Kinetics of calcium Cyanamid obtaining process from lime, carbon dioxide and ammonia

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ABSTRACT

In Uzbekistan, the main range of nitrogen fertilizers produced is ammonium nitrate, carbamide and ammonium sulfate, the use of which has led to acidification of millions of hectares of land for many years, which negatively affects the receipt of high yields of agricultural crops.

1. INTRODUCTION

Scientific research has established that the physiological calcium deficiency in soil salinity is one of the main factors limiting the salt tolerance of cotton and other crops. Therefore, the development of the production of mineral fertilizers on the basis of our own raw materials, especially calcium-containing and alkaline species such as calcium cyanamide and others, is important for growing crops in saline soils and limited water resources [1].

Calcium cyanamide is a slow-acting fertilizer and nitrogen from it is absorbed by plants more efficiently. When applied under autumn plowing, it is preferable to other nitrogen fertilizers and has a sterilizing effect on the harmful microflora of the soil.

Defoliants are of no small importance for obtaining high and high-quality crop yields.

Calcium cyanamide and its derivatives are a mild defoliant, unlike other defoliants, they relatively quickly lose their toxic properties, decomposing within 48-72 hours.

Industrial processing of calcium cyanamide provides a number of valuable products for various industries, including gold mining.

Calcium cyanamide opens up rich possibilities for the synthesis of both simple organic compounds (cyanides) and more complex organic substances that may be of importance in the manufacture of explosives, in the production of pharmaceutical products, plastics, artificial resins, dyes, etc.

Calcium cyanamide can be used to produce dicyanamide, which in itself may find limited use, but serves as the main source for the synthesis of guanidine, urea granules and other more complex substances.

Guanidine perchlorate, nitroguanidine and nitrocyandiamidine are substances that can be used in various explosive mixtures and are held in reserve by many leading countries.

The above compounds, as well as urea and thiourea derivatives, are beginning to play an increasing role in the synthesis of pharmaceutical products.

However, the production of such compounds as calcium cyanamide has not been established in our Republic, and this issue remains relevant to this day.

2. MAIN PART

In kinetic studies, first of all, we determined the order of the chemical reaction between calcium oxide, ammonia and carbon dioxide. In the experiments, the effect of changing the initial composition of one of the gas components of a chemical reaction was investigated with the relative constancy of the other component. Experimental studies were carried out by the excess method, in which an excess of ammonia was used in one series of experiments, and an excess of carbon dioxide was used in the other. The excess was high enough that the concentration of the excess component remained practically constant from trial to trial. The concentration of the other component, which was used to determine the order of the reaction, changed very significantly from experiment to experiment - several times.

Based on the results of experiments carried out at various initial concentrations of the gas component and the duration of obtaining calcium cyanamide, we obtain a series of curves in coordinates from the percentage of nitrogen in the product - $C_{\rm N2}$ and time - τ .

Further, to determine the order of the reaction, the method of initial rates was applied, according to which the CN_2 - τ curves were graphically differentiated to determine the rate of the process $(dCN_2/d\tau)$ at any time from the beginning of the reaction.

In the coordinates process speed - time, curves were plotted in accordance with the speed values $(dCN_2/d\tau)$. The constructed curves were extrapolated, and then the rate of the process was determined in the initial period $(\tau=0)$.

After that, a curve was constructed in the coordinates of the logarithm of the initial velocity - the logarithm of the initial concentration of the tested component. The constructed curve had the character of a

straight line, the slope of which to the abscissa axis showed the order of the reaction for the component under study, i.e. the particular order of the reaction for carbon dioxide or ammonia.

During the experiments, the duration of the calcium cyanamide synthesis process varied from 25 to 105 minutes in 15-minute increments, the NH₃:CO₂ ratio ranged from 4:96 to 96: 4. The charge was prepared on the basis of natural limestone of the Jamansai deposit.

The temperature of 800° C was kept constant, which turned out to be optimal in the previous experiments, the volumetric velocity of the initial gas mixture was 6000 h⁻¹.

According to classical concepts, the reaction order can be 0, 1, 2, and 3, as well as fractional. In this regard, the experimental data obtained were checked by the known equations and diagrams, which showed their discrepancy. Therefore, from a theoretical point of view, the reaction is not three-molecular, apparently, it has an order associated with the complex mechanism of the reaction of formation of calcium cyanamide.

The first series of experiments to determine the order of the reaction with respect to carbon dioxide was carried out at a ratio of $CO_2:NH_3 = 4:96, 7:93, 10:90$.

The second series of experiments to determine the order of the reaction with respect to ammonia was given at the ratios of carbon dioxide to ammonia 96:4, 93:7, 90:10.

According to the results of experiments (Figs. 1 and 2), it can be concluded that with the same duration of the process, ammonia accelerates the formation of calcium cyanamide more than carbon dioxide.

