The influence of chemical soils composition on the thermodynamic probability of the air nitrogen fixation

A K Podshivalova

Irkutsk State Agrarian University named after A.A. Ezhevsky, Molodezhny settlement, Irkutsk district, Irkutsk region, 664038, Russia

E-mail: chem.acad.38@yandex.ru

Abstract. According to the simulation results, the oxidation of air nitrogen in soils to the highest degree of oxidation (nitrate ion) is thermodynamically possible. Clay soils are favorable for the process of air nitrogen oxidation. Sandy soils are inert in this respect, and the processes occurring in them are determined by other participants of the studied thermodynamic systems. Soils containing limestone and slaked lime are characterized by the highest efficiency of fixation of air nitrogen. The thermodynamic probability of air nitrogen binding depends not only on the type of the main component of the mineral fertilizer, but also on the degree of its oxidation in the composition of the corresponding compound. The presence of nitrogen (+5) in the simulated systems creates thermodynamic prerequisites for reducing the energy barrier of the limiting stage of air nitrogen oxidation.

In previously published works [1-3] by the method of physicochemical modeling of the influence of nature of soil (clayey and sandy) and the composition of the mixed mineral fertilizers (nitrogen, phosphorus, potassium, limestone, and slaked lime) on the activity of the major nutrient elements, namely nitrogen and oxygen. Data indicating a positive effect of clay soils on oxygen activity were obtained. At the same time, the most significant increase in the chemical activity of oxygen is observed in systems containing limestone and slaked lime. Sandy soils do not affect the activity of oxygen. The activity of nitrogen is reduced on clay soils. Sandy soils, due to their inertia, do not affect the chemical activity of nitrogen.

The results of physical and chemical modeling presented in works [1-3] are consistent with the results of experimental work. Many researchers note the special role of liming in the processes of optimizing soil properties [4] and the action of mineral fertilizers [5-6].

The purpose of this work was to study the thermodynamic probability of air nitrogen binding, taking into account: 1) the principle feasibility of this process; 2) the influence of chemical soils composition; 3) the influence of mineral fertilizer components on the process under study.

As it is known, nitrogen is a kainosymmetric element, and this determines the special, in most cases difficult for studying and description, properties of its compounds. First of all, this applies to nitrogen oxides, since the kainosymmetricity of nitrogen provides features of the structure, properties and stability of all oxide compounds of this element.

The process of fixing air nitrogen is a sequence of nitrogen oxidation reactions with the formation of oxide forms and requires strict conditions, which is due to two factors: the energy barrier of the first stage of the reaction of nitrogen oxidation; metastability of the highest oxidized form of nitrogen.
The limiting stage of the nitrogen oxidation process is the initial stage, since the nitrogen molecule has a strong triple bond that breaks under very harsh conditions (under the action of an electric discharge). In this regard, the initial stage of oxidation of nitrogen molecules to nitrogen monoxide NO determines the final content of oxide forms in the studied thermodynamic systems.

The thermodynamic possibility of fixing air nitrogen by plants is known, which is confirmed by the fact of the existence and activity of nodule bacteria. However, nodule bacteria bind air nitrogen not in an oxidized form, but in a reduced form, in the form of ammonia nitrogen. In this regard, it should be noted that the existence of nitrogen in living organisms is generally characterized by reduced forms, in particular, the amino group in the composition of amines and amino acids.

On the other hand, plants absorb precisely the oxidized forms of nitrogen, and, thus, the assessment of the thermodynamic possibility of binding air nitrogen to form the final oxide form (nitrate ion) is quite relevant.

The study was performed using the method of physical and chemical modeling based on the software complex “Selector” [7-8]. The method is applicable to the study of both equilibrium and non-equilibrium chemical processes. The method is known to be used for studying processes occurring in soils [9].

The main sources of thermodynamic values were the works [10-13].

The final indicators of the systems were calculated as follows: Gibbs energy of the system, chemical potentials of the corresponding independent components, the number of solution components, the amount of emitted gases, the pH of the solution, the redox potential of the system.

Ten variants of each of the studied systems were calculated with a gradual increase in the content (to the maximum) of the corresponding component.

We modeled processes in the systems soil – mineral component – water – air, flowing in:

- clay soils, the main component of which is aluminum oxide Al2O3, which is part of the clay minerals: kaolinite, montmorillonite, illite;
- in sandy soils, the main component of which is silicon dioxide SiO2 (silica).

At the first stage, the efficiency of air nitrogen binding in soils containing the most important mineral fertilizers: phosphoric (calcium dihydroorthophosphate), nitrogen (ammonium nitrate), potash (potassium chloride), limestone (calcium carbonate) and slaked lime (calcium hydroxide) was studied.

At the second stage, we modeled the processes occurring in clay soils containing nitrogen-containing fertilizers (equimolar with respect to nitrogen) with different degrees of oxidation (from -3 to +5) of the main component.

