The comparative analysis of the mineral nitrogen fertilizers

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Abstract. According to the results of physical and chemical modeling, the chemical form of nitrogen fertilizers has a significant effect on the thermodynamic parameters of systems with their application. The chemical activity of nitrogen in sandy soils is higher than in clay soils, and decreases in the series: potassium nitrate - ammonium nitrate - urea - ammonia hydrate, i.e., decreases with the transition from the oxidized form of nitrogen +5 to reduced -3. Potassium and sodium nitrate are optimal with regard to the chemical activity of nitrogen in sandy soils. In clay soils, on the contrary, the maximum activity of nitrogen is provided by the use of urea containing a reduced form of nitrogen. The reactivity of oxygen is higher in clay soils and increases with the transition from oxidized to reduced forms of nitrogen. Therefore, to increase the activity of oxygen in sandy and clay soils, it is preferable to use urea and ammonia water. The binding efficiency of atmospheric nitrogen increases in the series: ammonia hydrate, urea - ammonium nitrate - potassium nitrate, and thus, systems containing highly oxidized nitrogen are favorable for fixing atmospheric nitrogen.

It was shown in [1-2] that mixed fertilizers are complex thermodynamic systems whose components mutually benefit each other. The nature and degree of influence also depend on the chemical composition of soils [3]. As a rule, the composition of the fertilizer used is described by the ratio nitrogen: phosphorus: potassium in terms of macrocell oxides. Moreover, the forms of macro-fertilizers are often not specified, which may not be of fundamental importance in the case of potassium and, to a lesser extent, phosphorus fertilizers, but it is important in relation to mineral nitrogen macronutrients.

Unlike potassium and phosphorus, nitrogen is a part of mineral fertilizers in various forms. This is due to the ability of nitrogen to exhibit various oxidation states in the compounds: a negative oxidation state of -3 and positive oxidation states from +1 to +5. In this regard, nitrogen compounds are characterized by various acid-base and redox reaction characteristics.

The following mineral nitrogen fertilizers are most widely used: potassium nitrate (oxidation state of nitrogen in the nitrate ion +5); urea and ammonia water (oxidation state of nitrogen in ammonia and its derivatives -3); ammonium nitrate (nitrogen atoms are present in oxidation states of -3 and +5). It is logical to expect that these compounds as the main component of nitrogen macronutrients in various ways affect the properties of systems with their application.

The purpose of the current work was to study the effect of the composition of mineral nitrogen fertilizers on the thermodynamic characteristics of soil – mineral fertilizer – water – air systems. The activity of nitrogen and oxygen, which are the most important participants in the metabolic processes...
in plants, and the thermodynamic probability of oxidation of atmospheric nitrogen were considered as the main indicators.

The study was carried out by the method of physicochemical modeling based on the “Selector” software package [4–5]. Despite the fact that the method was developed to study equilibrium (primarily geochemical) processes, taking into account the principle of partial equilibrium laid down in the method, the Selector software package can be used to study non-equilibrium processes. The scientific literature describes the application of the method to study the processes occurring in soils [6].

The thermodynamic data required for modeling are contained in [7–10].

The method allows one to calculate a fairly large number of system indicators. The most important indicators include the Gibbs free energy of a system, the chemical potentials of the components, the number of components of the solution, liquid and solid phases, the pH of the solution, and the redox potential of the system

The processes in the soil – mineral – water – air component systems were simulated:
- in clay soils, the main component of which is aluminum oxide Al₂O₃, which is part of clay minerals: kaolinite, montmorillonite, illite;
- in sandy soils, the main component of which is silicon dioxide SiO₂ (silica).

As follows from the curves shown in figure 1, the chemical activity of nitrogen in sandy soils is higher than in clay soils. It is most likely to assume that this is due to the inertness of sandy soils, due to the low chemical activity of silicon dioxide (silica). Aluminum compounds, due to a sufficiently high activity and pronounced amphotericity, are able to influence the state of nitrogen in the systems under study.