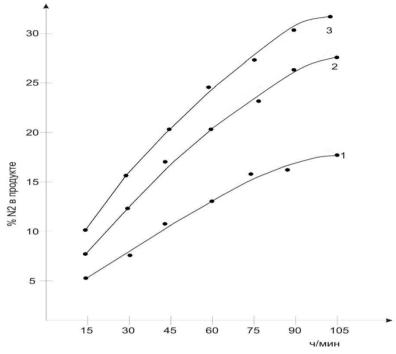
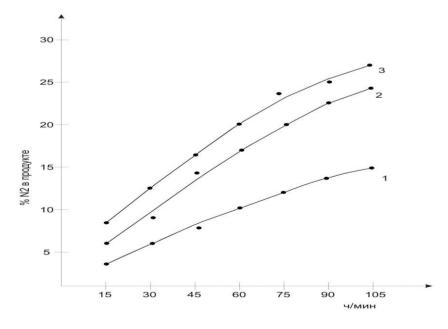
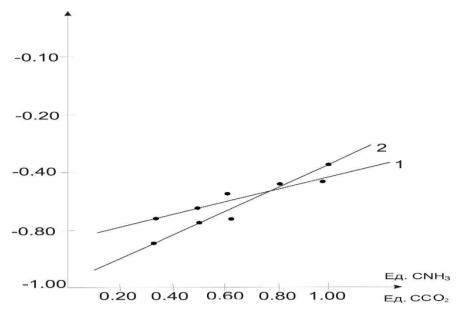


Figure: 1 Dependence of the nitrogen content in the product on the duration of the process and the concentration of ammonia in the gas mixture



1-4%, 2-7%, 3-10%

Figure: 2 Dependence of the nitrogen content in the product on the duration of the process and the concentration of carbon dioxide in the gas mixture



 $1-\Pi co_2=0,416, 2-\Pi NH_3=0,425$

Figure: 3 Dependence of the logarithms of the initial rates of the synthesis of calcium cyanamide on the logarithms of the concentration of carbon dioxide and ammonia in the initial gas mixture

The determination of the particular orders (Fig. 3) shows that the order of the formation reaction for carbon dioxide is 0.416, and for ammonia - 0.71205.

Since the reaction orders are fractional, this indicates that the process of chemical interaction of calcium oxide with ammonia and carbon dioxide is complex and its mechanism cannot be expressed by a simple stoichiometric equation.

Based on certain reaction orders, it can be considered that the heterogeneous process of the formation of calcium cyanamide from lime, ammonia and carbon dioxide is a complex process that includes a number of successive stages. In this regard, the overall speed will be determined by the speed of the slowest stage.

We put forward a hypothesis that the limiting stage of the studied process is the chemical interaction on the surface of a solid lime particle. To verify this, a number of experiments were carried out under optimal conditions for the synthesis of calcium cyanamide from lime, ammonia and carbon dioxide.

With the constancy of all other conditions of the experiment, changes were made: the duration of the process of exposure to the initial gas mixture from 15 to 120 minutes, as well as temperatures from 700 to 900° C.

Based on the experimental data (Fig. 4), graphs were constructed showing the effect of the temperature and duration of the process on the nitrogen content in calcium cyanamide.

The results of the analysis are in good agreement with the experimental data on the effect of temperature on the production of calcium cyanamide presented in this chapter.

The nature of the curves (Fig. 5) shows that in the initial period of the synthesis process they differ in steepness, which corresponds to the formation of a product at a high rate. With an increase in the duration of the synthesis process, the curves become flat, tending to a straight line, which reflects the achievement of an equilibrium yield of calcium cyanamide for the corresponding temperatures.

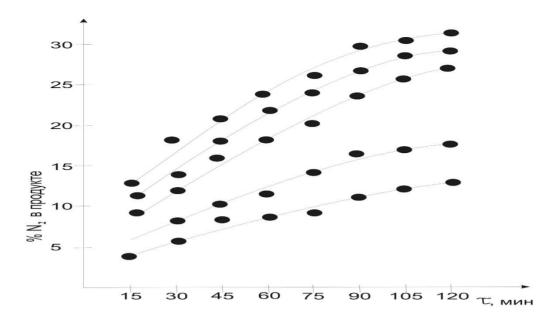


Fig. 4 Influence of the duration and temperature of synthesis on the nitrogen content in the product Based on the research results, it can be concluded that the limiting stage of the process of obtaining calcium cyanamide from lime, carbon dioxide and ammonia is the diffusion of the initial gas components through the product layer.

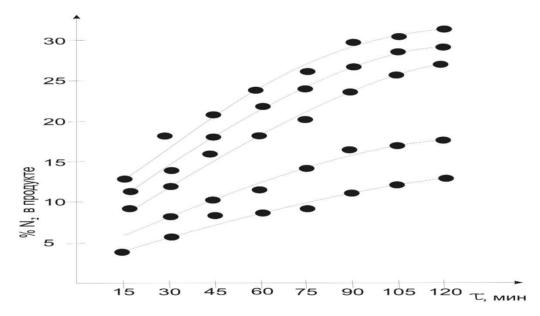


Fig. 5 Influence of the duration and temperature of synthesis on the nitrogen content in the product

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