



# **Historical Group**

**OCCASIONAL PAPERS**

**No 7**

**Nitrogen, Novel High-Pressure Chemistry, and  
the German War Effort  
(1900-1918)**

**Anthony S. Travis**

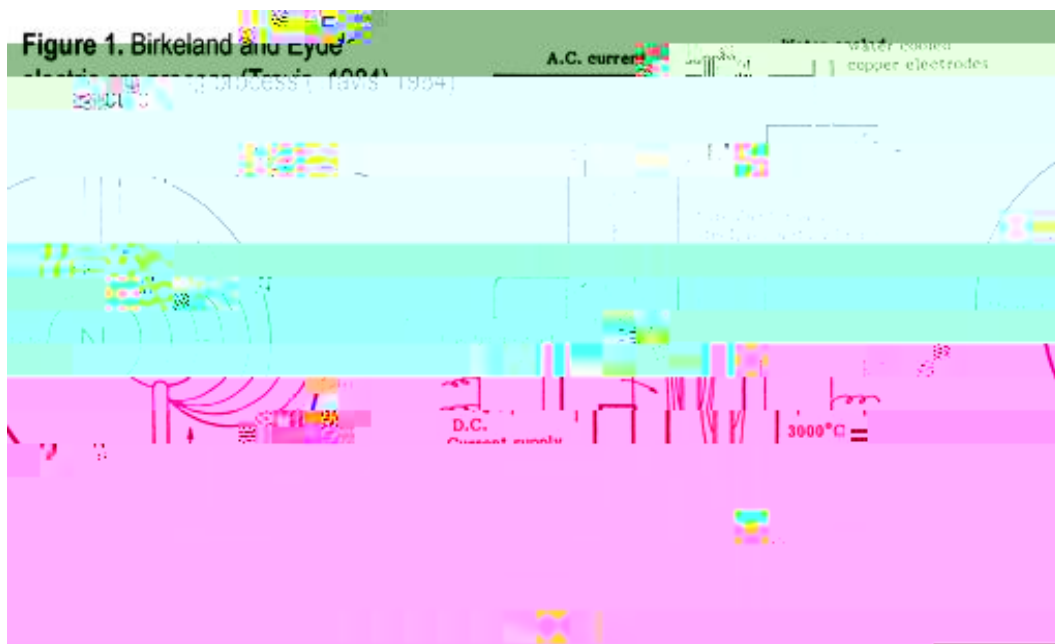
## Introduction

“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): 285-6.

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 even desperate episode in the conduct of what became known as the First Great War. “Nitrate”, a commodity essential to the production of modern explosives employed in warfare, mainly aromatic nitro compounds such as TNT 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 (Chilean saltpetre, or sodium nitrate), extracted from the mineral caliche, and the other nitrogen-containing chemicals of commerce, such as calcium cyanamide and ammonia, as sources of vast

electrodes (**Figure 1**). This arrangement enabled the working of large furnaces. The atmospheric nitrogen was captured as nitric oxide. A prototype was constructed at Arendal, Eyde's birthplace.



At the end of 1903, Birkeland and Eyde, jointly with the Swedish bankers Knut and Marcus Wallenberg, backed by the Enskilda Bank, Stockholm, set up the firm Elektrokemisk, followed by Notodden Saltpeterfabriker AG (1904) to undertake manufacture at Notodden, in Telemark, southwest of Oslo. On 2 May 1905, work started on a small factory, with three 500-kilowatt furnaces. Power for the Birkeland-Eyde process was supplied by the Tinfos hydroelectric station, opened in 1901.

The gas leaving the electric arc furnaces contained two to three per cent of nitric oxide. Rapid quenching in an aluminium vessel lowered the temperature, in order to prevent decomposition of the oxide. The cooled gas was passed through oxidation chambers, vertical iron tanks lined with acid-proof stone, to form dioxide, and then through an absorption system where the dioxide was converted into nitric acid.

