

Oppau 1921: Old Facts Revisited

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The likely causes for the explosion of an ammonium sulfate nitrate silo in Oppau 1921 are reviewed on the basis of publications from 1922 - 1926.

Ammonium sulfate nitrate is a mixture of 2 salts: ammonium nitrate (explosive) and ammonium sulfate (inert). The explosiveness of the mixed salt is mainly determined by the ratio of these 2 salts.

The influence of the mixed salt composition on the sensitivity to detonation impact had been thoroughly investigated before the accident as it was common practice to use small explosive charges to loosen the salt which had solidified during storage in the silo. About 20.000 blasting operations were carried out without any notable incident.

Experiments conducted after the accident revealed that several physical parameters (particle size, density, water content, homogeneity of crystal structure) also had an influence.

The introduction of a new drying process for ammonium sulfate nitrate (spray process, "Spritzverfahren") caused changes in all these parameters resulting in a salt with increased explosiveness. In addition a dust-like fine fraction with increased ammonium nitrate content was formed which accumulated at the edge of the silo.

It can be assumed that on the day of the accident at least one of the explosions for loosening the caked salt was carried out in the area of the fine fraction, thus initiating a detonation of this fine fraction and causing the detonation of further fractions with approximately "normal" nitrate content.

This accident is a strong example for the need of Management of Change (MOC) procedures, which are an integral part of today's process safety.

1. Background

On 21. September 1921 the explosion of an ammonium sulfate nitrate silo in Oppau killed 507 and injured 1917 people (the numbers of victims differ depending on the source, see Kast 1925a). Figures 1 and 2 show the destructions at the center of the explosion and in the immediate neighbourhood. The possible causes for this accident were determined by detailed investigations and published in a series of articles by Kast (1925b and 1926a).

The results of these investigations are well known in the "ammonium nitrate community", but their awareness in the general process safety community has decreased over the years. The increased interest in this accident on occasion of its 90th anniversary was an occasion to review the old reports on this topic.

There exist several reports from different investigation committees, but the publications of Kast summarize most findings. They are therefore used as main source together with the report of the Bayerische Untersuchungskommission (1922).

2. State of Knowledge before the Accident

2.1 Basics

Ammonium sulfate nitrate (ASN) is a mixed salt consisting of ammonium nitrate (AN) and ammonium sulfate (AS). It is produced in large scale as fertilizer and stored in silos. During storage ASN can cake forming a solidified mass impossible to handle for further loading and shipment.

It was common practice before the accident to use small charges of explosives (2 - 5 cartridges each with 2 g Parastralit) to loosen the caked ASN in the silo. Before the accident about 20,000 blasting operations were

carried out without any notable incidents. Figure 3 shows the drilling of the holes and the placement of the Perastralit cartridges in preparation of a blasting operation.

2.2 Explosive Properties of ASN

The explosive properties of ASN depend mainly upon the ratio of the components AN (explosive) and AS (inert). The ASN produced and stored in Oppau had an AN/AS ratio (by weight) of 50:50 ("Oppau salt"). The ASN composition which in the Trauzl lead block test could be induced to explode by booster charges corresponded to an AN/AS ratio of $> 55:45$. Based on these results, which were confirmed after the accident, it was assumed that the blasting operations for loosening the caked salt could be conducted safely. Basic condition for this assumption was the strict adherence to the correct AS/AN ratio of 50:50. This was achieved by frequent analyses. Another reason for regular analyses was the fact that the AN content of the mixed salt was an important specification feature of the fertilizer.



Figure 1: View of the explosion crater



Figure 2: Destruction in the neighbourhood of the exploded silo



Figure 3: Preparation of blasting operation

3. Accident Investigation

3.1 Facts around the Drying and Storage Process

The exploded silo was a wood construction with concrete foundation. It was used for drying as well as for storage of the mixed salt. The drying process had been changed at the end of 1920. Originally the ASN was dried with a drying screw. To obtain a product quality with less residual humidity, the spray process ("Spritzverfahren") was introduced and used exclusively since beginning of 1921. In the spray process the hot salt solution was sprayed with hot compressed air through an atomizer into the storage area. The dried salt fell to the ground like snow and was either removed at once by a conveyer belt in the silo or it formed heaps located at different places in the silo depending upon the spray direction.

