Identification of soluble chemical species of aluminum (Al) in the interstitial waters presents a great interest, in particular, to assess the potential toxicity of soluble aluminum in the large concentrations over the plants [1], because not all its soluble species are toxic to the same extent. The ion Al$^{3+}$, hydroxocomplexes Al(OH)$^{2+}$ and Al(OH)$^{2+}$ are the most toxic species, while the complexes Al - F and Al - organic ligand are less harmful. The concentration of soluble Al in the most natural waters is very small (10$^{-5}$ – 10$^{-6}$M), in conditions when the medium is almost neutral and concentrations of complexing agents are negligible, being generally controlled by gibbsite [2]. However, in soils which become acidic due to the oxidation of pyrite or sulfur the ion SO$_4^{2-}$ is the dominant anion. Soil acidity can increase and as a result of atmospheric rainfall containing sulfur compounds.

With increasing the SO$_4^{2-}$ concentration the Al$^{3+}$ activity (or concentration) grows exponentially [3]. At the same time modifies the relative stability of minerals in soils. In sulfate acidic soil solution the Al oxysulfate minerals, such as alunogen Al$_2$S(O)O$_4$.17(H$_2$O), alunite KAl$_2$[(OH)$_2$(SO$_4$)$_2$, jurbanite Al(OH)$_2$(SO$_4$).5(H$_2$O) and basaluminite Al$_4$(OH)$_3$(SO$_4$).5(H$_2$O) [4-6] are more stable than gibbsite. The identification of mineral species controlling Al solubility in acidic soil solution, rich in sulfate presents a difficult problem. Firstly, as has been shown by X-ray diffraction, solids can be amorphous. Secondly, to distinguish between the adsorbed and structural sulfate is an additional intricacy. In numerous studies the theoretical calculations have been carried out in order to determine the Al mineral species that form in the acidic sulfate environments of soils. In [7] the authors state that retention of sulfate by acid soils is a consequence of the solubility of basaluminite and/or alunite. The basaluminite solubility and its control over the Al concentration in aqueous acid sulfate systems has been examined recently for a series of natural acid waters [8,9]. Using Al, S and O K XANES - spectroscopy, combined with the elemental analysis of the groundwater precipitates it has been demonstrated that for pH values 4.0-5.2 the Al concentration is controlled by less crystalline mineral - hydrobasaluminite (with an empiric formula $\text{Al}_4(\text{OH})_{10}(\text{SO}_4)_{15}(\text{H}_2\text{O})$) that under conditions of relatively low humidity is very unstable and tends to dehydrate with formation of basaluminite. The same authors have demonstrated that concentrations of Al soluble within the pH 3.5-7.0 range in acidic sulfate soils are controlled by a mixture of amorphous Al hydroxide and basaluminite.

In the present paper it is investigated the distribution of soluble and insoluble Al$^{3+}$ species of soil solutions in the heterogeneous multicomponent system "basaluminite-saturated aqueous solution".

Theoretical part

The equilibrium model is based on the following assumptions:
- the Al$^{3+}$ concentration in soil solution is controlled by the basaluminite solubility:
  \[
  \text{Al}_4(\text{OH})_{10}\text{SO}_4.5\text{H}_2\text{O} + 10\text{H}^+ \leftrightarrow \text{Al}_4\text{Al}_2(\text{OH})_6(\text{SO}_4)_8.17\text{H}_2\text{O} + 10\text{H}_2\text{O} + 2\text{SO}_4^{2-}
  \]

  $K_s$ represents the product of the mineral solubility of aluminum. For convenience, the charges of ions will be omitted.

  Therefore, the Al$^{3+}$ion concentration is:
  \[
  [\text{Al}^{3+}] = \frac{[\text{Al}^{3+}]^{[\text{SO}_4^{2-}]}}{[\text{H}^{+}]^{10}}
  \]  

- the studied soil solutions are dilute solutions with a low ionic strength, so its influence can be neglected [10].

