Impact of phase composition on quality of ASN fertilizers

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Abstract. Ammonium Sulfate Nitrate (ASN) based fertilizers are very efficient fertilizers in modern agriculture. Designed to provide targeted nutrition and high yields, they combine the extended availability of Ammoniacal (NH₄) and rapid effect of Nitrate Nitrogen (NO₃) with the multiple agricultural benefits of Sulfur. Most of these products have some tendency to form agglomerates (caking) and dust during storage in a bulk of hundreds to thousands of tons. The severity of quality deterioration can be influenced by a number of factors, such as phase composition, moisture content, particle structure, mechanical strength, hygroscopic properties, product temperature, ambient conditions, storage time and pressure. ASN fertilizer is mainly a combination of the double salts 3AN·AS ((NH₄)₅(NO₃)₃SO₄) and 2AN·AS ((NH₄)₄(NO₃)₂SO₄). It is known that presence of these mixed salts has a strong impact on the quality of fertilizer. Seeing that X-ray Powder Diffraction analysis (XRPD) is commonly used to control the quality of industrially produced fertilizers, a new X-ray method has been developed. This new method is based on the determination of the ratio of the integral intensities of the diffraction lines of the 3AN·AS and 2AN·AS components. The ratio obtained by line profile analysis provides an effective screening test of the quality of fertilizer immediately after production. In accordance with ratio value it is possible to estimate quality changes of product during long-term storage.

1. Introduction

The current intensive agricultural utilization of soils requires regular and complex fertilizer application. Ammonium Sulfate Nitrate (ASN) is a granular fertilizer, which due to its simultaneous supply of Nitrogen and Sulfur considerably improves the fertility of the soil and therefore increases the growth and yield of the plants. Because ASN contains high ammonium nitrogen content it furthermore guarantees long-term and sustainable nitrogen supply and prevents the nitrogen from being washed out of the soil. In addition, ASN supports the availability of secondary nutrients like manganese, iron, and boron in the soil [1].

The physical state in which the fertilizer is produced is of considerable importance from an agronomic point of view and with regard to satisfactory handling, transport, storage and end-application in the field. Most ASN fertilizers tend to form lumps or agglomerates (caking) and dust, which is a major problem in fertilizer handling and storage. The fertilizer caking and dustiness can be affected by several factors, e.g. chemical composition, moisture content, hygroscopic properties, product temperature and storage time [2]. The various methods of reducing or eliminating caking in fertilizers basically involve production process control, storage conditions or addition of some...
anticaking agents. Furthermore, it is known that the phase composition of fertilizer immediately after production has a significant effect on its quality, especially during long-term storage [3].

X-ray Powder Diffraction (XRPD) analysis is mainly used as identification and quality control tool in the fertilizer industry. The identification of particular crystalline components of the fertilizer is carried out by the method of qualitative phase analysis. This method is based on comparing the diffractogram of each crystalline fertilizer component with the reference diffractogram from the Powder diffraction file database (PDF) [4]. Quantitative phase analysis is used to determine the content of the different phases that are present in an industrial fertilizer sample after identifying each phase [5, 6]. Overall, the quantitative analysis of ASN fertilizers can be quite difficult and problematic due to the extremely complex diffraction patterns with strongly overlapping Bragg diffractions. ASN type fertilizer can usually contain a number of components, typically four or more.

As reported in the literature, the double salts 3AN·AS ((NH₄)₅(NO₃)₃SO₄) and 2AN·AS ((NH₄)₄(NO₃)₂SO₄) (AN – ammonium nitrate, AS – ammonium sulfate) together with ammonium sulfate form the major components of ASN fertilizers [7]. Significant effects of 3AN·AS and 2AN·AS content on fertilizer quality parameters were found by diffraction analysis of high and low quality industrial samples immediately after production. Standard comparative method of qualitative analysis is not suitable for samples of ASN fertilizers by reason of complex and overlapped diffraction patterns (Figure 1). It is not possible to achieve satisfactory analysis accuracy by using it. On account of this, a new X-ray method has been developed providing an effective screening test for estimating changes in fertilizer quality during long-term storage. This new method is based on the determination of the ratio of integral intensities of selected diffraction lines of 3AN·AS and 2AN·AS components.