For sandy soils, nitrogen activity in systems involving nitrogen-containing compounds decreases in the series: potassium nitrate - ammonium nitrate - urea - ammonia hydrate, i.e. decreases with the transition from the oxidized form of nitrogen +5 to reduced -3. Therefore, potassium and sodium nitrate are optimal with respect to the chemical activity of nitrogen in sandy soils.

In clay soils, on the contrary, the maximum nitrogen activity is ensured by the use of ammonia nitrogen contained in urea. But at the same time, in a solution of ammonia, where a reduced form of nitrogen is also present, nitrogen activity is low, at the level of potassium and ammonium nitrate.

![Figure 1](image)

**Figure 1.** Dependence of the chemical potential of nitrogen on the composition of the nitrogen-containing compounds in mixtures.

This is in contrast to the chemical activity of oxygen (figure 2). Unlike nitrogen activity, this value is higher in clay soils and increases with the transition from oxidized to reduced forms of nitrogen.
contained in simulated mixtures. Therefore, to increase the activity of oxygen in sandy and clay soils, it is preferable to use urea and ammonia water.

![Graph](image_url)

**Figure 2.** Dependence of the chemical potential of oxygen on the composition of the nitrogen-containing compounds in mixtures.

The influence of the degree of nitrogen oxidation in the compounds on the thermodynamic probability of nitrogen fixation is considerably definitive, which was discussed in a slightly different way earlier.

![Graph](image_url)

**Figure 3.** Dependence of the content of nitrate ions on the composition of the nitrogen-containing compounds in mixtures.

As it follows from the data presented in figure 3, the atmospheric nitrogen oxidation is thermodynamically possible in all simulated systems, both in clay and sandy soils. Equimolar amounts of nitrogen-containing compounds (1 mol of nitrogen) were introduced into the calculations; therefore, amounts of nitrate ion in excess of 1 mol were formed due to the atmospheric nitrogen fixation.
From the curves (Figure 3) it follows that clay soils favor atmospheric nitrogen fixation, in which the nitrogen content of the nitrate ion can be more than 6 times the original nitrogen content of the nitrogen-containing compound. For sandy soils, the indicators are approximately two times lower.

Quantitative indicators of the atmospheric nitrogen fixation increase in the series: ammonia hydrate, urea - ammonium nitrate - potassium nitrate. In this case, the transition from the lowest to the highest degree of nitrogen oxidation in the compounds is clearly traced. Thus, systems containing highly oxidized nitrogen are favorable for the atmospheric nitrogen oxidation, and the implementation of the process consists in selecting conditions that lower the energy barrier of the first (limiting) stage of the multistage process of atmospheric nitrogen oxidation.

The conclusions are as follows:

1. The chemical composition of nitrogen fertilizers has a significant effect on the thermodynamic parameters of systems with their application.

2. The chemical activity of nitrogen in sandy soils is higher than in clay soils. For sandy soils, nitrogen activity in systems involving nitrogen-containing compounds decreases in the series: potassium nitrate - ammonium nitrate - urea - ammonia hydrate, i.e. decreases with the transition from the oxidized form of nitrogen +5 to reduced -3. Optimal in regard to the chemical activity of nitrogen in sandy soils are potassium and sodium nitrate. In clay soils, on the contrary, the maximum activity of nitrogen is provided by the use of urea containing a reduced form of nitrogen.

3. The chemical activity of oxygen is higher in clay soils and increases with the transition from oxidized to reduced forms of nitrogen. Therefore, to increase the activity of oxygen in sandy and clay soils, it is preferable to use urea and ammonia water.

4. The efficiency of atmospheric nitrogen fixation increases in the series: ammonia hydrate, urea - ammonium nitrate - potassium nitrate. Thus, systems containing nitrogen in the highest oxidation state are favorable for fixing atmospheric nitrogen.

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