# ALUMINIUM HOMOGENEOUS AND HETEROGENEOUS SPECIATION IN SOIL WATER EQUILIBRIA WITH THE MINERAL PHASE JURBANITE

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**Abstract.** A novel approach of graphical representations of complex equilibria based on numerical computerized methods, which quantitatively describe the repartition of various soluble and insoluble, inorganic and organic, monomeric and polymeric aluminium species in the heterogeneous multicomponent system "jurbanite – saturated aqueous solution" has been used. This method applies the thermodynamic relations together with the mass balance constraints, where the mineral phase is explicitly expressed. The factors influencing the distribution of soluble and insoluble aluminium species in aquatic natural systems in a large range of pH values have been considered. The used method predicts *Al* speciation for published soil solution data, assuming soil solutions are in equilibrium with jurbanite. The obtained results imply that the presence and dissolution of jurbanite in soils impacted by acidic deposition has a noticeably influence the soil solution *Al* chemistry. The developed new type of diagrams can be used to interpret data obtained within the framework of water quality monitoring programs.

## Introduction

Aluminum (*Al*) is the most abundant metal in the earths crust, comprising about 7% of its mass. Since many plant species are sensitive to micromolar concentrations of *Al*, the potential for soils to be *Al* toxic is considerable. Speciation of aluminium *Al* is a critical issue when assessing the effects of *Al* in soil solutions because not all chemical species of *Al* are equally toxic. Fortunately, most of the *Al* is bound by ligands or occurs in other nonphytotoxic forms such as aluminosilicates and precipitates. However, solubilization of *Al* is enhanced by low pH and *Al* toxicity is a major factor limiting plant production on acid soils; the toxic effect being dependent on the plant species and the concentrations of individual *Al* species in solution.

Acidic deposition constitutes one mechanism by which the atmospheric pollutants influence the soil equilibria. Thus, the release of toxic $Al^{3+}$ is one of the most serious consequences of soil acidification. Introduction of acidic rainwater in the soils results in a significant change in soil solution composition, especially in the $SO_4^{2-}$ concentration. In the soil water, $SO_4^{2-}$ is one of the major anions, generally ranging from $1.5 \cdot 10^{-4}$ to $1.25 \cdot 10^{-3}$ mol/L in the different natural waters. The sulfate activity of surface waters and ground waters is fairly constant and is set at $2.5 \cdot 10^{-3}$ mol·L$^{-1}$. In some of the natural systems the concentrations of inorganic monomeric aluminum are typically between $1 \cdot 10^{-4}$ and $2 \cdot 10^{-4}$ mol·L$^{-1}$ [1]. Under typical soil conditions, the *Al* activity is usually controlled by the solubility of gibbsite $A(OH)_{3(s)}$ or kaolinite [2]. However, in areas of sulfide oxidation, high concentrations of sulfate modify the aqueous geochemistry of *Al*. The acid sulfate soil waters contain generally high concentrations of dissolved aluminum. In acid sulfate drainage waters and leachate solutions from mine waste tailings and soils, the *Al* solubility appears to be controlled by a variety of basic *Al* sulfate phases (alunite, jurbanite etc.). Authors [3] suggested that the formation of basic aluminium sulfate (*BAS*) minerals $(K,Na)_n Al_x (OH)_y (SO_4)_z (H_2O)_m$, also named hydroxy-aluminium sulfate, may contribute to sulfate retention in soils. The identification of the mineral species controlling the solubility of Al in acidic waters rich in sulfate has presented researchers with several challenges. It is apparent that there are inconsistencies in the literature on the process regulating aqueous aluminum concentration in dilute acidic waters. If one intends to improve the models that have been developed to evaluate the degree and effects of surface water acidification it is essential that one develops a better understanding of the mechanisms of aluminum mobilization. The vast majority of these studies indicate the formation of a mineral species matching the stoichiometry of jurbanite, $AlOHSO_{4(S)} \cdot 5H_2O$. Authors [1] stated that the aluminum chemistry in the natural systems could not be described by the simple models of gibbsite equilibrium. The majority of soil water samples studied in this paper with pH below 5 was oversaturated with respect to jurbanite. Their best predictions were obtained by assuming a jurbanite type equilibrium for pH<5 and a gibbsite type equilibrium for higher pH values, but to what extent this really reflects the real processes was uncertain [1]. Additionally, Appelo and Postma [4] established that in groundwater the gibbsite model was reasonably accurate when pH>4.5 and a jurbanite model better for pH<4.5. Karathanasis and others [5] suggested the change occurring between pH 4.5–5 is the boundary for $Al^{3+}$ control between basic aluminum sulfates and aluminosilicates. The