On the day of the explosion the silo contained approximately 4,500 t ASN. The size of the crater formed by the explosion correlated to the explosion of 300 - 400 t ASN.

3.2 Search for the cause: first considerations

The hypotheses on possible causes for the explosion soon focused on factors which may have caused a deviation in the chemical composition of the mixed salt (higher AN content) resulting in an increased sensitivity to detonation impact. The following causes were discussed:

- Lack of care by operators induced by introduction of a new bonus system which was linked to the production quantity
- Introduction of the new spray process
- Deviations from the operating procedures resulting in the addition of wrong amounts of AS (too little) or AN (too high)

The review of operations diaries and analysis reports recovered from the surroundings of the exploded silo did not reveal any irregularities. However, this statement is qualified by the fact that the samples taken for analysis were average samples. Furthermore some of the samples taken after the explosion from a neighboring silo not involved in the explosion showed an AN content above 55 % (Kast, 1926b).

3.3 Factors influencing the explosive Properties of ASN

Though the chemical composition of ASN obtained from the changed drying process (spray process) remained unchanged (AN/AS ratio of 50:50), the physical properties differed from ASN obtained in the original drying process (drying screw). Therefore a series of explosion tests were conducted at the "Chemisch-Technische Reichsanstalt Berlin" to investigate the influence of various physical parameters on the explosive

properties of ASN (Kast 1926c). Additionally the influence of the test conditions (strength of confinement and brisance of the booster charge) were investigated.

The results are summarized in table 1. It can be seen, that the changes in physical parameters of the mixed salt (particle size, density and water content) caused by the transition to the new spray process all lead to an increased sensitivity to detonation impact.

Based on these results it is a realistic possibility that larger portions of ASN in the storage silo could be induced to explode by a sufficiently strong detonation impact, though the AN content did not significantly exceed 50 %.

Table 1: Results of the explosion tests of "Chemisch-Technische Reichsanstalt Berlin"

| Parameter | Influence of Parameter on sensitivity to detonation impact | Influence of spray process on parameter |
|-----------------------------|--|---|
| Particle Size | Increased by smaller particle size | Particle Size is smaller |
| Density | Increased by lower density | Density is lower |
| Strength of Confinement | Increased with increasing strength of confinement | No influence |
| Brisance of booster charge | Increased with increasing strength of booster charge | No influence (the same cartridges were used as before the process change) |
| Water content of mixed salt | Increased with decreasing water content | Water content is lower (4 % before vs. 2 % after process change) |

3.4 Influence of the spray process

The report of the Bayerische Untersuchungskommission (1922) discussed in detail the effects of the introduction of the spray process. Witnesses described that besides the main fraction having the desired chemical composition (AN/AS ratio of 50:50) a dust-like fine fraction with very low particle size was formed as byproduct. While the main fraction fell to the ground near the spray nozzle, the fine fraction floated in the air like dust and settled all over the silo. Those portions of the fine fraction settling at the edge of the silo were never removed but formed a layer of ca. 0.5 m corresponding to an estimated quantity of 100 t. The relative amount of fine fraction was estimated as 0.1 - 0.2 % of the total production quantity.

This observation explains the finding that some samples from the adjacent silo taken after the explosion had an AN content above 55 %. These analyses were isolated cases only valid for a limited area in the silo. Therefore these results are not contradictory to the analyses of the average samples taken for monitoring the process and which were in the specified range.

The hearing of witnesses as well as theoretical considerations confirmed that the spray process could yield a certain degree of inhomogeneity of the dried product.

AN and AS have different water solubilities, AS having a lower solubility. The mixed salt was obtained by adding solid AS to a hot concentrated AN solution in an amount corresponding to the desired AN/AS ratio of 50:50. The AS was not completely dissolved when the hot slurry was subjected to the spray process. So in the spray process there was a tendency of AS to crystallize first before AN resulting in a "demixing" of the mixed salt: instead of "mixed salt crystals" having the correct AN/AS ratio on a microscopic (or molecular) level, a certain fraction of the salt existed as a mixture of AN and AS crystals having the correct AN/AS ratio only on a macroscopic level. According to Kast (1926d) this inhomogeneity also resulted in an increased explosiveness. In the same way it can be explained that the dust-like fine fraction which accumulated at the edge of the silo, had an increased AN content above 55 %.

