The atmospheric nitrogen fixation thermodynamic probability study depending on the mixed mineral fertilizers composition

A K Podshivalova* and E S Gogol

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. The mixed mineral fertilizers component composition effect on the binding atmospheric nitrogen thermodynamic probability in soils was studied. The studies were carried out by the physical and chemical modelling method based on the Selector software package. The systems following final indicators were calculated: the Gibbs system energy, the corresponding independent components chemical potentials, the solution components amount, the evolved gases amount, the solution pH, and the system redox potential. The results obtained in this work make it possible to conclude that the atmospheric nitrogen fixation in a nitrate ion form is thermodynamically resolved, and the problem lies in finding conditions conducive to this process implementation. It was revealed that the thermodynamic probability of atmospheric nitrogen oxidation depends both on the mineral fertilizer main component and on this component form, in particular, on its redox or acid-base characteristics. According to the modelling results, limestone as a mixed mineral fertilizers component contributes to a significant increase in the binding atmospheric nitrogen thermodynamic probability with the most oxidized form formation. The nitrogen presence in mixed mineral fertilizers in the most oxidized form (the nitrogen oxidation state is +5) can contribute to the conditions' creation favorable for fixing atmospheric nitrogen. An increase in the urea and ammonium hydrate content in ammonia water, where nitrogen is in the maximum reduced oxidation state of -3, on the contrary, leads to a decrease in the atmospheric nitrogen binding thermodynamic probability to form oxide forms.

1. Introduction

In works number [1-2] the mixed mineral fertilizers components mutual influence was investigated by the physicochemical modelling method. It was revealed that the mixture components can have a significant mutual influence, which results in a change in their activity with the corresponding chemical systems new properties' emergence.

The data obtained as a research result [3-4], make it possible to identify conditions conducive to an increase in the mineral fertilizers main components' activity. In particular, it was found that limestone and slaked lime have an extremely favorable effect on oxygen activity [5]. The same components increase, albeit to a lesser extent, the phosphorus activity, somewhat reduce the potassium activity and practically do not affect the activity of nitrogen in the mixed mineral fertilizers composition.

The physicochemical modelling results presented in publications [1-5] agree with the experimental work results. Many researchers note the liming special role in the optimizing soil properties processes [6] and the mineral fertilizers effect [7-8].
When discussing the results obtained by the physicochemical modelling method, attention should be paid to the data indicating an atmospheric nitrogen fixation thermodynamically possible process, which is, in fact, a nitrogen oxidation multistage process with the oxide forms formation.

The harsh conditions for this process are due to two factors:
1) the nitrogen oxidation reaction first stage energy barrier;
2) the nitrogen the highest oxidized form metastability.

As you know, nitrogen is a kainosymmetric element, and this determines the special, in most cases difficult to study and describe, its compounds properties. First, what has been said applies to nitrogen oxides, which number and composition, at first glance, contradict the valence formal concepts.

The limiting stage, as already mentioned, is the nitric oxide nitrogen oxidation initial stage (II), which ultimately determines the nitrate ions final content in systems containing fertilizers mixed with mineral. The nitric oxide properties most important component (II) is an unpaired electron presence on the molecular antibonding \((\pi_e^-)\) - orbital, which causes interaction with other free radicals [9], including in the nitrogen further oxidation processes.

2. Materials and methods

In this work, we studied the mixed mineral fertilizers' composition effect on the nitrate ions content in the corresponding systems. The studies were carried out by the physical and chemical modelling method based on the Selector software package [10–11].

The thermodynamic quantities main sources were the works [12–15].

The simulated systems main parameters were determined based on the data presented in [16]. The indicated salts molar amounts corresponding to an area of 10 m² were introduced into the model. The number of \(H_2O\) - 2000 mol; air - 1000 g.

The systems following final indicators were calculated: the Gibbs system energy, the corresponding independent components chemical potentials, the solution components amount, the evolved gases amount, the solution pH, and the system redox potential.

We calculated 10 variants of the systems each with the corresponding compound different contents (with the maximum amount' gradual achievement indicated above).

3. Results and discussion

It was revealed that the thermodynamic probability of atmospheric nitrogen oxidation depends both on the mineral fertilizer main component and on this component form, in particular, on its redox or acid-base characteristics.

As already mentioned, according to the modelling results described in [1-5], such mineral fertilizers components as limestone and slaked lime have a particular effect on the increasing oxygen activity processes. Therefore, it is quite logical to assume that it is in these substances' presence in mineral fertilizers mixtures that the binding atmospheric nitrogen thermodynamic probability with the maximally oxidized form formation.

The corresponding systems' simulation results, presented in figure 1, confirm this assumption for calcium carbonate.

So, with the ammonium nitrate 1 mol, initial amount and the ammonium ion oxidation condition by atmospheric oxygen, the nitrate ion maximum amount in the solution should be 2 mol, but already at the calcium carbonate initial concentration it is 2.76 mol, then it increases and then remains at the achieved level. Of course, this process actual course scale may differ significantly from the calculated data, however, implementing this process fundamental possibility deserves attention and a more detailed study.

The points limited number in the calcium carbonate case is due to this substance lower solubility compared to calcium hydroxide.
Figure 1. Change in the nitrate ions amount in mineral fertilizers mixtures with an increase in the calcium carbonate or calcium hydroxide amount.

