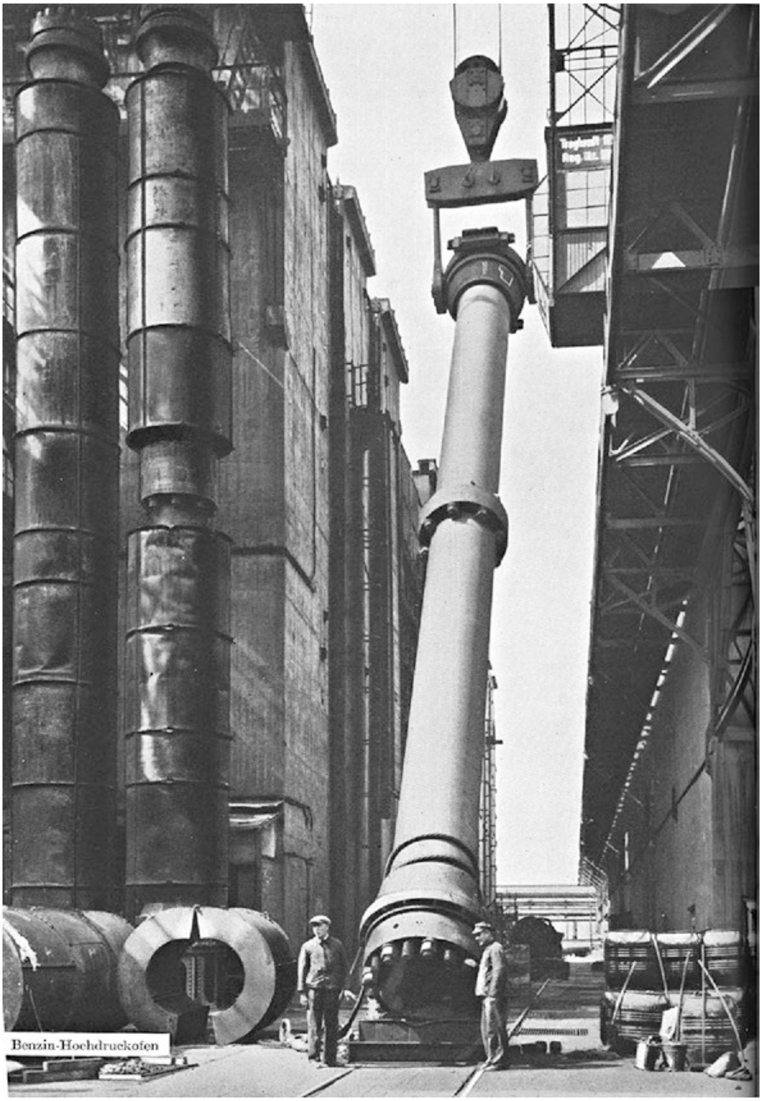


Fig. 5.14 Converter for production of synthetic motor fuel by hydrogenation of coal at the I.G. Farben Leunawerke, identical with converters used in synthesis of ammonia and methanol, 1930s. (*Erzeugnisse unserer Arbeit*. Frankfurt am Main: I.G. Farbenindustrie, 1938, opposite p. 179)

