

## EFFECT OF ACID AND ALKALI TREATMENTS ON SURFACE-CHARGE PROPERTIES OF SELECTED MINERALS

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**Abstract**—Bentonite, biotite, illite, kaolin, vermiculite and zeolite were treated with 0.1, 1.0 and 5.0 mol. dm<sup>-3</sup> HCl or NaOH. Suspensions of Na homoionic forms of the initial and the treated minerals were back titrated with 0.1 mol. dm<sup>-3</sup> NaOH. From back-titration data variable surface charge,  $Q_V$ , vs. pH dependencies and apparent surface dissociation constant distribution functions were estimated. Variable charge vs. pH curves were scaled against cation exchange capacity at pH 7.2 to obtain actual charge,  $Q_A$ , vs. pH plots. In general both treatments led to an increase of  $Q_V$ , while the  $Q_A$  value increased and decreased depending on the mineral and the treatment. Products of 5 mol dm<sup>-3</sup> NaOH action on zeolite and of 1 and 5 mol. dm<sup>-3</sup> NaOH on kaolin apparently developed a positive surface charge below pH ~3.7 and below ~4.3, respectively.

The heterogeneity of charge-generating surface groups was observed in natural minerals. During acid treatment, the number of weakly-acidic surface functional groups increased while the number of groups of stronger acidic character decreased. The opposite was found for alkaline treatment: the number of surface groups of intermediate acidity increased and that of low acidity decreased.

**Key Words**—Acidification, Alkalinization, Surface Charge, Surface Dissociation.

### INTRODUCTION

The surface charge of minerals influences soil microstructure, buffering and ion exchange (Thomas and Hargrove, 1984) and control the catalytic properties of the minerals (Breen *et al.*, 1995; Brown and Rhodes, 1995). Two types of charge can be distinguished in minerals: a permanent charge resulting from isomorphic substitution of higher valence cations by lower valence cations in the crystal structure, and a variable charge resulting from dissociation and/or association of protons by surface hydroxyl groups (Van Olphen, 1963). The prevalence of permanent charge exposed on basal planes of the particles is a common feature of most clay minerals. Both the absolute and the relative numbers of the permanent and the variable charge sites vary among the minerals.

Metal and Si oxides develop variable charge. On kaolinites, variable charge dominates both on the edges and on the basal Al and Si sites of the mineral (Ward and Brady, 1998). The permanent negative charge from isomorphous substitution of Al<sup>3+</sup> for Si<sup>4+</sup> is insignificant. The charge of kaolinite depends strongly on the particle size. This is more important than crystallinity. The high cation exchange capacity (CEC) found in some kaolinites was due to smectite layers on the surface of the kaolinite crystals (Chi Ma and Eggleton, 1999). Both permanent and variable charge sites on mineral surfaces are heterogeneous. Based on the IR spectra of NH<sub>4</sub><sup>+</sup>-saturated and KBr-exchanged smectites, Petit *et al.* (1999) found that the layer charges have permanent

low charge density and/or variable charge sites whereas the interlayers were characterized by high permanent charge density. Different proton interacting sites were found by Janek and Lagaly (2001) on freshly H-saturated and autotransformed smectites using potentiometric titration data. Sites with pK values of ~2.8 were assigned to protons exchanged for sodium ions and of ~11.3 to deprotonization of silanol groups. Hydrated Al<sup>3+</sup> ions in freshly proton-saturated dispersions were characterized by pK ≈ 6. This group of weakly acidic centers also included oligomeric hydroxoaluminum cations because the number of these sites increased during autotransformation and was accompanied by a shift in pK to ~5.5. Autotransformation removed all strongly acidic sites with pK ≈ 2.8. A specific form of Al oxyhydroxide with amphoteric properties, having two constants of deprotonation  $K_1 = 10^{-5}$  and  $K_2 = 0.32 \times 10^{-6}$ , was found by Mrad *et al.* (1997) as the product of Al<sub>13</sub> polycation transformation in Al-intercalated montmorillonite. The inhomogeneity of an illite charge indicating the existence of a multiplicity of energetically-distinct surface types was found by Sinityn *et al.* (2000) based on potentiometric titration. These surface sites included amphoteric silanol and aluminol groups, basal planar surfaces, and 'frayed edges'. The frayed edges were observed only in solutions of low ionic strength.