According to the results of modeling, the oxidation of air nitrogen in the studied conditions is thermodynamically possible, and to the highest degree of oxidation +5 (nitrate ion). This result is quite consistent with the above ideas about the limiting first stage of the oxidation process, as a result of which the subsequent stages are not energy-intensive and end in the formation of the final oxidized form.

Figure 1 shows the dependence of the content of nitrate ions in the clay soil – mineral fertilizers – water – air systems on the amount of aluminum oxide and the type of mineral fertilizer.

As it follows from the nature of the curves shown in figure 1, clay soils are favorable for the process of air nitrogen oxidation: the content of nitrate ion in the system increases with the increasing amount of aluminum oxide in the mixtures.
At the same time, the highest values of quantitative bound nitrogen are systems containing calcium hydroxide and calcium carbonate. The content of nitrate ion in the studied mixtures reaches 5.7 mol and reaches a plateau in systems with an aluminum oxide content exceeding 0.6 mol. According to the results of modeling, the yield of curves on the plateau is associated with the formation of the mineral gibbsite of the composition \( \text{Al(OH)}_3 \). Therefore, the probability of formation of the mineral gibbsite must be taken into account when applying fertilizers to clay soils that have an alkaline medium in solutions, in particular, limestone and slaked lime.

The positive effect of calcium hydroxide and calcium carbonate on the process of fixing air nitrogen is consistent with the previously identified [1] high oxygen activity in mixtures involving these compounds. Perhaps the increased activity of oxygen is the main factor contributing to the process of air nitrogen oxidation with the formation of a nitrate ion.

Clay soils containing nitrogen fertilizer (ammonium nitrate) have the lowest ability to fix air nitrogen in the studied systems. Despite the fact that in figure 1 the curves corresponding to potash and nitrogen fertilizers almost coincide, it should be noted that in the case of ammonium nitrate, the system initially contained one mol of nitrate ions in the composition of this compound, and its subtraction from the total amount will lead to even lower rates of air nitrogen binding. The obtained result is consistent with the data presented in [1] on the relatively low oxygen activity in clay soils containing nitrogen fertilizers, and thus confirms the assumption about the determining role of oxygen activity in the process of binding air nitrogen.
The results of modeling shown in figure 2 indicate, first of all, a significantly lower ability of sandy soils to bind air nitrogen in comparison with clay soils. The maximum amount of nitrogen bound to the nitrate ion in sandy soils is 3.5 mol, which is significantly lower than the corresponding value for clay soils.

In general, the sequence of influence of mineral fertilizer components on the final content of nitrate ions in the case of sandy soils is similar to clay soils. At the same time increase the content of the basic component of soil sand (silicon dioxide) characteristics of nitrogen fixation remain at the same level, in contrast to clay soils, where the values grow with the increase of content of aluminum oxide in the systems. Thus, sandy soils are quite an inert environment, in which the nature and intensity of exchange processes practically do not depend on the main component of the soil, but are determined by other participants of the studied thermodynamic systems.

As shown by the simulation results, the thermodynamic probability of air nitrogen binding depends not only on the type of the main component of the mineral fertilizer, but also on its state, in particular, the degree of oxidation in the composition of the corresponding compound.

The curves shown in figure 3 characterize the influence of the degree of oxidation of nitrogen, which is part of a nitrogen-containing fertilizer, on the efficiency of formation of nitrate ions in clay soils; the compounds corresponding to the composition of the most important nitrogen-containing fertilizers are equimolar with respect to nitrogen.

According to modeling data, the most favorable soils for fixing air nitrogen are those containing nitrogen in the highest degree of oxidation (+5 (potassium nitrate). The results are somewhat lower in the case of ammonium nitrate containing nitrogen in the highest oxidized (+5) and reduced (-3) degrees of oxidation. The lowest efficiency of air nitrogen binding is characterized by systems containing nitrogen in an exclusively reduced form – urea and ammonia water.
Therefore, the presence of highly oxidized nitrogen in the simulated systems creates thermodynamic prerequisites for reducing the energy barrier of the limiting stage of air nitrogen oxidation.

**Conclusion**

According to the results of modeling, the oxidation of air nitrogen in soils to the highest degree of oxidation (nitrate ion) is thermodynamically possible.

Clay soils are favorable for the process of air nitrogen oxidation. Sandy soils are inert in this respect, and the processes occurring in them are determined by other participants of the thermodynamic systems under study.

The most effective fixation of air nitrogen is characterized by soils containing limestone and slaked lime. Dihydroorthophosphate calcium occupies an intermediate position. Clay soils containing nitrogen fertilizer (ammonium nitrate) have the lowest ability to fix air nitrogen in the studied systems. The results obtained allow us to make an assumption about the determining role of oxygen activity in the process of binding air nitrogen.

The thermodynamic probability of air nitrogen binding depends not only on the type of the main component of the mineral fertilizer, but also on its degree of oxidation in the composition of the corresponding compound. The presence of highly oxidized nitrogen in the simulated systems creates thermodynamic prerequisites for reducing the energy barrier of the limiting stage of air nitrogen oxidation.

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