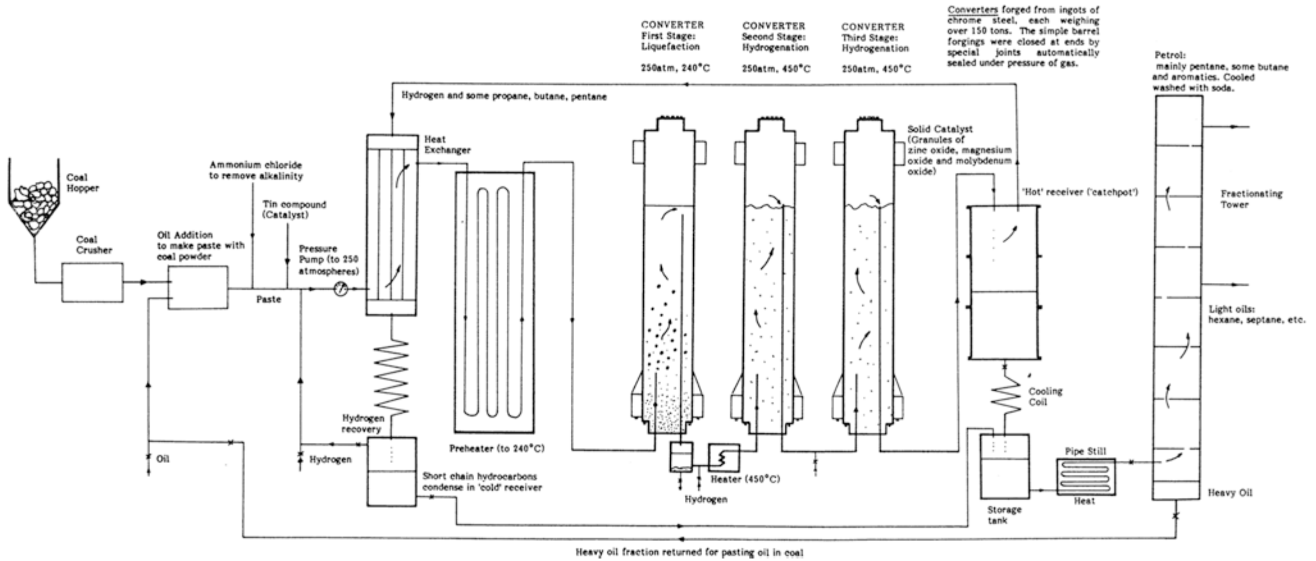


Fig. 5.15 Hydrogenation of coal, Imperial Chemical Industries, Billingham, based on the BASF coal-to-oil (Bergius) process

After the 1925 fusion of BASF with other leading German dye firms, creating I.G. Farben, Bosch became chairman of the corporation, which backed the Bergius process for conversion of coal to oil, as did American oil companies and ICI, which acquired British Empire rights to the process in 1927. Industrial scale production of synthetic fuel (Leunabenzin, Leuna petrol) was first achieved at Leuna in the same year, mainly through the efforts of Pier. In 1931, Bosch and Bergius were jointly awarded the Nobel Prize for "their contribution to the invention and development of chemical high-pressure methods" [51, 52].

The falling price of petroleum, due to the discovery of oil in Texas, meant that synthetic fuel was hardly viable, at least until the National Socialist autarky programmes were implemented. By 1936, Leuna was producing over a quarter of a million tons of motor fuel each year. In 1938, total German production exceeded 600,000 tons. During World War II, this output was tripled, particularly for use as a high octane aviation fuel by the Luftwaffe. ICI at Billingham commenced the erection of plant for manufacture of motor fuel after the British government in July 1933 introduced a preference on the price of home-produced petrol. Though the ICI product, introduced in 1937, was completely uncompetitive, from 1939 Billingham produced valuable aviation fuel, as required by the RAF. Meantime high-pressure industrial processes became widespread, encouraging the search for novel catalysts, and developments in petroleum technology. Engineering firms turned to the manufacture of high-pressure converters, compressors, boilers and autoclaves.

At the end of World War II, converters and other equipment at the Leunawerke were dismantled for use in the Soviet Union. The factory, rebuilt under ownership of the German Democratic Republic (GDR), was named after Walter Ulbricht (1893–1973), who had participated in formation of the Weimar-era German Communist Party and was a prominent politican in the GDR. Most of what remained at Leuna from the prewar and wartime period was demolished during the 1990s.

In the mid-1960s, the ammonia industry in western Europe and the United States underwent major technical improvements. M.W. Kellogg and Chemico introduced single train energy-integrated plants, replacing process technology that had changed little since the 1920s. Casale and Uhde, in addition to C.F. Braun, ICI, Kellogg, and Topsøe, were among the firms that introduced advanced technology systems. In the 1950s natural gas rapidly replaced coal as the source of hydrogen, particularly in the United States. Two decades later, coal-gasification processes were developed in response to the rising cost of petroleum.

Manufacture of synthetic ammonia continues to represent an important part of the chemical industry, with around 80 % consumed by the agricultural sector.[3] Yara International, successor to the Birkeland-Eyde enterprise, was by the

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[3] At the close of the 20th century, four products represented the mainstay of the ammonia-based fertilizer industry: granular ammonium nitrate; liquid anhydrous ammonia; ammonium nitrate; and urea. More recently, urea has come into favour, due to its higher concentration of nitrogen. This enables more careful application, with less damage to the environment. Composite fertilizers containing nitrogen, potassium and phosphorus, the concentrated three-component NPK products, were introduced in the mid-1920s by I.G. Farben as Nitrophoska.

