EFFECT OF PHOSPHATE ADDITIVES ON PHYSICAL-CHEMICAL PROPERTIES OF AMMONIUM NITRATE

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ABSTRACT

The composition of nitrogen phosphorus fertilizers is offered obtained by mixing of two components: the melt of ammonium nitrate and Central Kyzyl Kum’s phosphorite taken in such a proportion guaranteeing the end product production containing \( P_2O_5 \) in a range: 1.05-5.04 %. The effect of phosphate additive on the physical-chemical properties and trademarks of ammonium nitrate are studied. It has been shown that the introduction of phosphate additives in ammonium nitrate’s melt leads to a significant improvement of ammonium nitrate’s quality indicators.

Keywords: ammonium nitrate, phosphate raw material, nitrogen phosphorus fertilizer.

INTRODUCTION

Ammonium nitrate (AN) is the most widespread fertilizer in the world and the most efficient nitrogen fertilizer containing at least 34.4% of nitrogen [1]. It can be applied at all types of soils and for all plants being a basic and feeding fertilizer for them.

Currently the world production of ammonium nitrate exceeds 43 million tons a year. In the Uzbekistan, three Open Joint Stock Companies (OJSK): “Maxam-Chirchik”, “Navoiazot” and “Ferganaazot” did produce more than 1.7 million tons of ammonium nitrate by 2012. However ammonium nitrate is used not only as a fertilizer but as an explosive component [2]. Series of terrorist attacks worldwide including Uzbekistan state were carried out with ammonium nitrate oxidizer leading to necessity of tight security measures at its handling [3]. Thus, in particular, China, Brazil, Colombia, Algeria, and the Philippines began to consider ammonium nitrate as an explosive and banned its use as a fertilizer. The Uzbekistan’s State Joint Stock Company “Uzkimyosanoat” annually spends USD 25000 for special guard measures at transportation of each batch from its productive factory to a farmer’s field.

Therefore, nowadays for the producers of ammonium nitrate it is very important to apply agriculture nitrate-based fertilizers with a less explosive property retaining however high agrochemical efficiency. So we decided to obtain such a stabilized ammonium nitrate by the introduction of phosphorite raw material (PRM) (Central Kyzyl Kum, Uzbekistan) into usual ammonium nitrate’s melt.

EXPERIMENTAL

For the experiments the ammonium nitrate produced at Open Join Stock Company “Maxam-Chirchik” (34.6 % N) and the PRM (characterized with the following composition, mass %: \( P_2O_5 \) (total) – 17.20; CaO – 46.22; \( Al_2O_3 \) – 1.24; \( Fe_2O_3 \) – 1.05; MgO – 1.75; F – 2.00; \( CO_2 \) – 16.00; \( P_2O_5 \) (acceptable) : \( P_2O_5 \) (total) = 18.49 %) have been used. Ammonium nitrate was melted in a metal cup
on a hot plate. Into the melt the PRM was injected preliminary taken in an amount providing the end product’s $P_2O_5$ content in a range of 1-5%. At 180°C for 30 minutes it was thoroughly mixed. The cooled product was powdered and chemically analyzed. Acceptable form of $P_2O_5$ and CaO components were determined at test procedure based on application of 2% citric acid. The chemical composition of nitrogen phosphorus fertilizers (NPF) so obtained is shown at Table 1.

For PRM granulation the ammonium nitrate was melted at 180°C, then the calculated amounts of phosphates salts were introduced into a number of pool, carefully stirred for 30 minutes, poured smoothly into granulator represented with a metal cup with a perforated bottom (diameter of holes 1 mm). Pumped to the top of the cup the melt was sprayed from a height of 30 m down to a plastic film lying on the ground. After that the strength of granules of 2-3 mm in diameter obtained was determined using the special device MIP-10-1 according to Standard [4] based on measuring the strength (kg) needed for granules destruction. The static strength of granules (kg/granule) was calculated using the formula:

$$Y = \frac{20}{20} \left( \sum_{i=1}^{20} P_i \right)$$  (2)

where $P_i$ - the force required to break a single granule (kg);

$$P_{por} = \frac{V_1 - V_2}{V_2 - V_3} \times 100$$  (3)

where $V_1$, $V_2$, $V_3$ - volumes of the buretted (ml).

The porous AN used as a component of explosive mixtures possesses this rate acceding 20%.

To present the results of tests in MPa units the value calculated (2) was divided by 10.2. For comparison the strength of pure AN pellets with a diameter of 2-3 mm was measured as well.

Porosity of pellets was determined by the volumetric method [5]. The essence of the porosity of pellets according to this method was as follows. Into a 25 ml burette equipped with a crane a certain amount of cryoscopic benzene was put ($V_1$). Then 10 g of AN or NPF were put there and after 1-2 min the changes of the burette’s volume ($V_2$) were fixed. Then the crane was opened, the benzene located between the fertilizer’s granules was pulled down into the second burette (volume also 25 ml) and its volume was measured ($V_3$). Porosity $P_{por}$ (in percentages) was calculated according to formula (3):

$$P_{por} = \frac{V_1 - V_2}{V_2 - V_3} \times 100$$  (3)

where $P_{por}$ - the force required to break a single granule (kg);

Table 1. The chemical composition of nitrogen phosphorus fertilizer.