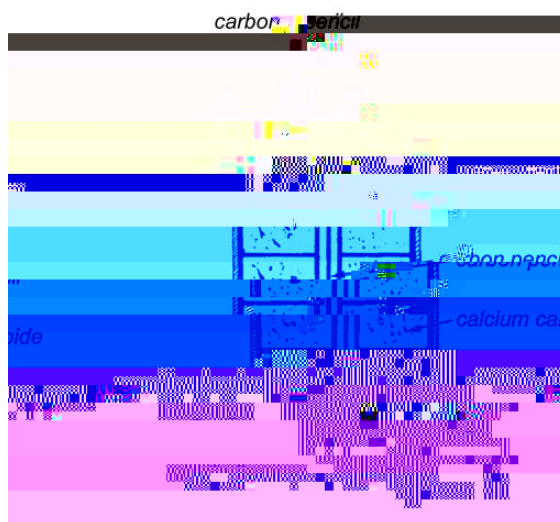
Details of the Birkeland-Eyde process were described by the chemist Otto N. Witt (1853-1915) on 25 November 1905 at the inauguration of the new technical chemistry institute at the Royal Technical College of Berlin (Königliche Technische Hochschule zu Berlin, also known as the Technische Hochschule Charlottenberg). 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 electrochemistry, thoroughly familiar with the Norwegian process after serving as a consultant to Birkeland and Eyde. Following Crookes, Witt also warned of future shortages of nitrates, suggesting that they would begin to

iron pipes surrounding an inner electrode. From the absorption towers, forty per cent nitric acid was obtained, which was either 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. There were considerable polemics over the most suitable type, or the number of each type, of arc furnace, Birkeland-Eyde or BASF, 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.

The yield of desired nitric oxide from the BASF electric arc was higher than from the Birkeland-Eyde arc. Also, the cost of the BASF furnace was lower, and repair and maintenance costs were not great. However, new and taller BASF furnaces were problematic in operation. In 1909, BASF commissioned the academic physicist Jonathan Zenneck (1871-1959) of 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 electric arc furnace and found that an increase in pressure had no advantage. Little came out of these efforts. The Birkeland-Eyde furnaces were found to be more efficient than the newer BASF furnaces. BASF pulled out in 1911, already heavily involved in another, quite different, way of fixing nitrogen based on the work of Haber.

Several other arc processes were developed, including, in 1902, one by Harry Pauling, citizen of Brandau, Bohemia, Austria-Hungary, in which a stream of fast moving air was blown against an arc created 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. Air blown up through a nozzle into the lower part of the arc was deformed into a flame (Lunge 1916, vol. 1, pp. 253-256). The process was adopted in the furnaces of Salpetersäure-



**Figure 2:** Early Frank-Caro Electric Oven for Calcium Cyanamide (redrawn from Ernest Kilburn Scott, *Nature*, 11 July 1912, p. 492).

In the improved cyanamide process, the absorption of nitrogen took place at the point of contact of the pencil with the carbide and continued gradually outward. After around twenty-five hours the current was switched off, and the furnaces left a further ten hours, by which time the nitrogen had been absorbed. The calcium cyanamide, appearing as a black-grey clinker, was turned out, crushed, ground, and packed in bags for shipping. The high operating temperature kept the power cost high.

That changed with the introduction of a rival 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 a catalyst. This enabled reduction of the operating temperature to 700-800°C. With inventor Constantin Krauss, Polzenius developed a manufacturing process. In 1904, it was taken up at Westeregeln, close to Magdeburg, central Germany, but proved uneconomic. Following improvements to the furnaces, the Deutsche Karbid Gesellschaft was founded on 31 May 1906 in Frankfurt am Main by Metallgesellschaft. A factory was erected at Knapsack, near Cologne. 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. In 1909, along with reorganization, the name of the company was changed to Aktiengesellschaft für Stickstoffdünger, and in the following year Krauss took over as manager. In 1911, the Knapsack site began the manufacture of calcium cyanamide in a continuous process.

Operation of the Frank-Caro process within Germany was delayed until 1908, when Frank and Caro came to an arrangement with Polzenius over the latter's cyanamide patent. From then on, addition of catalyst enabled a lowering of the operating temperature in all the furnaces that used the Frank-Caro process. 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 Carl von Linde process (1908).