beginning of the 21st century the world's leading producer of ammonia. (Norsk Hydro, since 2004, when the fertilizer business was spun off, has specialized in metals and energy.) Evonik Industries, successor to the early firms in which Frank and Caro were involved, is a leading manufacturer of specialty chemicals. Casale SA, successor from 2014 to Ammonia Casale, founded in 1921, continues to introduce improvements in ammonia and related technologies. Around 80 % of nitric acid made from synthetic ammonia is converted into ammonium nitrate for fertilizer and explosives.[4] American Cyanamid, apart from its entry into chemical engineering and synthetic ammonia, diversified into organic chemistry through acquisition of the Calco Chemical Company of Bound Brook, New Jersey, in 1929, and pharmaceuticals through Lederle and Davis & Geck, both of New York, in 1930 [53, 54]. AlzChem, at Trostberg, remains active in cyanamide chemistry. SKW Stickstoffwerke Piesteritz GmbH, successor to the Reichsstickstoffwerke, is the main German manufacturer of ammonia and urea.[5]

Footnote 3 (continued)

Ammonium nitrate, made from hot ammonia and nitric acid, after removal of water, is sprayed in a tower, where small lumps are formed, called prills. According to density, prills are used as fertilizer or in manufacture of explosives. Ammonium nitrate is highly explosive under certain conditions. In September 1921, a mixture of ammonium nitrate and ammonium sulphate at Oppau exploded, with loss of over 600 lives, in addition to 2,000 injuries. This followed detonation of a hardened mixture while it was being broken up with small explosive charges. Carl Krauch, the upcoming BASF high-pressure chemist, was responsible for reconstruction, which took just twelve weeks, and brought about his elevation to the managing board of BASF. In September 2001, there was another major accidental explosion of ammonium nitrate, this time at the Toulouse ammonia factory in France. In April 2013 there was a further explosion, in Texas.

[4] After 1918, Bamag (Bamag-Meguin from 1924) became a major supplier of nitric acid plants throughout Europe and Japan. The introduction of stainless steels overcame many of the corrosion problems. The most important feature of the ammonia oxidation plant, as introduced in Germany, was the special chrome-steel converter in which layers of catalyst were laid out horizontally. The catalyst, made up of a fine wire of platinum-rhodium alloy, was woven into a large circular gauze. The rhodium, representing 10 % of the catalyst wire, gave strength and minimized loss of platinum. Ammonia oxidation plants developed during World War I were to become the basis of all such installations in use until the 1950s and beyond (some oxidation plants that operated under conditions of high pressure were developed in the 1920s, though these were introduced generally after World War II). In 1926, ICI at Billingham constructed its first nitric acid plant for oxidation of synthetic ammonia. In 1939, the British Ministry of Supply took delivery of ten-foot diameter gauzes, which became the norm for industrial use. In the converter the ammonia is vaporized over warm water and mixed with air. The gas mixture is then sucked through the converter or pushed through at low pressure and the gauze electrically heated to start the reaction. The reaction mixture is rapidly removed, cooled and taken up into dilute nitric acid, or water. The uptake is slow and makes the operation expensive. Production of nitric acid by the platinum oxidation process continues to be maintained at high levels in civilian economies for reaction with ammonia to form ammonium nitrate ("nitram," etc.) fertilizer.

[5] Though production of calcium cyanamide increased during the 1920s, reaching a peak in 1928, its overall share of the fertilizer market declined. In the mid-1930s its agricultural applications were extended to use as an effective defoliant, based on herbicidal properties, and, before planting of crops, as seed-bed sterilizer. Studies on dicyanamide had been undertaken by Caro and colleagues shortly after 1900. It became important in the manufacture of melamine resins. Cyanamide found uses in the synthesis of sulpha drugs, and as an intermediate, including for acrylonitrile.

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Chapter 6
Conclusion: A Legacy of Synthetic Nitrogen

6.1 Homage to Inventors

The introductory remarks to this account of the early synthetic nitrogen industry, particularly its critical role in Germany during World War I, opened with allusions to myths surrounding Fritz Haber's personal role in waging war through his contribution to the manufacture of nitrogen products for explosives and involvement with gas warfare. Haber's contribution to the war through research into fixed nitrogen is often stated, and repeated, as fact. This is erroneous. He was, essentially, less a villain then an ambitious and arguably amoral servant of his country at war, as well as brilliant chemist and organizer of science in peacetime.

While several of the myths surrounding Haber are unfounded, the "myth" that is often ignored, that of the heroic inventor, generally tallies here, allowing for the fact that he drew on earlier work, and stimuli, of others, particularly Nernst (and required the collaboration of Robert Le Rossignol).