<table>
<thead>
<tr>
<th>The ratio of the AN:PRM</th>
<th>Humidity</th>
<th>N, %</th>
<th>$P_2O_5$ acceptable, %</th>
<th>$P_2O_5$ acceptable, %</th>
<th>CaO, %</th>
<th>CaO acceptable, %</th>
<th>CaO acceptable, %</th>
<th>P2O5 water solubility, %</th>
<th>P2O5 acceptable, %</th>
<th>CaO acceptable, %</th>
<th>CaO acceptable, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 : 7</td>
<td>0,28</td>
<td>34,6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 : 13</td>
<td>0,35</td>
<td>32,25</td>
<td>1,05</td>
<td>1,03</td>
<td>2,70</td>
<td>2,44</td>
<td>0,94</td>
<td>98,09</td>
<td>90,37</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 : 20</td>
<td>0,36</td>
<td>30,75</td>
<td>2,01</td>
<td>1,95</td>
<td>5,69</td>
<td>4,79</td>
<td>1,45</td>
<td>97,01</td>
<td>84,18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 : 30</td>
<td>0,42</td>
<td>29,15</td>
<td>3,00</td>
<td>2,87</td>
<td>8,35</td>
<td>6,60</td>
<td>1,52</td>
<td>95,66</td>
<td>79,04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100 : 40</td>
<td>0,56</td>
<td>27,10</td>
<td>4,10</td>
<td>3,83</td>
<td>11,01</td>
<td>8,05</td>
<td>1,57</td>
<td>93,41</td>
<td>73,11</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The caking of samples X (in MPa) was calculated using the formula (4):

\[ X = \frac{P}{S} \]  

(4)

where \( P \) - breaking effort (N), kg;

\( S \) - cross-sectional area of the sample, cm\(^2\).

Bulk density of the fertilizer granules (Ø 2-3 mm) was determined according to State Standard at temperature 25°C [6]. Determination of the dissolution rate of nitrogen phosphorus fertilizer’s granules was conducted according to State Standard; the method consisted of visual observation and dissolution time recording for fertilizer pellets (Ø 2-3 mm) lowered into distilled water at 25°C, bathed into a chemical glass of 100 ml volume.

The hygroscopic point of the fertilizer granules (Ø 2-3 mm) has been determined by exsiccator method [7] at 25°C. The determination of increase or decrease of humidity of substance at constant temperature and certain relative humidity of air was carried out for 3 hours. The required relative humidity of air was created in the exsiccator at the certain concentration of sulphuric acid.

RESULTS AND DISCUSSION

The chemical analysis of the products showed that the melt activates nitrate phosphate raw material, in other words it transforms the indigestible \( \text{P}_2\text{O}_5 \) into the digestible for the plants state (Table 1). If in the source of phosphate raw material the ratio of masses of digestible form to the total \( \text{P}_2\text{O}_5 \) form was only 18.49 %, the products of its interaction with the melt of ammonium nitrate obtained the value of such ratio in the range of 88.29 - 98.09 %. The products contained 25.24 - 32.25 % N, 1.05 - 5.05 % \( \text{P}_2\text{O}_5 \) and 2.44 - 9.02 % \( \text{CaO} \).

At Fig. 1 the values of strength of nitrogen phosphorus fertilizer’s granules obtained by mentioned above method are offered. The data at Fig. 1 show that the addition into a melt AN of ordinary phosphoric flour in an amount of 7 - 40 g per 100 g of AN increases the strength of granules - from 4.26 to 7.8 MPa, in other words it let to increase the strength of granules NPF over 2.6 - 5.0 times in compare with the strength of granules of pure AN. Increasing the mass of additives in phosphate raw material’s melt AN leads to an increase of their strength’s values.

Various impurities presented in the phosphate raw material (\( \text{CaO} \), \( \text{P}_2\text{O}_5 \), \( \text{Al}_2\text{O}_3 \), \( \text{Fe}_2\text{O}_3 \), \( \text{SiO}_2 \), etc.) do effect on the structural properties of the NPF granules. Introduced into the melt of AN special phosphate additives form the fine inclusions in the structure of crystalline blocks of a fertilizer. Reducing the size of the individual
crystals of salt and increasing of their packing density significantly promote the increasing of the fertilizer granules’ strength. It leads naturally to an increasing of the bulk density’s values - from 0.925 to 1.033 g/cm$^3$ versus the value of the bulk density of pure ammonium nitrate: 0.855 g/cm$^3$ (Fig. 2). Increasing of the bulk den-
-sity of fertilizer supports a decrease of porosity of the studied samples, and this in turn indicates an increase in the strength of NPF granules.