$Al^{3+}$ activity in solutions with pH<5 seems to be controlled by jurbanite, alunite, and gibbsite, depending on the $SO_4^{2-}$ activity in the soil solution. In solutions with pH>5 an amorphous $A(OH)_{3(s)}$ controls the *Al* activity [5].

As it was aforementioned, the determination of the total concentration of aluminium in soil solution has a low practical significance. Dissolved mononuclear Al occurs as aquo *Al*, as well as $OH^{-}$, $F^{-}$, $SO_4^{2-}$, and organic complexes. Although past investigations have often ignored non-hydroxide complexes of *Al*, it appears that organic and F complexes are the predominant forms of Al in dilute (low ionic strength) acidic surface waters. The concentration of inorganic forms of *Al* increases exponentially with decreases in solution pH. In order to better understand the effects of acid precipitation on soil and predict the toxic concentration of *Al* in soil solutions, it is necessary to have a tool to predict how the various species of *Al* will respond to changes in the composition of soil solutions. Chemical modeling represents a unique method for the prediction of aluminium behavior in soil solutions [6]. The main objectives of the present paper consist of the thermodynamic analysis and graphical representation of the distribution of various species of *Al* both in saturated aqueous solutions and solid phases. In this work, a new type of diagrams based on graphical and numerical computerized methods, which quantitatively describe the repartition of various soluble and insoluble, inorganic and organic, monomeric and polymeric aluminium species in heterogeneous multicomponent systems "jurbanite – saturated aqueous solution", has been used.

## Theory

Initially, some assumptions similar to [6] have been made. Firstly, the studied system is considered in a stable chemical equilibrium state, i.e. the influence of kinetic factors are neglected. Secondly, natural waters are considered as diluted solutions with a low ionic strength. In the third, the natural water is in balance with the mineral phase jurbanite in such a manner that the equilibrium concentration of aluminium ion $[Al^{3+}]$ can be estimated as a function of pH using following relations, where $K_S$ is the equilibrium constant (solubility product):

$$\begin{aligned} & AlOHSO_{4(S)} \cdot 5H_2O + H^+ \Leftrightarrow \\ & \Leftrightarrow Al^{3+} + SO_4^{2-} + 6H_2O, \\ & K_S = [Al^{3+}][SO_4^{2-}][H^+]^{-1}, \\ & [Al^{3+}] = K_S[H^+][SO_4^{2-}]^{-1} \end{aligned} \tag{1}$$

In the fourth, equilibrium reactions with the participation of *Fe* and *Mn* are not included in this model for some reasons (the most part of these metals may be present in the form of monomeric particles or as colloidal oxides taking part in complex redox reactions, and their chemical composition in acidic waters remains till now uncertain owing to the absence of a quantitative information concerning interactions between the *Fe* and *Mn* forms). In the fifth, organic substances in natural waters are considered in the form of the three-basic acids while two chemical forms of aluminium – organic matter are considered. In the sixth, the adsorption of anions ($F^-$ and $SO_4^{2-}$) is not included in model. Finally, in the seventh, $Al$-phosphate complexes can be presented in the form of $AlH_2PO_4^{2+}$, and $Al$-silicate complexes may be neglected. Besides the process of jurbanite dissolution (1), the set of possible concurrent equilibria in system "mineral phase - natural water", similar to [6] has been taken into account. The mass balance (MB) conditions in this system may be formulated on the basis of the method of residual concentrations, RC [6]. From the stoichiometric composition of jarosite $AlOHSO_{4(S)}$, the ratio follows:

$$\Delta C_{OH} = \Delta C_{SO_4} = \Delta C_{Al}, \tag{2}$$

where $\Delta C_i$ symbolizes the quantity of component *i* in the precipitate in one litter of solution.

