# A factual clarification and chemical-technical reassessment of the 1921 Oppau explosion disaster

the unforeseen explosivity of porous ammonium sulfate nitrate fertilizer

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# Keywords

# Summary

The Oppau factory was a chemical production facility constructed by the leading German chemical company BASF in the time period shortly before the First World War. The facility was located along the river Rhine, a few kilometers north of the town of Ludwigshafen in Germany. The purpose of the chemical manufacturing at Oppau was the production of nitrogen fertilizers on the basis of the then recently developed Haber-Bosch synthesis of ammonia. It was the first facility of its kind anywhere in the world.

On the morning of 21 September 1921, hundreds of tons of ammonium sulfate nitrate (ASN) fertilizer, kept in a storage silo at the Oppau factory site, decomposed explosively when piles of hardened fertilizer material were broken up with the help of explosives. The event, referred to as the Oppau explosion disaster, killed more than five hundred people, wounded nearly two thousand more, and destroyed a large part of the factory site and surrounding residential area. The incident remains one of the worst industrial disasters and most iconic hazardous material events of all times.

The Oppau explosion disaster is different from most other explosion disasters since it was not the result of an uncontrolled fire. The procedures leading to the disaster had actually been applied at the same facility thousands of times prior to the disaster. In spite of the exceptional assembly of notable experts summoned for the ensuing inquiries, the alleged causes of this industrial calamity – while partially identified – were never completely understood.

The objective of the present report is to clarify actualities and to ascertain the chemical-technical causes of the tragedy at Oppau, with the highest degree of certainty possible. To that end, this investigation has involved two main approaches. The first is a historical-technical approach, comprising a detailed reassessment of the original investigation material in light of the current state of knowledge within the science of energetic materials. The second is a chemical-technical approach, involving computerized thermochemical modeling of ASN decomposition, in an attempt to shed light on the energetic potential of ASN mixtures.

It is clarified how the understanding of energetic materials at the time of the accident was inadequate for an appropriate understanding of the phenomena involved. It is implied that the special physical characteristics imparted on the Oppau fertilizer material, by the application of a new spray-drying procedure some time prior to the accident, constituted an unforeseen disaster in waiting. The subsequent investigations thus struggled in their efforts to align experimental results and the conclusions extracted from these, with the theoretical framework of explosive materials then in existence.

The presented account renders a prime example of the dangers confronted at the intersection of large-scale chemical manufacture and a, to some degree, incomplete scientific foundation. Moreover, it underscores the unpredictable behavior of ammonium nitrate materials.

# Sammendrag

Oppaufabrikken var et kjemisk produksjonsanlegg oppført av det ledende tyske kjemikonsernet BASF i tidsperioden like før den første verdenskrig. Anlegget var plassert langs elven Rhinen, noen få kilometer nord for byen Ludwigshafen i Tyskland. Ved Oppaufabrikken ble det produsert nitrogenholdige gjødseltyper på grunnlag av den da nyutviklede Haber-Bosch-syntesen av ammoniakk. Anlegget var det første av sitt slag noe sted i verden.

Om morgenen den 21. september 1921 eksploderte en lagersilo på fabrikkområdet, en bygning som inneholdt store mengder med gjødsel i form av ammoniumsulfatnitrat (ASN). Eksplosjonen inntraff da hauger bestående av hardnet gjødselmateriale ble brutt opp ved hjelp av sprengstoff. Eksplosjonsulykken i Oppau tok livet av mer enn fem hundre mennesker, skadet omtrent to tusen og ødela en stor del av fabrikkanlegget og omkringliggende boligområder. Ulykken er fortsatt et av de verste industriuhellene i historien.

Eksplosjonsulykken i Oppau skiller seg fra de fleste andre eksplosjonsulykker ved at den ikke var et resultat av et ukontrollert brannforløp. Rutinene som førte til ulykken hadde faktisk vært anvendt tusenvis av ganger tidligere ved samme anlegg uten problemer. Til tross for at etterforskningsarbeidet ble ledet av fremstående eksperter, forstod man aldri årsakene til ulykken fullt ut, selv om viktige sammenhenger delvis ble klarlagt.

Formålet med denne rapporten er å klarlegge hendelsesforløpet og fastslå de kjemisk-tekniske årsakene til ulykken i Oppau med størst mulig grad av sikkerhet. Undersøkelsen omfatter to typer tilnærminger til problemstillingen. Den første er en historisk-teknisk tilnærming der det opprinnelige etterforskningsmaterialet har blitt revurdert i lys av oppdatert kunnskap om energetiske materialer. Den andre er en kjemisk-teknisk tilnærming der maskinvarebasert termokjemisk modellering av ASN-dekomposisjon har vært anvendt i et forsøk på å belyse det energetiske potensialet til ASN-blandinger.

Rapporten klarlegger hvordan forståelsen av energetiske materialer i den aktuelle tidsperioden var utilstrekkelig for å forstå de involverte fenomenene. Det er antydet at de spesielle fysikalske egenskapene til gjødselproduktet, som oppstod som et resultat av omlegginger i produksjonsmetoden kort tid før ulykken, i realiteten gjorde produktet langt farligere enn det hadde vært tidligere. Etterforskningen var ute av stand til å sammenstille konklusjonene fra de eksperimentelle resultatene med det teoretiske rammeverket som da eksisterte for energetiske materialer.

Historien om Oppaueksplosjonen er et godt eksempel på de farene som kan oppstå i skjæringspunktet mellom kjemisk produksjon på industriell skala og et vitenskapelig fundament som i noen grad er ufullstendig. Historien fremhever dessuten den til tider uforutsigbare oppførselen til ammoniumnitratholdige stoffblandinger.

# Content

# Preface

Scientists have for long been fascinated by – and equally fearful of – the ferocious, and at times unpredictable, behavior of energetic materials (explosives, propellants and pyrotechnics). Civilian and military researchers alike have always strived for a deeper understanding of the fundamental aspects that influence the safety of such materials. The work presented in this report was carried out by the author within the framework of a research project at FFI, among other things, dedicated to the attainment of such knowledge, mainly by using computational methods.

Due to the author's historical inclinations, the 1921 Oppau explosion disaster had been of interest for some time. A more concrete investigation on the matter was initiated towards the end of 2014, supported by knowledge accumulated in the FFI project. The work included a visit to Ludwigshafen in November 2015, involving a survey of the BASF facilities located there (part of which contains the areas of the former Oppau factory), as well as studies in the BASF corporate archives and the Ludwigshafen city archives.

The author would like to thank Dr. Stefan Mörz of the Stadtarchiv Ludwigshafen, who kindly provided documentary material, helped to establish relevant contacts and who generally was very helpful and supportive of the work that led to this account. His considerate efforts have been greatly appreciated by the author. The author would also like to thank the helpful staff of the BASF Corporate History and the BASF Visitor Center in Ludwigshafen, for valuable assistance and encouragement.

Furthermore, Dr. Ulrich Hörcher of BASF Ludwigshafen kindly forwarded a presentation he had held on the occasion of the 90th anniversary of the Oppau Explosion disaster. This presentation had been prepared on the basis of a review of the original investigation report. The library services at FFI are acknowledged for their expedient services and support in the provision of documentary material pertaining to the Oppau explosion disaster. Three anonymous reviewers of a previous version of this manuscript are also acknowledged for valuable comments and recommendations. Finally, the author would like to thank Åsmund Kaupang at the Department of Pharmaceutical Chemistry, University of Oslo, for corrections and valuable input to this manuscript.

**Important note**: The literature covering ammonium nitrate (AN) and its associated safety issues is vast. This text primarily addresses issues relevant for ammonium sulfate nitrate (ASN), and these may differ substantially from those that are applicable for other mixtures containing AN. There is a tendency in the literature to unduly lump together different compositions and incidents involving AN within the same, simplified narrative. Unfortunately, this now and then removes essential nuances and corrupts valuable lessons learned. Subsequently, this report does not incorporate material that is not deemed relevant for the Oppau explosion disaster, in particular with regards to issues concerning AN and fire. Interested readers should seek out the recent and comprehensive review by Vytenis Babrauskas in the *Journal of Hazardous Materials* (**2016**, *304*, 134–149), and the references contained therein.

# 1    The 1921 Oppau explosion disaster

In 1921, the Oppau factory was a major production facility belonging to what was then, and in fact still is, the leading global chemical company BASF (originally Badische Anilin- & Soda-Fabrik, but only the trademarked abbreviation has since maintained its relevance).[1,2] At the Oppau factory, nitrogen fertilizer products were manufactured on the basis of the then newly developed Haber-Bosch high-pressure synthesis of ammonia.

The Oppau plant was located along the river Rhine, near the small village of Oppau in Germany – then about 1.5 km north of BASF's main chemical factory at Ludwigshafen. Today, the village of Oppau (town from 1929) has become a suburb of Ludwigshafen (from 1938 onwards), and the Oppau and Ludwigshafen chemical facilities have merged into a single, continuous ~10 km$^2$ production site with tens of thousands of employees. It is currently the largest integrated chemical facility worldwide. Nevertheless, at the time of the Oppau explosion disaster, the Oppau and Ludwigshafen factories were two separate production facilities, both owned and operated by BASF, but located at some distance from each other.

At 07:32:14 local time, in the morning of Wednesday 21 September 1921, the Oppau factory was devastated by the first of a series of two titanic explosions.[3-13] The explosions took place four seconds apart, with the second explosion at 07:32:18 being considerably stronger than the first one. Together, they caused appalling loss of life and immense material destruction (see Figure 1.1). Although the sequence of two consecutive explosions will be an important point in the discussion later on, the incident will, as is customary, consistently be referred to as the Oppau explosion (in singular) throughout most of this text.

The death toll resulting from the two explosions varies somewhat according to the source material, but according to the official German investigations, the number of dead and missing (comprising victims that were either non-identifiable or not found) was listed as 559,[*] the number of wounded as 1977 and the number of homeless as 1870.[3,5,8] Other sources operate with a number of more than 7000 left homeless.[1]

The associated material damages were also colossal (Figure 1.1).[7] A considerable area of the southwestern end of the production site, the place in which the explosion originated, was completely obliterated. The rest of the factory was more or less severely damaged, taking the site out of production for months (until 9 December 1921).[1] Around the center of the explosion, only a very large, mostly circular, explosion crater remained, measuring 96 m in width, 165 m in length and 18.5 m in depth (approximately 12 000 m$^3$ in volume). The slightly peanut-shaped explosion crater is sketched in Figure 1.2.[7] The crater was largely filled with ground water after a short period of time.

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[*] Figures in the 560s are usually quoted in contemporary texts. Yet, the author has been unable to locate reliable source materials from the relevant time period that actually contain these numbers, so the origin of these oft-quoted figures is unknown.

Out of 300 buildings located at a distance of 480 m, 96 of them (close to a third), were completely destroyed. In the town of Oppau, which had about 7500 inhabitants and was located 550 to 1500 m away from the center of explosion, 1036 buildings located at a distance of up to 600 m were fully collapsed, 928 buildings located at a distance of up to 900 m were severely damaged, and the remaining 89 buildings were mildly affected. At the Ludwigshafen factory, located some 1.5 km in the southern direction, roofs were torn off and window frames dislocated. Material damages could be detected as far away as 75 km from the center of the explosion. The sound of the explosion was clearly audible in Munich, nearly 300 km southeast of Oppau, and reputedly in Zürich and Göttingen.[12]



Figure 1.1    *An iconic aerial photograph taken of the BASF Oppau factory following the devastation of the 1921 explosion, looking towards the factory site in a northeastern direction, with the Rhine in the background. The photograph was taken by a pilot from the French airline Compagnie Aérienne Française (now defunct) and published on the 1 October 1921 by L'Illustration (a weekly French newspaper published from 1843 to 1944).[13] The two tall chimneys to the left belong to the central power station, with the area of ammonia high-pressure synthesis located behind them. The ASN storage silo 110 was located in the crater at the front center, with the remnants of the large ASN concrete storage silos 182 and 112 lying just behind, and the heavily damaged sulfuric and nitric acid production areas to the right (see also Figure 1.2). The two tall chimneys in the center/right belong to each of the two ammonium sulfate factories, with large concrete storage silos located in between. (The picture is reproduced with permission from Stadtarchiv Ludwigshafen.)*

*Figure 1.2   Overview of the southwestern part of the Oppau factory site as of 1921, with an
              expansion of the Oppau explosion crater and a rough sketch of silo 110 that
              contained the ASN involved in the disaster, prior to the explosion. The figure has
              been reproduced on the basis of handmade drawings and depicted models
              contained in the final Reichstag commission report (for accuracy, the passage
              running from the annex of silo 110 to building 111 has been lowered one floor
              compared to the model depicted in the report, a mistake in the prepared model that
              was pointed out in the Reichstag commission report).[7]*

# 2 The course of investigations into the Oppau explosion disaster

Due to the very large scale of the destruction resulting from the Oppau explosion, both human and material, the incident immediately became a major event of both national and global proportions. At the time, it was the most severe accident in the history of the chemical industry, and it has remained among the worst industrial disasters up to the present day.

The Oppau disaster was also exceptional in a historical and societal context, as it took place during a tumultuous period in German history, shortly after the defeat in the First World War – and at a time of social unrest, political turbulence and economic upheaval. The numerous non-technical (political and socioeconomic) aspects of the disaster, such as the vast press coverage (often exaggerated, heavily politicized or sometimes wildly inaccurate or downright misleading), ensuing emergency relief efforts, political maneuvering, material reconstruction, insurance settlements and economic compensations, will not be detailed any further. These aspects of the disaster have now been thoroughly chronicled,[2,12,13] and then particularly in the recent and very comprehensive book by Sanner.[13]

Already at the day of the explosion, the Bavarian state parliament (Landtag) decided in the afternoon to form a commission (henceforth referred to simply as the Bavarian commission) set to investigate the facts and causes of the disaster.[8] One week later, on the 28 September 1921, the national parliament of the Weimar Republic (Reichstag) decided to form a parliamentary commission of investigation (from here on referred to simply as the Reichstag commission).[3-7] It was decided that the two commissions should mostly work independently of one another, but they were also to hold joint public meetings (usually held in Oppau, Ludwigshafen or Berlin). In addition to the two governmental investigations, the company BASF joined the inquiries, providing documentation and otherwise supporting the investigation efforts.

The Bavarian commission consisted of five members, both scientific-technical experts and representatives from industrial worker unions.[8] It was decided that the Bavarian commission should focus, in particular, on the clarification of chemical-technical matters relating to production, storage and transportation of ammonium nitrate (AN), ammonium sulfate (AS) and ammonium sulfate nitrate (ASN) – fertilizer products that were quickly assumed to be the root cause of the disaster. Their work consisted generally, but not exclusively, of the collection and study of documentary material (plans, drawings, protocols etc.), as well as of the questioning of relevant personnel, witnesses and experts.

The Reichstag commission had eight (later seven) members, consisting of politicians representing a broad spectrum of the Reichstag. The commission appointed a number of subjugated specialists tasked with the various scientific-technical parts of the investigation.[3-7] Several of these experts are known historical figures in the annals of energetic materials. These figures embodied the absolute prime of German expertise available at the time (relevant to the matters involved) and therefore merit some supplementary contextual information.

