
Calcium Cyanamide Studies

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

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

Mineral fertilizers play a key role in the development of agricultural production, because almost 50% of the cultivated yield is attributed to the use of mineral fertilizers. Therefore, the production of mineral fertilizers is constantly increasing. For example, the use of mineral fertilizers in agriculture in 1994-1995 was 121.8 mln and it reached to 134.1 million tons in 1997-1998 [1]. Today, only in China, 40 million tons of mineral fertilizers are being produced. In 1994-2000, 17 nitrogen and 11 phosphorus fertilizers producing plants were built in this country. Russia, Kazakhstan, Ukraine, Belarus, and the Republic of Uzbekistan in Central Asia are among the countries with phosphorus raw material reserves and developed fertilizer production industry.

The main assortment of nitrogen fertilizers produced in our country consists of ammonium nitrate, urea and ammonium sulfates. These fertilizers are physiologically acidic, and as a result of their use for many years, millions of hectares of agricultural land have become acidic, so it has a negative effect on increasing the productivity of agricultural plants.

Application of calcium cyanamide to the soil at the time of plowing is more effective than other forms of nitrogen fixation. In addition, calcium cyanamide neutralizes the harmful microflora of the soil. Important products can be made from calcium cyanamide for a variety of industries, including those used in the gold mining industry. However, the production of fertilizers like calcium cyanamide has not been established in our Republic, and this issue remains relevant to this day.

Temperature is one of the most important technological parameters of calcium cyanamide synthesis in the carbide-free method.

The synthesis of calcium cyanamide was carried out at different temperatures under the

following initial conditions:

1. It was prepared by burning the chalk from the Kitab mines on the basis of the initial slaked lime
2. Layer is prepared on the basis of CaO
3. The size of the layer granule is 2-3 mm.
4. Layer volume - 10 ml.
5. The average initial layer's weight is 4.82 gr.
6. The drying temperature of the initial layer is 600° C.
7. Duration of transfer of initial gaseous mixture is 90 minutes.
8. The fusion temperature in the range of 50°C is from 700 to 900°C
9. The ratio of CO₂ to NH₃ is 1:9.
10. Volumetric velocity of the initial gaseous mixture is 6000 hour⁻¹.

Further analysis and absorption of the exhaust gases resulting from the transfer in the experimental device was done as follows:

1. 7 N sulfuric acid solutions was added to the absorber with a 10% reserve for 15 minutes, in the amount of gas mixtures.
2. With a 10% reserve, it was placed in the absorber for 15 minutes in the amount due to the release of gas mixtures from the 40% NaOH solution.
3. Absorbers are replaced with their contents every 15 minutes.
4. Absorbed exhaust gases in the absorber are collected in a gas collector to measure their total volume through a gas counter.

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 layer, its solidity is higher compared to the initial layer [2-4]. The white color in the resulting product confirms the absence of free carbon. Based on the content of calcium cyanamide CO₂ and CN⁻¹- ions, the qualitative analysis presented in section 2 was carried out. The result of these analyzes showed that CO₂ и CN⁻¹- ions were not present. The nitrogen content in the synthesized calcium cyanide depends on the process temperature.

Table 1 Nitrogen retention in the product depends on the temperature of calcium cyanamide synthesis

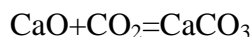
T _{Synthesis} , °C	700	750	800	850	900
N ₂ , %	15,2	24,1	30,2	28,1	21,8

From the obtained data, it can be seen that the retention of nitrogen in the obtained product increases to 30.2% at 800°C, reaching a maximum at the beginning with the increase in temperature. Then, as it grows, it decreases.

The lack of nitrogen below the temperature of 800°C is caused by the incomplete reaction during the synthesis of calcium cyanamide, and its low amount with increasing temperature is caused by the thermal decomposition of ammonia, which is one of the initial components, above the temperature of 800°C. The change of the amount of nitrogen in the obtained product corresponds to the results [8-10].

It should be noted that carbon dioxide gas is found in the product at temperatures below 800°C.

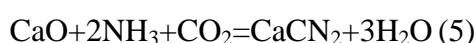
This is due to the fact that the chemical reaction in the partial formation of calcium carbonate gas under the given conditions is as follows:



At temperatures of 800°C and above, under hermetic conditions, the equilibrium of this reaction shifts to the left, and therefore the presence of calcium carbonate in the obtained products was not seen.

According to the literature review, a number of gaseous components may be involved in the process of synthesis of calcium cyanamide, the presence of them depends on the used initial materials and a number of processes involved in the production of calcium cyanamide. In the composition of the emitted gases in the factors indicated above carbon monoxide, carbon dioxide, ammonia, hydrogen cyanide, nitrogen, hydrogen, water vapor and others are found.

The composition and amount of emitted gases was determined according to the given methodology, as well as stoichiometric calculation of the effect of substances according to the reaction:



As the temperature rises during the synthesis of calcium cyanamide, the amount of ammonia and carbon dioxide decreases, and that of ammonia decreases relative to carbon dioxide. When the temperature increases from 700 to 900°C, the amount of ammonia decreases by 7.46%, and that of carbon dioxide decreases to 0.60% [6]. As the temperature rises, the amount of nitrogen increases by 2%. and hydrogen increases by 6% in the gases released from the synthesis of calcium cyanamide which is from 700 to 900°C.

When it comes to carbon monoxide, its amount is minimal and practically does not depend on temperature.

The amount of carbon monoxide in the range of temperatures can be up to 0.18-0.25%.

The amount of methane in the exhaust gases is in the range of 0.22-0.31%.

