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**Development of electrochemical methods of neutralization of nitric oxides, using lump electrodes with developed surface in aqueous solutions****Abstract**

Nitrogen oxides were electrochemically oxidized into nitrates with the goal of decreasing pollution of environment. Results showed that increasing of concentration of electrolyte and increasing the volume of passing gas mixture increases current output. But increasing the current density decreases current output. Results were obtained by using Photo electric colorimeter.

**Keywords:** Nitrogen oxides, electrooxidation.

**Introduction**

It is known that the combustion of fuel into the atmosphere large amount of gaseous substances which are not peculiar to the natural composition of the atmosphere, ie non-polluting. These include nitric oxide, and (II), which is produced especially intense when the temperature of combustion exceeds 10,000. Nitrogen oxides are mainly of anthropogenic origin are nitrogen oxide (II) – NO.

Nitrogen oxides are also present in the emissions of enterprises of some branches of chemical industry in the process of nitration, the manufacture of superphosphate, nitric acid cleaning of metals, manufacture of explosives. But the main source of emissions containing nitrogen oxides (II), is transportation. NO is not irritating to the respiratory tract, and therefore one can not feel it. When inhaled NO reacts with hemoglobin unstable compound, which transforms hemoglobin to methemoglobin, whose concentration in the blood of 60-70% is considered lethal.[3]

As the distance from the emission source an increasing amount of NO becomes NO<sub>2</sub>, irritates the mucous membranes. On contact with moisture in the body, nitrous and nitric acids, which corrode the walls of the alveoli of the lungs, like many other acids. If time does not prevent access of fluid in the alveoli, the lung edema can lead to death.[10] Oxides of nitrogen should be considered as substances

presenting a serious risk to human health. In this context, it becomes apparent that the need to find ways to neutralize nitrogen oxide(II) in the place of it's formation.[6]

At present there are ways to neutralize nitrogen oxide (II) present in the exhaust from cars, by restoring him to the nitrogen with the catalytic system. In addition, the methods developed by the oxidation of nitric oxide (II) in the presence of catalysts. Thus, the existing methods of disposal of nitric oxide (II) is reduced to its oxidation or reduction in the presence of catalysts and reagents. However, the methods of chemical oxidation or reduction of nitrogen oxide (II) have a low speed, require additional reagents and expensive catalysts, which are rapidly being poisoned in the presence of sulfur and lead. In this regard, the development of new methods for decontamination of nitric oxide (II) by its oxidation or reduction, precluding the use of catalysts, is now an urgent problem.[1]

The aim of the work is to establish patterns of electrochemical oxidation of nitrogen oxides using a lump of electrodes in aqueous solutions.

**Existing methods of neutralization of nitrogen oxides.***1 High-temperature catalytic purification*

As proposed by reducing hydrogen, a mixture of nitric oxide, carbon (II), natural gas, petroleum, coke and rich gases, vapors and kerosene, fuel oil and others. Practical application in the industry have found natural gas sulfur content shall not exceed 20 mg/m<sup>3</sup>.

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In the metals used as catalysts Pt, Pd, Rh, Ru, Ni, Cu, Cr, Fe, and alloys of Ni-Cr, Cu--Cr, Zn-Cr, etc., deposited on oxides of aluminum, zinc, silica, ceramics and natural materials. In UKL-7 units, 3 and AK-72 used palladium catalyst APK-2 (Al<sub>2</sub>O<sub>3</sub> with 2% Pd). The recovery process of NO<sub>x</sub> proceeds at 720-770°C, volumetric and linear gas velocities, respectively, 15000-25000 h<sup>-1</sup> and 1.0-1.5 m / s. To achieve the residual concentration of nitrogen oxides in the range 0.002 – 0.008% (vol.) support 10% excess of the stoichiometric natural gas.