The equilibrium concentration of $[Al^{3+}]$ ion is determined from the equilibrium constant $K_S$ (1). From the equations of the MB conditions [6] for a given pH, taking into account the relation (2) and equations of law of mass action (LMA), a system of five equations with five unknown quantities $[F], [Org], [SO_4], [PO_4]$ and $\Delta C_{Al}$ is derived, which may be easily solved by computerized numerical methods. Then, the residual concentrations $C_i^r$ of the component *i* are calculated, knowing the initial composition of heterogeneous mixture, e.g. the quantities $C_i^0$. Using the LMA and MB combined equations, it is possible to calculate the diagrams of distribution of aluminium ion both in solid and liquid phases (species in aqueous solution), i.e. the diagrams of heterogeneous chemical equilibrium (DHCE) [7]. The following equations for calculation of the species partial molar fractions $\gamma_i$ in the heterogeneous system, where the reactions presented in [6] proceed concomitantly, can be written:

$$\gamma_S = \frac{\Delta C_{Al}}{C_{Al}^0}, \gamma_{Al} = \frac{[Al]}{C_{Al}^0},$$

$$\gamma_{ij}=\frac{i[Al_i(OH)_j]}{C_{Al}^0},\gamma_{PO_4}=\frac{[AlH_2PO_4]}{C_{Al}^0}$$

$$\gamma_{f,j}=\frac{[AlF_j]}{C_{Al}^0},\gamma_{O1}=\frac{[AlOrg]}{C_{Al}^0},$$

$$\gamma_{O2}=\frac{[AlHOrg]}{C_{Al}^0},\gamma_{S1}=\frac{[AlSO_4]}{C_{Al}^0}, \qquad (3)$$

$$\gamma_{S2}=\frac{[Al(SO_4)_2]}{C_{Al}^0},\gamma_{tot}=\frac{C_{Al}^r}{C_{Al}^0}.$$

Within the thermodynamic approach, previously developed [6-10] and extended in this paper for the solid phase with a more complex composition, we have been demonstrated that the total Gibbs energy $\Delta G_{S,tot}$ values for the examined complex processes, where a large set of simultaneous reactions takes place, are calculated by the following equation:

$$\Delta G_{S,tot}=-RT\ln\frac{C_{Al}^r}{C_{Al}^0}-RT\ln\frac{C_{SO_4}^r}{C_{SO_4}^0} \qquad (4)$$

The diagrams of heterogeneous chemical equilibria (DHCE), externally, are similar to diagrams of species distribution in the homogeneous systems. The last usually are fitted in the coordinates $\gamma_i(pH)$, as in absence of polynuclear complexes the partial molar fractions of species $\gamma_i$ in aqueous solution (more frequently, notated as $f$ or $\alpha$) are functions only of the solution pH and do not depend on initial concentrations of components. In the case of heterogeneous equilibria, the partial molar fractions of species also depend on the initial composition of mixture and, for a given pH, are functions of five variables $\gamma_i=f\left(C_{Al}^0,C_F^0,C_{SO_4}^0,C_{Org}^0,C_{PO_4}^0\right)$. In this case it is reasonably to fit diagrams in coordinates $(\gamma_i, pH)$ while values of other quantities are kept constant.