The aim of this work was to monitor the quality of ASN fertilizer and its changes by means of the new X-ray powder diffraction method during 4 months of bulk storage with respect to the phase composition immediately after production.

2. Experimental

2.1. Materials and physical characteristics of fertilizer materials

All analyzed samples of ASN type fertilizer in this work originate in large – scale industrial production.

In the handling and storage of fertilizers, it is important to ensure that the quality is maintained right up to the point of usage: especially no caking and minimal dust content. The most important fertilizer quality parameters – caking tendency and dustiness were measured on devices that are not commercially available, but was designed special for characterization of these fertilizer properties in our laboratory. The aim of the caking test is to hold the fertilizer sample placed in a cylindrical mold under pressure during required time interval. Then the force required to break the sinter of fertilizer is measured and defined by the unit of force Newton (N). The method used to measure fertilizer dustiness is based on the determination of the dust proportion that is separated by the airflow from the fertilizer granules. Dustiness is given as a percentage (%). An accurate method for determining the amount of water in fertilizer samples is Karl Fischer (KF) titration. It is a chemical analysis procedure based on the oxidation of sulfur dioxide by iodine in a methanolic hydroxide solution. Volumetric water content of fertilizer samples was measured with 870 KF Titrino plus titrator.

2.2. X-ray method for 3AN·AS/2AN·AS ratio determination

The powder patterns of fertilizer samples was collected within the 2θ range 10–60° with a Rigaku MiniFlex 600 X-ray diffractometer equipped with scintillation counter, using β-filtered Cu Kα radiation. As mentioned the new X-ray method is based on determination of the ratio of integral intensities of selected diffraction lines of the 3AN·AS and 2AN·AS double salts. This ratio was obtained by line profile analysis of selected diffractions in the range of Bragg angles, where is the overlap with diffractions of other fertilizer components as small as possible (18.10 – 19.15 ° 2θ). The range of angles with the smallest overlap was determined using a diffractogram obtained by combining individual simulated diffractograms of all fertilizer components (Figure 1).
Simulated diffraction patterns of particular constituents were calculated using structure data from Inorganic Crystal Structure Database (ICSD) [8]. The X-ray method correlating the ratio of integral intensities of mixed 3AN·AS/2AN·AS salts with qualitative properties such as caking tendency and fertilizer dustiness provides an effective quality screening test immediately after production. It has been empirically found that if the ratio reaches a value less than 1.2, it can be estimated that the fertilizer will be more resistant to dramatic deterioration due to storage conditions, especially after moisture absorption. On the other hand, if the ratio value is more than 1.4, it can be expected that the metastable salt 3AN·AS will abruptly transform into stable salt 2AN·AS and qualitative parameters of fertilizer will be significantly worse [9]. The rate of such recrystallization increases with increasing relative humidity during storage. In the range of values of 1.2 - 1.4, this estimate is ambiguous, but only a minimum of samples with such a ratio value falls within the stated interval. The limit ratio values were found by gradual assignment of the ratio of integral intensities to the measured qualitative parameters of samples of real fertilizers obtained by other physical methods.

3. Results and discussion
For granular ASN fertiliser, degradation and caking is the most important problem in storage conditions. In the early research phase, a number of ASN based industrial samples were observed to deteriorate in the form of increased caking three months after production, while caking immediately after production was low (less than 20 N). The only significant difference found between them was the 3AN·AS/2AN·AS integral intensity ratio obtained by XRPD analysis. Results of XRPD analysis, caking test and water content analysis by Karl Fischer titration immediately after production and then after 3 months of storage in laboratory conditions (temperature 23 – 25 °C, relative humidity 40 – 60 %) are shown in Table 1.
Table 1. Results of XRPD analysis, caking test and water content determination

| Sample                         | 3AN·AS/2AN·AS ratio | Caking tendency (N) | Water content (%) |
|--------------------------------|---------------------|---------------------|-------------------|
| Sample 1 after production      | 1.95                | 15.9                | 0.92              |
| Sample 1 after three months    | 1.55                | 87.1                | 1.06              |
| Sample 2 after production      | 1.64                | 6.0                 | 0.62              |
| Sample 2 after three months    | 1.45                | 71.2                | 0.93              |
| Sample 3 after production      | 1.10                | 0.0                 | 0.82              |
| Sample 3 after three months    | 0.98                | 60.6                | 0.99              |
| Sample 4 after production      | 0.95                | 0.0                 | 0.69              |
| Sample 4 after three months    | 0.80                | 57.8                | 0.94              |