Among the appointed experts was Emil Bergmann (1857–1922), chemist and the first director of the Chemisch-Technische Reichsanstalt (CTR) in Berlin, the institution responsible for the greater part of the explosive-technical investigation pertaining to the Oppau explosion (this institution was discontinued following the Second World War, as it was completely dismantled by the Soviets).[12] Bergmann was an experienced specialist within propellants and explosives, and an experienced administrator of institutions dealing with such matters.[14]

Another appointed expert was Hermann Kast (1869–1927), chemist and departmental director in charge of explosives at the CTR from 1921.[15] Kast was perhaps the most central figure in the investigation complex relating to the Oppau explosion, and he is an important character in the history of explosives, as well as the author of a well-known treatise on the subject.[16] Kast was a untiring researcher, and the work must have taken its toll – Kast died unexpectedly of heart failure during a recreational journey in the Tyrolean Alps in 1927.[15]

Another appointee was Fritz Lenze (1866–1946), an experienced explosives expert and director of the CTR from 1923 to 1932 (after the death of Bergmann).[17] Included was also Alexander Gutbier (1876–1926), then a professor of electrochemistry, colloid chemistry and chemical technology at the Technische Hochschule Stuttgart.[18]

Yet other appointed experts included the chemist and explosives expert Ernst Richard Escales (1863–1924),[19] the founding editor of the journal *Zeitschrift für das gesamte Schiess- und Sprengstoffwesen* (a forerunner to the current journal *Propellants, Explosives, Pyrotechnics*) in 1906 and prolific author on the subject, also known for his large multivolume treatise on explosives (including a volume on AN explosives).[20] Escales was also the editor of several other, non-related, technical journals.[19]

Another distinguished figure and appointed expert was Lothar Wöhler (1870–1952) of the Technische Hochschule Darmstadt.[21] Aside from their extensive general knowledge on energetic materials, Escales and Wöhler had both made landmark contributions to explosives technology; Escales through his development of Ammonal (aluminized AN mixtures),[22] although other contributors to Ammonal were probably equally or more important, and Wöhler through his development of compound (composite) detonators.[23]

Although not included among the appointed technical experts, other famous chemists and well-known figures in the history of energetic materials involved themselves in the elucidation of events surrounding the Oppau explosion. Some of the more prominent ones include the Polish-German industrial chemist Nikodem Caro (1871–1935), co-developer of the important Frank-Caro cyanamide process for nitrogen fixation, the German physical chemist Kurt Arndt (1873–1946), known particularly for his work in applied electrochemistry (such as in the preparation of sodium perborate), the German-Greek chemist and world-renowned explosives expert Phokion Papa Naoúm (1875–1950),[24] another author of influential books and articles on explosives,[25] and the Swiss chemist Alfred Stettbacher (1888–1961), a noted author of a standard text on explosives.[26] Other knowledgeable experts, not mentioned here, were also involved.

In addition to the substantial investigations undertaken in Germany, the Chemistry Research Board of the Department of Scientific and Industrial Research in Britain (a now defunct government science agency) obtained relevant material samples from Germany and investigated them carefully at the Royal Arsenal, Woolwich (since closed, but then the premier center for government research on ammunition and energetic materials in Britain) and at the Government Laboratory.[9-11] Many of the contributors were renowned scientists, like the Scottish chemist and explosives expert Sir Robert Robertson (1869–1949), the chemist and engineer Sir Richard Threlfall (1861–1932), the Nobel laureate Sir William Henry Bragg (1862–1942), geologist Arthur Francis Hallimond (1890–1968), geologist Herbert Henry Thomas (1876–1935) and the Woolwich Research Department explosives and munitions specialist Godrey Rotter (1879–1969). A detailed account of the lives and merits of these scientists is outside the scope of the present work, but it could advantageously, with relevance to AN, be noted that Robertson was a pioneer in the introduction of Amatol (cast mixtures of trinitrotoluene and AN) during the First World War in Britain – a decisive contribution in military explosives technology.[27,28]

Taken together, the zenith of available expertise within energetic materials chemical technology in Europe at the time was summoned to clarify the actualities and causes of the Oppau explosion disaster – a testimony to the importance attached to the task. Moreover, such an ensemble of intellectuals has rarely, or perhaps never before, been amassed for the investigation of an industrial calamity. As such, when taken together with the sheer severity of the Oppau disaster, this merits an in-depth analysis of exactly what was revealed during these investigations.

In the aftermath of the Oppau explosion, due to the establishment of the first ammonia factory (according to Haber-Bosch synthesis) in the USA by the Atmospheric Nitrogen Corporation at Syracuse, New York, in August 1921, the US National Research Council (NRC) formed a "Committee on the Investigation of the Explosibility of Ammonium Compounds".[12] The committee was established to investigate the properties and behavior of AN, alone or in admixture with other ammonium compounds, during transportation, storage and use.[29] It was chaired by none other than the American chemist Charles Edward Munroe (1849–1938), the discoverer of the Munroe effect and one of the most distinguished figures in the field of explosives, both in the USA and internationally.[30] The safety of AN was therefore in focus on both sides of the Atlantic during the early 1920s.

Still, in spite of the eminent assemblage of skill, the Oppau explosion disaster would prove hard to fully comprehend, leaving a confusing legacy that lingers to the present day. In this report, a plausible explanation for this state of affairs will be presented, essentially attributing the source of the confused legacy of the Oppau investigations to a lack of congruence between the empirical knowledge gained from experimental testing and the maturity of the theoretical framework of energetic materials then in existence. Thus, while the probable causes of the disaster were mostly elucidated, these being connected to very distinctive physical, possibly also chemical, characteristics imparted upon the Oppau fertilizer product as a result of modifications in its production process, the investigators never completely clarified why the ASN fertilizer material had shifted in its receptiveness towards detonative impulses. At the time, the sensitivity of (potentially) explosive compositions was believed to be almost exclusively connected to their

chemical properties, and not the physical ones. The investigators then skillfully managed to uncover the importance attached to the physical characteristics of the fertilizer material, but the requisite theoretical framework for explaining the importance of these effects did not surface before the 1940s and 1950s, apparently too late to influence and correct the legacy of the Oppau explosion disaster.

# 3    Establishment of the Oppau factory

The history of the Oppau factory is intrinsically linked to the development of the Haber-Bosch synthesis of ammonia, arguably the most consequential application of chemical technology in history, and a topic much too far-reaching to be comprehensively dealt with in this text. Detailed accounts of the development and industrialization of the high-pressure synthesis of ammonia are plentiful, ranging from the scholarly to the more mundane, from accounts written by, or concerning, people directly involved to more generalized overviews, company-specific histories and popularized works.[2,31-40]

The unequivocal importance and contradictory nature of the Haber-Bosch process (technology being equally important to the world food production through nitrogenous fertilizers as to the manufacture of munitions through propellants and explosives), combined with the complex personalities of some of the central figures involved, have made it one of the most fascinating stories of the chemical sciences.

For the purposes of this account, a cursory historical summary will suffice. On the basis of scientific breakthroughs in the high-pressure catalytic synthesis of ammonia from elemental nitrogen and hydrogen in the period 1905–1908 by Fritz Haber (1868–1934), then professor of physical chemistry and electrochemistry at the Technische Hochschule Karlsruhe, and his gifted British assistant Robert Le Rossignol (1884–1976),[31,32] contact was established with BASF in 1908.

Following a successful demonstration of Haber's and Le Rossignol's tabletop apparatus for ammonia synthesis, for BASF representatives on 2 July 1909, the progressive director-general of BASF at the time, Heinrich von Brunck (1847–1911), initiated an aggressive developmental effort at BASF towards the possible industrialization of Haber's ammonia synthesis.[39] The effort was led by Carl Bosch (1874–1940),[33,34] an exceptionally skilled chemist-engineer who had joined BASF in April 1899, working under Rudolf Knietsch (1854–1906), a famed BASF chemist who had pioneered the company's efforts in the sulfuric acid contact process and chlorine liquefaction.[1,2]

The development of the high-pressure synthesis of ammonia progressed quickly at BASF. After a breakthrough in February 1911, Bosch eventually worked out the technicalities associated with the construction of large, double-walled steel converter tubes, capable of resisting both the high pressures (several hundred atmospheres), and the embrittlement (decarbonization) and weakening of carbon steel by hydrogen under such conditions.[33] In parallel, Alwin Mittasch (1869–1953), together with his colleagues Hans Wolf (1881–1937) and Georg Stern (1883–1959), succeeded in the development of an affordable iron-based catalyst for the conversion process (Haber had previously employed an expensive osmium catalyst).[35]

The first ammonia was produced at the BASF Ludwigshafen site on 18–19 May 1910.[39] The production totaled only about 5 kg as of July 1910, when a large converter was first put in operation, and then swelled to an average of about 30 kg/day of ammonia in 1911 (11 000 kg in

total that year). On the 5 February 1912, the daily production at Ludwigshafen reached 1000 kg.[35,39]

The BASF leadership had become convinced of the technical feasibility of industrial-scale ammonia synthesis according to the Haber-Bosch technology in April 1911, and plans for a new production facility moved forward. A final decision was made in November of 1911, and the construction of the 500 000 $m^2$ Oppau factory began on 7 May 1912. The first ammonia was officially produced at Oppau on 9 September 1913 (although some operations had started already during the late summer), following a construction period of a mere 15 months. The daily production of ammonia reached 10 tons on 24 October 1913, and would grow considerably in the years to come.[35]

The Oppau factory was originally constructed for the production of ammonia and its subsequent conversion to ammonium sulfate (AS) fertilizer with sulfuric acid. Owing to their development of the contact process for the production of sulfuric acid during the 1890s, BASF had by this time become the world's leading manufacturer of sulfuric acid. The resulting production of AS totaled 26 280 tons in 1914.[35] However, as a result of Germany's involvement in the First World War (1914–1918), the developments at Oppau were expanded.

An allied naval blockade deprived Germany its imports of both Chilean nitrates (sodium nitrate) for the production of propellants and explosives, as well as of foreign pyrites (feedstock for production of sulfuric acid). Consequently, Germany was on a course to run out of munitions by the spring of 1915.[39,41]

Due to Germany's precarious position with regards to nitrate raw materials for munitions manufacture, Bosch forwarded a bold proposal to the Ministry of War, a deal occasionally known as the "saltpeter promise".[40,41] Experiments with catalytic conversion of ammonia to nitric acid had only been undertaken by BASF at a laboratory scale by September 1914, but an efficient and inexpensive catalyst for this oxidation process (a mixed iron-bismuth catalyst that could replace the expensive platinum usually employed) had already been developed at BASF in February 1914 by Christoph Beck (1887–1960), working with Mittasch.[36,39] With this in mind, Bosch promised in a meeting with the War Ministry in late September 1914 that, given adequate financial support, BASF could establish an industrial plant for the production of sodium nitrate from ammonia at Oppau within six months of the day of the meeting.[40,41] After an understanding was reached, Bosch delivered on his promise, and a plant with a monthly capacity of 5000 tons of sodium nitrate started deliveries in May 1915.[39-41]

In yet another bold effort, a completely new and even larger facility for the production of ammonia and its conversion to nitric acid was built near the small village of Leuna on the southern outskirts of Merseburg, on the Saale River in central Germany, then well out of reach of hostile troops or airplanes, and with ample local supply of water and coal.[42] Construction started on 19 May 1916, and the first ammonia was produced on 27 April 1917.[2,35,39,42] Together, these massive undertakings would eventually supply all the needed nitrate raw materials to the German war machine, essentially lengthening the First World War by several

years. This momentous contribution to the war effort and the rise of a military-industrial complex greatly contributed to the conception of this conflict as the "Chemists' War".

In spite of its dualistic nature, the high-pressure synthesis of ammonia earned Fritz Haber a Nobel Prize in Chemistry in 1918 (for the ammonia synthesis) and Carl Bosch a Nobel Prize in Chemistry in 1931 (for the introduction of high-pressure chemistry),[32,33] of which the latter was shared with the coals-to-fuels pioneer Friedrich Bergius (1884–1949). The 1931 awards marked one of those few times in history that a Nobel Prize has been awarded for technical advancements.

# 4 The Oppau explosion and ammonium sulfate nitrate

During the final year of the First World War, all output of ammonia from Oppau was consumed in the manufacture of nitrates for munitions, and the production of AS resumed only in June 1919. The Oppau factory was a completely integrated operation, covering all stages of production, from the reception of coal, production of gases (including purification and compression) and synthesis of ammonia, to conversion into solid nitrogen fertilizers, storage of nitrogen fertilizers in silos and shipment of finished goods. In 1920, the Oppau factory employed about 70 chemists and engineers, about 3000 factory workers and approximately the same number of craftsmen.[35]

Though the events of the First World War had been upsetting for the lives of Fritz Haber and Carl Bosch, the tribulations following the disastrous explosion on the morning of 21 September 1921 were perhaps even worse, at least for Bosch. Haber was located in Frankfurt that fateful morning, approximately 70 km northeast of Oppau, and felt the shock of explosion there as "equivalent to an earthquake".[40] Bosch, by this time director-general of BASF, was at home in his spacious villa in Heidelberg, more than 20 km southeast of Oppau.[34] The explosion rattled the villa's windows, and the massive cloud of dust enveloping the Oppau production site was ominous. Bosch rushed to the factory, only to find the site in absolute turmoil.

Reputedly, Bosch handled the chaos and its immediate aftermath in an exemplary manner, including the delivery of an emotional address at the commemorative service held for the victims of the tragedy, four days after the explosion (on Sunday 25 September), an arrangement with at least 70 000 participants.[2,12,13,34,40] However, soon afterwards, Bosch collapsed and disappeared for months, allegedly never recovering fully from the tragedy.

As the investigations progressed following the disastrous explosion, it was quickly established that the explosion was not directly related to the Haber-Bosch process and its associated hardware, which was mostly intact (Figure 1.1), but had originated in a storage silo for ASN fertilizer (Silo 110, see Figure 1.2), a fertilizer product that had emerged in the factory's assortment comparatively late. This storage silo contained approximately 4500 tons of ASN at the time of explosion. Furthermore, it could be estimated that no more than roughly 10% of that quantity had decomposed explosively. It is an often repeated and sensationalistic misapprehension of the Oppau explosion that the entire quantity of ASN kept in silo 110 had exploded. However, a discussion of the exact scale of explosion will be postponed until one of the final sections of this account.

Moreover, the possibility that the explosion had originated in a cache of high explosives, somehow smuggled into silo 110, with a criminal intent, was dismissed as entirely unrealistic, much due to the large quantities of explosive material involved.[8] The contents of silo 110 consequently became the focal point of all inquiries into the disaster. The properties, production and storage of ASN at Oppau will therefore be described in some detail.

As stated previously, as a result of the war effort, the Oppau factory had acquired the capacity, not only to convert ammonia to AS, but to transform ammonia into nitric acid, thereby rendering possible the production of valuable nitrate fertilizers. Huge quantities of AN had been produced during the war for use in military explosives. As the hostilities ended, the production of AN for agricultural fertilizers was initiated. It was a much valued product for intensive farming due to its superior nitrogen relative to the sodium nitrate (Chilean nitrate) usually employed. However, in order to remedy the deleterious hygroscopic and deliquescent characteristics of AN, two different product modifications were implemented.[7]

The first modification consisted of the addition of potassium chloride to AN, resulting in a conversion to a mixture of ammonium chloride and potassium nitrate, a product referred to as potassium ammonium nitrate (Kaliammonsalpeter in German). This product is a source of two primary plant nutrients (nitrogen and potassium).