Table 2 Temperature dependence of the balance of ammonia and carbon dioxide.

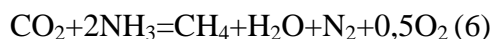
Synthesis temperature, °C	The amount of nitrogen in the product, %	Ammonia balance (% at baseline)			Carbon dioxide balance (% at initial)	
		In the product	In exhaust gases	Defecation	In the product	Gases exhausted
700	15,2	1,30	95,40	3,30	5,84	94,16
750	24,1	2,24	93,25	4,51	10,12	89,88
800	30,2	2,98	91,62	5,40	13,42	86,58
850	28,1	2,72	90,56	6,72	12,24	87,76
900	21,8	1,99	89,94	8,07	8,96	91,04

Table 3 The composition of the exhaust gases in the temperature dependence of the synthesis of calcium cyanamide

Temperature °C	Composition of exhaust gases, %					
	NH ₃	CO ₂	N ₂	H ₂	CO	CH ₄
700	84,48	9,26	1,46	4,37	0,18	0,25
750	82,72	8,86	2,00	6,00	0,20	0,22
800	81,37	8,54	2,40	7,19	0,19	0,31

850	79,23	8,53	2,94	8,82	0,25	0,23
900	77,02	8,66	3,46	10,37	0,21	0,28

Based on this, it can be concluded as follows, the content of gaseous compounds used for the synthesis of calcium cyanamide is very small, and they are not additional reaction products, but carbon monoxide and methane compounds.



When increasing the temperature of calcium cyanamide synthesis from 700 to 800°C, the content of carbon dioxide in the emitted gases decreases.

After increasing the temperature above 800°C, it first increases and then decreases as the temperature rises

The decrease in the amount of nitrogen in the product leads to the fact that carbon dioxide undergoes a chemical reaction to form a small amount of calcium cyanamide.

Experimental studies on the effect of temperature on the synthesis of calcium cyanamide show that with an increase in temperature, the amount of nitrogen in the product reaches a maximum at 800°C, and the nitrogen content decreases with further temperature increase. In all experiments, the product obtained was white, confirming the absence of free carbon. The product was formed in the form of solid granules and was 32% at the optimum temperature of 800°C, which is practically 1.5 times more than that of calcium cyanamide by the carbide method.

An analysis of the composition of gases released from the reactor was established, in which the content of ammonia and carbon dioxide decreases as soon as the synthesis temperature increases, the content of ammonia decreases more than that of carbon dioxide. The content of carbon monoxide and methane in the exhaust gases is minimal (ranging from 0.19 to 0.31%), and carbon monoxide and methane are not considered as some non-existent reaction products.

The synthesis of calcium cyanamide from lime uses mutual mixtures of carbon dioxide and ammonia gases. In recent years, ammonia production technology has improved, its cost is still high compared to expander gas. In order to reduce the consumption of expensive ammonia and to reduce the cost of calcium cyanamide, important issues are raised, and the ratio of ammonia and carbon dioxide should be kept at a constant rate. A number of experimental experiments were carried out to solve this problem, and lime layer was presented for the initial conditions. As a result of research analysis, the ratio of $\text{CO}_2:\text{NH}_3$ is changed from 12:1 to 1:12. The results of the research are presented in table 4 below.

Table 4 the content of nitrogen in the synthesis products of calcium cyanamide in the components of reaction gas mixtures

$\text{CO}_2:\text{NH}_3$ ratio	12:1	9:1	5:1	3:1	1:1	1:3	1:5	1:9	1:12
Nitrogen content in the product, %	26,76	25,90	25,08	25,69	25,90	28,65	29,38	31,27	31,34

The given data show that the amount of ammonia in the initial gas mixture has a greater influence than the amount of carbon dioxide. For example, when increasing the ratio of $\text{CO}_2:\text{NH}_3$ from :1 to 12:1, the amount of nitrogen in the product increased from 25.9 to 26.76, and the ratio from 1:9 to 25.9 increased by 31.27%, i.e. by 5.37%. By increasing the ratio of $\text{CO}_2:\text{NH}_3$ more than 1:9, the amount of nitrogen in the product does not practically increase,

in which case $\text{CO}_2:\text{NH}_3=1:9$ can be considered a convenient option.

The intensity of interplanar distance of calcium cyanamide is small compared to the samples taken at 750°C , and vice versa, the intensity of interplanar distances of unreacted calcium oxide was considered to be large, for the synthesis of calcium cyanamide, it is considered optimal to have the process at 800°C .

When the synthesis temperature is increased to 800°C , the intensity of the interplanar distances in the diffractograms for calcium cyanamide ($d=2.99; 2.46; 2.26; 2.08; 1.89; 1.85$) and for unreacted minimal calcium oxide ($d=2.46; 1.61; 1.43 \text{ \AA}$).

In conclusion, the intensity of interplane distances in the diffractogram at a temperature of 900°C decreases for calcium cyanamide ($d=2.99; 2.79; 1.85; 1.70 \text{ \AA}$), and increases for unreacted calcium oxide ($d=2.41; 1.70; 1.45; 1.33 \text{ \AA}$). Based on the above, it can be safely assumed that the cyanamide at optimum temperatures is low and the migration of ions occurs quickly in the bottom of the granules, and also the process of formation of active calcium oxide is quickly limited. As the temperature increases, the rate of formation of active calcium oxide increases, which leads to an increase in the cumulative rate of the process. Thus, on the basis of chemical and X-ray analysis, it is confirmed that the synthesis of calcium cyanamide from limestone, ammonia and expansion gas has a convenient temperature of 800°C .

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