It can be seen from Table 1 that in the final stored product the phase conversion, depending on the moisture content and initial ratio value caused an increasing tendency to caking. Values of ratio 3AN·AS/2AN·AS decreased after three months of storage, which means that metastable salt 3AN·AS has partially transformed into the more stable salt 2AN·AS. The degree of such transformation depends on initial ratio value and as above mentioned on water content of sample [10]. Samples with a higher value of ratio immediately after production (Sample 1 and 2) have slightly more considerable tendency in caking than samples with a lower ratio after production. It can be said that samples with a lower ratio values are more stable in terms of phase transitions and consequently caking tendency.

Another series of experiments continued with the testing of industrial grade ASN fertilizers with three different 3AN·AS/2AN·AS ratios (Table 2 – 4). Thereafter these three products were stored in large piles (hundreds of tons) separately with respect to 3AN·AS/2AN·AS ratio value. During four months of storage, tests were carried out to investigate the effect of phase composition and its changes on fertilizer quality parameters, in particular the tendency of caking during long-term storage. Samples were taken monthly from each pile and the caking, dustiness, water content and 3AN·AS/2AN·AS ratio were monitored.

Samples in Tables 2 – 4 are labelled as follows: the numbers 1 – 3 indicate the average value of the 3AN·AS/2AN·AS ratio immediately after production. Letters A and B describe the origin of the sample from storage test – A means that sample was taken from the upper layers of the pile, B indicates that sample was from the lower layers of the pile. The values of each parameter shown in Table 2 are averaged out of five parallel measurements.

The moisture content of the product is usually considered to be the most important factor in promoting caking [11]. Tables 2 – 4 shows that the moisture uptake during storage is most significant in top layers of piles. It is a natural phenomenon that comes mostly from ambient moisture in warehouse. With prolonged exposure of the material to elevated humidity, caking can become quite deep. Although the water content of the samples from each fertilizer pile is roughly the same after four months of storage, the tendency to caking is very different.

Table 2. Results of XRPD analysis and tests for caking, dustiness and water content in industrial ASN fertilizer with average value 3AN·AS/2AN·AS = 1.11 immediately after production during four months of storage.

| Average value of 3AN·AS/2AN·AS ratio = 1.11 immediately after production | 1st month | 2nd month | 3rd month | 4th month |
|--------------------------------------------------------------------------|-----------|-----------|-----------|-----------|
| 3AN·AS/2AN·AS ratio                                                      | 0.90      | 0.96      | 1.13      | 0.49      | 0.92      | 1.13      | 0.92      | 1.08      | 0.46      | 1.04      |
| Water content (%)                                                       | 1.48      | 1.44      | 1.95      | 1.38      | 1.96      | 1.24      | 2.08      | 1.45      |           |           |
| Caking tendency (N)                                                     | 31.1      | 18.3      | 21.5      | 15.0      | 16.9      | 12.1      | 19.6      | 17.5      |           |           |
| Dustiness (%)                                                           | 0.23      | 0.23      | 0.44      | 0.23      | 0.40      | 0.24      | 0.35      | 0.18      |           |           |
Table 3. Results of XRPD analysis and tests for caking, dustiness and water content in industrial ASN fertilizer with average value $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio = 1.27 immediately after production during four months of storage.

| 1. Average value of $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio = 1.27 immediately after production | 1st month | 2nd month | 3rd month | 4th month |
|---|---|---|---|---|
| 2-A | 2-B | 2-A | 2-B | 2-A | 2-B | 2-A | 2-B |
| $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio | 1.54 | 1.31 | 1.08 | 1.25 | 1.02 | 1.39 | 0.67 | 1.44 |
| Water content (%) | 1.12 | 0.91 | 1.86 | 1.29 | 1.94 | 1.21 | 1.95 | 1.32 |
| Caking tendency (N) | 24.5 | 23.3 | 13.3 | 25.0 | 6.4 | 14.8 | 73.7 | 19.9 |
| Dustiness (%) | 0.35 | 0.30 | 0.46 | 0.28 | 0.58 | 0.53 | 0.80 | 0.30 |