Concomitantly with the process (1) it has also been taken into account a set of possible equilibria in the system "mineral-soil solution", presented in the table 1. In the soil solution Al is present in various forms, including soluble hydroxy-, fluoro- and sulfate complexes, as well as organic complexes. There are also more phosphate complexes and polymeric species of Al. The organic acid contained in the soil can be considered as a triprotic acid H Org[1,3]. It has been taken into account the formation of two complexes of aluminum with ligand Org$^3$, AlOrg and AlHOrg$^2$. As polysynthetic species of aluminium the
polynuclear Al hydroxocomplexes will be considered (dimer $\text{Al}_2\text{(OH)}_4^{2+}$ and trimer $\text{Al}_3\text{(OH)}_4^{3+}$). Polymeric species with large molecular mass $\text{Al}_i\text{(OH)}_i$, where $i = 6, 8$ and 13 will not be taken into account, since they are basically not formed in the soil solution because of low polymerization kinetics. Concomitantly, the organic acids in soil solution inhibit their formation [1,3]. Aluminum phosphate complexes can be represented in the form of $\text{AlH}_2\text{PO}_4^{2-}$. The Al silicate complexes are ignored because of their weak complexation properties.

The mass balance (MB) conditions for the examined systems can be formulated on the basis of the method of residual concentrations (RC) [11,12]:

$$c_{\text{AI}}^0 = c_{\text{AI}}^r + \Delta c_{\text{AI}} = \sum_{j=0}^{\infty} \sum_{l=0}^{j} \left[\text{Al}_j\text{(OH)}_j^{2-}\right]^l + \sum_{j=1}^{\infty} \left[\text{AlF}_j^{3-}\right]^l + \left[\text{AISO}_j^{4-}\right]^l + \left[\text{Al(SO}_4^{2-}\right]^l$$

(3)

$$c_{\text{PO}_4}^0 = c_{\text{PO}_4}^r + \Delta c_{\text{PO}_4} = \sum_{m=0}^{\infty} \sum_{l=0}^{m} \left[\text{H}_m\text{PO}_4^{m-}\right]^l + \left[\text{AlH}_2\text{PO}_4^{2-}\right]^l$$

(4)

The quantities $c_i^0$ and $c_i^r$ (mol/L) in the equations (3)-(7) represent respectively the analytical and residuals concentrations of the component $i$ in the considered heterogeneous system, while $\Delta c_i$ symbolizes its quantity in precipitate in one liter of solution [13-15]. At the same time, within the CR method the following relationships result: $\Delta c_{\text{OH}} = -\Delta c_i$, and $c_{\text{H}_i}^r = -c_{\text{OH}}^r$. In the equation (8) $c_{\text{OH}}^r$ denotes the excess of the $\text{H}^+$ ions in respect to hydroxyl ions in the two-phase mixture $c_{\text{OH}} = -c_{\text{OH}}^r$. Based on the stoichiometric conditions of the considere Mineral with a general composition, $\text{Al}_i\text{(OH)}_i\text{SO}_4 \cdot 5\text{H}_2\text{O}$ the following relations can be derived:

$$\Delta c_{\text{OH}} = \frac{1}{10} \Delta c_{\text{SO}_4} = \frac{1}{4} \Delta c_{\text{Al}}$$

(8)

The Al$^{3+}$ equilibrium concentration is determined by the relation (2). From the MB conditions (3)-(7), for a specific pH value, taking into account the relations (10) and the equations of the law of mass action (LMA) deduced from the table 1, we obtain a system of 5 nonlinear equations with 5 unknown variables, $\Delta c_i$, respectively, which can be easily solved by using numeric computerized methods [13-15]. Next, the residual concentrations of the $i$ component are calculated, $c_i^r$, knowing the initial composition of the heterogeneous mixture, in other words, the quantities $c_i^r$.