Changes in pH may alter mineral charge via adsorption or desorption of non-exchangeable cations, mineral structure destruction and/or alteration (Rampazzo and Blum, 1991; Warren *et al.*, 1992; Yeoh and Oades, 1981). Breen *et al.* (1995) studied the effects of 6 mol. dm<sup>-3</sup> HCl treatments for 30, 300 and 900 min at 95°C on acidic sites of two montmorillonites using

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thermal desorption of cyclohexylamine. Samples treated for 30 min exhibited Bronsted acidities commensurate with the exchange capacities of the parent materials. A reduction in acidity was observed after longer treatment times and this was attributed to the presence of fewer exchange sites due to the depopulation of the octahedral sheet. Natural weathering of an illite-smectite produced an increase in CEC due to dissolution of illite-smectite and the appearance of smectite as a separate phase (Šucha *et al.*, 2001). Suraj *et al.* (1998) observed improvement in the exchangeability of kaolinites on acid activation. During the activation, the crystalline structure of kaolinite transformed thermally to amorphous metakaolin and preferentially released the octahedral  $\text{Al}^{3+}$  ions from the clay structure opening these sites for substitution by other metal ions. When the substituted metal ion had a lower charge the net negative charge at the site enabled adsorption of cations. Additionally  $-\text{Al}-\text{OH}$  and  $-\text{Si}-\text{OH}$  bonds were formed, acting as cation exchange centers. Dekany *et al.* (1999) found that the ion exchange capacity of a sepiolite may be completely eliminated by acid treatment. Acid treatment caused a permanent reduction of the global negative charge of the Al-pillared vermiculite layers (del Rey-Perez-Caballero and Poncelet, 2000). Šucha *et al.* (2001) found a decrease of CEC and Mg content in naturally weathered montmorillonite due to structural dissolution and precipitation of amorphous  $\text{SiO}_2$ . Sun Kou *et al.* (2000) observed a dramatic increase in strong acidity after Al or Zr pillaring of a montmorillonite, depending on starting salt concentration, period of ageing, and temperature.

Rassineux *et al.* (2001) found that the reaction of a Wyoming-type bentonite with pH 13.5 solutions at 35 and 60°C for periods of 1 to 730 days did not alter the total CEC or the CEC after neutralization of the octahedral charge; however a slight increase in the average layer charge was observed. Baccouche *et al.* (1998) found that an interstratified illite-smectite treated with 1 to 5 mol  $\text{dm}^{-3}$  NaOH solutions on reflux for 2–24 h increased the CEC due to formation of zeolitic products. Similar phenomena were observed by Ruiz *et al.* (1997) who found that the laminar structure of the starting bentonite was converted into spherical units of zeolitic nature by alkaline treatment in distilled and seawater media with simultaneous increase in CEC. Natural zeolites (clinoptilolite and mordenite) treated for 8 or 16 h with 2 mol  $\text{dm}^{-3}$  NaOH solution at 103°C increased their CEC by more than a factor of 2 (Shin-Jyung Kang *et al.*, 1998).

Jozefaciuk and Bowanko (2002) studied effects of acid and alkali treatments on surface areas and adsorption energies of selected minerals. To have a more detailed picture of the complex effects of acid and alkali attack on these minerals, the same materials and treatments were studied in the present work, concentrating on surface charge behavior.