## Results and discussion

The analysis of data illustrated on Fig. 1 and 2 reveals that the thermodynamic stability area of jurbanite becomes considerably larger by increasing the total (analytical) concentration of aluminium ion. The presence of sulfate can dramatically alter the *Al* solubility under acidic conditions, where other, less soluble minerals than gibbsite, can control the aqueous geochemistry of aluminum. These minerals include alunite $KAl_3(OH)_6(SO_4)_2$, jurbanite $Al(OH)(SO_4)\cdot 5(H_2O)$, and basaluminite $Al_4(OH)_{10}(SO_4)\cdot 5(H_2O)$.

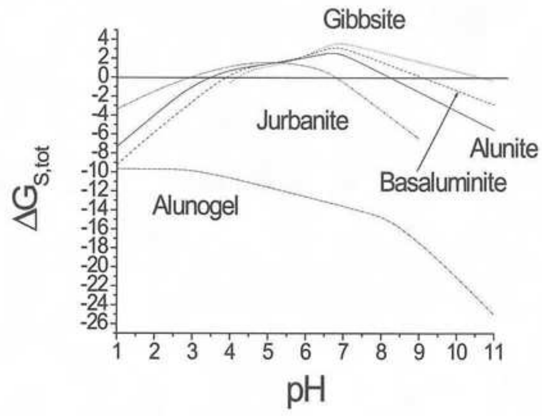

**Fig.1. Total Gibbs energy versus pH in the system "saturated aqueous solution – mineral". Concentrations (M): $C_{Org}^0$, $C_{PO_4}^0$ = 1·10$^{-4}$, $C_F^0$ = 5·10$^{-6}$, $C_{Al}^0$=$C_{SO_4}^0$ = 1·10$^{-3}$.**

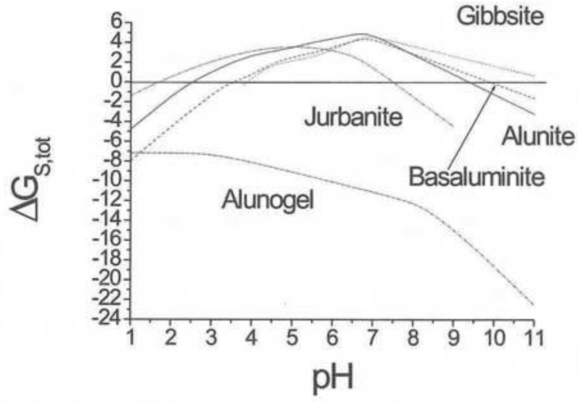

**Fig.2. Total Gibbs energy versus pH in the system "saturated aqueous solution – mineral". Concentrations (M): $C_{Org}^0$, $C_{PO_4}^0$ = 1·10$^{-4}$, $C_F^0$ = 5·10$^{-6}$, $C_{Al}^0$=$C_{SO_4}^0$ = 1·10$^{-2}$.**

The analysis of Fig. 1 and 2 shows that the thermodynamic stability areas of the *Al* hydroxyl-sulfate minerals become considerably larger at increasing total (analytical) concentrations. Under the examined conditions alunogel is thermodynamically unstable. Our data confirmed the early finding [11] that jurbanite is stable up to the pH range of 3–5 and alunite is stable at higher pH values than jurbanite, up to 4–7, depending on the sulfate activity (Fig. 1 and 2). Above these pH limits gibbsite is the most stable phase. DHCE for the investigated system are represented in Fig. 3 and 4. The diagram reflects clearly the distribution of various aluminium chemical forms both in the solid phase and saturated solutions. Partial molar fractions of soluble aluminium forms are changing strongly at the pH value of dissolution – formation of the solid phase. For a given total concentration of aluminium in acidic and neutral solutions the equilibrium concentrations of mononuclear and polynuclear aluminium hydroxo - complexes are negligible.