As a second catalyst bed is used tablet Al<sub>2</sub>O<sub>3</sub>. The service life of the catalyst 3 years, the loss of Pd is 3-5% per year (caused by weight). During the period of operation of the catalyst activity is reduced, and the concentration of nitrogen oxides increased from 0.002-0.003 to 0.008-0.01% when the content of NO<sub>x</sub> at the inlet of 0.1% (vol.).

The first stage of the process is the combustion of methane and the conversion of oxygen:



Incomplete combustion of methane produced hydrogen and carbon monoxide:

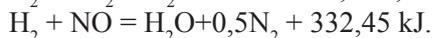
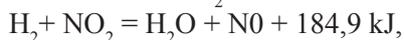


They can be oxidized by oxygen to carbon dioxide and water.

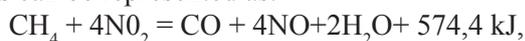
Allocated for these reactions heat leads to a significant increase in the temperature of the gas. The adiabatic heating of the gas-vapor mixture in the oxidation of 1% oxygen is 160 ° C. Therefore, to avoid overheating of the catalyst and at the same time ensuring its ignition temperature (450-550 CC), the oxygen content in the exhaust gas is maintained within 3.2%. When restoring a hydrogen-oxygen content of 4.4% O<sub>2</sub>, as in this case, the adiabatic heating is 130-140 ° C.

Thus, the reduction of nitrogen oxides involves all three of the reducing agent: H<sub>2</sub>, CO, CH<sub>4</sub>.

But it is more likely to react with nitrogen oxides in the catalyst is hydrogen. And at the first stage of nitrogen dioxide is reduced to nitric oxide NO, and then the last to N<sub>2</sub>



Similarly NO<sub>x</sub> interacts with carbon monoxide. The total reaction of natural gas with nitrogen oxides can be represented as:

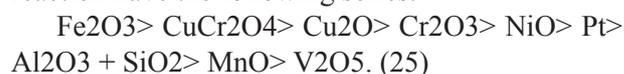


Under the operation of the catalyst APK.-2 is the optimal ratio of

[CH<sub>4</sub>]: [O<sub>2</sub>] = 0.55 – 0.56. Defiksation of nitrogen oxides in a reducing atmosphere (CH<sub>4</sub> excess of O<sub>2</sub>) leads to the appearance in the exhaust gas along with CO [0.15% (vol.)] ammonia and hydrogen.

Activity of the catalysts by hydrogen reduction of nitrogen oxides based on noble metals decreases in the order: Ru> Os> Rh> Ir> Pt> Pd.

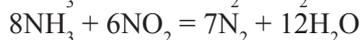
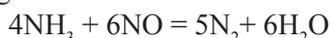
Reduction of nitrogen oxides by carbon monoxide in the presence of oxygen is hampered and may stop completely in excess of the stoichiometric oxygen content of carbon monoxide. When restoring a mixture of carbon monoxide it interacts only with the NO<sub>2</sub>-tested by the activity of the catalysts for this reaction have the following series:



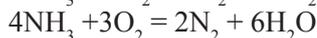
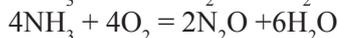
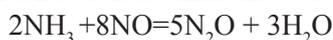
High-temperature catalytic purification process is organically linked with the technology of obtaining nitric acid. In its implementation can not only organize the vicious cycle of energy technology, but also give a significant amount of steam to the side. [1, 8].

## 2. Selective catalytic reduction of nitrogen oxides

The essence of selective recovery thermocatalytic NO<sub>x</sub> to molecular nitrogen is ammonia, which, under certain conditions selectively reacts with nitrogen oxides and does not react with oxygen:

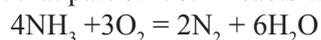


However, depending on the type of catalyst is also possible the restoration of NO<sub>2</sub> to NO and oxygen oxidation of ammonia to N<sub>2</sub> and N<sub>2</sub>O:



Comparison of the equilibrium constants of the main and side reactions indicate a preference for reduction reaction of nitrogen oxides with ammonia in comparison with the reaction of ammonia with oxygen .. In Russia, the selective catalytic purification is used in units with low-temperature regenerative turbine. Selective reduction of NO<sub>2</sub> and NO ammonia to molecular nitrogen is equal to the rate at temperatures of 250 – 450° C on catalysts of plati-

num, copper oxides, vanadium, magnesium, etc., in contrast to non-selective process thermocatalytic selective reduction of nitrogen oxides is carried out at any concentration of oxygen in the tail gas to the achievement of 98% purity or more. For example, alyumovanadievyy catalyst AVK-10M (10% vanadium) at a volume rate of gas flow 15 000 h<sup>-1</sup>, the linear velocity of 1 m / s and a temperature of 375 – 450 ° C provides a degree of recovery NOx 98 – 98.5% and has a lifetime 2 – 3 years. When the ratio of NH<sub>3</sub>: NOx equal to (1.1-1.5): 1, content of nitrogen oxides in exhaust gases does not exceed 0,002 – 0,003%. Travel time of the catalyst 2-3 years, during this period the degree of purification is reduced to 96%, the residual ammonia in the treated gas is less than 0.01% (v). Flow of ammonia at 25-30% confidence against excess stoichiometry of 2.5-3.0 kg for each tenth of a percent of nitrogen oxides contained in the feed gas. Slight excess of ammonia due to the fact that part of it still reacts with oxygen:



As catalysts for selective reduction of nitrogen oxides tested a variety of metals (including precious) metals, metal oxides, spinels, perovskites in pure, mixed and deposited species. The catalytic activity of catalysts in the 200-350° C and a speed of 10 thousand h<sup>-1</sup> decreases in the sequence:

Pt>MgO>V<sub>2</sub>O<sub>5</sub>>CuO>Fe<sub>2</sub>O<sub>3</sub>>Cr<sub>2</sub>O<sub>3</sub>>Co<sub>2</sub>O<sub>3</sub>>MnO<sub>2</sub>>NiO>Ag<sub>2</sub>O>ZnO>Bi<sub>2</sub>O<sub>3</sub>>Al<sub>2</sub>O<sub>3</sub>>SiO<sub>2</sub>>PbO<sub>2</sub>.

Palladium is sharply reduced their activity during the process. Have high activity of manganese oxides, vanadium, iron, chromium, copper and cobalt.

The disadvantages of this type of treatment include the difficulty of accurate dosing of small amounts of ammonia in the gas after the absorption column and distribute it in the gas stream, as well as education paths after cleaning nitrite-nitrate ammonium. To eliminate the formation of the past temperature of the gases emitted into the atmosphere after recuperation turbine support above 200° C.[8]

The scheme of the process of selective reduction of NOx in the production of nitric acid is described below.

Tail gases from the absorber enter the heater and a temperature of 50 ° C heating block are sent to the gas BGL – 172. the latter consists of a regenerator heat, convective and radiant heaters and air heater.

In the heating unit tail gases first pass through

the regenerator, where heated to 290° C. It uses advanced heat gases after the gas turbine, where the temperature is lowered from 370 to 146° C. After the regenerator tail gas passes through a convective heater, heated flue gases. The temperature of tail gas increases from 290 to 453° C, and smoke – is reduced from 935 to 390° C. Then the tail gases are fed to the Radiant heater, and heated flue gases, which are heated from 453 to 780° C and the gases are fed into the mixer 5. for more complete utilization of flue gas heat air to the burner of natural gas, preheated to 200° C, and the flue gases are cooled at the same time from 390 to 250° C.

In mixer, hot tail gases are mixed with ammonia and fed to the reactor catalyst cleaning. The reactor is a horizontal cylindrical device with a layer of alyumomedtsinkovogo catalyst (ACM-10), height 800 mm and a volume of 22.8 m<sup>3</sup>. duration of the catalyst – 3 years. Selective catalytic reduction NOx with ammonia at a temperature of about 350° C and 1.14 MPa. The linear gas velocity of 0.4 m / s, and the volume rate – 7500 m<sup>3</sup> / h per 1 m<sup>3</sup> of catalyst. After the heat recovery unit to heat and pressure energy in the gas turbine purified gases are mixed with the flue gas and emitted into the atmosphere. 10.8 Appointment of turbines is the same as for non-selective reduction of nitrogen oxides.[8]

The content of NOx in the exhaust gases does not exceed 0.006% by vol., Ammonia – 0.01%.