The second modification, which gradually replaced the first one, consisted of the addition of AS to AN, giving a product referred to as ammonium sulfate nitrate (Ammonsulfatsalpeter in German). The term Leuna saltpeter (Leunasalpeter in German), with reference to BASF's Leuna factory, is sometimes used as a synonym for ASN. This product is a source of both primary (nitrogen) and secondary (sulfur) plant nutrients. The mixture of AN and AS forms either a mixture of the two compounds, or double salts (2AN·AS or 3AN·AS), depending on the manufacturing process and mixing ratios employed.

The formation of double salts from AN and AS has been known since 1909, from work published by the Dutch physical chemist Franciscus A. H. Schreinemakers (1864–1945), and was therefore well established by the time of the Oppau explosion.[43] Historically, however, the term ammonium sulfate nitrate (ASN) has not referred to any specific composition of AN and AS in fixed proportions, causing much confusion, and cluttering the historical descriptions of the events at Oppau.

For reasons that will be explained later, the ASN produced at Oppau had a nominal composition of 50% by weight of AN and 50% by weight of AS (within the accuracy of the production methods employed), and its content of mechanical mixtures versus double salts was not fully controlled. This 50:50 ASN is sometimes simply referred to as the Oppau salt, a term that will be adopted also in this text for this particular ASN product. In Germany at the time, the salt was commonly called Mischsalz (mixed salt).

As the double salt 2AN·AS in its pure form contains 54.8% AN and 45.2% AS, close to the proportions employed at Oppau, the product involved in the Oppau explosion is often, but imprecisely, simply identified as the 2:1 double salt (or a 55:45 mixture by weight). A complete characterization of these AN-AS double salts has been elusive, and the crystal structures of the two AN-AS double salts were first reported in 2010.[44,45]

# 5    Production of ammonium sulfate nitrate at the Oppau factory

In Figure 1.2, the southwestern part of the Oppau factory site is sketched (as of 1921), encompassing also the contours of the explosion crater resulting from the explosion on 21 September 1921, as well as an expanded plot of that crater, containing both the outlines of the ASN (Oppau salt) storage silo 110 at center and a drawing of the silo prior to the explosion (the latter as seen looking in a roughly southern direction). This figure has been prepared on the basis of illustrations contained in the investigation material from the Reichstag commission.[7]

The link between the contents of silo 110 and the explosion crater is self-evident. Figure 5.1 contains a photo, taken some time prior to the explosion, of the ill-fated silo 110. A detailed assessment of all structural damages resulting from the explosion on 21 September 1921, affecting the Oppau factory site, can be found in the work of Goebel and Probst.[46]
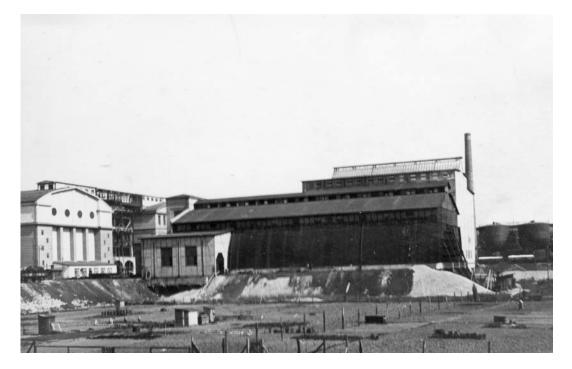


*Figure 5.1    Photograph of the ill-fated silo 110 at the Oppau factory, taken some time prior to the great explosion (looking in a roughly eastern direction). The southwestern ends of the two large storage silos 182 and 112 are visible to the left. (The picture is reproduced with permission from Stadtarchiv Ludwigshafen.)*

Silo 110 (Figures 1.2 and 5.1), the purpose of which was cooling, drying and temporary storage of ASN, was located at the very southwestern end of the factory site. Silo 110 was mostly a wooden construction, 61 m in length and 31 m in width, with an arched wooden roof. Its floor level was located 4.12 m below the filled ground level of the factory site, with the lower part of the silo consisting of a 5 m tall concrete foundation wall, the foremost part of which was buried (see drawing in Figure 1.2 and photo in Figure 5.1).[7]

The production of ASN took place in the neighboring building 111. Beneath the flooring of silo 110, a passage (2 m tall and 2.8 m wide) contained a conveyor belt running to the large (172 m long, 31 m wide and 20 m tall) concrete and brickwork storage silo 112 via an extension of building 111 (Figure 1.2). Due to the fluctuating seasonal demand for agricultural fertilizers – being in need in the spring and autumn – substantial storage facilities were essential. The storage capacity of silo 112 was as much as 50 000 tons of fertilizer (77 000 $m^3$). It contained 7000–7500 tons of ASN on the day of the Oppau explosion,[6,7] none of which exploded, despite its close proximity to silo 110 and the substantial damages inflicted upon it by the blast as well as the fact that a railway carriage placed between building 111 and silo 112 had been hurled into it by the force of the blast. An identical neighboring storage silo, designated silo 182 (Figure 1.2), was empty at the time. Silos 112 and 182 were dedicated exclusively to fertilizer storage.[7]

A schematic overview of the production of ASN taking place in building 111 at the Oppau factory is provided in Figure 5.2, an outline reproduced on the basis of a hand-drawn illustration contained in the investigation material from the Reichstag commission.[7] The manufacturing process employed aqueous ammonia, nitric acid and solid AS as the starting materials, all provided from other parts of the Oppau factory site. A brief overview of the preparation of these starting materials will be presented before proceeding to the production of ASN in building 111.

Hydrogen gas for the first ammonia produced at the Ludwigshafen test factory had been obtained from the nearby chloralkali electrolysis plant. For the Oppau factory, a more affordable mode of hydrogen production was needed. It was successfully developed by Wilhelm Wild (1872–1951), working in collaboration with Bosch.[2]

In separate gas generators, producer gas (mostly $N_2$ and CO) was generated from moist air and lignite (brown coal), and water gas (mostly $H_2$ and CO) was prepared by leading steam (diluted with some air) through glowing coke.[38] The gas mixtures were scrubbed with water in towers, then mixed and circulated over activated charcoal to remove hydrogen sulfide, resulting in a gas stream (mainly) composed of nitrogen, hydrogen and carbon monoxide, diluted with some carbon dioxide and water vapor.

Carbon monoxide and water in the resultant gas mixture were then shifted towards carbon dioxide and hydrogen through the water gas shift reaction in order to improve the yield of hydrogen, an important innovation. The gas mixture was compressed to 25 atmospheres, and the carbon dioxide was removed by washing the gas mixture with water (the carbon dioxide was subsequently exploited in the production of AS, as detailed later).

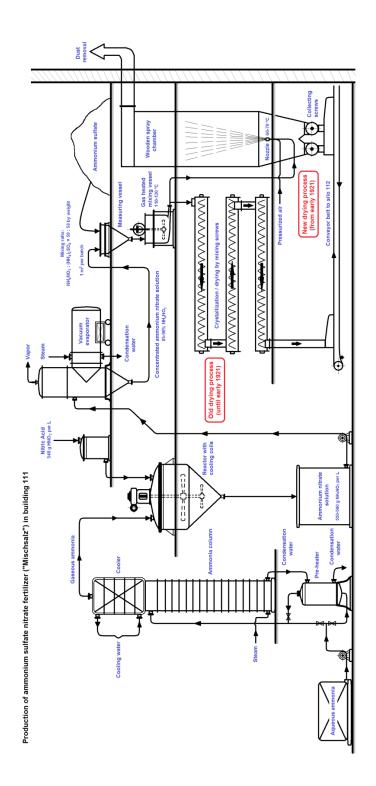*Figure 5.2* *Outline of the manufacturing process for ASN (Oppau salt) in building 111 at the*
*Oppau factory as of 1921. The figure has been reproduced on the basis of a*
*handmade drawing contained in the final Reichstag commission report.[7,8]*

The CO$_2$-free gas mixture was then further compressed to 200 atmospheres, and the last residues of carbon monoxide and other contaminants were removed by absorption in a cuprous ammonium formate solution, an invention by Bosch's colleague Carl Krauch (1887–1968). The nitrogen-hydrogen ratio of the purified compressed gas mixture was then adjusted to the stoichiometric ratio by addition of pure nitrogen, obtained through fractional distillation of air.[39]

Ammonia was obtained from the purified gases by high-pressure synthesis in double-walled, cylindrical steel converters at 200 atmospheres and 600 °C.[7] The resulting ammonia was dissolved in water, giving an approximately 25% solution that was stored in large tanks at the factory site. Nitric acid was obtained from the ammonia by catalytic combustion with air (the Ostwald process), followed by absorption of the nitrous oxides with trickling water in large absorption towers (the nitric acid production area is marked in Figure 1.2).

For the production of AS, the method by which ammonia was simply converted with sulfuric acid, obtained from the contact process, had been largely abandoned by the time of the Oppau explosion, because of its high costs and unwanted dependence on foreign raw materials (pyrites, mainly imported from Spain). The AS was now prepared, more economically, from gypsum (calcium sulfate) mined in a quarry (purchased by BASF in 1913) in nearby Neckarzimmern.[35]

Finely divided gypsum was slurried in a 6–8% aqueous AS solution. The slurry was fed into a stirred reactor (25 m$^3$) in which ammonia (from the Haber-Bosch synthesis) and carbon dioxide (from the preparation and purification of hydrogen gas by the water gas shift reaction, see above) were introduced, resulting in a self-heating reaction (kept at 50 °C by cooling). The precipitated limestone (calcium carbonate) was removed by filtration, and the resulting AS liqueur was marginally acidified with sulfuric acid and then concentrated in lead-lined evaporators.[7] The precipitated AS was then separated from the mother liqueur in centrifuges.[8] An important consequence of this mode of AS manufacture, was the introduction of small quantities of chloride (up to 0.3%) into the finished ASN, an impurity originating from the gypsum starting material.[8] Non-absorbed ammonia from the conversion process was reacted with sulfuric acid separately, but this share of the total AS formed, amounted to only ~3%.[7]

A proper understanding of the final steps in the preparation of ASN, taking place in building 111, is essential for the identification of possible causes of the Oppau explosion. The process is outlined in Figure 5.2.[7,8]

Gaseous ammonia was first obtained from the aqueous ammonia solution in a distillation column. The gas was then fed into a wrought iron reactor vessel (equipped with stirring and cooling coils) containing the dilute nitric acid. An excess of 0.2% of ammonia was applied consequently, the end point being determined through manual titration. The resultant AN solution was gathered in a storage tank and fed to a cast iron vacuum evaporator. Originally, the AN solution would now have been evaporated to dryness and mixed with solid AS, with partial double salt formation taking place upon storage of this mixture. However, this procedure had swiftly been abandoned and the AN was taken further in the production process as a concentrated aqueous solution (Figure 5.2).

Instead, in the final steps of the production of ASN, the concentrated AN solution was fed, in portions of 1 m$^3$ per batch, through a cone-shaped measuring receptacle into a gas-heated and stirred mixing vessel. Three dumping wagons containing solid AS (transported to building 111 by railway carriage), the contents of which had been adjusted to assure a correct mixing ratio of equal weights of AN and AS, were then shuffled into the mixing vessel. By stirring and heating at 110–120 °C, a viscous mass formed, a mass which would solidify immediately upon cooling. An analogous procedure was employed for the preparation of potassium ammonium nitrate, with the AS being replaced by solid potassium chloride.[7] The most crucial step of this procedure – the cooling and drying of the heated reaction mixture – will be detailed in the next section.

# 6 Drying of ammonium sulfate nitrate at the Oppau factory

As described in the previous section, the warm and viscous ASN slurry, obtained from the concentrated AN solution and solid AS in the mixing vessel of building 111, was led into covered sheet metal channels equipped with mixing screws. Air was blown through the channels to cool and dry the material. The mass would then solidify and break into small lumps (Figure 5.2), which were transported to storage on conveyor belts. During the winter of 1920/21, however, this mode of cooling and drying had been replaced with a new spray-drying procedure.[7,8]

Heated pipelines would bring the liquid mass of ASN slurry from the mixing vessel to a spray-nozzle, where the mass was atomized using compressed air (Figure 5.2). The admixture of pressurized air to the liquid mass would bring down its temperature from 110–120 °C in the mixing vessel and pipelines, to about 60 °C in the spray-nozzle.

The new spray-drying procedure gave rise to a snow-like and powdery ASN product, a material with a lower moisture content than that produced using the previous drying method. These characteristics facilitated the spreading of the material and thus its use as an agricultural fertilizer. The spray-drying initially took place in wooden, ventilated spray-chambers ("spray-stables") in building 111 (Figure 5.2), wherein the sprayed powdery material was collected on conveyor belts and transported for storage in silo 112. However, spray-drying later took place in silo 110, with the fertilizer slurry being led via a pipeline from building 111 into silo 110. For the ASN involved in the Oppau explosion, only the material prepared by the spray-drying process in silo 110 is relevant, and this potentially has major implications for the causes of the Oppau explosion disaster.

From the 27 April 1921 and onwards, the spray-drying of ASN was conducted in the free space of silo 110. According to the Bavarian commission, which comprehensively mapped the preparation of ASN at Oppau, two distinct periods for spray-drying of fertilizer material directly in silo 110, preceding the explosion on 21 September 1921, was distinguished.[8]

During the first period of spray-drying, lasting until the end of May 1921, the ASN slurry was spray-dried into overlapping fertilizer heaps on variable locations throughout silo 110, the piles covering each other in irregular patterns. At the end of this period, most of the fertilizer material contained in the northeastern part of silo 110 was removed. About 3200 tons of spray-dried, hardened ASN then remained in the southwestern part of silo 110, and about 300 tons along the eastern wall of the northeastern half of the silo.[8]

The second period of spray-drying in silo 110 started at the end of May 1921 and lasted until the 19 September 1921, only two days before the great explosion. The spray-drying procedure was now conducted in a different manner than during the first period. During this second period, the spray-nozzle was kept in a fixed position along the midline of the silo, at a 45° angle and a

height of 4.5 m, with the nozzle continually pointing in the direction of openings built into the floor of the silo. This row of holes led to the transport channel running beneath the silo (containing the conveyor belt running to silo 112 via building 111). Most of the sprayed material therefore fell directly through the floor openings and was immediately transported away on the conveyor belt. However, since the spray-jet was wider than the floor openings, over time, an elongated, horseshoe-shaped wall of fertilizer, approximately 15 m long, developed around the floor openings. The resultant fertilizer wall was referred to as the "bunker".[8]

During spray-drying, the air of silo 110 was filled with fertilizer dust, limiting visibility to a few meters. The problem was exacerbated by the very dry and hot climate prevailing through the summer of 1921 (for the Rhineland-Palatinate, the year 1921 was actually the driest on record between 1881 and 2011).[12] The dust gradually settled on roof beams, on the floor, on top of fertilizer material from the previous spraying period and along the outer walls of the silo as a loose white layer with a thickness of 35–45 cm, turning the inside of the silo to what was described by witnesses as resembling a winter landscape.[†] This fluffy material was not removed.[8]

For three days during the second period of spray-drying, from the 2 September until the 4 September, yet another modified drying procedure was tested out. Pure AN solution ("blank" solution) was sprayed onto the conveyor belt running beneath silo 110 towards building 111. In building 111, solid AS was then added shovel-wise to the conveyor belt before the material was transported away for storage in silo 112. Hence, this material was not stored in silo 110. The quantity of material involved totaled some 150 tons each of AN and AS, giving ~300 tons of such dry-mixed ASN.[6] This quantity of material was not particularly large when taking into account that an average of 200 tons of ASN was sprayed daily in silo 110, when spray-drying was conducted there.[8] According to witnesses, any solid AN deposited along the walls of silo 110 as a result of the modified procedure was rightfully regarded as potentially hazardous and carefully scraped away afterwards. The significant implications of all the facets of the different spray-drying procedures conducted at Oppau will be discussed later.