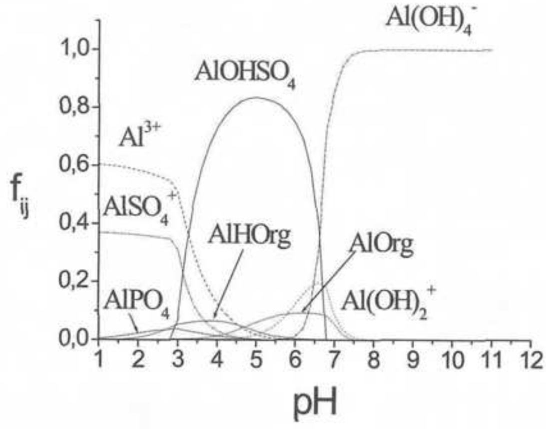

**Fig.3. Diagrams of heterogeneous chemical equilibrium in the system "saturated aqueous solution – jurbanite". Concentrations (M): $C^0_{Org}, C^0_{PO_4}$ = 1·10$^{-4}$, $C^0_F$ = 5·10$^{-6}$, $C^0_{Al} = C^0_{SO_4}$ = 1·10$^{-3}$.**

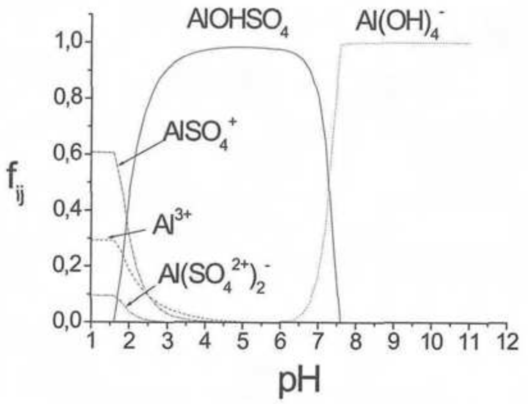

**Fig.4. Diagrams of heterogeneous chemical equilibrium in the system "saturated aqueous solution – jurbanite". Concentrations (M): $C^0_{Org}, C^0_{PO_4}$ = 1·10$^{-4}$, $C^0_F$ = 5·10$^{-6}$, $C^0_{Al} = C^0_{SO_4}$ = 1·10$^{-2}$.**

The $Al^{3+}$ activity is strongly correlated with the soil solution pH and it increases as pH decreased. The presence of inorganic ligand, fluoride ion $F^-$, does not practically affect the solubility of jurbanite, while the organic ligand $Org^{3-}$ has a little influence. The solubility of jurbanite increases under alkaline condition. The anionic hydroxo – complex $Al(OH)_4^-$ in alkaline media becomes the prevailing species. From Fig. 3 and 4 one can clearly see that the thermodynamic area of jurbanite stability increases with the increase of the analytical concentrations of aluminium and sulfate ions in the heterogeneous mixture.

In the case of $C^0_{Al} = C^0_{SO_4}$ = 1·10$^{-2}$ M in the strong acidic solutions in the pH region up to 2.0 the predominant species is $AlSO_4^-$.

## Conclusions

The factors influencing the distribution of soluble and insoluble aluminium species in aquatic natural systems in a large range of pH values have been considered. The MB conditions take into consideration all the chemical forms present in aqueous and solid phases, including inorganic and organic mononuclear and polynuclear forms. Using data from several published sources, the used method demonstrates how the change in soil solution composition affects *Al* solution chemistry in equilibrium with jurbanite. It has been found that the $SO_4^{2-}$ concentration has a substantial influence on the distribution of aluminium speciation in acidic soils, while the concentrations of organically complexed and fluoride complexed *Al* are minimal in the pH range studied. Our thermodynamic analysis for a series of different soil solution compositions shows that at decreasing the $SO_4^{2-}$ concentration, the amounts of toxic forms of $Al^{3+}, AlOH^{2+}$ and $Al(OH)_2^+$ are greatly increased while the concentrations of $Al-F$, $Al-SO_4$ and $Al-Org$ are reduced. The obtained data regarding the factors influencing Al speciation, based on the constructed DHCE diagrams, are in good agreement with the previous results obtained by authors [1-5, 11]. The results presented here suggest that the formation of *BAS* minerals plays a major role in sulfate retention in S-impacted soils.

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