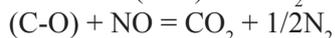
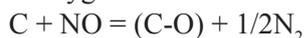
Compared with non-selective methods, this method allows to reduce natural gas consumption by 15%, excludes the use of expensive catalyst APK-2 in the exhaust gases are no carbon monoxide and methane.

Purification of gases from nitrogen oxides in the manufacture of non-concentrated nitric acid on oxide catalyst alyumovanadievom AVK-10 in the presence of ammonia does not always satisfy the requirements of the residual ammonia content in the purified gas. Using the so-called two-layer catalyst achieves a high degree of purification from nitrogen oxides and ammonia.

The two-layer catalyst layer consists of alyumovanadievogo (AVC-10 AVC-10M, AVC-10SH) and a layer of iron-chrome (STK-1, STC-2, MIR-482, CTK-482-MF) of the catalyst. Volume ratio is 1:1. optimal conditions for purification of the following: T = 250-290° C, P = 0.4 MPa, space velocity of 7000 h<sup>-1</sup>. content of nitrogen oxides in the initial gas flow of 0.1-0.3., the ratio of NOx: NH<sub>3</sub> = 1: (0.8-1.1). [5,8,9]

### 3 The decomposition of nitrogen oxides reducing heterogeneous

At high temperatures (500-1300 ° C) defiksation of nitrogen in the exhaust gas can be carried out on the solid carbonaceous materials, particularly coal, coke, graphite. In such processes, the carbon acts as a catalyst, and fuel. The catalytic action of carbon associated with the formation of complexes of carbon – oxygen:



However, the relatively rapid loss of activity of these catalysts leads to the fact that the decomposition of nitrogen oxides, particularly in the initial range of the specified temperature range, is incomplete. In this regard, in order to increase the degree of decomposition of NOx suggested, for example, to enter into graphite sodium carbonate. With increasing temperature, the degree and speed of the recovery increases: at 800 ° C the degree of reduction of NOx using coke can reach 96%, and at 1000 ° C is close to 100%. High temperature processes such a negative impact on their technical and economic performance, although much of the energy potential neutralizes gases used may be useful.[7]

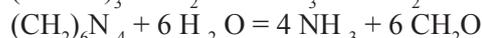
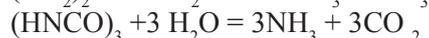
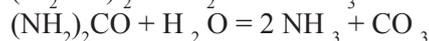
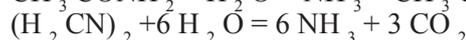
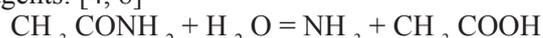
Comparative analysis of the effectiveness of reducing

Flue gas cleaning by reduction of nitric oxide to nitrogen and oxygen on the catalyst is a complex task due to the following circumstances:

1) The presence of ash in the flue gases and sulfur oxides, pollutants and toxic catalyst;

2) The need for higher temperature gas from the catalyst (typically 400 ° C compared to the temperature of ash collection). In practice, in the heat mainly develop two areas of flue gases of nitrogen oxides: selective non-catalytic reduction of nitrogen oxides (SNCR) process and the selective catalytic reduction of NOx (SCR) process. As the reducing agent used ammonia or chemical compounds capable of easily decomposed with the release of ammonia. Difficulties with the use of nitrogen-containing compounds in the design begin dosing and dispensing reagent in the boiler. Unlike ammonia and monoethanolamine, agents can not be converted to a gaseous state, since the melting temperatures they begin to decompose, forming high molecular weight compounds with high melting points. In this regard, adopted in the case of ammonia flow sheet with dilution reagent porom, air or flue gases can not be applied. All of these reagents should be administered directly to the appropriate temperature