The same applies to Carl Bosch, largely as a result of his mixed training in chemistry, engineering and metallurgy. While their contributions were in many ways both different and separate, they are jointly remembered through the high-pressure ammonia process that carries their names. High-pressure industrial chemistry derived from a nexus of changing needs, new corporate and public ideologies, new technologies, and new directions in academic chemistry [1]. A measure of the level of success of high-pressure ammonia synthesis at BASF, and of the tremendous prestige accorded to Haber and Bosch, was the total failure to imitate the process elsewhere before 1918, and the status and efforts of postwar commissions sent to examine the BASF Oppau ammonia facility. The British failed on a technical level when they sought to achieve the ambitious goal of catching up with BASF from scratch, notwithstanding the skilled scientists who had studied physical chemistry in Germany, including with Haber. Inspections at Oppau by British and American chemical experts in 1919, apart from hindrances placed in

A.S. Travis, *The Synthetic Nitrogen Industry in World War I*,
SpringerBriefs in History of Chemistry, DOI 10.1007/978-3-319-19357-1_6

the way by BASF, and to a lesser extent the French occupying forces, yielded little of value; the technology was simply too complex and too innovative.

Haber's laboratory work demonstrated the possibilities of high-pressure ammonia synthesis on an industrial scale. Unlike most other chemists whose activities straddled the worlds of academic and applied organic chemistry, Haber chose the uncertainties of the emerging physical chemistry, at first with a survey of the applications of electrochemistry, and later through the thermodynamics of gas reactions. By clever manipulation of thermodynamics and kinetics, and with the introduction of a suitable catalyst, he showed that the synthetic ammonia reaction gave yields that some considered impossible, and others could not achieve due to the limitations of their apparatus, as well as various flaws. By making the reaction continuous, with unreacted gases recirculated to the steel converter, Haber, with the aid of Robert Le Rossignol, developed the benchtop apparatus designed to impress industrial chemists from BASF. It was all the more remarkable because of the very low yield—that had discouraged other chemists—a problem overcome by the recirculation of unreacted gases. In July 1909, this apparatus, demonstrated at Karlsruhe Technische Hochschule, served its intended purpose. Haber's reward was a profit sharing arrangement with BASF, directorship of his new Kaiser Wilhelm Institute in Berlin, and the Nobel Prize. He was also generous financially to Le Rossignol for his outstanding laboratory work (and acknowledged in his Nobel Lecture the joint studies with Greenwood).

Though BASF financially supported Fritz Haber's scientific work, he played no part in the industrial scaling up. To go from a benchtop model to a full-size industrial plant was a big leap. That took a team of BASF chemists, metallurgists, and proto-chemical engineers, led by Carl Bosch—delving into a wide range of problems, concerning materials of construction, compressors, catalysts, instruments, supply and purification of hydrogen and nitrogen, and drawing on prior developments in chemical and other technologies—over four-and-a-half years to realize. The pursuit of a single invention dedicated to chemical manufacture had never before relied on so many skills. It was driven to a satisfactory conclusion under one unyielding, single minded and tenacious individual, Carl Bosch, whose brute force process bound nitrogen with hydrogen on a scale suited to manufacture. Bosch's role was recognized by senior management. His reward was rapid promotion, to chairman of the board of BASF, and of I.G. Farben in 1925 (until 1935). His role in the development of high-pressure industrial chemical synthesis was also acknowledged with the Nobel Prize received jointly with Friedrich Bergius in 1931.

These remarkable scientific and technological innovations should not, however, detract from other achievements in nitrogen fixation. They had started out as activities of independent inventors, or as a desire for diversification at dye-manufacturing and other chemical firms, with the promise of profits from contributing to increased agricultural yields. Notably, Nikodem Caro was involved with Adolph Frank in the invention of a successful electrothermal process for nitrogen fixation, applied in Europe and elsewhere, particularly by the American Cyanamid Company at Niagara Falls. The Frank-Caro process remained in use in Norway until 2002. No less important was Kristian Birkeland's work. Though the original source of inspiration is uncertain, that hardly matters. His simulator of lightning was undoubtedly the most successful of the electric arc methods. It was, conveniently, invented in a country where cheap hydroelectricity could be made available in abundance. Casale, Fauser and Claude also deserve their rightful places among the individual inventors of 20th-century nitrogen fixation processes.

