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IMPROVEMENT OF THE PROCESS OF IMPROVING THE QUALITY OF UREA GRANULES

The object of research is the process of improving the quality of urea granules by processing. The subject of research is the physicochemical properties of granular urea after processing with a new composite. Granular urea has a wide range of uses, but during storage and sale it is capable of caking with a significant loss of its flowability, static and dynamic strength of granules. When transporting over long distances, these phenomena cause inconvenience in loading and unloading operations, and also affect the quality of the supplied goods. Therefore, the search for methods to improve its quality is still important. The paper considers the results of theoretical studies of ways to improve the quality of granular urea. As a rule, at most enterprises, an additive is introduced into the urea melt – urea-formaldehyde concentrate, which promotes the formation of isometric forms of urea crystals and reduces the growth rate of faces with the third pinacoid. Due to the toxicity of formaldehyde, the market for such urea is limited. The results are presented for laboratory tests of the processing of urea produced by pouring without a fluidized bed, a new anti-caking composite – a hydrolyzed solution of protein raw materials from the family of fibrillar proteins with a protein raw material concentration of 10 %. The main purpose of the granule processing was to improve the quality of urea through the use of a new composite anti-caking agent, which leads to an increase in the shelf life without changing the physicochemical properties and provides an environmentally friendly condition. As a result of laboratory studies, a decrease in moisture absorption was revealed. It has been established that the proposed anti-caking agent exhibits a hydrophobilization effect. The effectiveness of the conditioning action of the proposed composite has been proven, which consists in achieving fixation of a hydrophobic coating of natural origin on the surface of fertilizer granules and, as a consequence, reducing the percentage of caking of fertilizers. The disadvantages of the developed composite were also established, namely: the fact of a decrease in the static strength of granules after processing was established. Therefore, work on improving the composition of the composite will continue.

Keywords: *granular urea, modifier additives, anti-caking composite, granule flowability, surface treatment, moisture absorption, static strength.*

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1. Introduction

Urea modification by introducing additives into its composition or coating granules with various substances is aimed at increasing the efficiency of its use in agriculture and animal husbandry. As a result of the use of modifiers, the flowability of urea during its transportation, storage and use is preserved, the strength of the granules increases, hydrolysis and nitrification in the soil slows down, and the nutritional value increases due to the introduction of additional nutrients, in particular, microelements. Urea is a water-soluble fertilizer, therefore it is capable of caking (crumbling), and with prolonged storage, urea loses its static and dynamic strength, therefore its storage is a problem for some farms. Urea can lose flowability due to the formation of adhesion contacts between the particles. There are three main types of contacts: cohesive, phase and liquid. Cohesive contacts arise if there are no adsorption layers of air molecules or other substances on the collision surface of particles. The effect of loads on the proportions during the transportation of fresh, well-dried urea, when the adsorption of gases and vapors on its surface is minimal, leads to an increase in the number of cohesive contact points and to product compaction. An effective way to combat cohesive compaction is to cool a granular product: as its temperature decreases, the adsorption of air on the surface increases, making it difficult or eliminating cohesive contact [1, 2].

Weather conditions also affect the strength of the pellets. In [3], to assess the influence of weather conditions on the quality of urea, a set and processing of statistical data on the quality of urea in summer (July) and winter (December) time was carried out. According to the results of the aforementioned study, in the summer there is a decrease in the strength of the granules and an increase in their moisture content. It has also been found that temperature significantly affects the strength of the granules. At lower cooling temperatures of granules, their strength increases [4]. To increase the strength of urea granules, as well as to increase the proportion of granules with a diameter of 2–4 mm, the cooling conditions for droplets in the process of floatation are changed by increasing the height of the granulation tower [5, 6]. However, these methods do not provide sufficient indicators of granulometric composition and strength of granules for consumers. To improve the quality of urea, various modifying additives are also used [7, 8]. Today, at most enterprises, to increase the strength of granules into the melt, a synthetic resin from the group of aminoplasts is dosed, the product of polycondensation of urea with formaldehyde is urea-formaldehyde resin (UFR), which promotes the formation of isometric forms of urea crystals and reduces the growth rate of faces with the third pinacoid [9]. UFR is introduced into the urea melt at the stage of evaporation before granulation [10]. Due to the toxicity of formaldehyde, the market for such a product is limited. There is also a method of processing the finished product by spraying or powdered anti-caking agents of various compositions [11]. However, the anti-caking composites on the market do not fully meet the requirements for the product in the absence of UFR, therefore, the search for new composites is an urgent line of research.