region of the boiler or in the form of aqueous solutions (water soluble acetamide monoethanolamine, urea and methenamine) or in suspension (cyanuric acid and melamine). They are before entering the reactor to be converted to ammonia. This restriction is essential, and therefore a set of reagents is mainly limited to liquid ammonia (a few changes only dosing scheme), ammonia water and urea, which is relatively easily hydrolyzed at moderate temperatures. The mechanism of hydrolysis and decomposition of reagents: [4, 8]



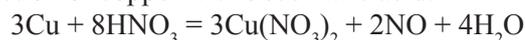
### Materials and methods

#### Sample preparation

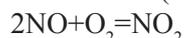
Sample preparation consists of 2 parts:

#### 1. Obtaining of nitrogen oxides

The obtaining of nitric oxides is based on the reaction of copper with 30% nitric acid.



Nitric oxide (II) is oxidized in the air:



By this reactions we have a mixture of NO+NO<sub>2</sub>

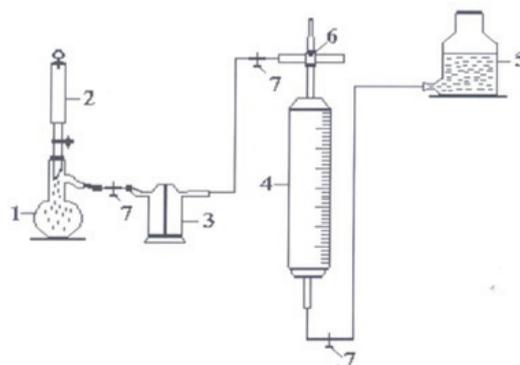


Figure 1 – Scheme of device for obtaining of nitric oxides

Elements of device:

- 1) Wurtz flask
- 2) Burette
- 3) Tishchenko vial
- 4) Burette for measuring the volume of gas
- 5) The vessel to create pressure in the system
- 6) Three-way valve
- 7) Clips

Calculating the mass of copper for obtaining 750 ml(volume of burette) of nitric oxide:

### 2. Neutralization of nitrogen oxides

After obtaining the mixture of nitric oxides we close the clips, then we put off the hose from Tishchenko vial and put it on the electrolyzer. Electrolyzer filled with KOH. Electrolytic space divided by cationic membrane(mark MK-40). Both electrodes are made from iron. Anode is made as plate with space where pieced electrodes are put, and is put into electrolyzer. Cathode is put into membrane. Then we take the current density 100 A/m<sup>2</sup>, open the clips and look at the electrolysis process.

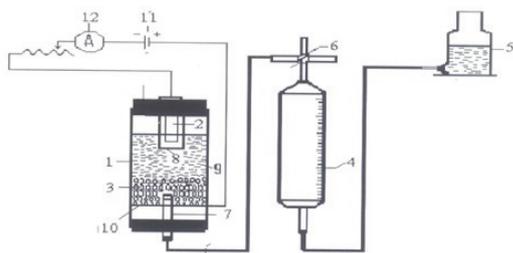
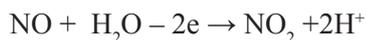


Fig. 2 – Scheme of device for neutralization of nitrogen oxides

Elements of device:

- 1) Electrolyzer
- 2) Cathode
- 3) Anode
- 4) Burette
- 5) The vessel to create pressure in the system
- 6) Three-way valve
- 7) Valve to create the constant rate of gas
- 8) Membrane MK-40
- 9) Electrolyte
- 10) Anode
- 11) Source of current
- 12) Ampermeter

Reactions, that take place during electrolysis:



Nitric oxide(II) could be oxidized by atomic oxygen, that obtained on anode:



There is also a reaction of the resulting nitrogen dioxide with potassium hydroxide with the formation of nitrite and nitrate ions and nitrite ions, in turn, can be oxidized further to nitrate ions:



and the interaction of an excess of oxygen immediately proceeds with the formation of nitrate ions:



After all volume of gas passed through the electrolyzer, we close the clips, turn off the source of current. Then we take the solution from electrolyzer for analysis.