Within the thermodynamic approach elaborated earlier [16-19] and extended in this paper on the solid phase with a more complex composition, it can be demonstrated that the total Gibbs energy values $\Delta G_{i,tot}$ for the examined complex processes, where dissolution-precipitation reaction (1) and those from the table 1 take place concomitantly, can be calculated with the following equations:

$$\Delta G_{i,tot} = -RT \ln \frac{c_i^r}{c_i^0} - RT \ln \frac{c_{\text{OH}}^r}{c_{\text{OH}}^0}$$

(9)

In order to calculate the Gibbs energy $\Delta G_{i,tot}$ referred to one mole of aluminum, we will use the expression:

$$\Delta G_{i,tot} = -RT \ln \frac{c_i^r}{c_i^0} - RT \ln \frac{c_{\text{OH}}^r}{c_{\text{OH}}^0}$$

(10)

The solid phase $\text{Al}_i\text{(OH)}_i\text{SO}_4 \cdot 5\text{H}_2\text{O}$ is stable if $\Delta G_{i,tot} > 0$. The condition $\Delta G_{i,tot} = 0$ corresponds to the beginning of dissolution/precipitation of basalluminite.

Using the combined equations of LAM and MB, the distribution diagrams of the aluminum ion both in the solid and liquid (species in aqueous solution) phases, so called the diagrams of heterogeneous chemical equilibria (DHCE) can be calculated [2,12].

For the studied system the heterogeneous system the following equation for calculation of partial molar fractions of species, $\gamma_i$ , where the reactions listed in table 1 are take place concomitantly:

$$\gamma_S = \frac{\Delta c_{\text{Al}}}{c_{\text{Al}}^0}, \gamma_{\text{tot}} = \frac{c_{\text{Al}}^r}{c_{\text{Al}}^0}, \gamma_{\text{Al}} = \frac{[\text{Al}]}{c_{\text{Al}}^0}$$

(11)

place concomitantly

$$\gamma_{\text{F}_i} = \frac{\Delta c_{\text{F}_i}}{c_{\text{F}_i}^0}, \gamma_{\text{F},i} = \frac{[\text{F}_i]}{c_{\text{F}_i}^0}$$

$$\gamma_{\text{OH}} = \frac{[\text{OH}]}{c_{\text{OH}}^0}, \gamma_{\text{SO}_4} = \frac{[\text{SO}_4]}{c_{\text{SO}_4}^0}$$

$$\gamma_{\text{PO}_4} = \frac{[\text{PO}_4]}{c_{\text{PO}_4}^0}$$

(12)

The index "tot" symbolizes the sum of the partial molar fractions of all the soluble species. From the expressions (3) - (10), the following relation results:

$$\gamma_{\text{S}} + \gamma_{\text{tot}} = \gamma_{\text{S}} + \gamma_{\text{Al}} + \sum_{j=1}^{\infty} \sum_{l=0}^{j} \gamma_{\text{F},i} + \gamma_{\text{O}_1} + \gamma_{\text{O}_2} + \gamma_{\text{S}_1} + \gamma_{\text{S}_2} + \gamma_{\text{PO}_4}$$

After their outer appearance DHCE look like diagrams of distribution of species in a homogeneous system. The last, as a rule, are constructed in the coordinates $\gamma_i$ (pH), because in the absence of polynuclear complexes the partial molar fractions of species $\gamma_i$ in aqueous solution

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Equilibrium constants used in thermodynamic calculations are functions only on pH of solution and do not depend on the initial concentrations of components. In the case of heterogeneous equilibria, the partial molar fractions of species additionally on the initial composition of the mixture and for a fixed value of pH are functions of five variables \( y_i = f \left( C_0^{\text{Al}}, C_0^{\text{F}}, C_0^{\text{SO}_4}, C_0^{\text{Org}}, C_0^{\text{PO}_4} \right) \). In this case it is rational to construct the diagrams in coordinates, while the values of other quantities are maintained constant.