In the calcium hydroxide presence, as follows from figure 1, the binding' atmospheric nitrogen process is much less efficient. The nitrate ion initial value corresponds only to this component content in the initial ammonium nitrate, the maximum value slightly exceeds the ammonium ion additional oxidation result, which is the initial nitrogen-containing fertilizer part.

Figure 2. Change in the mineral fertilizer mixtures redox potential with an increase in the calcium carbonate or calcium hydroxide amount.
The above results are confirmed by a clear correlation between the nitrate ions concentration and the corresponding systems redox potential (figure 2).

Binary systems based on calcium carbonate have a higher oxidative potential, which, along with other consequences, can contribute, among other things, to the atmospheric nitrogen effective fixation with a nitrate ion formation.

The results presented in figure 3 indicate the atmospheric nitrogen binding thermodynamic probability dependence not only on the component type that is the mixed mineral fertilizer part but also on its oxidation state.

An increase in a nitrogen-containing compound amount in mixtures with calcium dihydrogen phosphate has a different effect on the nitrate ions content. The nitrate ion molar amounts increase in mixtures containing potassium nitrate practically does not change in mixtures with ammonium nitrate and decrease in mixtures with urea and ammonia hydrate.

Therefore, it can be assumed that the nitrogen present in the mixed mineral fertilizers in the most oxidized form (the degree of nitrogen oxidation is +5) can contribute to the conditions' creation favourable for the atmospheric nitrogen fixation. An increase in the urea and ammonium hydrate content in ammonia water, where nitrogen is in the maximum reduced oxidation state of -3, on the contrary, leads to a decrease in the atmospheric nitrogen binding thermodynamic probability to form oxide forms.

4. Conclusion
The results obtained in this work make it possible to conclude that the atmospheric nitrogen fixation in a nitrate ion form is thermodynamically resolved, and the problem lies in finding conditions conducive to this process implementation.
It was revealed that the atmospheric nitrogen oxidation thermodynamic probability depends both on the mineral fertilizer main component and on this component form, in particular, on its redox or acid-base characteristics.

According to the modelling results, limestone as a mixed mineral fertilizers component contributes to a significant increase in the binding atmospheric nitrogen thermodynamic probability with the most oxidized form formation.

The nitrogen presence in mixed mineral fertilizers in the most oxidized form (the nitrogen oxidation state is +5) can contribute to the conditions’ creation favourable for fixing atmospheric nitrogen. An increase in the urea and ammonium hydrate content in ammonia water, where nitrogen is in the maximum reduced oxidation state of -3, on the contrary, leads to a decrease in the atmospheric nitrogen binding thermodynamic probability to form oxide forms.

References
[1] Podshivalova A K 2019 Soil Influence on the mixed mineral fertilizers components activity The Krasgau Herald 207 31-6
[2] Podshivalova A K 2019 Oxygen activity as a function of the composition of mixed fertilizers IOP Conf. Ser.: Earth Environ. Sci. 315 052056
[3] Podshivalova A K 2020 The influence of chemical soils composition on the thermodynamic probability of the air nitrogen fixation IOP Conf. Ser.: Earth Environ. Sci. 548 52002
[4] Podshivalova A K 2020 The comparative analysis of the mineral nitrogen fertilizers IOP Conf. Ser.: Earth Environ. Sci. 548 52010
[5] Podshivalova A K and Butorina N V 2020 Limestone and slaked lime influence physical and chemical modelling on the mixed mineral fertilizers components activity IOP Conf. Ser.: Earth Environ. Sci. 677 52025
[6] Karpova A Yu, Isupov A N, Bashkov A S and Bortnik T Yu 2013 Lime Influence on the aluminium movable forms contained in the turf-sub-salt soil and the field crops yield The Udmurt University Herald. Biology series. Earth Sciences 6-3 50-2
[7] Yakovleva L V, Lobzeva G A and Boytsova E A 2016 Liming influence on the phosphates state in sod-podzolic sandy loam soil The St. Petersburg State Agrarian University bulletin 45 98-102
[8] Kirpichnikov N A and Andrianov S N 2007 Effect and aftereffect of phosphorus fertilizers on sod-podzolic heavy loamy soil at liming varying degrees Agrochemistry 10 14-23
[9] Zelenin K N 1997 Nitrogen Oxide (II): New features of the long-known molecule Soros educational magazine 10 105-10
[10] Karpov I K, Chudnenko K V and Kulik D A 1997 Modeling chemical mass transfer in geochemical processes: thermodynamic relations, conditions of equilibria and numerical algorithms American Journal of Science 297 767–806
[11] Karpov I K, Chudnenko K V, Kulik D A and Bychinskii V A 2002 The convex programming minimization of five thermodynamic potentials other than Gibbs energy in geochemical modeling American Journal of Science 302 281–311
[12] Glushko V P 1972 Thermal Constants of Substances iss 6, part 1 (Moscow, Russia: AUISTI) p 370
[13] Glushko V P 1974 Thermal Constants of Substances iss 7, part 1 (Moscow, Russia: AUISTI) p 344
[14] Yokokawa H 1988 Tables of thermodynamic properties of inorganic compounds Journal of the national chemical laboratory for the industry 83 27-118
[15] Reed R, Prausnitz J and Sherwood T 1982 Properties of Gases and Liquids: a Reference Guide (Leningrad: Chemistry) p 592
[16] Kryshchenko V S and Golozubov O M 2010 Agro-landscapes soil monitoring problems: the structure and model of data Agrochemical Herald 5 9-11