### Methods

Optical density of obtained nitrates was measured by photo-colorimetric method at wavelength 410 nm.

### Procedure of measuring optical density

1 mL of sodium salicylate(0.5% aqueous solution) is added to 10 mL of sample, then the mixture is evaporated to dryness in porcelain bowl. After cooling, dry residue is moisten by 1 mL of sulfuric acid and left for 10 minutes. Then the contents of the bowl is diluted by distilled water and put into volumetric flask for 50 ml, after that 7 mL of 10 n sodium hydroxide is added into the flask. After cooling to room temperature mixture in flask is diluted by distilled water till mark and collorimetried on photo electric calorimeter.[2]

### Results and discussion

#### Influence of current density on current output

In this case we can say that current output decreases while current density increases (fig.3). This could be explained by this fact: current goes to secondary process – formation of atomic oxygen.

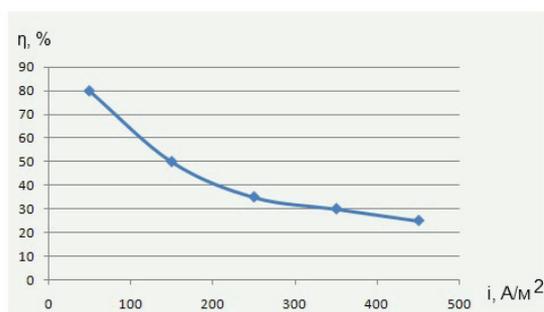


Fig. 3 – Dependence current output – current density

#### Influence of volume of passing gas on current output

This case shows us that increasing of volume of passing gas increases current output (fig.4).

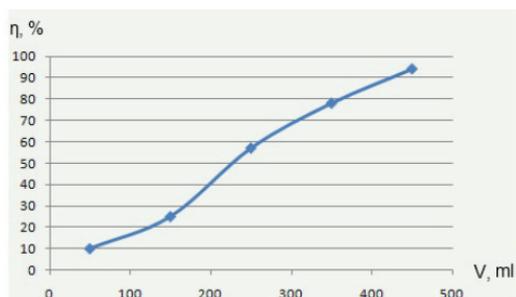


Fig 4 – Dependence current output – volume of passing gas

#### *Influence of concentration of electrolyte on current output*

In this situation we could see that current output increases if concentration of electrolyte increases (fig.5).

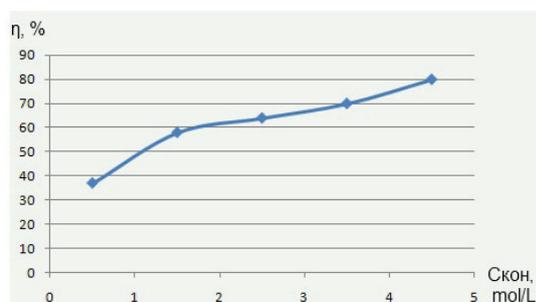


Fig. 5 – Dependence current output – concentration of electrolyte

#### **Conclusions**

The application provides a lump electrode patterns of the oxidation of gaseous nitric oxide (II) and to establish the mechanism of the process. For the first time were established regularities of oxidation of nitric oxide (II) to lump the electrodes with a developed surface, and it will be a Serious contribu-

tion to the science of electrochemistry of gases, in particular, the electrochemistry of gaseous nitrogen compounds. Based on the patterns created by the opportunity to develop ways to neutralize harmful environmental gas – nitric oxide (II). As a result of oxidation of gaseous substances in aqueous solutions it is possible to obtain different nitrogen compounds, which are widely used in various sectors of the industry (preparation of synthetic fertilizers, ammonia, nitric acid, and organic nitrogen compounds – dyes and pharmaceuticals).

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