## MATERIALS AND METHODS

Bentonite (Chmielnik, Poland), biotite (Chongyang, Korea), illite (Yongdong, Korea), kaolin (Vimianzo, Spain), vermiculite (Lovec, Bulgaria) and zeolite (Wolsong, Korea) were studied. The bentonite contained <5% feldspars and quartz. Traces of albite and anorthite were present in the biotite and of talc in the vermiculite. The illite was a dioctahedral muscovite amended with a very small amount of quartz and traces of anorthite. The kaolin contained ~5% of quartz and traces of mica. Two zeolite group minerals: stilbite and natrolite were dominant components of the zeolite used. A more detailed description of the samples is given in Jozefaciuk and Bowanko (2002).

The minerals were treated for 2 weeks at room temperature with HCl or NaOH solutions of 0.10, 1.0 and 5.0 mol  $\text{dm}^{-3}$  at a 1:50 solid:liquid ratio. Acid treatments are abbreviated below using symbols 01H, 1H and 5H and alkaline ones as 01OH, 1OH and 5OH, where the numbers correspond to the reagents' concentrations. The control samples were treated with distilled water. The treatment suspensions were occasionally shaken. After 1 week, the treatment solutions were renewed. After 2 weeks the solids were separated, washed with 1 mol  $\text{dm}^{-3}$  NaCl solution by centrifuging to the lack of Al (ICP AES) in the supernatants, and used for further studies. The washing was applied to remove any dissolved and surface ions which could remain in the treated minerals and eventually precipitate during further experiments.

Titration measurements were performed using a Radiometer Copenhagen autotitration unit equipped with Orion Research combined electrodes. A back titration procedure (Duquette and Hendershot, 1993a,b) was used with a few modifications as described by Jozefaciuk and Shin (1996a). A suspension of 1 mol  $\text{dm}^{-3}$  NaCl, containing 1.00 g (dry mass) of the Na homoionic form of the mineral was kept at pH ~2.9 by additions of small increments of 1 mol  $\text{dm}^{-3}$  HCl during 30 min of mixing. For an additional 3 min of mixing the pH was controlled, and if changed by more than 0.02 units, the suspension was centrifuged and the pretreatment repeated. From the final suspension, half of the supernatant liquid and the remaining suspension were titrated with 0.100 mol  $\text{dm}^{-3}$  NaOH in 1 mol  $\text{dm}^{-3}$  NaCl solution at a rate of 30  $\mu\text{l}/\text{min}$ . The amount of the titer consumed between pH 3 and 9 was recorded with a step of 0.2 pH unit. The measurements were performed in four replicates with the deviation not exceeding 6.2% (suspensions) and 15% (supernatants). The titration curves of all supernatant liquids were similar to a titration curve of 1 mol  $\text{dm}^{-3}$  NaCl pH = 3 solution, indicating that the dissolution of the solid phase under experimental conditions was negligible. It is important to note that in the above procedure, equilibrium conditions are not reached, so the titration curves

can be used only for comparative purposes. A 24 h equilibrium titration of a soil consumed up to twice as much titer as a continuous titration similar to that used in the present work and considerable dissolution of the solid phase occurred as was seen from titration of the supernatant liquids (Jozefaciuk and Shin, 1996a).

Applying constant and high concentrations of neutral salt during titration has a few advantages. It minimizes titration of exchange acidity (replacing exchange protons by neutral salt cations), dilution effects (changes of variable charge with salt concentration), dissolution of solid phase, and allows for a better development of variable surface charge (surface groups dissociation is less hindered by electrostatic effects at high ionic strengths).

The amount (moles) of base consumed by the suspension,  $N_{\text{susp}}$ , minus the amount consumed by the supernatant,  $N_{\text{sol}}$ , was assumed to be equivalent to the increase of the variable surface charge of the solid phase,  $\Delta Q_V(\text{pH})$ , during titration:

$$\Delta Q_V(\text{pH}) = N_{\text{susp}} - N_{\text{sol}} \quad (1)$$

The  $\Delta Q_V(\text{pH})$  accounts for an increase of negative charge and a decrease of positive charge.