The procedure for constructing DHCE includes the next necessary steps:

i) The calculation of thermodynamic stability area of the mineral. For this purpose from equation (9) or (10) the Gibbs energy values shall be determined.

ii) The calculation with equations (11) the partial molar fractions \( \gamma_i \) of all the species containing the aluminum ion within the thermodynamic stability area of basaluminite established in the previous stage.

iii) In order to complete the diagram, in the case of aqueous homogeneous solution, the partial molar fractions shall be calculated from the equations used for constructing usual distribution diagrams. In this case, under the conditions of mononuclear species formation the \( \gamma_i \) values do not depend on the initial concentrations of the components.

**Results and discussions**

It is well known that the pH value of saturated solutions is one of the major factors ("master" variable) that influences the distribution of aluminum in both minerals and soluble inorganic and organic species. The diagrams \( \Delta G^\theta_{\text{tot}}(\text{pH}) \) allow easy the determination of thermodynamic stability area of basaluminite in function on the initial composition of multicomponent systems.

In the calculations carried out in this paper the analytical concentrations of aluminium, the inorganic ligands, fluorine and phosphate ions as well as the organic ligand have been kept constant, \( C_0^{\text{Al}} = 1 \times 10^{-4} \text{M}, C_0^{\text{F}} = 5 \times 10^{-6} \text{M}, C_0^{\text{PO}_4} = 1 \times 10^{-4} \text{M} \) and \( C_0^{\text{Org}} = 1 \times 10^{-4} \text{M} \). The pH range of variation was of 1 ÷ 11. The analysis of the data presented in figure 1 shows that the thermodynamic stability area of the mineral

<table>
<thead>
<tr>
<th>Chemical reactions</th>
<th>log( \gamma )</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}^{3+} + H_2O = \text{AlOH}^{2+} + H^+ )</td>
<td>-4.99</td>
<td>( K_1 )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 2H_2O = \text{Al(OH)}^{+} + 2H^+ )</td>
<td>-10.00</td>
<td>( K_2 )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 4H_2O = \text{Al(OH)}^{4+} + 4H^+ )</td>
<td>-23.00</td>
<td>( K_4 )</td>
</tr>
<tr>
<td>( \text{Al}_2(\text{OH})_6(\text{SO}_4)<em>2(\text{OH})</em>{10-} + 10H^+ = 4\text{Al}^{3+} + 5\text{SO}_4^{2-} + 15H_2O )</td>
<td>22.5</td>
<td>( K_S )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + F^- = \text{AlF}^2+ )</td>
<td>7.02</td>
<td>( K_{f1} )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 2F^- = \text{AlF}_2^- )</td>
<td>12.76</td>
<td>( K_{f2} )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 3F^- = \text{AlF}_3^- )</td>
<td>17.03</td>
<td>( K_{f3} )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 5F^- = \text{AlF}_5^- )</td>
<td>19.73</td>
<td>( K_{f4} )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + \text{SO}_4^{2-} = \text{AlSO}_4^{+} )</td>
<td>29.92</td>
<td>( K_{f5} )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + 2\text{SO}<em>4^{2-} = \text{Al(}</em>{2}\text{SO}<em>4\text{)}</em>{7-} )</td>
<td>3.01</td>
<td>( K_{f6} )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + \text{Org}^{3-} = \text{AlOrg}^- )</td>
<td>8.39</td>
<td>( K_{f7} )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + H^+ + \text{Org}^{3-} = \text{AlHOrg}^+ )</td>
<td>13.09</td>
<td>( K_{f8} )</td>
</tr>
<tr>
<td>( H_2O + H^+ = HF )</td>
<td>6.15</td>
<td>( K_w )</td>
</tr>
<tr>
<td>( 2\text{Al}^{3+} + 2H_2O = 2\text{Al}_2(\text{OH})_2^{4+} + 2H^+ )</td>
<td>-6.3</td>
<td>( K_{f10} )</td>
</tr>
<tr>
<td>( 3\text{Al}^{3+} + 4H_2O = 3\text{Al}(\text{OH})_4^{5+} + 4H^+ )</td>
<td>-12.1</td>
<td>( K_{f11} )</td>
</tr>
<tr>
<td>( \text{Al}^{3+} + H_2\text{PO}_4^{2-} = \text{AlH}_2\text{PO}_4^{4+} )</td>
<td>3.1</td>
<td>( K_{f12} )</td>
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<tr>
<td>( \text{PO}_4^{3-} + H^+ = \text{HPO}_4^{2-} )</td>
<td>12.0</td>
<td>( K_{f13} )</td>
</tr>
<tr>
<td>( \text{PO}_4^{3-} + 2H^+ = \text{H}_2\text{PO}_4^{4-} )</td>
<td>19.21</td>
<td>( K_{f14} )</td>
</tr>
<tr>
<td>( \text{PO}_4^{3-} + 3H^+ = \text{H}_3\text{PO}_4 )</td>
<td>21.36</td>
<td>( K_{f15} )</td>
</tr>
</tbody>
</table>
becomes considerably larger with increasing the total (analytical) concentration of the SO$^{2-}$ ion.