On 6 November 1908, the Cyanidgesellschaft, with the backing of Deutsche Bank, created a subsidiary, Bayrische Stickstoffwerke AG, in Munich, for the manufacture of the lime-nitrogen, Kalkstickstoff, in Germany. (Degussa had withdrawn from the partnership; in 1899 its research chemist Johannes Pflieger [1867-1957] improved on the cyanide process developed by Hamilton Y. Castner.) Adolph Frank and Nikodem Caro were the principals of Bayrische. Albert Frank worked in administration until 1916, when following the death of his father he joined the board. A large factory was built at Trostberg, Bavaria, supplied with electricity from a hydroelectric power station on the River Alz, a tributary of the Inn ("Trostberg: From Fertilizers to Construction Chemicals"). The hygroscopic catalyst calcium chloride was later replaced with, for example, calcium fluoride, as well as other alkali and alkaline earth salts.

By 1914, annual global production of cyanamide was 120,000 tons, with one-quarter manufactured in Germany. The crude product containing approximately twenty

On 12 March 1900, Ostwald advised the BASF management that he had devised a method for preparing ammonia from its elements based on the application of elevated temperature in the presence of an iron wire catalyst (Stoltzenberg 2004, p. 80). However, when the method was tried at BASF it was found that the ammonia was not formed directly (but perhaps from iron nitride). The scientist in charge of the evaluation was Carl Bosch.







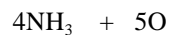
The converter had to be re-designed to prevent, or at least minimize, this difficulty. The development work continued

ammonia came from a coke-



with the Haber-Bosch process, had not been idle. Alwin Mittasch worked on improvements to the oxidation since early 1914. 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. This was important, since there were shortages of platinum, previously available from the Ural Mountains in Russia. It was Mittasch's success which enabled Carl Bosch in October 1914 to guarantee that new enlarged plant at Oppau would meet the needs of the BASF contract with the military from around March or April 1915 (Stoltzenberg 2004, p. 131).

Converting ammonia to nitric acid involved the oxidation of ammonia, of seven to ten per cent volume, mixed with air to give nitric oxide.



In April 1918, von Ludendorff, Supreme Commander of the German Army in Flanders, failed to hold back British forces on the coasts of Belgium and France. This decisive event would bring an end to the war. In the final stages, Germany was producing 650 tons of synthetic ammonia per day. Of this Oppau was responsible for 250 tons and Leuna for 400 tons (Hartley 1919, p. 211). German output of cyanamide, much of it converted into nitric acid for the manufacture of explosives, was close to an annual rate of 600,000 tons. Following the cessation of hostilities, it was estimated that there was the potential in Germany for peacetime manufacture of 500,000 tons of nitrogen products annually, as fertilizer: sixty per cent from the Haber-Bosch process, and twenty per cent each from the gas works and cyanamide factories ("Nitrogenous Fertilizers", 1920). The future of the Haber-Bosch process had been assured by the needs of wartime.

## **Conclusion**

The almost four-year stalemate that followed the Battle of the Marne in September 1914 made heavy demands on the producers of nitrogen compounds employed in the manufacture of explosives. At that time both the Allies and the Central Powers were reliant on imported Chilean nitrate for production of the nitric acid required to nitrate, mainly aromatic, organic chemicals. For the Central Powers the availability of this vital commodity ceased following the Battle of the Falkland Islands in December 1914. German industry turned to the processes for capturing atmospheric nitrogen that had developed from around 1900: the cyanamide and, increasingly, Haber-Bosch processes were of critical importance. This stimulated technical improvement and the massive expansion of these processes, as well as major developments in the production of concentrated nitric acid by catalytic oxidation of ammonia. The Haber-Bosch process came to the forefront from 1916 mainly as a result of the decision to erect a new works at Leuna, and the demands of the Hindenburg programme of state-led industrial organization. The war inaugurated a new era in industrial chemistry,