Production of AS at Oppau around the time of the explosion disaster totaled some 600 tons per day, of which approximately 100 tons was further processed into either ASN or potassium ammonium nitrate.[7] The annual production of ASN at Oppau amounted to 8252 tons in 1919 (first year of production), 52 614 tons in 1920 and 62 940 tons in 1921. For comparison, the production of potassium ammonium nitrate was 13 tons in 1917 (first year of production), 4216 tons in 1918, 13 734 tons in 1919, 16 761 tons in 1920 and then declining rapidly to 312 tons in 1921.[7] For the most part, ASN had gradually replaced potassium ammonium nitrate.

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[†] It is important to keep in mind that this layer of loose ASN material covered the older and more hardened fertilizer material located beneath. The presence of the caked fertilizer material therefore necessitated the blasting operations, something which would probably not have been the case if only the loose ASN material was present. In addition, also the powdery ASN material would consolidate over time.

# 7    Disintegration of ammonium sulfate nitrate at the Oppau factory using safety explosives

During the course of the investigations into the Oppau explosion, it quickly became obvious that the explosion had originated in the stock of ASN kept in silo 110, and that it was immediately occasioned by the application of cartridge safety explosives used to break up congealed piles of fertilizer material. A discussion of the apparent risk aspects associated with the application of such a drastic procedure on a material containing a known explosive component (AN), and the evaluations undertaken by BASF in advance, to ensure safety (or lack of such), will be postponed to a later section. In this section, the procedures themselves will be detailed, so as to adequately fundament the upcoming discussion.

In spite of the addition of AS to AN, in an attempt to somewhat diminish the hygroscopic nature of the latter, by formation of ASN, the 50:50 ASN material prepared at Oppau nevertheless had a strong tendency to solidify on storage. The work associated with the removal of fertilizer material from silo 110 was delegated to a subcontracted transport firm called Kratz.[3,5] These efforts regularly involved the use of explosives to ease the removal of hardened fertilizer material.

The relevant high explosive in these operations was Perastralit, a cartridge safety explosive manufactured by the company Sprengstoffabriken Hoppecke AG in Würgendorf, on the basis of surplus military explosives (old artillery shells). According to the manufacturer, Perastralit was a mixture of 90 parts of the military explosive Ammonal (the German version of Ammonal consisted of 72% AN, 16% aluminium and 12% trinitrotoluene) and 10 parts of the military explosive Perdit (72% AN, 10% potassium perchlorate, 15% nitro compounds and 3% wood flour). The composition of Perastralit should therefore equal 72.0% AN, 1.0% potassium perchlorate, 12.3% nitro compounds (mainly dinitrotoluene), 14.4% aluminium and 0.3% wood flour.[7]

In reality, this explosive was apparently poorly mixed at the factory and analyses conducted after the Oppau explosion revealed that the composition could vary considerably from one cartridge to another, as could the appearance. In Table 7.1, the results of chemical analyses of different cartridges of Perastralit, as reported by German investigators, are listed together with the analogous results from analyses conducted as part of the investigation in Britain (using cartridges sent from Germany).[7,10]

Prior to the commencement of blasting operations in the fertilizer silos at Oppau, other explosives had been tested out by BASF, including Koronit (a chlorate explosive), Perwestfalit (an AN explosive resembling Perastralit) and trinitrotoluene (TNT). The actual blasting operations were first conducted using the explosive Astralit (an AN explosive similar to Perastralit, but without any perchlorate) before going over to Perastralit exclusively from February-March 1921 and onwards.[3,4,6,7]

*Table 7.1    Results from the chemical analyses of Perastralit carried out in Germany and Britain after the Oppau explosion disaster.[7,10]*

| Component | Analyses by BASF and Wöhler [%][a] | Analyses by Beyersdorfer [%][b] | Analyses by the Woolwich Research Department [%] |
|---|---|---|---|
| Ammonium nitrate | 59.0–64.0 | 31.1 | 65.1 |
| Potassium perchlorate |  | 4.9 | 2.4 |
| Nitro compounds[c] | 19.3–23.0 | 31.0 | 20.2 |
| Aluminium[d] | 13.4–15.7 | 19.4 | 10.3 |
| Wood flour | 0.5–1.0 |  | 2.0 |
| Moisture[e] |  | 10.9 |  |
| Remainder |  | 4.8 |  |

[a]Interval values from several analyses. [b]Paul Beyersdorfer (1886–1971) in Frankenthal, particularly known for his work in the sugar industry, on dust explosions, and later also on glass materials. This analysis was obviously heavily influenced by moisture, eroding the AN content. [c]Trinitrotoluene (TNT) included. [d]In the form of chopped foil according to the results from Britain. [e]Some cartridges had obviously been severely affected by moisture.

As seen from Table 7.1, the chemical composition of the Perastralit explosive varied significantly from one cartridge to another, and it did not coincide with the factory specifications. The use of two surplus military explosives (Ammonal and Perdit) as starting materials apparently caused large fluctuations in the resulting Perastralit.

Perastralit does not have a particularly high detonation pressure when compared to the other explosives used in the testing programs, that will be detailed later, but its aluminium content gives it a relatively high temperature of detonation.[‡] Nevertheless, the effect of the varying composition of Perastralit was addressed specifically in separate experimental trials during the investigations following the Oppau explosion,[6] and it was found that it could not have been of decisive importance.

The blasting operations in the fertilizer silos at Oppau were accomplished in various manners. Regularly, 2–5 cartridges of Perastralit were applied. The cartridges were equipped with standard detonators (nr. 8), containing 2 g of mercury fulminate each, and ignited using either a fuse or electrical ignition. On some occasions, 5–10 cartridges of Perastralit, even up to 18

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[‡] According to technical information located by the author in the BASF corporate archives, Perastralit in the lead block test yielded an expansion value of 369.5 cm$^3$ when including the contribution from the detonator, and 349.8 cm$^3$ without the 19.7 cm$^3$ contribution from the detonator (No. 8, copper casing, TNT base charge). See section 9 for details on the lead block expansion test.

cartridges, could be loaded in a single borehole.[8] On a single occasion, 25 boreholes containing a total of 150 cartridges were ignited simultaneously by electricity.[7,8] No damaging effects had been detected, and thousands of such blasting operations had been conducted safely by the time of the Oppau explosion. Such operations were estimated by the factory management to have included as many as 20 000–30 000 successful shots.[3-7]

Notably, although a very large number of successful blasting operations on hardened fertilizer material had been conducted at Oppau, most of these had not been undertaken on the spray-dried ASN material in silo 110. The contents of this silo had been removed with the help of explosives two times during 1920, but that could not have been on spray-dried material. In May-June 1921, after the initial period of spray-drying in silo 110 had been completed, 100–120 shots with Perastralit were carried out (without incident) to remove the fertilizer material in the northeastern part of the silo, described in the preceding section.[3,4] It is important to keep in mind the different implementations of the spray-drying process during the first and the second periods of spray-drying in silo 110.

The second period of spray-drying in silo 110 was completed on 19 September 1921, and the removal of fertilizer material from the silo was started on the 20 September. The first blasting operation was, according to witnesses, carried out that afternoon, although some such operations may have been undertaken earlier that day (the source material is not entirely consistent).[7] The blasting took place on the ~2.5 m tall horseshoe-shaped wall surrounding the spray-nozzle and the floor openings of the silo (at the end opposite to the nozzle-head). Most probably, the operations involved 13 shots, consuming a total of some 50 cartridges of Perastralit.[3,4,6]

Just before 07:00 on the next morning, the day of the ill-fated operation, the chief blaster Hermann Humpe (1882–1921)[12] was observed by witnesses while preparing a blasting operation, using an iron tube and a shovel handle to prepare a borehole and then loading it with 1–3 Perastralit cartridges and a fuse from an ammunition box (electrical ignition was not available). It is assumed that the boreholes were placed somewhere around the outer slopes of the aforementioned horseshoe-shaped wall ("bunker"), at least partly in the freshest and loosest fertilizer material contained there. The boreholes were placed 80–120 cm apart and loaded with Perastralit, detonators and fuses. It was determined that the chief blaster had, at most, 66 cartridges available this morning. In all likelihood, the first Oppau explosion at 07:32:14 coincided with the first shot of this blasting operation.[7]

When the particulars of this sequence of events are taken together, a quite remarkable set of conspicuous circumstances emerges, above all as seen from today's vantage point. Thousands upon thousands of shots with high explosives had evidently been accomplished safely on ASN fertilizer material stored at the Oppau factory. About a hundred shots or so were completed successfully on the ASN kept in silo 110 that was spray-dried according to the first procedure (used from the 27 April until the end of May 1921). Then, rather suddenly, when ASN that had been spray-dried according to the second procedure (used from the end of May until 19 September 1921) was broken up with explosives, a disastrous decomposition of a large part of this fertilizer material followed already at the first shot on the second day of such operations.

The significance of the timing of these events cannot be ignored, yet it was only slowly realized at the time. Today, this remains one of the most common and unfortunate misconceptions about the Oppau explosion disaster – that somehow, tens of thousands of shots had been performed safely on the same type of fertilizer material, for then to fail disastrously as a random incident on the 21 September 1921. In reality, as a result of the adoption of a new drying procedure for ASN at Oppau, and the loosening of this particular material with high explosives, a disastrous decomposition followed rather swiftly.

# 8    The purity of the ammonium sulfate nitrate produced at the Oppau factory

In the previous sections, factual descriptions of the history and layout of the Oppau factory, the production of ASN, its subsequent drying and storage in silos and the sequence of the events leading up to the calamity on the morning of the 21 September 1921, as well as the catastrophe's immediate aftermath and ensuing inquiries, have been narrated. Now, the more subtle parts of the investigation efforts – those that relate to the clarification of the fundamental causes of the incident – will be explicated. As the account progresses, the original material will be strengthened through the application of modern methods, methods better equipped to quantify the energetic phenomena involved than the more rudimentary approaches available in the 1920s.

As the sequence of events leading up to the Oppau explosion were clarified, meaning the actualities pertaining to how the explosion obviously had originated in the ASN in silo 110, and how it was immediately occasioned by the loosening of caked fertilizer material there with the explosive Perastralit, the much harder task of charting the detailed energetic behavior of ASN manufactured at Oppau was in full swing. For obvious reasons, the chemical composition of the ASN fertilizer material, and the identity of possible contaminants contained in it, became an early focal point during the investigations.

Through time, a common characteristic of great disasters, most pronounced in the ones that become prominent media events, is the virtual flood of propositions relating to facts and causes that is promoted by those believed to have relevant insight. In this respect, the 1920s were no different.[12,13] In the aftermath of the Oppau explosion, numerous assertions relating to possible contaminants in the Oppau salt were forwarded from all corners of the scientific community. These contaminants were believed to dangerously heighten the material's sensitivity towards thermal and mechanical stimuli.[7,8,12]

The list of possible contaminants included species such as sulfuric acid, nitrites (particularly ammonium nitrite), azides, hydrazine, chlorates, perchlorates, elemental sulfur and even the hideously explosive compound nitrogen trichloride. The absence of such contaminants was conclusively established through a series of exhaustive chemical analyses on scattered fertilizer material from silo 110, as well as material salvaged from storage silo 112. Moreover, no truly convincing explanation for the formation of these contaminants could be advanced. The proposed formation of Ammonal-like mixtures (well-known explosives) through the introduction of small metal particles into the ASN material during manufacture, could not be substantiated either. The analyses carried out in Britain also ruled out the presence of sulfides, sulfites, thiocyanates and pyridine, impurities associated with AS prepared by other methods (using ammonia from coke-oven gas). Only a miniscule amount of organic matter as carbohydrates (~0.03%) could be detected.[9]

Although the presence of conspicuous contaminants was refuted, the Oppau salt nevertheless contained some known impurities. Aside from its varying moisture content (approximately 1–4%), the ASN produced at Oppau, as mentioned previously, contained up to 0.3% chloride due to the sodium chloride contained in the gypsum starting material used for the production of AS, as well as some of the gypsum itself. In addition, the Oppau salt could contain up to 0.35% rust (iron oxides), something which imparted a yellow to brown color on the fertilizer material. The rust originated from the iron-based production equipment. As a matter of fact, both chlorides and iron oxides can influence thermal characteristics of ammonium nitrate to a significant extent,[47-49] and this was also understood in the 1920s (at least to a certain degree).[8]

Perhaps the most contentious issue tackled during the investigations of the Oppau explosion disaster was the crucial subject of whether the fertilizer material stored in silo 110 had a composition that deviated significantly from the factory specifications, by containing an excess of AN relative to AS. The grander part of later discussions relating to the Oppau explosion has also been centered on this topic.

To settle the matter, a number of samples were collected by investigators shortly after the explosion, including scattered material from silo 110, as well as samples from the damaged storage silo 112. Analyses of the samples were conducted both in Germany and in Britain.[3-9] All relevant chemical analyses conducted by BASF during the production of the involved materials were closely scrutinized as well.

In summary, although many ambiguities remain (after all, none of the fertilizer material that actually decomposed was available for analysis), no definite evidence was ever amassed to corroborate the assertion that the ASN produced at Oppau during the relevant period contained a significant excess of AN. Contrariwise, no analysis of the content of AN relative to AS in the fluffy ASN material, that lined most of silo 110 as a result of the new spray-drying procedure, was apparently ever conducted by BASF or others. Thus, this issue very much remains unsettled to the present day.

The factory guidelines for production of ASN at Oppau strictly specified a 50:50 ratio by weight of AN relative to AS. The fertilizer material was analyzed by BASF following production for its moisture level and its total nitrogen content, but not the separate shares of AN and AS. As the fertilizer was prized and sold on the basis of its nitrogen content, the factory and the customers had opposing financial interests regarding the outcome of the nitrogen analyses. The factory aimed for the highest possible value of nitrogen, thereby obtaining the best possible prize for its fertilizer product, whereas the customers naturally had an interest in a low value for measured nitrogen, so as to pay as little as possible. These divergent incentives are important to keep in mind, because in ASN, composed of AN (containing ca. 35.0% N in pure form) and AS (containing 21.2% N in pure form), the nitrogen content increases as the proportion of nitrate relative to sulfate rises. The analyses conducted by BASF, therefore, had no particular reason for underestimating the content of AN in the fertilizer, rather the opposite.

A large number of control samples were taken out at several phases during production, and analysis protocols kept at Oppau. These were successfully recovered after the explosion and showed no significant anomalous deviations in the analysis results, relative to the fertilizer specifications.[3,5] Furthermore, the investigations could not demonstrate that any carelessness or negligence during production had taken place, possibly influencing the mixing ratios of the two fertilizer components. It was believed, at least by some fractions (due to political conflicts prevalent at the time), that such carelessness could have been perpetrated by the factory personnel at Oppau as the result of a salary reward system that was in function at the time of the accident (productivity at the cost of safety).

Out of a total of 42 samples of ASN salvaged from the remnants of the mostly collapsed silo 112 after the explosion, 5 samples contained more than 60% AN by analysis (all from the northern part of the ASN heaps in silo 112).[3,5] However, 2 of those 5 samples were taken from the same location. In addition, these samples may have been weathered due to the collapsed state of silo 112 after the explosion. It was speculated that rain or other influences could have affected the state of the material in an uncontrollable manner. The validity of the analyses was therefore in doubt, although water would probably lower the AN content rather than increase it (because of its greater water solubility relative to AS).

