Limestone and slaked lime influence physical and chemical modelling on the mixed mineral fertilizers components activity

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Abstract. A binary systems' components mutual influence thermodynamic assessment containing limestone or slaked lime in a mixture with nitrogen-containing, potassium-containing and phosphorus-containing mineral fertilizers has been carried out. The systems under study the following indicators were taken into account: the Gibbs system energy, the corresponding components chemical potentials, the solution components amount, the evolved gases amount, the solution pH, and the system redox potential. The results obtained made it possible to conclude an increase in the oxygen chemical activity in systems containing limestone and slaked lime. At the same time, the slaked lime introduction gives an increasing oxygen activity significantly greater effect than the limestone introduction. The maximum effect concerning an increase in oxygen activity is achieved with the limestone and slaked lime introduction in doses of approximately 2 t/ha in the mixed mineral fertilizers' composition. The phosphorus activity increases with calcium carbonate and calcium hydroxide increasing amounts in mixtures. The potassium activity is lower than that of phosphorus. Nitrogen has the lowest activity, which is possibly due to the low-activity gaseous nitrogen present in the system, although, as shown by the simulation results, there is its transformation thermodynamic probability into a nitrate ion. Binary mixtures based on calcium carbonate have a higher oxidation potential in comparison with calcium hydroxide.

1. Introduction
Many researchers note the liming special role in the soil properties optimization processes and the mineral fertilizers effect [1-2]. Taking into account the many parameters on which the result depends (climatic conditions, soil type, fertilizers component composition, fertilizer application rates, plant species, etc.), it is very difficult to determine whether and to what extent to those chemical compounds components mutual influence manifests itself, which are the mixed mineral fertilizers part. In this regard, it seems advisable to the corresponding chemical systems thermodynamic analysis.

The work aim was to study binary mixtures corresponding to the mineral fertilizers' composition by the physicochemical modelling method based on the Selector software package [3-4]. It is known to use the Selector software package to study the processes occurring in soils, including those associated with the mineral fertilizers use [5-8].

The thermodynamic quantities main sources were the works [9-12].
2. Objects and research methods

System simulation was performed:

1. Calcium carbonate - ammonium nitrate - water - air
2. Calcium carbonate - calcium dihydrogen phosphate - water - air
3. Calcium carbonate - potassium chloride - water - air
4. Calcium hydroxide - ammonium nitrate - water - air
5. Calcium hydroxide - calcium dihydrogen phosphate - water - air
6. Calcium hydroxide - potassium chloride - water - air

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 the above systems every 10 variants with calcium carbonate (limestone) and calcium hydroxide (slaked lime) different contents.

3. Results and discussion

Of the greatest interest in the results obtained is the change in the independent components chemical potentials in binary systems 1-3 with an increase in the calcium carbonate amount and binary systems 4-6 with an increase in the calcium hydroxide amount. The points missing number in figure 1 and subsequent figures with the calcium carbonate participation in comparison with the calculated number is due to this substance limited solubility.

![Figure 1](image.png)

**Figure 1.** The oxygen chemical potential dependence on the calcium carbonate content in mixtures.

From the data obtained it follows that there is a significant increase in oxygen activity in the limestone and slaked lime presence. This is evidenced by a rather sharp decrease in the oxygen chemical potential in the above binary systems with an increase in the calcium carbonate and calcium hydroxide (figure 1) molar amounts (figure 2).
Figure 2. The oxygen chemical potential dependence on the calcium hydroxide content in mixtures.

In this case, the oxygen chemical potentials in mixtures with the calcium hydroxide participation must be approximately two times lower than in mixtures with the calcium carbonate participation. This means that the slaked lime equimolar amounts introduction has an increased oxygen activity significantly greater effect than the limestone introduction.

As follows from the curves shown in figures 1 and 2, both calcium carbonate and calcium hydroxide presence in binary mixtures with other salts gives approximately an increase the same picture in the oxygen chemical activity in systems with the ammonium nitrate and potassium chloride participation.