Table 4. Results of XRPD analysis and tests for caking, dustiness and water content in industrial ASN fertilizer with average value $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio = 2.25 immediately after production during four months of storage.

| 2. Average value of $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio = 2.25 immediately after production | 1st month | 2nd month | 3rd month | 4th month |
|---|---|---|---|---|
| 3-A | 3-B | 3-A | 3-B | 3-A | 3-B | 3-A | 3-B |
| $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio | 1.78 | 2.10 | 0.84 | 2.07 | 0.50 | 1.32 | 0.51 | 1.66 |
| Water content (%) | 1.23 | 1.05 | 1.80 | 1.19 | 1.83 | 1.41 | 2.02 | 1.48 |
| Caking tendency (N) | 34.7 | 40.0 | 10.0 | 23.9 | 4.7 | 31.0 | 352.1 | 20.5 |
| Dustiness (%) | 0.19 | 0.14 | 0.97 | 0.19 | 1.25 | 0.28 | 1.53 | 0.19 |

However, it has been found that the $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ phase ratio also has a significant effect on the fertilizer caking tendency. Overall, the fertilizer with the lowest $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio after production (1) has the lowest caking tendency after four months storage test. On the other hand, severe caking of the top layers of pile was observed for the fertilizer with highest $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio after production (3-A).

Generally, increasing relative humidity during storage accelerate the $\text{3AN} \cdot \text{AS} \rightarrow 2\text{AN} \cdot \text{AS}$ transformation which results in a lower $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio (Figure 2b). It has been found that higher relative humidity values promote the adsorption of water vapour onto the crystal surface, which enhances ion mobility [12]. The rate of $\text{3AN} \cdot \text{AS} \rightarrow 2\text{AN} \cdot \text{AS}$ transformation is not only affected by the humidity but as well by the initial ratio value after production. It can be assumed that high $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio values immediately after production will lead to abrupt $\text{3AN} \cdot \text{AS} \rightarrow 2\text{AN} \cdot \text{AS}$ transformation due to the moistening of product in storage conditions. The low value of the $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio immediately after production causes that recrystallization to be gradual and likely not to cause severe caking (Figure 2a).

Figure 2. Relation between caking tendency and $\text{3AN} \cdot \text{AS}/2\text{AN} \cdot \text{AS}$ ratio (a) and influence of water content on ratio (b) of samples taken after 1 month of storage.
Dustiness together with caking is an important factor negatively affecting fertilizer quality. Products that generate dust make fertilizer handling and storage difficult. A larger surface of the dust particles can lead to a greater susceptibility to wetting, which in turn increases the probability of caking and reduces the shelf life. Hence, this quality parameter is given along with caking.

Figure 3 shows that caking of fertilizer is connected with $\text{3AN} \cdot \text{AS}/\text{2AN} \cdot \text{AS}$ ratio values due to very similar trends during storage. Further, it can be observed that water content influences the dustiness values rather than $\text{3AN} \cdot \text{AS}/\text{2AN} \cdot \text{AS}$ ratio. Results after 4th month of storage represent an exception to these observations, considering the strong increase of caking in upper layers of piles with higher ratio values after production (2-A and 3-A).

![Figure 3: Trends in $\text{3AN} \cdot \text{AS}/\text{2AN} \cdot \text{AS}$ ratio, water content, dustiness and caking of fertilizer samples during storage test after 1st month (a), 2nd month (b), 3rd month (c) and 4th month (d).](image)

4. Conclusion

This research about ASN type fertilizer indicates that caking and degradation problems of product are related to the phase composition of fertilizer immediately after production. It was found that standard search/match XRPD analysis is not suitable for this type of fertilizer because of very complex diffraction patterns. New X-ray method based on the determination of the ratio of the integral intensities of the diffraction lines of the $\text{3AN} \cdot \text{AS}$ and $\text{2AN} \cdot \text{AS}$ components of fertilizer was evolved with respect to all present phases. This method appears to be very fast, effective and reliable tool in screening tests of fertilizer quality immediately after production. It offers a possibility to estimate the undesirable quality changes related to phase transformation during storage. It should be noted that measured parameters can be affected by sample inhomogeneity in pile due to the large volumes of...
produced fertilizer, morphology of crystallites in the sample and by some other production and storage conditions.

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