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The production of calcium nitrate by the air high-voltage ac plasma torch

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Abstract. The article discusses the production of calcium nitrate by the plasma method. A method is proposed that can be used in small-tonnage production of nitrogen mineral fertilizers. It is an alternative to the traditional Haber method, which has a number of significant drawbacks. The nitrogen oxides used were obtained using a high-voltage AC plasma torch, which has improved performance characteristics. Specific energy consumption is 8.88 kWh/kg of calcium nitrate, which is somewhat higher than in traditional methods for producing nitrogen fertilizers.
Keywords: high-voltage AC plasma torch, nitrogen oxides, nitrogen fertilizers, calcium nitrate.

1. Introduction

Along with phosphate and potash fertilizers, nitrogen fertilizers are one of the three main types of fertilizers necessary for the full development of crops. However, nitrogen fertilizers are the most common and important type of fertilizer.

The high level of demand for nitrogen fertilizers in comparison with other types of fertilizers is explained, in particular, by the fact that their use has the most direct impact on the yield. In addition, nitrogen is stored in the soil for a relatively shorter time than phosphorus or potassium, which makes it necessary to regularly apply nitrogen fertilizers to achieve results.

Without the use of fertilizers, the current amount of land would already be enough to feed no more than 3 billion people. According to the UN, at the end of 2021, almost 7.9 billion people lived on earth. Increasing the intensity of agriculture, including the use of fertilizers, seems to be the only solution to the problem of food security.

According to the National Research University Higher School of Economics, at the end of 2019 [1], the capacity of nitrogen fertilizer amounted to 107.1 million tons. With a total consumption of all types of fertilizers 190.5 million tons.

In most cases, the production of nitrogen fertilizers is highly localized due to high capital costs and high productivity of existing chemical plants [2]

At present, the main methods for obtaining nitrogen fertilizers are synthesis from nitric acid and ammonia [3]. Both of these substances are produced using hydrogen in a catalytic chemical process, which in turn is produced predominantly from natural gas. Due to the instability of hydrocarbon prices, the cost of production of nitrogen fertilizers can vary significantly over time. At the same time, political tension significantly complicates the functioning of the nitrogen fertilizer market. As can be seen, the increase in gas prices has already caused a massive shutdown of nitrogen fertilizer companies in Europe, and the political situation in the world has significantly changed the supply chains of fertilizers and the availability of nitrogen fertilizers for different parts of the world.

The electric arc production of calcium nitrate is based on the plasma synthesis of nitrogen oxides in air at high temperature. With a relatively low output of nitrogen oxides (mainly nitrogen monoxide), an important advantage of this method is the available raw material (prepared air). The concentration of useful products largely depends on the temperature, residence time, and cooling rate of the synthesis products. With relatively slow cooling of the products, the resulting nitrogen oxides are again partially converted into nitrogen and oxygen. Rapid cooling of the mixture prevents this process. The resulting nitrogen monoxide is subjected to catalytic oxidation with the formation of nitrogen dioxide, which has acidic properties. Due to the low efficiency of the first plasma devices,

the plasma method was no longer used in industry. One of the main reasons for this was the low marginal productivity of such plasma installations.

The Haber method replaced the previous method due to its high efficiency, relatively low cost and high productivity. At present, with the development of alternative energy, it is possible to create installations for electric arc synthesis, taking into account the functioning of alternative energy power plants, which makes it possible to use it in the local production of nitrogen fertilizers [4].

2. Experimental part

The proposed solution is based on a high-voltage three-phase AC electric arc plasma torch developed at the IEE RAS [5] (Fig.1).

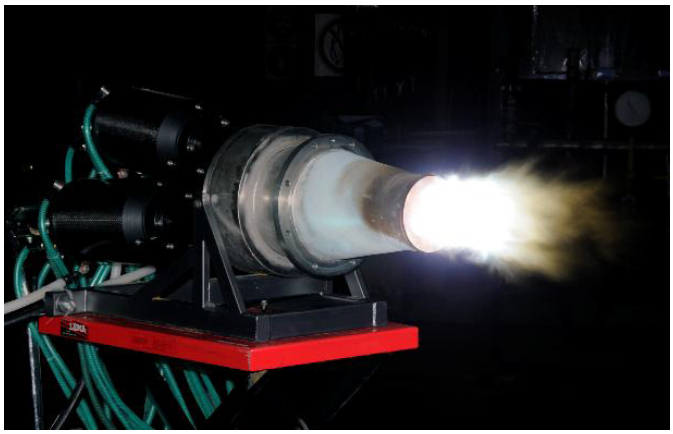

Fig.1. The AC plasma torch.

Characteristics of the plasma torch: power 150–500 kW, plasma gas: air, nitrogen, carbon dioxide, mixtures of nitrogen and oxygen (1:1 mol.), thermal efficiency – 95%, electrode service life 2000 hours [6].

Fig.2 shows the current-voltage characteristic of the plasma torch and Fig.3 shows the dependence of the voltage drop across the arc and the power of the plasma torch on the flow rate of the plasma-forming gas (air).