The difference in the system behaviour with the calcium dihydroorthophosphate participation is associated, as can be assumed, with the composition \(3\text{Ca}(\text{PO}_4)_2 \cdot \text{Ca(OH)}_2\) hydroxoapatite formation in an amount of 0.1 mol. Obviously, in connection with this poorly soluble substance composition oxygen to binding in the calcium hydroxide and calcium carbonate 2-5 mol amounts range, the increase in oxygen activity is somewhat reduced.

On the other hand, in general, the calcium carbonate positive effect on the oxygen activity in mixtures affects, as can be seen in figure 1, only in this substance amounts range up to 3.5 mol in the nitrogen- and potassium-containing mineral fertilizers case and up to 5 mol in mixtures with phosphorus-containing fertilizers. For calcium hydroxide (figure 2), an increase in oxygen activity is observed in this substance investigated amounts entire range, although the most significant increase in this characteristic occurs in the calcium hydroxide amounts range up to 5 mol. Therefore, the maximum effect on increasing oxygen activity is achieved when limestone and slaked lime are applied in doses of approximately 2 t/ha as mixed fertilizers part.

The nitrogen, phosphorus and potassium chemical activity, which are nitrogen-, phosphorus- and potassium-containing compounds part, in the calcium hydroxide (figure 3) and calcium carbonate presence (figure 4) is different.

The most active is phosphorus. The phosphorus activity increases with an increase in the calcium carbonate and calcium hydroxide amounts in binary systems, and in the calcium hydroxide case (in the range of 3 - 5 mol) this increase is more pronounced.
The revealed relationship between the phosphorus fertilizers activity and soil liming was noted in [2]. Potassium activity is lower than that of phosphorus; moreover, this component decreases activity as the calcium carbonate and calcium hydroxide amounts increase in their concentrations range from 2 to 3.5 mol, and then the corresponding curve reaches a plateau.

Figure 3. The nitrogen, phosphorus, potassium chemical potentials dependence on the calcium hydroxide content in mixtures.

Figure 4. The nitrogen, phosphorus, and potassium chemical potentials' dependence on the calcium carbonate content in mixtures.
Nitrogen has the lowest activity. This is due to the low-level nitrogen gas present in the system, although, as will be shown below, there is its transformation thermodynamic probability into a nitrate ion.

![Figure 5](image1.png)

**Figure 5.** The system redox potential dependence on the calcium carbonate and calcium hydroxide content in mixtures.

![Figure 6](image2.png)

**Figure 6.** The nitrate ion amounts dependence in solution on the calcium carbonate and calcium hydroxide content in mixtures.

The simulation results indicate a calcium carbonate and calcium hydroxide significant effect on the systems redox characteristics under study (figure 5). Binary systems based on calcium carbonate have
a higher oxidative potential, which, along with other consequences, can contribute, inter alia, to the atmospheric nitrogen fixation with a nitrate ion formation.

The data obtained in this work indicate that the atmospheric nitrogen oxidation with a nitrate ion formation in solution is thermodynamically allowed in the system under study (figure 6).

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.

It should also be noted that all the patterns identified in the work are manifested, as a rule, with calcium carbonate and calcium hydroxide amounts up to 5 mol, which corresponds to the limestone and slaked lime introduction into the soil at approximately 2 t/ha.

4. Conclusions
There is a significant increase in the oxygen activity in mixed fertilizers in the limestone and slaked lime presence. This is evidenced by a rather sharp decrease in the oxygen chemical potential in the above binary systems with an increase in the calcium carbonate and calcium hydroxide (figure 1) molar amounts (figure 2).

The slaked lime equimolar amounts introduction gives an increasing oxygen activity much greater effect than the limestone introduction.

The phosphorus activity, in contrast to the potassium and nitrogen activity, increases with an increase in the calcium carbonate and calcium hydroxide amounts in binary systems, and in the calcium carbonate and calcium hydroxide case calcium carbonate and calcium hydroxide (in the range of 3 - 5 mol), this increase is most pronounced.

Binary systems based on calcium carbonate have a higher oxidation potential in comparison with calcium hydroxide. Under these conditions, the atmospheric nitrogen oxidation with a metastable nitrate ion formation in solution is thermodynamically permitted.

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