In summary, the introduction of the spray process can have resulted in the presence of the following salt fractions:

- A fine fraction (estimated quantity 100 t) at the edge of the silo with an AN content > 55 % sensitive to detonation impact from the Perastralit cartridges used for loosening the caked salt
- An unknown quantity of salt having an AN/AS ratio of approximately 50:50, but sensitive to a strong detonation impact due to changes in particle size, density, water content and inhomogeneous crystal structure.

3.5 Likely Chain of Events

Based on the results from chapters 3.3 and 3.4 the following chain of events could explain the explosion:

- Introduction of the spray process at the beginning of 1921
- Accumulation of a fine fraction with AN content > 55 %. This fine fraction is sensitive to detonation impact from Perastralit cartridges.
- The accumulation of the fine fraction is not noticed since it is located at the edge of the silo and since the main fraction has the required AN/AS ratio.
- The physical parameters of the main fraction have changed, causing an increased sensitivity to a strong detonation impact
- The blasting operation on 21.09.1921 for loosening the solidified salt was carried out at least partially in the area of the fine fraction thus initiating a powerful detonation
- The detonation of the fine fraction acts as booster for further ASN with correct AN/AS ratio, which due to changed physical parameters is able to explode

4. Assessment

The chain of events described in 3.5 is in accordance with all known facts and therefore most likely offers an explanation for the explosion of 21.09.1921. However, a definite proof is not possible due to the destruction caused by the explosion. In particular the ASN fractions which were able to explode (due to higher AN content or changes of physical parameters) had disappeared during the explosion. Therefore the exact contribution of each factor to the increased sensitivity to detonation impact (AN content, particle size, density, water content, homogeneity of crystal structure) cannot be determined. But the chronological sequence of events strongly supports the assumption that the introduction of the spray process was the reason for the explosion. This view is supported by the fact that the accident occurred already at the 2nd blasting operation carried out after the introduction of the spray process.

5. Handling of ASN Today

The use of explosives to loosen solidified salt is forbidden since the 1921 explosion. Since it is possible today to prevent caking by treatment with anti-caking additives, there is no need for further measures to improve the handling of the fertilizer.

6. Conclusions: Relevance for Process Safety Today

The following lessons which can be learned from the accident in 1921, are basic rules of process safety now for many years, but should be recalled on this occasion:

- Management of Change: before implementation of a process change the consequences to process safety must be checked and the safety concept must be updated
- In particular the influence of the process change upon the safety characteristics of the handled materials must be determined
- If a process has an extremely high hazard potential, it must be impossible that one single fault (e.g. a deviation from the correct chemical composition of ASN) can activate this hazard potential

7. Summary

The likely causes for the explosion of an ammonium sulfate nitrate silo in Oppau 1921 are reviewed on the basis of publications from 1922 - 1926.

Before the accident it was assumed that the sensitivity to detonation impact of ammonium sulfate nitrate (ASN) only depends on the ratio of the two components ammonium sulfate (AS) and ammonium nitrate (AN). Experiments conducted after the accident revealed that several physical parameters (particle size, density, water content, homogeneity of crystal structure) also had an influence.

The introduction of a new drying process for ammonium sulfate nitrate (spray process, "Spritzverfahren") caused changes in all these parameters resulting in a salt with increased explosiveness. In addition a dust-like fine fraction with increased ammonium nitrate content was formed which accumulated at the edge of the silo.

A chain of events is proposed which explains the explosion of the silo and which comprises the following essential elements:

- Introduction of the spray process at the beginning of 1921
- Accumulation of a fine fraction with AN content > 55 %. This fine fraction is sensitive to detonation impact from Perastralit cartridges.
- The blasting operation on 21.09.1921 for loosening the solidified salt initiates a detonation of the fine fraction

- The detonation of the fine fraction acts as booster for further ASN with correct AN/AS ratio, which due to changed physical parameters is able to explode

Reference

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