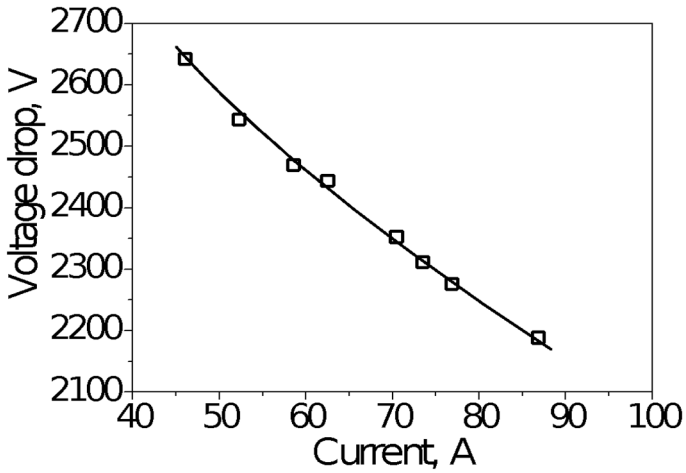

Fig.2. Volt-ampere characteristic of the plasma torch.

IEE RAS conducted experiments to study the synthesis of nitrogen oxides in air plasma. A photograph of the installation is shown in Fig.4.

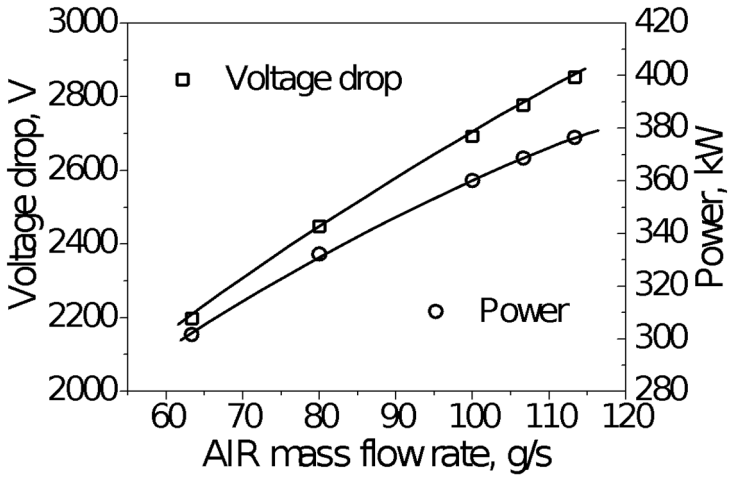

Fig.3. Dependence of the power and voltage of the arc voltage on the flow rate of the plasma-forming gas. Arc current 90 A.

To determine the composition of products after plasma treatment, a water-cooled sampling probe is placed in the plasma-chemical reactor. The concentration of nitrogen oxides (NO and NO_2) was determined using a mass spectrometer calibrated with calibration gas mixtures.

Fig.4. Photograph of the plasma torch and plasma-chemical reactor.

It has been experimentally established that a plasma-chemical plant with a high-voltage plasma torch makes it possible to obtain product gas with a nitrogen oxide concentration of up to 3.5%. wt. (mainly nitrogen monoxide). The enthalpy of the air plasma generated by the plasma torch is 6.12 MJ/kg of air.

The application of this method for the synthesis of nitrogen oxides for the production of calcium nitrate ($Ca(NO_3)_2$) was evaluated.

The sequence of stages for obtaining calcium nitrate is as follows: 1 – electric arc synthesis of nitrogen monoxide from air using a plasma torch; 2 – production of nitrogen dioxide by catalytic oxidation; 3 – absorption of nitrogen dioxide by calcium hydroxide and further oxidation to nitrates.

Table 1. Energy consumption for obtaining synthesis products

Substance	Yield, kg/kg of air	Energy costs	
		MJ/kg	kW·h/kg
Nitrogen monoxide (NO)	0.035	174.86	48.57
Nitrogen dioxide (NO_2)	0.051	114.04	31.68
Nitric acid (HNO_3)	0.074	83.24	23.12
Calcium nitrate ($Ca(NO_3)_2$)	0.191	31.98	8.88

The table shows that the energy costs for the production of calcium nitrate are quite high and currently cannot compete with the cost of nitrogen fertilizers obtained in the classical way. And this technology will not be in demand in countries with large production of nitrogen fertilizers. However, new technologies in renewable energy and plasma technologies for producing nitrogen fertilizers make it possible to build small plants (container type) powered by wind or solar generators with a capacity of 50–100 kW, capable of producing nitrogen fertilizers in quantities sufficient for farms up to 100 hectares. Consumables for this technology will be wind, sun, water and lime (one of the cheapest and most common substances on earth). Moreover, the resulting nitrogen fertilizers will be environmentally friendly. There will be no carbon dioxide emissions during their production, and the cost of nitrogen fertilizers produced by such a plant will not depend on the price of gas and the political situation in the world.

3. Conclusion

The development of modern plasma technology makes it possible to take a fresh look at the electric arc synthesis of nitrogen oxides. The proposed method allows organizing small-scale production of calcium nitrate (an important nitrogen fertilizer) using local raw materials. Thus, the further use of electric arc synthesis of nitrogen oxides for the production of nitrogen fertilizers is advisable for local use in relatively large farms or in places with complex fertilizer delivery logistics.

4. References

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