Though today many of these names are almost forgotten, efforts are being made to retain reminders of their heritages. At Rjukan, a Birkeland-Eyde furnace, an acid tower dating from 1911, and various buildings, in addition to the complete transport network, including railways and train ferry terminals, survive. They are included in a UNESCO World Heritage Site proposal (2014) for commemorating the impact of industries powered by hydroelectricity at Rjukan and Notodden [2]. The Norwegian Industrial Workers Museum at Rjukan includes several exhibits related to the Birkeland-Eyde process. Abandoned Frank-Caro furnaces and a Linde nitrogen plant remain in place at the Odda facility. The Norwegian Museum of Hydro Power and Electricity covers historical developments at Odda and Tyssedal. The Deutsches-Chemie Museum Merseburg includes several items of equipment from the early days of synthetic ammonia manufacture at Merseburg/Leuna. The Carl Bosch Museum Heidelberg emphasizes the work of the Nobel laureate on high-pressure chemistry, with appropriate exhibits.

6.2 Autarky

> The 'false momentum, propelled not by consumer demand, but by the contingencies of war.'
>
> Peter J. T. Morris

The electrothermal developments related to the capture of nitrogen brought about significant and far-reaching changes in the chemical industry between 1900 and 1914. Only at the end of that period did high-pressure chemistry offer a viable, rival process to the electric arc and cyanamide processes. That was the through the Haber-Bosch synthetic ammonia process inaugurated in September 1913. Unlike the operators of electric arc and cyanamide processes, there was at first limited interest at BASF in nitric acid made by oxidation of synthetic ammonia [3]. Nevertheless, elsewhere in Germany oxidation of ammonia from gas and coke oven works to nitric acid, as well as at the Trostberg cyanamide facility, had been introduced on a small scale. Thus all the new nitrogen-based processes that would be required to serve the Kaiser's army and navy from August 1914 were already in place, even if the scales of operation were not great, and in most cases technical difficulties still had to be overcome.

The stalemate that began in the autumn of 1914, the resulting war of attrition, and the urgent need for military resources, particularly high explosives, would bring about a new strategy in the conduct of war, at first on the German side. It was based, as Fritz Haber later described it, on the "internal connection" between war and the exact sciences [4]. This harbinger of change was recognized within every industrialized nation.

Haber was referring to the vast military-academic-industrial complex in which he was intimately involved, as academic, adviser, and soldier. More than at any other time before, the relationships were reliant on scientific advances and the latest technological innovations. It required men of extraordinary ability, commitment, organizational skills, and even stubborness, including leading academic and industrial chemists, notably Emil Fischer, Carl Duisberg, and, especially, Fritz Haber and Carl Bosch. This was indeed "The Chemist's War" carried out on an unprecedented scale, most particularly in the sizing up and development of products and processes for capturing nitrogen, converting the products into nitric acid, nitrating aromatic compounds, and manufacturing ammonium nitrate and sulphate. And Merseburg was, in its vastness and diversity, the iconic manufacturing facility.

The British and French also brought together similar arrangements between state agencies, the military, chemical manufacturers, and universities, as did the Americans even before they entered the war in April 1917 [5]. These accelerated moves into new and more efficient technologies, revived the fortunes of some firms, and kept several others that might otherwise have gone to the wall in business.

Peacetime conditions would rarely have justified the great capital expenditures involved in such ventures. Research and development without economic goals was put into practice, often aimed at finding substitutes (ersatz products) for materials no longer readily available. Outstanding, as described here, was the urgent need in Germany to replace the mineral nitrate from South America in order to sustain the long and hard stalemate, especially after it was realized that the conflict would not be a "war of movement" but of drawn out and inconclusive campaigns. Of those caught up in the endeavour to satisfy the needs of the military, it was Fritz Haber who, by association, and conviction, remains the scientist most connected with the German war effort. Yet despite the many claims to the contrary, and even the reminiscences of Alwin Mittasch, started during World War II—Mittasch was then of the opinion, correctly, that his 1914 work on ammonia oxidation contributed towards Germany's ability to continue fighting after the spring of 1915 [6–8]—the ammonia synthesis that Haber devised was not, at least until 1916, an overriding factor in munitions manufacture. No less significant: but for the war, and especially the long stalemate, the enormous Haber-Bosch and other factories, sponsored, directly and indirectly, by the Reich, would not have become available, perhaps for decades, to provide the fertilizer required to feed humankind.

