Evaluation of acidic-alkaline properties of various minerals through thermodynamic constants of their hydrolytic dissociation

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During the last decades a serious effort was mounted to calculate acidic-alkaline properties of minerals as an important characteristic of their stability both in melt and solution systems (D.S. Korzhinsky, A.A. Marakushev, V.A. Zarikov, D.Burt *et al.*). In particular, main ideas were selected in the special book: 'Acid-alkaline properties...' (1982). Nevertheless, the problem of the general thermodynamic description and comparison of various mineral groups and species is open now from this point of view. In this relation rather simple and effective approach is suggested below to create the wide system of conventional numerical values.

There are several data bases including sets of thermodynamic constants or other characteristics of hydrolytic mineral reactions, such as Karpov (1981), Bowers *et al.* (1984), Ball, Nordstrom (1991). Some universal characteristics of different types of dissolution reactions can be calculated with the help of these or other data bases. Depending on the chemical environment, these characteristics reflect various types of interactions.

The simplest type of reactions, chosen from Bowers *et al.*(1984) and illustrated in the Table1 (first column), has been used in this study. Taking such "ideal" acid solution without complex- and secondary phase formation, but with some real level, e.g. 10^{-4}mol/kgH_2O, for every produced aqua-ion activities, we calculate the necessary pH value, providing equilibrium. Ion activity products, commonly known in chemistry, have been based on the same conception of standard state of solutions. The proposed values can be named as **conventional indices of acidic-alkaline stability** (CIAAS) of minerals in solutions.

To check the accuracy of pH calculation, some reactions of hydrolytic dissociation have been calculated with the help of different data bases (Table 1, pH_{1-3}). In addition to demonstrate the efficiency of the suggested approach, just same indices for a set of calcium minerals are presented in the right column of Table 2. Really, the good agreement between their decrease from top to bottom along with the drop of mineral solubility is obvious. In the first stage the hydrolytic dissociation of 40 oxides, silicates, alumosilicates, carbonates, sulphates and sulphides has been estimated. We can repeat, that these reactions are true only in rather acid solutions and inconsistent with the near-neutral, and especially alkaline pH values. Moreover, it is well

TABLE 1. Calculated pH at 25°C for the simplest type of hydrolyses reactions using various data bases

Reactions	pH_1	pH_2	pH_3
$CaMg(SiO_3)_2 + 4H^+ = Ca^{2+} + Mg^{2+} + 2SiO_{2(aq)} + 2H_2O$	9.24	8.97	9.54
$Mg_2SiO_4 + 4H^+ = 2Mg^{2+} + SiO_{2(aq)} + 2H_2O$	10.04	10.08	9.54
$KAl_2(AlSi_3O_{10})(OH)_2 + 10H^+ = K^+ + 3Al^{3+} + 3SiO_2(aq) + 6H_2O$	4.26	4.07	6.0
$KMg_3Al_2(AlSi_3O_{10})(OH)_2 + 10H+ = K^+ + 3Mg2+ +3Al^{3+} + 3SiO_{2(aq)} + 6H_2O$	7.82	8.33	9.5
$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$	9.71	–	9.54
$FeCO_3 + H^+ = Fe^{2+} + HCO_3^-$	9.26	–	9.53
$KAl_3(OH)_6(SO_4)_2 + 6H^+ = K^+ + 3Al^{3+} + 2SO_4^{2-} + 6H_2O$	4.11	–	–
$(H_3O)Fe_3(SO_4)_2(OH)_6 +5H^+ = 3Fe^{3+}+ 2SO_4^{2-} + 7H_2O$	–	2.92	–
$PbS + H^+ = Pb^{2+} + HS^-$	–6.85	–4.78	–
$ZnS + H^+ = Zn^{2+} + HS^-$	–3.36	–3.62	–

pH_1 - Bowers *et al.*,1984; pH_2 - Ball, Nordstrom, 1991; pH_3 - Karpov, 1981

TABLE 2. Selected characteristics of hydrolyses reactions for a set of calcium minerals by Bowers *et al.*, 1984

Reactions	$\mathrm{lgK_1}$	$\mathrm{pH_1}$
$CaO + 2H^+ = Ca^{2+} + H_2O$	32.60	18.30
$(CaSiO_3 + 2H^+ = Ca^{2+} + SiO_{2(aq)} + H_2O)$	13.62	10.81
$CaMg(SiO_3)_2 + 4H^+ = Ca^{2+} + Mg^{2+} + 2SiO_{2(aq)} + 2H_2O$	20.97	9.24
$CaAl_2Si_2O_8 + 8H^+ = Ca^{2+} + 2Al^{3+} + 2SiO_{2(aq)} + 4H_2O$	27.06	5.88
$CaMg(CO_3)_2 + 2H^+ = Ca^{2+} + Mg^{2+} + 2HCO_3^-$	2.52	9.26
$CaSO_4 = Ca^{2+} + SO_4^{2-}$	−4.27	–
$CaF_2 = Ca^{2+} + 2F^-$	−10.04	–

known, that totally different reaction of nonstoichiometric type is more common and important for nature, when both hydrolysis of soluble ions and appearance of relatively insoluble minerals on the surface of initial matrix take place.

Table 3 shows some calculated examples of more complicated decomposition of different feldspars, replacing by assemblages of the secondary minerals. In this case both pH and other ion activities are dependent on the new-formed buffer associations.

These features of real processes could be taken into account in the particular physical-chemical models and are developed by the authors too. Nevertheless, we do not know any other chance to get the numericalcharacteristics for the fast quantitative estimations of efficiency of natural geochemical barriers, when rather complicated mineral assemblages are involved into water-rock interaction. Both applied and environmental geochemistry could be the perspective areas for new approach. In particular, forecast of the scale of acid mine drainage process and environmental pollution was developed in the USA, Canada (Proceedings of..., 1994) and some other countries. Our approach give a possibility to compare 'the maximal acid potential' of sulphide ores and the 'neutralizing potential' of carbonate or silicate wall-rock. Authors believe, that it is the key reason for evaluation of the theoretical methods under discussion.

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TABLE 3. Calculated buffered pH and molality of cations for the more complicated reactions of feldspars decomposition (using Karpov, 1981)

Initial feldspars	New-formed secondary minerals	pH	$\lg m_{K,Ca,Na}$	$\lg m_{Al}$	$\lg m_{Si}$
$KAlSi_3O_8$	$AlO(OH)$, SiO_2, $KAl_2(AlSi_3O_{10})(OH)_2$	9.26	−4.41	−7.96	−3.92
$CaAl_2Si_2O_8$	$AlO(OH)$, SiO_2 $CaAl_2Si_4O_{12}{\cdot}4H_2O$	9.76	−4.21	−7.22	−3.78
$NaAlSi_3O_8$	$AlO(OH)$, SiO_2	10.63	−2.98	−6.34	−3.21