The DHCE diagrams for different concentrations of sulfate are presented figure 2-5. These diagrams reflect explicitly the distribution of various chemical species of aluminium in both the solid and liquid phases. The partial molar fractions of soluble aluminium species change substantially at the pH value of sedimentation-solubilization of solid phase.

For the studied compositions of mixture, in acidic and neutral solutions, the equilibrium concentrations of mononuclear hydroxocomplexes are small, while the polynuclear species do not almost form within the entire range of pH and the concentration of sulfate. The concentration of the toxic aluminum ion decreases significantly with increasing C$^{\text{SO}_4}$, and for C$^{\text{SO}_4} = 1 \cdot 10^{-2} \text{ M}$ becomes insignificant. The predominant species in alkaline environments is the anionic hydroxocomplex Al(OH)$^4^-$. With the increase of the concentration of sulfate ions the stability areas of other soluble species are substantially modified. In the case C$^{\text{SO}_4} = 2.5 \cdot 10^{-3} \text{ M}$ and C$^{\text{SO}_4} = 1 \cdot 10^{-2} \text{ M}$, in the range of pH variation 4.0 – 5.0 the complexes AlOrg and AlHOrg$^+$ prevail, while for C$^{\text{SO}_4} = 1 \cdot 10^{-3} \text{ M}$ this range of pH narrows, and for C$^{\text{SO}_4} = 1 \cdot 10^{-2} \text{ M}$ the formation of these complexes is blocked by the predominance of aluminum complexes with the sulfate ion, AlSO$^{4+}$ and Al(SO$_4$)$_2$ (fig.5). In figure 6 the variation of the partial molar fraction of solid phase - basaluminite is given, depending on the pH and C$^{\text{SO}_4}$. As one can see, the areas of the mineral existence, i.e. of the heterogeneous system coincide with the thermodynamic stability of this mineral (fig. 1), at the same time the $\gamma_s$ values increase with increasing the C$^{\text{SO}_4}$ values.
Conclusions
Within the method of residual concentrations, using the mass balance conditions that take into account all the possible chemical species present both in aqueous and solid phases, a method of thermodynamic calculation of complex chemical equilibria in soils containing mineral-phase basaluminite in real conditions has been developed.

The areas of thermodynamic stability of basaluminite for a wide range of the variation of pH and different values of sulfate ion have been determined. A new type of distribution diagrams, which describe quantitatively the distribution of soluble and insoluble species of aluminium in heterogeneous multicomponent system "basaluminite-saturated aqueous solution" has been presented. In the studied system the \( \text{SO}_4^{2-} \) ions play an important role in regulating the distribution of soluble and insoluble species. The increasing the \( \text{SO}_4^{2-} \) concentration leads to decreasing of residual concentration of aluminium in solution, \( C'_d \). The obtained data are in good agreement with the experimental data reported previously in the literature.

References

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