The addition of phosphate raw material into the melt of ammonium nitrate also reduces the porosity and specific surface area of the internal NPF granule (Fig. 3). The experimental data indicate that the addition into the ammonium nitrate’s melt of phosphate raw material taken in above mentioned amount reduces the porosity of the obtained NPF granules (∅ 2-3 mm) from 9.15 to 7.08 %.

The data of NPF caking showed the fertilizers’ caking values decreasing from 2.77 to 1.7 kg/cm$^2$, that is 1.6 times according to the increase of phosphate additives mass from 7 to 40 grams. At the optimum mass ratio of the entered phosphate additive and the melt (AN: PRM = 100:40) the NPF caking reduced by 2.7 times compared to the caking of pure ammonium nitrate: 4.67 kg/cm$^2$.

We also determined the rate of dissolution of AN and NPF granules (Table 2). The data indicate that the introduction of a phosphate additive into the melt of ammonium nitrate fertilizer’s granules their dissolution rate is reduced in compare with the pure ammonium nitrate. At the increasing of mass portion of phosphate raw material from 7 to 40 % the obtained NPF granules’ samples demonstrate the increasing of dissolution period for them from 66.4 to 100.8 seconds in compare with granules made of pure nitrate: 46.8 seconds, thus it increases by 2.2 times. Reducing of the NPF granules dissolution rate, from our pint of view, occurs as a result of granules strength’s increasing: the more is strength of granules, the slowly is the dissolution of fertilizer’s granules.

The delayed solubility of NPF granules to a certain degree has a positive effect on the absorption of the fertilizer’s nutrients by plants through their root system, in the other words the granules containing phosphates will gradually give nutrients, resulting in significantly increase of their efficiency.

The hygroscopic points’ values of fertilizer samples were the following: for AN – 62.0 %, AN:PRM = 100:7 – 54.5 %, AN:PRM = 100:20 – 54.0 % and for AN:PRM = 100:30 and AN:PRM = 100:40 – 53.5 %.

The relative air’s humidity at the Uzbekistan is the following: monthly mean minimum – 46%, monthly mean maximum – 74 %, mean yearly – 60 %. According to Pestov’s scale [7] all Uzbekistan’s nitrogen-phosphorous fertilizers are hygroscopic. They are more hygroscopic than the parent ammonium nitrate. Despite of that the presence of water indissoluble components of phosphate additive and formation of crystallohydrates prevent from melting of end-product and accordingly reduces the negative influence of hygroscopy on agglutination in storage of ammonium nitrate.

<table>
<thead>
<tr>
<th>Mass ratio AN:PRM</th>
<th>N, %</th>
<th>P$_2$O$_5$, %</th>
<th>Time of granules dissolving, sec</th>
<th>Average value</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0,0</td>
<td>34,6</td>
<td>---</td>
<td>51 51 42 47 43</td>
<td>46,8</td>
</tr>
<tr>
<td>100:7,0</td>
<td>32,25</td>
<td>1,05</td>
<td>68 58 71 66 69</td>
<td>66,4</td>
</tr>
<tr>
<td>100:13,0</td>
<td>30,75</td>
<td>2,01</td>
<td>80 64 79 78 76</td>
<td>75,4</td>
</tr>
<tr>
<td>100:20,0</td>
<td>29,15</td>
<td>3,00</td>
<td>82 89 75 81 88</td>
<td>83,0</td>
</tr>
<tr>
<td>100:30,0</td>
<td>27,10</td>
<td>4,10</td>
<td>96 94 81 92 93</td>
<td>91,2</td>
</tr>
<tr>
<td>100:40,0</td>
<td>25,24</td>
<td>5,04</td>
<td>104 104 106 94 96</td>
<td>100,8</td>
</tr>
</tbody>
</table>
CONCLUSIONS

The possibility of obtaining of nitrogen phosphorus fertilizers by phosphate raw materials (Central Kyzyl Kum) introducing into a melt of ammonium nitrate was studied. The chemical composition of fertilizers showed that the phosphate raw material in the molten nitrate is activated, in other words the indigestible $P_2O_5$ in the raw material transforms into digestible state suitable for plants. This allows turning phosphate raw materials into an effective phosphorus fertilizer without using the scarce acid reagent.

The introduction of phosphate raw materials of Central Kyzyl Kum into a melt of ammonium nitrate leads to significant quality improvements (strength, bulk density, porosity, caking, hygroscopity and the dissolution rate of granules) of the ammonium nitrate.

This method is basic for new fertilizers producing at OJSC “Navoiazot”. The granulated nitrogen phosphorus fertilizer possesses an excellent physical, chemical and production characteristics. It does not deteriorate and corresponds to TSh 6.1-00203849-111:2007 State Standard. From the beginning of 2009 more than 200000 tons of nitrogen phosphorus fertilizers have been produced casting USD 37.5 millions and sent to consumers.

REFERENCES