More significantly though, small pockets of AN-rich material could also have formed in some parts of the stored ASN as a result of cleaning carried out in the AN vessel in building 111, loosening crusts of AN material that were later transported to silo 112.[7] Scattered fertilizer material from silo 110 was also recovered, and all these samples conformed to the specifications. Likewise, fertilizer samples from silo 112 and scattered material from silo 110 were sent to Britain. Meticulous analyses carried out there could not detect any significant deviation from the product specifications.[9]

While analyses on available ASN, from samples extracted both prior to and after the explosion, could not establish the existence of fertilizer material with a composition deviating significantly from the specifications (except the samples mentioned above), the situation is evidently not straightforward regarding the fertilizer material spray-dried in silo 110, a considerable part of which was consumed in the explosion. When the hot liquid mass of AN, AS and ~8% water was spray-dried (see previous section), separation of the two fertilizer components was conceivable. This was a subject of much discussion and controversy following the explosion disaster.[3,4,7,8] After all, due to the greater water solubility of AN compared to AS, the liquid fertilizer mass fed to the spray-nozzle consisted of AS particles suspended in a warm, supersaturated aqueous solution of AN and AS. The ensuing crystallization and drying during the atomization process was a poorly controlled event.

During the first period of spray-drying in silo 110 (from the 27 April until the end of May 1921), samples were continually taken out at various locations in the silo and analyzed for their nitrogen content. No irregularities were detected. However, since the fertilizer material during this period was spray-dried into small piles throughout the silo, covering each other in irregular patterns, no major separation of AN and AS was to be expected. The moisture content of the spray-dried material was also analyzed and found to be ~4% – a relatively high value.[8] A high

moisture-content most probably suppressed separation of the components during the spray-drying process and facilitated the formation of double salts.

During the second period of spray-drying in silo 110 (from the end of May until 19 September 1921), the spray-nozzle was stationary, and most of the dried material fell directly onto the conveyor belt running below silo 110 and was transported away. However, as already detailed, a considerable part of the spray-dried material missed the floor openings to the conveyor belt running beneath and deposited around the openings as a horseshoe-shaped wall. In addition, fine dust floated beyond this "bunker" and settled as a powdery material lining most of silo 110.

Importantly, although samples were taken out of the mentioned fluffy surplus material during production, this material was only analyzed for its moisture content, and not its nitrogen content. The material was found to be considerably drier than the material prepared during the first period of spray-drying, having a moisture content of only ~2%. This low moisture content was, at least partly, due to the especially dry and hot weather prevailing in the summer of 1921.[8,12] Furthermore, since the nitrogen content of the fluffy material was never determined, the presence of excess AN is conceivable, perhaps even likely. The lack of any specific analyses of the amount of AN relative to AS in this fluffy ASN material was later a source of criticism towards BASF, particularly by Escales.[6]

It was speculated by the Bavarian commission that during spray-drying of ASN, the material from the center of the spray-cone would be enriched in larger particles of the less water-soluble AS, falling onto the conveyor belt, while finer dust from the outer edges of the spray-cone would be enriched in AN, floating out into the silo.[8] These suspicions were strengthened by analysis of the fine material that gathered in the dust compartments above the spray-chambers ("spray-stables") in building 111 (Figure 5.2). This dusty material contained up to 75% AN. Spray-experiments carried out during the investigation could also support the hypothesis that a partial separation of the fertilizer components during spray-drying was feasible.

Nevertheless, the Reichstag commission contended the significance of this supposition, arguing that the higher temperatures and better ventilation (sometimes aided with a ventilator) in the spray-chambers of building 111, relative to those of silo 110, accelerated the drying process to such an extent that a partial separation of components was possible only there.[3,4] In hindsight, taken together with the fact that the Oppau explosion was synchronized with the use of high explosives on the fluffy fertilizer material deposited during the second period of spray-drying in silo 110, such a separation does not seem unrealistic. However, such a separation may not be essential either. Further discussion of this notion will follow in the sections to come.

Aside from the chemical analysis, the samples of ASN that had been sent to Britain were also submitted to a range of other analytical procedures.[9] For instance, the ASN material was separated into different fractions by gravity, and the optical properties of these fractions were examined by geologists. X-Ray analyses and experiments on the hardening of the salt by pressure, as well as a large number of experiments that sought to determine whether it possessed explosive properties, were conducted. Many of these will be detailed later.

# 9 Testing of the explosive capabilities of ammonium sulfate nitrate prior to the Oppau explosion disaster

At the time of the Oppau explosion, the explosive properties of AN were already quite well recognized, having been established by the Dutch chemist Cornelis A. Lobry de Bruyn (1857–1904) in 1891.[50] However, AN was considered more as a "relative explosive" than an explosive by itself,[8] in the sense that it usually mandated the use of additives, and in its pure form was known to detonate only under the most severe conditions.[29] On the other hand, AS possesses no such properties, but its ammonium content nevertheless represents some fuel-value in admixtures with oxidizing materials.

Thus, ASN was therefore understood by BASF to hold an explosive potential that depended on the ratio nitrate to sulfate. In order to establish the requisite quantities of AS required to extinguish the explosive potential of AN, and thereby allow the safe disintegration of caked ASN with explosives, BASF chemists set out to survey the explosive properties of such mixtures.

In particular, three BASF scientists, among them the distinguished chemist Carl Müller (1857–1931), had examined the explosive characteristics of potassium ammonium nitrate and ASN through the Trauzl lead block expansion test.[6] The Trauzl test, named after the Austrian chemist, industrialist and explosives expert Isidor Trauzl (1840–1929), was a standard method for testing the strength of explosives at the time.[51] A tinfoil-wrapped sample (10 g) was introduced into a cavity (125 mm deep, 25 mm in diameter), drilled into a cylindrical lead block (200 mm tall, 200 mm in diameter). The sample was equipped with a standard copper detonator (nr. 8) containing 2 g of mercury fulminate, tamped with quartz sand and fired electrically. The net volume increase of the resulting pear-shaped cavity was then measured by filling it with water (the 61 cm$^3$ cavity volume, usually also the ~17 cm$^3$ contribution by the detonator, were subtracted). A standard value of reference was that of TNT, which gives a net expansion of approximately 300 cm$^3$.

In the first part of the investigations undertaken by BASF, conducted early in 1918 and primarily directed towards potassium ammonium nitrate-type mixtures, a number of AN mixtures were tested in the lead block. Then, in a series of tests taking place from mid-December 1919 until January 1920, AN-AS mixtures, both double salts and simple mechanical mixtures, were tested in the lead block.[6] Some of the results are reproduced in Table 9.1. From this point on, mechanical (dry) mixtures of AN and AS will be referred to as AN-AS, while the term ASN will be reserved for AN and AS that have been contacted in aqueous solution, as they were at Oppau.

*Table 9.1    Net expansions of AN-AS mixtures and ASN in the Trauzl lead block test.[6]*

| Composition | Net expansion [$cm^3$][a] |
|---|---|
| Oppau salt: 50% AN - 50% AS (as ASN) | 3 |
| 2AN·AS (double salt)[b] | 7–9 |
| Oppau salt with 0.36% $Fe_2O_3$ | 7–11 |
| 55% AN - 45% AS (mixture) | 5–11 |
| 60% AN - 40% AS (mixture) | 35–39 |
| 75% AN - 25% AS (mixture) | 126–129 |
| 75% AN - 25% AS (double salt + AN) | 126–131 |
| 100% AN | 150–156 |

[a]For these values, only the 61 $cm^3$ cavity volume has been subtracted in the calculation of the net expansion, as the contribution of the detonator often depended on the test sample. The given ranges are the results of two parallel shots for each compound/mixture. [b]The double salt corresponds to 55% AN - 45% AS by weight.

On the basis of the experiments (Table 9.1), it was concluded that below a threshold value of about 60% AN, ASN held little or no explosive potential. Furthermore, a pronounced difference between the double salt versus mechanical mixtures could not be established. To provide a safety margin relative to the composition of the 2AN·AS double salt, both with regard to its explosive potential and tendency towards congealment, a slight excess of AS was employed, resulting in the 50:50 ratio by weight of AN and AS employed in the ASN produced at Oppau.

Although a very limited number of experiments on the potential explosive capabilities of potassium ammonium nitrate were conducted at larger scale than that employed in a lead block test, such large-scale testing was apparently never carried out with ASN.[6]

Only two months prior to the Oppau explosion, on the 26 July 1921, a terrible explosion accident had hit the explosive factory of Lignose AG in the town of Kriewald (today Krywałd, near Knurów, in Poland).[52,53] A railway wagon containing congealed AN had exploded while workers had tried to loosen the material with the help of explosives, killing 19 people, injuring 23 others and destroying the entire factory located there.[6,12,52,53] In Kriewald (Krywałd) and Schyglowitz (today Szczygłowice), all windows were broken, and the roofs had been torn off many of the houses there.[52]

BASF apparently became aware of this incident only after the Oppau explosion, and it was surmised during the ensuing Oppau investigations that perhaps BASF would have reconsidered their procedures in the light of the Kriewald accident, had they known about it.[12]

However, considering the fact that the railway wagon at Kriewald contained pure AN, this conjecture is doubtful, and the incident could only have served to advance some general reservations. In light of the testing conducted by BASF in 1919/20 (Table 9.1), as well as of separate testing undertaken on pure AN by others, the BASF researchers apparently had no misapprehensions concerning the explosive properties of undiluted AN, as the very purpose of their testing had been to establish the requisite addition of AS necessary to eliminate this potential. Still, the incident at Kriewald is a clear indication of the overall insignificance attributed to the potential explosivity of AN at the time (not necessarily by BASF), despite the evidence to the contrary.

Following the Oppau explosion, and in the discussions that had erupted in scientific circles regarding the dangers posed by AN, some notable testimonies to its purported insensitivity were forwarded, particularly by researchers experienced in the handling and production of Ammonal – by then an important AN explosive.[54] Munroe, in charge of the American efforts seeking to pin down the explosive characteristics of AN, concluded that "ammonium nitrate when stored by itself in wooden receptacles and apart from explosive substances is, for transportation and storage, not an explosive".[29] Such ambivalence regarding the energetic properties of AN is tangible all the way up to present times.

# 10 Testing of the explosivity of Oppau ammonium sulfate nitrate after the Oppau explosion disaster

It was realized by the scientific-technical experts engaged in the Oppau disaster investigations that the experiments undertaken by BASF on ASN and AN-AS mixtures using the Trauzl lead block test were to some degree incomplete, with respect to shedding light on the blasting operations undertaken to fragment the caked fertilizer material.

In the lead block test, only a small sample (10 g) is initiated with a standard blasting cap, and it was known at the time that some explosives that are relatively inert towards detonation initiated by a standard blasting cap, could nonetheless be successfully detonated with the help of a reinforcing middle charge (booster) consisting of a powerful secondary explosive. In addition, the experiments in the lead block had not properly examined the influence of the physical characteristics of the fertilizer material, such as the particle size distribution, porosity/density or temperature. Therefore, in the aftermath of the Oppau disaster, a series of comprehensive test programs were carried out to probe the shock sensitivity of ASN and AN-AS mixtures in minute detail, both in Germany and in Britain.[6,7,10,55]

It is not of primary importance for the discussion herein to explicate the large number of detonative tests conducted on the Oppau salt (50:50 ASN), much because they, on the whole, only attested to its inertness. A cursory overview will therefore suffice.

Testing of the sensitivity towards mechanical shock in a standard falling weight (drop hammer) machine provided only very slight indications of incipient decomposition, much less than for pure AN.[7,10] Likewise, friction was shown to have little or no effect on the Oppau salt.[7,10]

The Oppau salt was found to be more stable towards thermal stimuli than AN. A heating experiment with Wood's metal (eutectic Bi-Pb-Sn-Cd alloy) bath gave vigorous effervescence at 280 °C, but no explosion, even at 360 °C.[7] The content of iron oxide and chloride impurities in the Oppau salt did not seem to have influenced its thermal stability to an appreciable extent. Various experiments with intense local heating of the Oppau salt by either cook-off-type testing over free flame or through use of pyrotechnic heating charges, whether conducted in a sheet metal container, steel tube, steel shell, glass tube or the like, provided no evidence to corroborate a notion that the ensuing thermal decomposition of the Oppau salt was capable of transitioning into fully self-sustained explosive decomposition.[7,10]

Both at the CTR (Berlin) and in Britain, similar small-scale testing in the Trauzl lead block, as conducted by BASF prior to the Oppau explosion, was carried out and gave analogous results (Table 9.1).[7,10] Attempted shock-initiation of the Oppau salt at the kilogram scale in an iron pipe (36 cm length, 8.3 cm inner diameter, 4 mm wall thickness) using a booster charge of pressed picric acid (370 g) failed to induce self-sustaining detonation of the fertilizer material.[7]

As part of the British investigation efforts, charges of Oppau salt from the ~10 g scale (½ ounce) up to the ~100 kg scale (250 pounds) were subjected to strong detonative impulses.[10] This included tests in small cylindrical steel bombs (with the Oppau salt heated to as much as 155 °C prior to testing), in 18-pounder shells with tetryl booster charges (30 g), in 2-inch mild steel steam pipes (2–3 feet length and 0.23 inch wall thickness) with various booster charges (including tetryl, picric acid, Perastralit and pentaerythritol tetranitrate), in 4-inch cast iron pipes (6 feet length, ⅛ inch internal diameter) sunk in the ground and, finally, two grand experiments in a plugged 60-pounder gun jacket (14 feet long) containing 250 pounds Oppau salt with either a combined Perastralit (200 g) and tetryl (20 g) booster charge or a large tetryl (1 pound) booster.

The British report concludes in clear terms that the testing had brought out "the fact that the salt cannot propagate a detonation even for short distances", that "no definite evidence is provided that any of it detonated at all", even under conditions of heavy confinement, and that the Oppau salt could only augment the violence of explosion of the initiator-booster to a negligibly small extent.[10]

Richard Escales reported that he had, with the help of coworkers, conducted a series of sixteen tests on ASN material that had been "sent from the factory" (using detonators and Perastralit cartridges that had been seized by the police after the Oppau explosion).[6] These tests were carried out in small wooden chests (typical dimensions were 20×14×15 cm) containing a few kilograms of ASN. It was, however, difficult to extract any conclusive results from these experiments. At least partial gas-formation ("gassing") of the ASN salt was detected, but no pronounced blast effect. It could not be ascertained whether this gas-formation took place consistently or only under especially advantageous conditions. The probable cause of the gassing was ascribed to the strong heat-pulse provided by the aluminium content in the Perastralit charges, and the gassing was not believed to be fully self-perpetuating.

In essence then, the investigations carried out in Germany and Britain could only further substantiate their incapability of imparting a detonation to the Oppau salt of the correct 50:50 composition. In the guidelines prepared in April 1923 by the central German regulatory authorities for explosives and munitions manufacture, concerning preparation, properties, handling and storage of AN and ASN, it was spelled out in clear terms that 50:50 ASN "is no explosive".[56] Furthermore, in light of the demonstrated inability to amass unambiguous evidence to support the assertion that the ASN contained in the ill-fated silo 110 on the day of the explosion had a composition deviating markedly from the 50:50 BASF specification (as narrated in a previous section), the true cause of the Oppau explosion seemed more enigmatic than ever.