Thus, *the object of research* is the process of improving the quality of urea granules by processing.

The subject of research is the physicochemical properties of granular urea after processing.

The aim of research is to improve the quality of urea granules by processing through the use of new anti-caking composites, increasing the shelf life without changing the physical and chemical properties and ensuring environmental friendliness.

2. Methods of research

A new composite anti-caking agent has been created, namely: a hydrolyzed solution of protein raw materials from the family of fibrillar proteins with a concentration of protein raw materials of 10 % mass particles (m. p.). In the presented studies, let's use samples of urea containing UFR (formaldehyde concentration=0.06 % ppm) and without UFR, which met the requirements of DSTU 7312:2013. Urea. Technical conditions. The dose of the anti-caking agent was 1 kg/t of the product with a formaldehyde content of 0.06 % and 1.5 kg/t of urea without formaldehyde content. The anti-caking agent was applied using a laboratory nozzle. The method for determining the dose of anti-caking agent is weight. In the course of laboratory tests, the main indicators of efficiency were taken as caking, moisture absorption, static strength of granules before and after moisture absorption. Samples for research were processed with a new composite. The reference samples are analyzed for moisture content using an infrared moisture meter; the static strength of the granules is determined using a device – a granule strength meter IPG-1M (manufacturer «Unikhim OS», Yekaterinburg, Russia). To determine moisture absorption in static conditions, a climatic chamber with a relative humidity of 70 % was used. The residence time of the processed samples of samples and reference samples in conditions of high humidity at a temperature of 17 °C is 5 days. Traceability was determined by the height of the stuck together sample columns in relation to the entire sample %. Also, the parameters of caking in ambient conditions were determined after 5 days of stay at a temperature of 17 °C; pressure of 1 atm; relative air humidity 40 %.

3. Research results and discussion

The averaged results of laboratory tests of the quality of urea obtained by the pouring method without a fluidized bed (with and without UFR) when treated with a new composite anti-caking agent are presented in Table 1.

A negative point is a decrease in the static strength of the granules, caused by the introduction of additional moisture into the granule by the solvent of the composite, which rearranges the crystal lattice. According to the molecular kinetic approach, to the determination of the equilibrium shape of a polyhedron (the Stransky and Kaishev method), moisture evaporation occurs in places where the atom bond is weakest, that is, inflection points (breaking) are formed, also called the position on the crystal. In the process of processing, the fracture points are regrouped. By wetting the crystal, moisture is absorbed, breaking the Periodic Bond Chain. The indicator of moisture absorption and flowability turned out to be positive. The proportion of caking during sample processing decreased in all cases. After moisture absorption, the moisture content in the treated sample of urea without UFR was 16 % less than the moisture content of the reference sample of the urea sample without formaldehyde and 14 % less than the moisture content in the reference sample with formaldehyde content of 0.06 %, which confirms the effectiveness of the conditioning effect. The anti-caking composite based on fibrillar proteins prevents the formation of crystallization-type contacts between the particles (the formation of agglomerates).

Table 1

Average results of urea quality after treatment with a new composite

Mass fraction of formaldehyde, %	Mass fraction of anti-caking agent, kg/t	Mass fraction of H_2O, %	Granulometric composition				Static strength of granules		Mass fraction of H_2O, %		Caking after moisture absorption	
							before	after	before	after		
			fractions size				moisture absorption		moisture absorption		40 % humidity	70 % humidity
			<1 mm	1–2 mm	2–3 mm	3–4 mm						
			%				kgf/granule		%		%	
0.00	0.0	0.11	1.0	0.7	94.2	4.1	1.10	0.88	0.11	0.15	3	50
0.00	1.5	0.13	1.0	0.9	93.8	4.3	1.02	0.72	0.13	0.12	5	30
0.06	0.0	0.10	0.8	1.0	94.5	3.7	1.00	0.91	0.10	0.14	2	0
0.06	1	0.11	0.6	1.0	95.4	3.0	1.03	0.77	0.11	0.12	2	0

4. Conclusions

The developed composite anticaking agent exhibits a hydrophobilization effect, which leads to a decrease in the moisture absorption rate. The effectiveness of the conditioning action of the proposed anti-caking agent is proved, which consists in achieving fixation of a hydrophobic coating of natural origin on the surface of fertilizer granules and, as a consequence, reducing the caking of fertilizers. The proposed anti-caking composite requires improvement, since after application the static strength of the granules decreases. Therefore, work on improving the composition of the composite will continue. The substance of natural origin, included in the composition of the anti-caking agent, is environmentally friendly, therefore, processed urea can be used in pharmacology, cosmetology and in animal husbandry, which significantly expands its sales market.

