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ANALYSIS OF THE FREE CARBON CONTENT IN THE SYNTHESIS OF CALCIUM CYANAMIDE

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Annotation
Technical solutions have been developed to create a technology for the production of calcium cyanamide from lime, carbonate anhydride and industrial ammonia. A technological scheme for the production of nitrogen fertilizer and an effective defoliant - calcium cyanamide was developed and the optimal technological parameters of the process were determined at the experimental plant. An experimental batch of calcium cyanamide was produced.

Keywords: Carbon dioxide, ammonia, expander gas, calcium cyanamide, off-gases.

Application of nitrogenous fertilizers, mainly alkaline forms of calcium cyanamide, is one of the most economical and effective methods of neutralizing soil acidity. This is one of the third properties of calcium cyanamide, according to which commercial calcium cyanamide is better than other alkaline forms of nitrogen fertilizers due to the presence of free lime and the ability to neutralize bound calcium.
The fourth characteristic of calcium cyanamide is that calcium cyanamide and its derivatives are considered to be particularly common defoliants for artificial removal of cotton leaves before harvesting by machine [2].
Unlike other defoliants, calcium cyanamide completely decomposes in soil to ammonia and calcium carbonate within 48-72 hours [3] and quickly loses its weak toxic properties.
Decomposition of calcium cyanamide, calcium carbonate and ammonia products is involved in neutralization of saline soils, and ammonia can also play the role of nitrogen fertilizers.
The characteristic of calcium cyanamide is that it is one of the best anti-wilt preparations.
The properties that distinguish calcium cyanamide from other types of mineral fertilizers are very important, so that every year a certain part of cotton (30% in some districts) is lost due to wilt disease.
Another important aspect of calcium cyanamide is that it is particularly safe compared to more common nitrogen fertilizers such as ammonium nitrate.
Because of this problem, a number of developed countries refuse to use ammonium nitrate in agriculture [5].

Until now, the carbide method for the production of calcium cyanamide has undergone some improvements [6], as a result of which the duration of the process cycle has been reduced from more than 60 hours to 52 hours, the productivity of the furnaces has increased from 2.5 t/day to 52 t/day, vertical furnaces have been replaced by rotary ones, the use of elemental nitrogen increased from 30 to 85%. However, the production process of calcium cyanamide by the carbide method has become cyclical, long-term, labor-intensive, energetic, multi-stage and inefficient, and has been carried out in factories in Germany, Italy, France, the United States and other countries using catalyzed additions of potassium chloride or potassium fluoride.

The difference between obtaining "white" calcium cyanamide by the carbide-free method and black calcium cyanamide by the carbide method is based on the following general reaction:

$CaCO_3+4NH_3+CO_2=CaCN_2+(NH_4)_2CO_3+2H_2O$ (1)

The use of some additives in the initial batch also gives some positive effects in the synthesis of calcium cyanamide, but they are not always available in nitrogen production plants to build a calcium cyanamide production plant there. Therefore, it is necessary to purchase these additives in the parties or to produce them on site. It requires additional capital, as well as labor and energy consumption, which increases the cost of the product.

Thus, it was necessary to research effective technologies for the synthesis of calcium cyanamide with recycling without catalytic additives.

Researches on the synthesis of calcium cyanamide by the carbide-free method conducted by Sh. A. Yakubov and O.Kh.Panjiev [10] without adding any catalytic additives to the initial charge, in which the gaseous mixture of carbon monoxide and ammonia were exposed to calcium oxide granules, play a clear role.

As indicated above, the possibility of free carbon formation in calcium cyanamide plays a major role. Therefore, during the synthesis of calcium cyanamide by the carbide-free method, we made a thermodynamic calculation of the probability of free carbon formation in the composition of the mixture of carbon (IV) oxide and ammonia gases to calcium oxide. The formation of free carbon occurs according to the following chemical reaction:

$2NH_3 + CO_2 = C + N_2 + 2H_2O + H_2 + Q$

A thermodynamic calculation was performed in the range of 873-1373^{0}K with a temperature step of 100^{0}K for the given starting gas. According to Hess's law, the thermal effect of the above chemical reaction under standard conditions at constant pressure was calculated by the following formula:

$\Delta H^o_{298}=\Sigma\Delta H^o_{пр} - \Sigma\Delta H^o_{ис}$

In this formula, $\Sigma\Delta H^o_{пр}$ is the algebraic sum of the heat of the product produced as a result of a chemical reaction carried out under standard conditions, cal/mol. $\Sigma\Delta H^o_{ис}$ is the algebraic sum of the heat generated in the initial components under standard conditions, cal/mol. According to the results of the above calculations, the enthalpy is $\Delta H^0298=2257,2$ cal/mol. This proves that the reaction under investigation is endothermic under standard conditions. The entropy change (ΔS^0298) of the above reaction was found to be 106.28 cal/mol.degree. After that, it was determined that the reaction under study was reversible. The result of the calculation is the change in Gibbs energy showed that it is equal to ΔG^0 =298 cal/mol. The obtained result indicates the thermodynamic probability of the reaction. Consequently, our experimental study under standard conditions did not confirm this conclusion, and therefore it was decided to perform further thermodynamic calculations at higher temperatures. For

this, the Kirchhoff equation was used and the temperature dependence of the heat capacity was deduced. Based on this relationship, the thermodynamic parameters of the reaction were calculated, the results of the calculation are presented in Table 1.

Table 1

Т.к.	873	973	1073	1173	1273	1373
ΔH_T^0, col/mol	25406	25979	26240	26313	26675	26573
ΔG_T^0 col/mol	25962	23598	20624	17100	13050	8477

The thermodynamic parameters of the reaction, depending on the results, were calculated. Studying the data, the entire temperature range (873-1373°K) shows that the reaction heat is endothermic. The reaction decreases with increasing heat temperature up to 1173°K, and then they increase a little. In the following calculations, we determine the value of Gibbs energy change.

These data indicate that the absolute value of the Gibbs energy change decreases with increasing temperature. Experiments were conducted at high temperatures to obtain a gas mixture of calcium cyanamide under the action of carbon dioxide and ammonia calcium oxide.

As a result of the research, a granular white product was obtained. The volume of the product is reduced compared to the initial volume of the product; its strength is higher compared to the initial volume. The white color in the resulting product confirms the absence of free carbon. The obtained calcium cyanamide was qualitatively analyzed depending on the content of CO_2 and CN^{-1}- ions. The result of these analyzes showed that CO_2 and CN^{-1}- ions are not clearly present.

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