# 11    Thermochemical modeling of ammonium nitrate-ammonium sulfate decomposition

Given the failure to unveil an intrinsic explosive danger posed by the BASF ASN (Oppau salt), the investigations carried out following the Oppau explosion found it prudent to chart the sensitivity of various mechanical AN-AS mixtures for comparison (as an addition to the testing undertaken by BASF, prior to the accident), hoping to shed light on how the ratio of its two constituents could attenuate the receptivity towards shock stimuli. The researchers strengthened their analysis with thermochemical considerations.[7] At this point, however, the original findings will be reassessed through the application of modern computational methods, using tools that can much more accurately derive such thermochemical values. The new analyses will deliver valuable insight and provide the first clues to how the theoretical foundation in existence at the time misled the efforts to disentangle the causes of the explosion disaster.

In Figure 11.1, the values calculated by the Reichstag commission specialists for the heat of explosion of AN-AS mixtures are graphed. With the techniques available at the time, these values were calculated by choosing mixtures corresponding to convenient stoichiometric ratios of the two salts, followed by postulating a sensible decomposition reaction with associated explosion products ($H_2O$, $N_2$, $SO_2$, $H_2$ and/or $O_2$) and calculating a heat of explosion through a straightforward, essentially enthalpic analysis.[7]

Using the thermochemical computer code EXPLO5 V6.02,[§] the isobaric heat of combustion at 1 atmosphere can be calculated using the same stoichiometric points. These values are also graphed in Figure 11.1. For convenience, the sign has been reversed for all heats of decomposition, both in Figure 11.1 and in the figures to follow, facilitating the graphical presentation.

As is apparent in Figure 11.1, the computational analysis closely trails the original curve set up in the 1920s.[7] However, since the values for the heat of combustion of the AN-AS mixtures mapped in Figure 11.1 are based on the isobaric conversion of AN-AS at atmospheric pressure, this analysis does not accurately model the decomposition as a detonation process (the use of the term explosion is therefore somewhat dubious in this context). Nevertheless, in the isobaric analysis, a pivot point at the ~55:45 AN-AS weight ratio, corresponding to the stoichiometry of the 2AN·AS double salt, is manifest in Figure 11.1. This event occurs due to the transition from an oxidizer-lean decomposition zone below the 55:45 point, to an oxidizer-rich decomposition zone above this point. At the 55:45 point, the decomposition products consist almost exclusively of $H_2O$, $N_2$ and $SO_2$ (Figure 11.1).

In conclusion, based on this simplistic analysis, resulting in the curves of Figure 11.1, the ratio interval up to 55:45 AN-AS was identified as particularly critical regarding the energetic behavior of AN-AS, identifying a 55:45 pivot point at which the heat of decomposition

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[§] **Important note**: For all calculations involving EXPLO5 V6.02, the number of chemical species included in the actual calculations is considerably larger than the dominant products discussed in the main text and given in Figures 11.1–11.3.

transitions from rising steeply with the AN content into a slower growth afterwards.[7] Yet, the experimentally obtained lead block expansion values (Figure 11.1) point towards 55:45 to 65:35 as the interval in which the energetic behavior of AN-AS becomes more pronounced. The action in the lead block appears somewhat "delayed" relative to the rise in the heat of combustion up to the 55:45 point. This discrepancy was duly noted by Kast, who admitted that the theoretical methods of the time were incomplete.
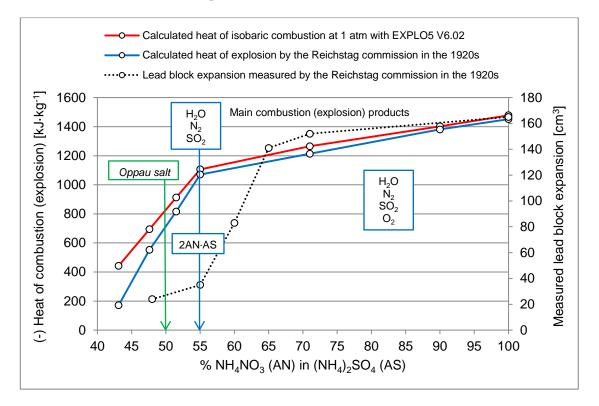


*Figure 11.1  The (negative) heat of explosion of AN-AS mixtures as calculated by the Reichstag commission in the 1920s (blue line), compared to the (negative) isobaric heat of combustion of the same mixtures calculated with EXPLO5 V6.02 (red line). The experimental lead block expansion values (with the contribution from the detonator included) measured by the Reichstag commission for such mixtures are also plotted (dotted line). **Note**: Only the major reaction products are indicated.*

Naoúm and Aufschläger presented a similar thermochemical analysis to that of the Reichstag commission in Figure 11.1, in their 1924 publication on the energetic behavior of AN-AS mixtures, in which they identified the same 55:45 pivot point (based on the doctoral work of Aufschläger, supervised by Naoúm).[55] These authors also, in analogy to the Reichstag commission, contrasted this behavior of AN-AS mixtures to the dissimilar behavior of AN-potassium chloride mixtures (that displayed no pivot point).

The Oppau explosion, however, is almost certainly coupled to detonation rather than isobaric combustion. In a detonation event, in contrast to an isobaric combustion at atmospheric conditions (Figure 11.1), the detonation products first reach equilibrium at the end of a narrow reaction zone, at very high pressures and temperatures, and subsequently expand towards ambient conditions. In this high-pressure pathway, possible detonation products may be constrained by phase transitions. In the 1920s, the theoretical frameworks that could model such a detonation event did not yet exist, and the scientists had, to a large extent, to rely on their chemical-physical intuition. Because of this, the scientific-technical experts in the investigating commissions failed to appreciate an important aspect of the AN-AS decomposition behavior, during a detonation event.

Displayed in Figure 11.2 are the values for the heat of detonation of AN-AS mixtures at a constant bulk density of 1.1 g·cm⁻³ (typical value for the density of much of the fertilizer material contained in silo 110 at Oppau), calculated by using the thermochemical computer code EXPLO5 V6.02, applying the Becker-Kistiakowsky-Wilson (BKW) equation of state (EOS) for gaseous detonation products and the Murnaghan equation of state for compressible condensed products.



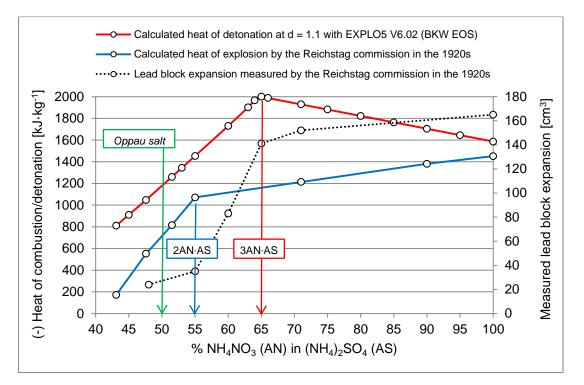Figure 11.2  *The (negative) heat of detonation of AN-AS mixtures calculated with EXPLO5 V6.02 at a constant density of 1.1 g·cm⁻³ (using the BKW EOS) compared to the (negative) heat of explosion (combustion) as calculated by the Reichstag commission in the 1920s. The experimental lead block expansion values (with the contribution from the detonator included), measured by the Reichstag commission for such mixtures, are also plotted.*

Upon application of the more recent model of detonation, a different picture to that of the simplified analysis in Figure 11.1 now arises. The heat of detonation of AN-AS mixtures rises steeply up to a pivot point at the ~65:35 AN-AS ratio, corresponding to the stoichiometry of the 3AN·AS double salt, and then decreases slowly towards pure AN (Figure 11.2). Unlike the thermochemical analysis conducted in the 1920s, the heat developed by the AN-AS mixtures continues to rise sharply beyond the 2AN·AS (55:45) point, up to the 3AN·AS (65:35) point.

This has important implications, because it suggests that mixtures of AN and AS have dispositions for explosivity that does not weaken beyond the 55:45 AN-AS ratio, but rather beyond the 65:35 ratio. Although merely indicative, the trend in the experimentally obtained lead block expansion values obtained by the Reichstag commission, also plotted in Figure 11.2, shows a rather startling correspondence to the trend in the values for the (calculated) heat of detonation, as both curves reach their maxima in the vicinity of the 65:35 ratio. By application of the Jacobs-Cowperthwaite-Zwisler (JCZ3) EOS for the gaseous detonation products in the calculations, instead of the BKW EOS, the same crucial 65:35 pivot point is identified.

In conclusion, from a modern theoretical standpoint, the AN-AS mixtures gather explosive potential rather quickly in the 50:50 to 65:35 AN-AS interval region, making any AS-lean zones in the Oppau fertilizer material, contained in silo 110, even more consequential than the investigators in the 1920s could possibly have appreciated from their theoretical understanding at the time.

What factors determine the dissimilar trends seen in Figures 11.1 and 11.2? Modern tools can elucidate the chemical composition of the detonation products (using free energy minimization techniques), furthering our understanding of the explosive behavior of AN-AS mixtures. In Figure 11.3, the quantity of gaseous detonation products and the detonation temperatures of AN-AS mixtures are plotted, as calculated with EXPLO5 V6.02, at a constant density of the AN-AS mixture at 1.1 $g \cdot cm^{-3}$ (the fertilizer material that exploded at Oppau probably had a density lower than this, but this is relatively inconsequential for the conclusions extracted from the calculations).

The 65:35 pivot point, pronounced in both Figures 11.2 and 11.3, is apparently associated with the formation of $H_2O$, $N_2$ and $H_2SO_4$ as the sole prominent detonation products (the calculated numbers are associated with some degree of uncertainty because the compressibility factors in Murnaghan EOS may be inaccurate, particularly for sulfuric acid). Significantly, the larger part of the sulfuric acid is formed in condensed (liquid) form. The distinction between an oxidizer-lean zone below the 65:35 point, and an oxidizer-rich zone above the same point, is now associated with the formation of sulfuric acid (Figures 11.2 and 11.3), and not sulfur dioxide (Figure 11.1), as the determining sulfur reaction product.

Sulfuric acid is a detonation product with sulfur in its highest possible oxidation state (+VI). The specialists of the 1920s apparently considered sulfur trioxide as the only plausible initial sulfur(VI) detonation product, but then, at high temperatures, such as those prevailing in a detonation event, sulfur trioxide is quantitatively dissociated into sulfur dioxide and oxygen. As a result, only these latter species were considered as credible final products, such as in Figure

11.1. As the sulfur trioxide dissociation process is endothermic, some of the evolved heat of detonation is consumed, lowering the detonation temperature. This is the origin of at least some of the differences between Figures 11.1 (isobaric conversion) and 11.2 (detonative conversion).
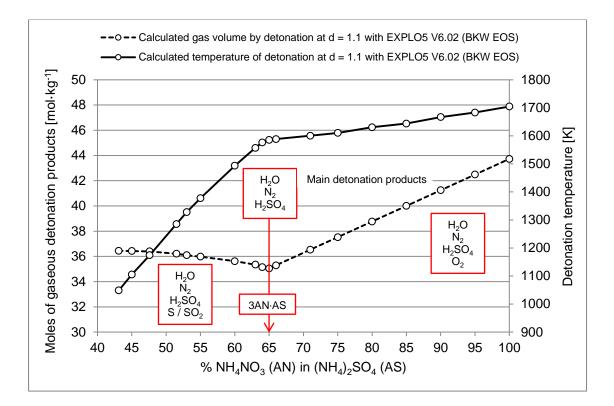


*Figure 11.3 The quantity of gaseous reaction products and detonation temperatures of AN-AS mixtures calculated with EXPLO5 V6.02 at a constant density of $1.1 \ g \cdot cm^{-3}$ (using the BKW EOS). **Note**: Only the major reaction products are indicated.*

What is then the central role of sulfuric acid in the detonative conversion of AN-AS? At the very high pressures prevalent during detonation, any sulfur trioxide formed may react with the water formed (a major reaction product) and give sulfuric acid in a condensed form, despite of the high temperatures, thus "locking it" from further decomposition and releasing substantial heat in the process. If the detonation products are then allowed to undergo isentropic expansion to reach room temperature and atmospheric pressure, the product distribution is, according to the calculations, only mildly affected. The high-pressure detonation pathway therefore constrains possible reaction outcomes and can invalidate some the postulated decomposition reactions considered in the 1920s.

Consequently, as a prediction of non-volatile, condensed phase sulfuric acid among the possible explosion products was outside the capabilities of the time, the reaction temperatures were

probably underestimated, and the reaction product gas volumes calculated by the experts in the Reichstag commission show a lower variability than those plotted in Figure 11.3.[7] This may have impeded their understanding of the energetic characteristics of AN-AS and ASN. Naoúm and Aufschläger experimentally detected the presence of sulfuric acid in the explosion products of AN-AS mixtures during their studies, but had scant chances of appreciating its importance.[55]

Another illuminating facet can be extracted from Figure 11.3. While the detonation temperature rises sharply up to the 65:35 point, the associated gas volume remains fairly constant throughout the preceding interval. Above the 65:35 point, however, the detonation temperature rises only slowly while the quantity of gaseous explosion products shows a steady increase. The result of these opposing trends is that measured parameters of the detonative performance of AN-AS mixtures, such as the detonation velocity, detonation pressure and specific energy (a measure of an explosive's capability of performing pressure-volume work – much like that measured in the lead block expansion test), which all rely on the combination of both detonation temperature and the evolved gas volume, all exhibit quite steady monotonous increases (data not shown) – concealing the importance of the 65:35 pivot point.

As a final point, although speculative, the presence of sulfuric acid among the ASN decomposition products could shed light on another aspect of the Oppau explosion. After the disaster, the press was rife with testimonies and speculations regarding the irritating and noxious character of the gas and dust cloud formed as a result of the explosion.[12,13] Although the majority of these assertions was rooted in entirely unrelated matters, particularly in the legacy of the First World War, and the German development and use of chemical warfare agents, a combined dust cloud and sulfuric acid aerosol (possibly also containing other irritating sulfur reaction products) could indeed have had a detectable, unpleasant influence on people in the vicinity of the Oppau factory after the explosion.

# 12 Experimental testing of the explosivity of ammonium nitrate-ammonium sulfate mixtures

As a result of the Oppau disaster, a variety of mechanical AN-AS mixtures and ASN spiked with AN were subjected to a comprehensive experimental test program in Germany, in order to probe their susceptibility towards detonative impulses.[7,55] Some of the testing on the 50:50 ASN Oppau salt has already been detailed in a previous section.

Impact testing (using drop hammer) of 50:50, 60:40 and 70:30 AN-AS mixtures, as well as with pure AN, revealed the anticipated increase in impact sensitivity with rising AN-content (becoming definite first at the 60:40 AN-AS ratio), but the method was far too crude to allow for definitive interpretations.[7]

Extensive shock-testing of ASN, with or without extra AN, was undertaken by the Reichstag commission experts, using sealed wrought iron cylinders (8–10 cm diameter, 27–37 cm length, 4 mm wall thickness) filled with ~1–3 kg salt mixture (at a loading density close to $1.0 \ g \cdot cm^{-3}$) and equipped with booster charges of pressed picric acid (~100–500 g).[7] Upon testing ASN with 41–45% AN content under such conditions, only partial explosive decomposition ensued. Testing of ASN spiked with additional AN, giving a total AN content in the range of ~62–68%, gave complete explosive decomposition of the entire charge. A comparable result was obtained by using a mechanical mixture of 65% AN and 35% AS. Rather predictably, an even more pronounced explosion was achieved by using a charge consisting of pure AN (at a loading density of $0.76 \ g \cdot cm^{-3}$).