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CALCULATIONS OF TWO-FLOW REGENERATION OF ACTIVATED METHYLDIETHANOLAMINE SOLUTION

The object of research is the stage of regeneration of the spent solution of purification of process gas from CO_2 in the production of ammonia with a capacity of 1360–1500 t/day, in a two-section plate regenerator-recuperator. The calculations confirmed the possibility of replacing the monoethanolamine absorbent solution (MEA) with activated methyldiethanolamine solution (aMDEA) for a two-flow purification and regeneration scheme. One of the most problematic places is the lack of a mathematical model of two-flow regeneration of a new absorbent. During the study to determine the composition of the vapor-gas mixture used the method of material balance, which takes into account the temperature of the upper and lower parts of the regenerator and proposed numerical integration to calculate the number of plates of the regenerator.

An algorithm and a program of multivariate calculations have been developed and implemented in Excel, which provide for variation of concentration parameters over a vapor-gas mixture. Thermal calculations take into account the endothermic reactions of CO_2 desorption, water evaporation and determine the specific heat consumption for solution regeneration. The decrease of specific heat consumption for regeneration of activated aMDEA solution from 4.4 to 3.11 MJ/m^3CO_2 was determined in comparison with MEA solution. The approximations of the equilibrium pressure of CO_2 over the MDEA solution on the degree of carbonization of solution and the desorption temperature are approximated. The kinetic calculation of the regenerator established the number of plates equal to 14 when the number of 31 plates in a standard regenerator-recuperator. The calculated number of plates determines the reliable regeneration of the solution in one apparatus to the required degree of carbonization of coarsely (0.35) and finely regenerated (0.1) solutions. The reduction in the number of plates when using aMDEA is due to taking into account the properties of this solution, in particular, the difference in the equilibrium pressure of CO_2 over aMDEA compared to MEA. The real possibility of using 40 % aMDEA solution instead of 18 % MEA solution on existing two-stream absorbers and regenerators without changing the technological scheme is established.

Keywords: *process gas, carbon monoxide (IV), methyldiethanolamine, piperazine, two-section plate regenerator, numerical integration.*

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1. Introduction

The regeneration of waste solutions obtained during the purification of process gas from carbon monoxide (IV) in the production of ammonia takes place in strippers (regenerators) – packed or disc-shaped. Physicochemical basis of regeneration is provided in [1]. Technological schemes for the regeneration of solutions of monoethanolamine (MEA) and potash, design features of the regenerators are considered in [2, 3]. In works [4, 5], a comparative analysis of schemes and methods of purification from carbon monoxide (IV) is provided. The method of purification with the use of an activated solution of methyldiethanolamine (aMDEA) with a concentration of up to 50 %, activated with piperazine $C_4H_{10}N_2$ (PZ, diethylenediamine) with a concentration of up to 5 %, has become widespread [6, 7]. Examples of the design and industrial implementation of this method are a single-flow technological scheme of purification from CO_2 with an ammonia capacity of 1,550 t/day [8] and amine purification with an ammonia capacity of 1,000 t/day [9]. Note that, unlike the purification stage, much less attention is paid to the aMDEA regeneration stage. Thus, the authors of [10] investigated the energy consumption for the regeneration of the mixed absorbent MEA/MDEA. A decrease in the energy of regeneration when using this solution in comparison with the MEA solution has been proven. In [11], the influence of the MDEA/PZ ratio on the energy consumption of regeneration of the flue gas cleaning solution of a coal-fired power plant was studied. In the study [12], the simulation of single-stream regeneration of the spent aMDEA solution in a tray desorber with an ammonia capacity of 600 t/day was carried out. The results of modeling the two-flow regeneration of the MEA solution are given in [13].

Simulation of two-flow purification of process gas from CO_2 with an activated solution of aMDEA is described by the authors of this work in [14]. The proposed material is a logical continuation of the specified work and reflects in-depth attention to the calculation aspects when introducing this method, especially for large-scale production. Therefore, the development and implementation of calculations of precisely two-stream solution regeneration is relevant. Thus, *the object of research* is the stage of regeneration of the spent solution for cleaning the process gas