Peter Morris, the leading historian of I.G. Farben technology during the interwar period, has demonstrated that BASF's tremendous appetite for risk, and confidence in success, grew and was maintained following the triumphs of synthetic alizarin (1870) and indigo (1897). These were peacetime triumphs, important components of civilian economies, as was synthetic ammonia, though its strategic significance was known long before 1914. The Haber-Bosch process, despite its technical superiority, achieved supreme status, particularly among the Allies, only well after the German loss of nitrate supplies from Chile aggravated a growing awareness that the war would be long and drawn out. The conditions of war, with state support for expansion—notably at first of calcium cyanamide—provided the potential for tremendous future profits after the war.

The success of the Haber-Bosch process before the end of the war encouraged even greater risk taking in the late 1920s once high-pressure coal-to-oil conversion was adopted. But the economic conditions were not by any means normal. The single-minded support by Carl Bosch and Carl Krauch of high-pressure industrial chemistry would almost bankrupt I.G. Farben by 1930, particularly as new and abundant reserves of petroleum were discovered in the United States and the Near East. It took until the mid-1930s before that risk taking could be justified, and the corporation saved, with the generation of vast self-sufficiency, or autarky, programmes as dictated by the National Socialists [9]. The same can be said of the work from the mid-1920s of Walter Reppe (1892–1969) on catalytic reactions of acetylene under conditions of high pressure. Industrial application, as with the calcium cyanamide process, was facilitated by the existence of the calcium carbide industry. It enabled a response to the British monopoly on natural rubber, particularly after restrictions on the supply from Malaya were imposed. The well-developed acetylene chemistry, through its application to synthetic rubber production, heralded a new era of synthetics, brought on by autarky programmes [10, 11].

The expansion of Haber-Bosch ammonia production particularly during 1916–1917, was, just like the later Reppe acetylene-based developments, driven by a "false momentum, propelled not by consumer demand, but by the contingencies of war" [12]. That was true also of the Bergius synthetic fuel process, which became important only as conditions for preparation of war approached. Bosch and a few others at BASF had believed early on that a peacetime momentum would drive the future of high-pressure chemical industry, not only away from dependence on synthetic dyestuffs but also into completely new areas of industrial chemistry. Commercially, in the short term, that was a disaster. The need for backing the development of costly high-pressure processes was a main contributor to the merging of German chemical firms in 1925, apart from other considerations, such as the threat from foreign rivals that had made substantial headways in the dyes business, as well as alternative high-pressure ammonia processes. Ironically it was the traditional products, synthetic dyes, as well as pharmaceuticals and photo products, which provided the profits that sustained the behemoth I.G. Farben into the mid-1930s [13].

The scientific and technological brilliance of the Haber-Bosch ammonia synthesis was the outcome of a high risk, and extremely expensive, venture that was perhaps not necessarily seen to be the final way forward for capture of atmospheric nitrogen, even though it was recognized to be the best process available among the synthetic variants. This was also recognized by Allied investigators in 1919, when acknowledging that the German ammonia factories were ready for reverting to peacetime production of fertilizer with the minimum of disruptions. In the long-term, therefore, high-pressure industrial chemistry was the chemistry of the future, but it came about only through the "false" contingencies of war and self-sufficiency in preparation for war (Fig. 6.1).

Fig. 6.1 Artist's impression of barge transporting tanks of nitric acid on the River Rhine with the BASF/I.G. Farben Oppau factory in the background, mid-1930s. Nitrogen products were also critical to Hitler's rearmament programmes. (*Erzeugnisse unserer Arbeit*. Frankfurt am Main: I.G. Farbenindustrie, 1938, p. 171)

In summary, the commitment to the Haber-Bosch ammonia process was propelled by the same high-risk strategies aimed at self sufficiency in Germany that inaugurated synthetic alizarin and indigo, and would be followed by commitment to other high-pressure industrial processes. The latter, in particular, included the emergence of Reppe chemistry, as a "counter-weight" based on availability of carbide-derived acetylene, and new polymers, notably Buna synthetic rubber [14]. Without the buildup of the German military in the 1930s there would have been no economic incentive to continue with synthetic petroleum and synthetic rubber, both reliant on high pressures and use of catalysts. Similar circumstances in 1915–1916 created the momentum for improvement and expansion of synthetic ammonia production, and the development of the modern processes for large-scale conversion of ammonia into nitric acid.

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SpringerBriefs in History of Chemistry, DOI 10.1007/978-3-319-19357-1