In another test series at the CTR in Germany, carried out under analogous conditions to the test series above, Oppau salt obtained from silo 112 of the Oppau factory site was tested, either in its pure form or spiked with added AN.[7] Testing of these materials with total AN contents of 48–55% gave only partial explosive decompositions. Conversely, testing of mixtures with a total AN content of 60% gave full explosive conversion, and an even more manifest explosive behavior was achieved using mixtures containing 65% AN in total. Moreover, it was proven that the explosive decomposition was detonative in nature, and not merely a deflagration (rapid combustion) process.[7]

A number of additional tests, conducted in iron tubes, steel grenades, cardboard containers or even large wooden barrels (75 cm in height, 45 cm in diameter, containing 130 kg salt consisting of ASN with or without added AN), were painstakingly carried out by the German investigators, probing the influence of a number of factors, such as the loading density, the confinement, the AN/AS grain sizes, the booster size/identity, the salt moisture content and the charge temperature.[7]

Some significant correlations could be established as a result of the testing, and the first clues to how the explosive potential of AN-AS mixtures may be seriously perturbed now surfaced. Most importantly, the Reichstag commission experts,[7] as well as the independent work published by

Naoúm and Aufschläger,[55] clearly demonstrated the importance of AN/AS grain sizing. An increase in the grain size of the AS component and a decrease in the grain size of the AN component, in mechanical mixtures of the two, acted to heighten the explosive potential of the mixture substantially. This is a consequence of the fact that the transfer of heat of decomposition depends on the relative surfaces of the two salts, with the AN being the heat source and the AS the heat sink.

Testing of AN-AS mixtures at different grain sizes in the wrought iron cylinders (10 cm diameter, 37 cm length, 4 mm wall thickness) at the ~2.5 kg scale with pressed picric acid boosters (100 g), at loading densities in the range of 0.9 g·cm$^{-3}$, revealed that mixtures containing as little as 40% AN (40:60 AN-AS) could sustain an explosive decomposition, when the graining of the AN was fine (<1 mm) and that of the AS was coarse (1.5–2 mm).[7]

The finest conceivable "mixtures" of AN and AS are naturally the fully formed ASN double salts. In contrast to the conclusions drawn by BASF on the basis of their experimental testing prior to the Oppau explosion, Naoúm and Aufschläger detected a clear difference in explosivity between mechanical 50:50 AN-AS mixtures and 50:50 ASN prepared through an aqueous route (which allowed for efficient double salt formation), as in the production method employed at the Oppau factory (Figure 5.2).[55]

Naoúm and Aufschläger, in particular, advanced the proposition that kinetic and thermochemical trends thus opposed each other in determining the explosivity of AN-AS mixtures. On the one hand, from a thermochemical point of view, the exothermic combustion of the ammonium in AS by the oxygen surplus in AN adds to the energy output and explosivity of the salt mixture. On the other hand, from a kinetic point of view, the initial endothermic dissociation of AS drains heat from the exothermic decomposition of AN, thereby slowing the kinetics of the AN decomposition and lessening the explosivity of the salt mixture. The kinetic trend is obviously heavily influenced by the grain sizes of the two components.

Unsurprisingly, it was found that an increase of the moisture content of the salt mixture dampened its explosive power (results obtained through lead block expansion tests).[7] Actually, the aforementioned 1923 regulatory guidelines issued by German authorities on AN and ASN, specifically identified 3% water (in pure AN) as a threshold value for the substantial attenuation of the explosivity of AN.[56] With regards to the thermochemical modeling of AN-AS decomposition presented in the previous section, the presence of a few percent of water in the AN-AS mixtures does not significantly affect the results (data not shown).

Increasing the temperature of the AN-AS mixtures increased their willingness to undergo explosive decomposition, but only at temperatures on the order of 70 °C, which is probably too high to be of relevance for the fertilizer material in silo 110 at Oppau.

In USA, the NRC committee on AN, headed by Munroe, tested the explosivity of mechanical AN-AS mixtures by firing a cartridge of blasting gelatin in contact with the mixture (a few tens of pounds) contained in a keg placed on a lead block.[29] Using 100 g blasting gelatin cartridges for initiation, charges with 90:10 AN-AS and 80:20 AN-AS mixtures detonated (though not

when using 50 g blasting gelatin cartridges for initiation), but charges with 70:30 AN-AS or 60:40 AN-AS mixtures did not.

Thus, when the results of the German, British and American small-, intermediate- and large-scale testing narrated above is contemplated in its totality, we may conclude that both AN-AS mixtures or 50:50 ASN spiked with AN only exhibit fully developed and self-sustaining explosive behavior when the total content of AN reaches the 60–65% level, unless heavily skewed by external factors such as excessive temperatures or segregation of the components into mixtures of fine-grained AN and coarse-grained AS (a rather unrealistic scenario when taking into account the aqueous manufacturing route employed at Oppau for ASN). In hindsight, considering the thermochemical aspects presented in Figures 11.2 and 11.3, there is an overall impression of conformity between the experimental testing and the modern theoretical framework, but not with the framework in existence at the time of the Oppau explosion.

# 13 Porosity and hot spot ignition mechanisms: An only partially understood breakthrough in the Oppau explosion investigations

The material presented in the preceding sections has deliberately omitted to delve into certain characteristics of utmost importance for the fertilizer material involved in the Oppau explosion. These concern its physical structure, specifically its density and associated porosity. These parameters are almost certainly of paramount importance for exposing the triggering factor of the disastrous event at Oppau in 1921, as they relate to the introduction of the new spray-drying procedure for ASN fertilizer in silo 110, shortly before the disaster. This connection was partially realized at the time, and an attempt will be made herein to further substantiate the role of the porosity as perhaps the single most important cause of the Oppau explosion, and to explain how its importance could not have been realized at the time. The ultimate cause may perhaps still be a surplus of AN in part of the Oppau salt contained in silo 110, but that point may never be unequivocally established.

The awareness of the association between the physical structure of an explosive material and its receptivity towards impact and shock initiation is one of the most consequential pieces of insight in the history of energetic materials. It is also one of the least understood, least appreciated and most anonymous facets of modern explosives technology.

Nonetheless, the majority of all modern high-explosives for civilian applications, from simple dry AN blasting agents (based on porous prilled AN combined with fuel oil to give ANFO) to the moisture-resistant water-gel slurries or water-in-oil emulsion explosives (whether in cartridge form or in bulk), owe their existence to the recognition that controlled physical imperfections introduced into such mixtures (either in a factory or on-site, by the use of porous constituents, occluded air, gas-evolving additives, hollow microspheres etc.) are decisive for their functionality and safety.[57-64]

For long, manufacturers of gelatin dynamite products (gelatinous nitroglycerine-nitrocellulose colloids) had noticed some peculiarities, linking the sensitivity of such products to their age. As a typical example, in a 1930s patent from a formerly major dynamite manufacturer (DuPont of USA), it is stated that "The sensitiveness, or propagating power of gelatin dynamites varies notably, depending on the composition and grade, and also to a marked degree on the density of the explosive; the higher the density, the lower the propagating power, other things being equal. The propagating power of gelatin dynamites decreases with age because of a gradual increase in density, this increase being due to the loss of small air bubbles entrapped in the gelatins at the time of manufacture".[65]

The concept was understood only in a practical sense, and not from a theoretical standpoint, at least not from a comprehensively one. A sensible framework that could link features of the physical condition of explosive materials to their shock sensitivity was eventually developed during the 1940s, spearheaded by the Tasmanian-born British surface physicist Frank Philip

Bowden (1903–1968).[66-75] In collaboration with Abraham David Yoffe (1919–), Bowden eventually published an influential book on the subject.[76]

It was hypothesized that minute gas spaces confined in the energetic material would compress adiabatically when shocked/impacted to furnish localized zones of very high temperatures, regions referred to as "hot spots". Decomposition reactions could then develop from these and eventually transition the process into detonation. The conversion of energy by the detonation shock wave to the heat energy necessary for inducing chemical reactions was thus facilitated, and the detonation front was henceforth believed to be thermally heterogeneous, with local spots of high temperature.

Besides occluded gases, other significant hot spot formation mechanisms include friction between sliding or impacting surfaces (between energetic material particles and/or grit particles in the mixture), localized adiabatic shear of materials during mechanical failure, viscous heating of rapidly extruded material between impacting surfaces and cavity collapse with associated hydrodynamic shock focusing.[69-77] Hot spots have recently been observed experimentally in solid composites subjected to ultrasonic irradiation.[78]

The bearing of the aforementioned concept on the analysis of the Oppau explosion is both profound and decisive. It provides a window through which to observe and scrutinize the struggles of the Oppau investigators, perhaps dispelling some uncertainties and answering some of the persistent questions.

A revealing passage contained in the British investigation material on the Oppau explosion runs as follows: "In one experiment a most intense initiation by means of a charge of penta-erythrite nitrate was applied to Oppau salt compressed to a high density, these conditions being considered favourable for propagation of explosion".[10] Today, a knowledgeable applier of blasting agents might balk at such an assertion, knowing that high densities can make such a mixture almost impervious to shock initiation. Throughout, the investigations carried out in Britain appear entirely ignorant of the concept of porosity as a latent sensitivity-enhancer.[**] During testing there, the loading density varied in the approximate interval of 1.1 to 1.5 $g \cdot cm^{-3}$ and mostly in the high loading density region of $\geq 1.2$ $g \cdot cm^{-3}$.[10]

The Reichstag commission technical experts, on the other hand, through an impressive amalgamation of experimental testing and physicochemical intuition, eventually came to acknowledge the significance of the physical characteristics of the ASN fertilizer material involved in the explosion at Oppau.[6,7]

This understanding was developed gradually through the early 1920s. In his 1924 declaration on the Oppau accident, Escales discusses a possible connection between the implementation of the

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[**] In fairness, it should be kept in mind that the British investigators had to conduct their testing on fertilizer material in the condition as it was received from Germany (consisting of compacted and hardened material), and was most probably unaware of the discussion in Germany regarding the spray-drying process and the resultant powdery ASN material. Nevertheless, the exact wording in their report, on several occasions, clearly conveys an impression of complete ignorance regarding porosity as a latent sensitivity-enhancer.

new spray-drying procedure, its influence on the congealment of the ASN material (and thereby also the density) and its possible impact on the explosivity of the resulting material, but could not conclude on the matter.[6]

In what is perhaps the most remarkable series of passages in the entire investigation material relating to the Oppau explosion, it is succinctly pointed out by Kast, that the mode of ASN manufacture had been altered shortly before the accident at Oppau (the introduction of spray-drying), and a product of different physical characteristics had resulted. The new powdery material, containing a more irregular particle size distribution, was understood to possibly harbor an anomalous explosive potential relative to the old ASN material. Crucially, the commission experts point out, this notion was apparently entirely unknown to BASF.[7]

As a corollary to the viewpoint outlined above, one may ask whether BASF should have been able to foresee the possibility of an abnormal sensitivity harbored by the powdery ASN fertilizer material. In fact, at the time, was such a notion prevalent among experts at all? Yet again, as stated in the opinion of the Reichstag commission experts, the notion that the physical condition of a substance could influence its explosive properties "was not generally known, even among experts".[7] The historical fact that researchers came to fully appreciate this concept first during the 1940s appears to further validate this assertion.

Concerning the density of the Oppau salt contained in silo 110, it was estimated that ~500 tons had a density of 1.3 $g \cdot cm^{-3}$, ~1100 tons had a density of 1.1–1.2 $g \cdot cm^{-3}$, ~1200 tons had a density of 1.0 $g \cdot cm^{-3}$ and ~500 tons had a density of 0.9 $g \cdot cm^{-3}$. The assumed density of the remainder of the 4500 tons of ASN believed to reside in silo 110 on the day of the Oppau explosion was not clarified further.[7]

Was low-density 50:50 ASN actually proven to exhibit an anomalous explosive potential? Again, shock-testing of AN-AS mixture was undertaken in wrought iron containers (10 cm diameter, 37 cm height, 4.5 mm wall thickness) filled with ~1.5–2.5 kg salt mixture and equipped with booster charges of pressed Ammonal or picric acid (100 g).[7] When the loading density of the salt mixture was lowered to 0.75 $g \cdot cm^{-3}$, a more or less complete explosive decomposition of 50:50 AN-AS could be positively established, both with Ammonal or picric acid booster charges. Nevertheless, it is important to keep in mind that the results from the testing of mechanical AN-AS mixtures are not directly applicable to ASN prepared by the aqueous route, such as that produced at the Oppau factory.

In another test series, 65:35 AN-AS mixtures were shock-tested in iron or steel containers, and it was established that the explosive effect of such mixtures diminished rapidly when the loading density was increased. The mixtures became almost inert above a loading density of ~1.2 $g \cdot cm^{-3}$.[7] The incoherence between these results and the testing conducted in Britain, which was apparently firmly based on the idea that high loading densities were beneficial, is therefore significant.[10]

Had the investigators now finally pinned down the true cause of the Oppau explosion? While the results of the testing of low-density AN-AS mixtures narrated above undeniably represented

a breakthrough in the Oppau investigations, it must be conceded that it is all too easy, in retrospect, to attribute a greater degree of comprehension to the investigators of the 1920s, than can actually be established on the basis of their contemporary records. As a matter of fact, in trying to make sense of their testing, from a theoretical standpoint, the experts engaged in some quite far-fetched speculations, presenting part of it as "obvious".[7]

In reality, the heightened sensitivity of porous, low-density AN-AS was not ascribed to the low density of the material as such, but rather to the "swirling up" of the loose salt by the pressure wave before the explosion, the material "in this condition being more easily brought to decomposition".[7] During testing, several of the containers were therefore deliberately filled with reduced quantities of salt mixture so as to leave a cavity above the mixture, and testing was conducted with the containers in both upright and lying conditions. Alas, although the importance of the porosity was partially revealed by the Oppau investigators in an empirical sense, they failed to elucidate it from a theoretical standpoint. Hot spot-like ignition mechanisms were apparently never contemplated.

In 1926/27, Kast published an extended article, presented piecewise over seven journal issues, on the explosivity of ammonium salts, including AN and AN-AS mixtures.[79] In it, Kast presents a comprehensive test program for the explosivity of AN, taking into account the particle sizes and loading densities. Results from the testing of 60:40 and 70:30 AN-AS mixtures are also presented. Again, although low loading densities (0.64–0.98 $g \cdot cm^{-3}$) were apparently indispensable for a successful detonation, Kast did not really expound on the issue.

Munroe, the distinguished explosives expert in charge of the American NRC committee set to investigate "the conditions and associations under which $NH_4NO_3$ develops explosive characteristics", could report in 1924 that the "susceptibility of $NH_4NO_3$ to initiate detonation and its capacity to propagate detonation are effected by the extent to which it is confined and the degree to which it is comparted".[80] It is clearly spelled out that testing had uncovered that the certainty of initiating detonation in AN decreased with an increase in the density of the AN.[80,81] Thus, AN tended to become "dead pressed". Even so, the true significance of this finding, and its relevance for the Oppau explosion, was apparently not appreciated.

A weakness of nearly all the experimentation conducted in the wake of the Oppau disaster is the relatively modest scale of materials employed. The concept of critical diameter (occasionally called failure diameter), that is to say, the smallest cross-sectional area of a bare test material that can sustain a stable (steady-state) detonation reaction – and an important concept in the understanding of explosives – was poorly developed at the time. The critical diameter of AN materials can be very substantial, on the order of 10 cm and above, thus greatly influencing the outcome of the testing of the explosivity of such materials. However, this effect will to a certain extent depend on the confinement (strong confinement facilitating detonation of smaller charges), and it is difficult to fully assess its bearings on the Oppau investigations.

During the 1950s, the Bundesanstalt für Materialprüfung (the Federal Institute for Materials Testing, a descendant of the CTR) in Germany published some new results from testing of the

explosivity of ASN.[82] Using a strong 3 kg booster charge of pressed RDX (hexogen, cyclonite) in a 1 $m^3$ box containing 1000 kg ASN, an explosion was seemingly triggered with ASN containing as little as 37.5% AN (~1:1 AN-AS molar ratio). However, an explosion in the same ASN was not propagated in a buried 2 m long wooden box (40×40 cm) when using a 1 kg booster charge of pressed RDX. Loading densities are once again absent, and it is difficult to assess the actual significance of these tests, but they underline an important conclusion, namely that given particularly favorable circumstances (particle distribution, adequate boostering, low-density material and confinement), 50:50 ASN as that manufactured at Oppau could also plausibly propagate explosive decomposition.

Hermann Kast, on behalf of the Reichstag commission, concludes his final report by attributing the Oppau explosion to alterations in the physical condition of the Oppau fertilizer material by introduction of the spray-drying procedure and the ensuing increased potential for explosive decomposition.[7] In spite of the technical mastery, however, the legacy of the Oppau investigations is much less clear than alluded to in that concluding statement.

Kast's final report, although published in 1925/26, was mostly complete by 1923 (the cause of the delay was not clarified), and the critical experimental testing of low-density AN-AS material, detailed previously, was complete by 1922.[7] Despite of this, the 1924 summary by Kast on the conclusion of the Oppau investigations does not place a pronounced emphasis on the posited dangers of spray-dried, low-density ASN, nor does the general declaration of the Reichstag commission.[3]

As a result, when commenting on Kast's 1924 summary and its appended statements, the widely circulated American journal *Industrial & Engineering Chemistry* reported soberly that "This report, in common with reports of other investigations, throws no additional light upon the true cause of the disaster, which, though admittedly caused by blasting, took place under conditions that have not been duplicated experimentally".[83]

If we then turn to the work carried out in Britain, it is stated in the introduction to their 1924 report that, after completion of their work, the British committee had had the opportunity to read the final report of the official German investigation.[9] It is duly pointed out that the conclusions of the German investigation "agreed very closely with those of the Board" (Chemistry Research Board in Britain).

It is telling that the British investigators, who so openly flaunted their finding that the Oppau salt had not detonated despite of "the most powerful compression" – this notion being such an obvious misconception relative to the German findings (which had identified the importance of *low* compression) – still felt that their interpretation of the Oppau explosion closely matched that of the Germans. In the discussions following presentation of the British report, issues touching on the porosity and the associated loading densities did not enter the discussion.[11]

Despite its scientific merits and academic credentials, the 1924 German disclosures on the causes of the Oppau explosion did not come across, at least internationally, as particularly enlightening,[3-6,8] something which has clouded the scientific legacy of the investigation efforts.

The less widely circulated, but more conclusive, 1925/26 report by Kast does not appear to have been able to correct the legacy of the investigations.[7] Why was this final report published only as a supplement to a specialized scientific journal? Why were its conclusions not more widely publicized in the press?

Perhaps Kast's untimely death in 1927 curtailed any continued discussion, or the accident was simply out of the public's mind by then. Nevertheless, on the basis of the treatment herein, it is suggested that there existed a fundamental lack of agreement at the time, concerning the realities uncovered during experimental testing and the general state of the science of energetic materials. That is to say, the incomplete understanding of certain phenomena, such as the process of detonation for condensed explosives (the energies involved, the products formed) and the apparent absence of a developed notion of hot spot-type ignition mechanisms, impeded the comprehension of the sequence of events leading to the Oppau explosion, and of the results of the experimental testing undertaken in the wake of the disaster.

Because such a lack of congruence existed, Hermann Kast and his associates may not have been sufficiently equipped to establish causality to a full extent, but found themselves limited to unravel certain correlations experimentally and forward more uncertain conclusions. Perhaps were there even serious disagreements among the specialists. With time, thought processes matured, the scientific insecurity abated and, in 1925/26, Kast had a secure enough footing, at least experimentally, to more openly forward his interpretations of the actual cause of the explosion disaster.

The underdeveloped state of knowledge, concerning the physical aspects of explosives and detonation phenomena, may as well have been a symptom of the relatively homogeneous make-up of the technical workforce within the explosive industry of the 1920s. The entire industry was then completely dominated by chemists, something which had been the state of affairs since the beginning of the modern explosives industry in the 1860s. Physicists entered this field at a later stage, and then particularly in the aftermath of the Second World War (1939–1945).

In the wake of the final 1925/26 report by Kast, a critical publication appeared shortly afterwards, and it may support the notion that scientists within the field of explosives at the time lacked physical insight. In a quite stinging article, Lupus criticized the results of the Oppau explosion investigations, arguing that the whole subject was regarded too narrowly from the chemical standpoint, and that the physical side of explosives had been badly neglected.[84] The extent to which these opinions found an attentive audience at the time is, to this author's knowledge, unknown. Yet, this physical-chemical dichotomy is in essence the true scientific legacy of the Oppau explosion investigations.

# 14    The mystery of the two consecutive explosions

One final feature of the Oppau explosion merits discussion. The Oppau explosion was actually a series of two explosions placed four seconds apart in time, something which was asserted by many witnesses and later proven with certainty on the basis of seismographic data.[85]

The first explosion was estimated to have involved some 70–80 tons of ASN fertilizer material, while the second, and considerably more powerful explosion, was assessed to have consumed some 300–400 tons of fertilizer material (resulting in a ~1:4 to ~1:5 output ratio of the two explosions).[3,4] Taken together, this comprised approximately 10% of the 4500 tons of ASN contained in silo 110 on the day of the disaster.

Many of the speculations pertaining to the two consecutive explosions make for a rather confused reading. As a result, the discussion herein is kept to a minimum, and only the most plausible suppositions will be treated. The problem was, and remains, the fact that while the two explosions were undeniably linked in some manner, four seconds is far too long for there to have existed any sort of direct detonative or shock wave-induced transfer from one explosion to the next one. Accordingly, any linkage must have been either thermal in nature or of an entirely different sort altogether. In addition, due to the very large explosive output of either explosion, both must have originated from the explosive decomposition of ASN fertilizer material contained in silo 110, and cannot have had any other source of origin (such as ruptured gas containers or something of that sort).

Given the highly insensitive character of ASN towards any type of influence, whether thermal or mechanical in nature, as clearly evidenced by the testing conducted after the Oppau disaster, it was exceedingly difficult to imagine how the first explosion could have sufficed to somehow heat up a large portion of the remaining fertilizer material to such an extent that it would proceed to explosively decompose, presumably detonating, after a few seconds. Even under the most favorable conditions, the investigators were not able to duplicate any such behavior of ASN during testing.

As can be seen from Figure 1.2, the crater resulting from the two consecutive explosions was somewhat constricted along its length, giving the crater a distinctive pear- or peanut-shape. It may therefore have originated from the overlap of two individual craters, one larger (in the northeastern part) and one smaller (in the southwestern part), and a surmised coupling of these craters to each of the two consecutive explosions was quickly promoted. However, due to the unequal distribution of fertilizer material in the silo at the time of the explosions, particularly of hardened and congealed material (some 3000 tons at the location of the smaller crater and some 300 tons in the vicinity of the larger crater), as well as the positioning of the silo relative to the filled ground level of the factory site (see Figure 1.2), the shape of the crater need not have originated solely from the unequal output of the two explosions.

There exists a notable incongruence between the 1924 reports and the later 1925/26 report by Kast on this issue,[3-5,7] and the attempted linkage of the unequal crater sizes with the dissimilar

outputs of the two explosions will not be pursued any further in this account (an elaborate discussion on this point can located in Kast's final report).[7]

In the end, the most likely explanation for the two separated explosions was coupled to the blasting operations that brought about the disaster in the first place. Even though the exact procedure followed by the chief blaster on the fateful morning of the Oppau explosions is unknown, it was surmised, in analogy with other such operations, that 6–8 boreholes placed 80–120 cm apart were loaded with Perastralit and had been ignited through fusing.[7] Therefore, the entire length of boreholes amounted to a substantial 8–10 m, and a significant amount of time (on the order of a minute) could pass from the ignition of the first fusing to the last fusing in the sequence. Unlike the use of electrical ignition, the use of fusing gave rise to individual shots, separated in both time and space.

As a result of the way the blasting operations were carried out, the two consecutive explosions on the morning of 21 September 1921 were most probably linked to two separate shots of Perastralit. The first shot coincided with the first explosion and was spatially restricted. Due to the fertilizer material loosened thereby, reducing the loading density of surrounding fertilizer material, the circumstances for a larger and more destructive explosion were favored. Four seconds later, a second shot of Perastralit was triggered (either by the fusing or because of the effect of the first explosion), giving rise to the final disastrous explosion.

Concerning the mystery of the two consecutive explosions, there is little to add from today's vantage point. Given the inertness of ASN materials, there is every reason to believe that the two separated explosions were connected to two separate shots of Perastralit, and not to any thermal event linking the ASN involved in the two.

# 15 Conclusions and some consequences of the Oppau explosion

Industrial disasters are usually the result of the unfortunate convergence of a series of interconnected, individually improbable, events. In the case of the Oppau explosion disaster, the introduction of a new spray-drying procedure, conducted in a most ill-fated manner by the use of a stationary nozzle head, when combined with the exceptionally hot climate of the summer of 1921, resulted in the formation of low-density ASN fertilizer material with very low moisture content.

High temperature and dryness both hinder the formation of ASN double salt. In addition, there are grand reasons to suppose that the ASN material was, at least to some degree, enriched in AN relative to the 50:50 AN-AS factory specifications (as narrated, BASF did not control the nitrogen content of the porous material actually involved in the disaster), and that it was endowed with an unfavorable particle size distribution.

Unbeknownst to BASF, and even to experts in explosive materials for that matter, these conditions, particularly the porosity of the fertilizer material, favored its explosivity to a large extent. When charges of safety explosives were set off in such powdery material (which covered piles of older and more consolidated fertilizer material located below), perhaps strongly confined by surrounding hardened fertilizer material, a calamitous detonative transfer from the Perastralit cartridges to the ASN followed.

Furthermore, given the unpredictable scale-dependency of energetic phenomena, it remains unclear whether more elaborate testing by BASF – undertaken before the blasting operations were conducted in the new ASN material – could have uncovered the heightened sensitivity of the spray-dried material in advance. Either way, it is difficult to comprehend the safety evaluations that allowed blasting operations to be carried out directly on 50:50 ASN material, when it was known through prior testing, that only a modest enrichment of AN, giving a 60:40 ASN material, sufficed for it to attain distinctly explosive properties.

Naturally, in the wake of the Oppau explosion disaster, blasting operations in fertilizer materials were prohibited by German authorities. Only mechanical means were allowed from that point on for the loosening of hardened material.[12,13]

One aspect of the Oppau explosion has had profound implications. Following the disaster, in the latter part of the 1920s, BASF, then part of the vast chemical industrial conglomerate I.G. Farbenindustrie AG, developed a successful method for the production of ammonium nitrate-limestone fertilizer (in globular form).[86] In the spring of 1929, this product, under the name of Kalkammonsalpeter IG, was marketed by I.G. Farbenindustrie as a new nitrogen fertilizer material. This fertilizer contained 35% calcium carbonate and had a nitrogen content of 20.5% N.[87]

In Britain, Imperial Chemical Industries (ICI) launched a similar AN-limestone product to the German Kalkammonsalpeter, with a somewhat lower nitrogen content of 15.5%, under the name Nitro-Chalk.[88-90] In USA, analogous products were later known under the names Cal-Nitro (by Synthetic Nitrogen Products Corporation) or A-N-L (Ammonium Nitrate-Limestone).

Currently, AN-limestone fertilizers are most often referred to as calcium ammonium nitrate (CAN), a most unfortunate label due to the widespread confusion with another major type of calcium-nitrogen fertilizer material composed of calcium nitrate-ammonium nitrate double salts.[††]

The transition from ASN to AN-limestone fertilizers,[‡‡] originally touted as an improvement from a safety perspective (at least in cases where the AN content in the ASN is excessive), has not been an enhancement from a security perspective, due to the greater potential for illicit use of AN-limestone,[91] relative to ASN, in improvised explosive devices.[§§]

As a matter of fact, a new ASN fertilizer material has lately been resuscitated as a nitrogen fertilizer material with reduced potential for misuse (marketed under the name Sulf-N® 26 by Honeywell).[92,93] This granular ASN product has a ~1:1 AN-AS molar ratio overall, and the two salts are combined to an ASN product through a fusion process at high temperatures (~180–210 °C).[92] The fused ASN product consists almost entirely of a $2AN \cdot AS$ double salt (~70% by weight) in combination with free AS (~30% by weight),[93] and contains only very small quantities (≤5% by weight in total) of the more dangerous $3AN \cdot AS$ double salt or free AN.[92]

The introduction of fused ASN, as a safer variant of this class of fertilizer materials, is a fitting closure to this work. Indeed, had it not been for the Oppau explosion disaster, ASN materials would perhaps not have been targeted by the special hazardous material regulations in many parts of the world, in terms of transportation and storage, which they currently are.

The Oppau explosion disaster is a difficult topic with which to deal and does not admit of any easy answer, and the author shall venture no further here. Hopefully, by making the details of the original German investigation materials available to an international audience, further progress is probable. Yet, it can be acknowledged that the events at Oppau on the 21 September 1921 have not relinquished all their secrets – and probably never will. Still, by recognizing the limitations of the science of energetic materials at the time, we are now in a more privileged position to evaluate the ensuing investigation efforts and the consequences arising therefrom.

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[††] The hydrated double salt $5Ca(NO_3)_2 \cdot NH_4NO_3 \cdot 10H_2O$ with 18.8% Ca, 14.4% N from nitrate and 1.1% N from ammonium is the most common product. This product is usually called Kalksalpeter in Germany and Norway. Due to its low content of AN, it is sometimes referred to simply as calcium nitrate. This product should therefore not be confused with AN-limestone fertilizers. The confusion arising from the use of the term calcium ammonium nitrate is remarkably prevalent and unduly resilient, even among professionals.

[‡‡] The production of ASN fertilizer was eventually restarted by BASF, and it is still an important nitrogen fertilizer product. However, unlike the spray-drying conducted at Oppau, drying of ASN is today achieved through granulation, and anti-caking additives are added.

[§§] AN-limestone is more directly applicable than ASN, and it can also be more easily refined than ASN. As should be evident from the treatment herein, properly prepared ASN, containing somewhat more AS than that contained in the Oppau salt, is more or less completely inert towards detonative impulses.

Indisputably, the multifaceted legacy of the Oppau explosion disaster continues to challenge our perceptions of the at times unpredictable behavior of ammonium nitrate.

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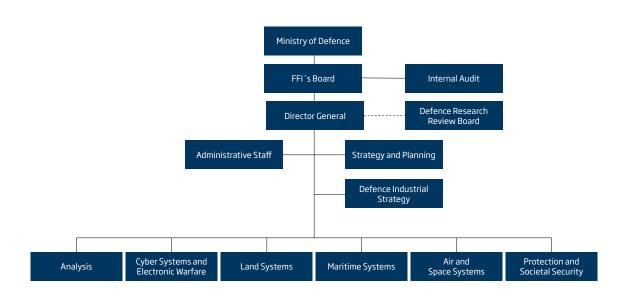
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