To find the actual surface charge,  $Q_A$ , vs. pH dependence, the  $Q_V(\text{pH})$  curves were shifted against the vertical axis to meet the actual charge value at pH 7.24. The latter was taken as a CEC of the minerals, estimated by measurements of exchangeable  $\text{Ca}^{2+}$  in  $0.25 \text{ mol dm}^{-3}$  calcium acetate, with AAS. The eventual occurrence of a positive surface charge at pH 7.24 was ignored.

The variable charge vs. pH data were interpreted in terms of dissociation/association of surface functional groups using site-heterogeneity theory (De Wit *et al.*, 1990; Huang, 1981; Jozefaciuk and Shin, 1996b; Koopal *et al.*, 1987; Nederlof *et al.*, 1991, 1993). Because this theory is now quite standard, it is outlined only briefly.

Assuming that the variable charge originates from dissociation of surface acidic groups of kind  $i$ :  $\text{SOH}_i = \text{SO}_i^- + \text{H}_s^+$  ( $\text{H}_s^+$  denotes a proton in a plane of dissociation) and the (intrinsic) dissociation constants  $K_i$ :

$$K_i = [\text{SO}_i^-][\text{H}_s^+]/[\text{SOH}_i] \quad (2)$$

where the brackets denote surface activities, the variable charge at a given pH is:

$$Q_V(\text{pH}) = \sum_{i>1}^n [\text{SO}_i^-](\text{pH}) = \sum_{i>1}^n N_i \alpha_i(K_i, \text{pH}_s) \quad (3)$$

where  $\alpha_i(K_i, \text{pH}_s) = [\text{SO}_i^-]/[\text{SOH}_i]$  is the degree of ionization of groups of kind  $i$  and  $N_i = [\text{SOH}_i]$  is their amount. For any pH during the titration:

$$Q_V(\text{pH})/N_t = \alpha(\text{pH}) = \frac{\sum_{i>1}^n \alpha_i(K_i, \text{pH}_s) N_i/N_t}{\sum_{i>1}^n \alpha_i(K_i, \text{pH}_s) f(K_i)} \quad (4)$$

where  $N_t$  is the total number of surface groups and  $f(K_i) = N_i/N_t$  is the fraction of  $i$ -th groups. Using

condensation approximation (Nederlof *et al.*, 1993), the  $f(K_i)$  values are:

$$f(K_i) = 1/N_t \Delta Q_V(\text{pH})/\Delta K_i; \quad K_i = [\text{H}_s^+] \quad (5)$$

and in logarithmic scale:

$$f(\text{p}K_i) = 1/N_t \Delta Q_V(\text{pH})/\Delta \text{p}K_i; \quad \text{p}K_i = \text{pH}_s \quad (6)$$

The distribution function of surface dissociation constants, i.e.  $f(K_i)$  vs.  $K_i$  dependence, can be calculated knowing both surface protons' activity ( $\text{pH}_s$ ) and  $N_i$  values. The mineral edges, basal planes, surface coatings and destruction products may have different shapes and different charges, thus varying in surface potential values. For  $\text{pH}_s$  (and  $K_i$ ) calculations, based on the diffuse double-layer theory, a single potential value spread uniformly over all surfaces of the same shape is a common assumption, which seems to be invalid in the present case. Also, there still exists much controversy on the application of DDL theory to surface chemistry (McBride, 1997). Therefore, the surface proton activity was replaced by the solution activity and  $N_t$  was taken as  $N_{\text{max}} = \text{maximal value of } (N_{\text{susp}} - N_{\text{sol}})$  measured within the experimental window and, instead of the intrinsic, the distribution functions of apparent surface dissociation constants,  $K_{\text{app}}$ , were determined:

$$f(\text{p}K_{\text{app},i}) = 1/N_{\text{max}} \Delta Q_V(\text{pH})/\Delta \text{p}K_{\text{app}}; \quad \text{p}K_{\text{app}} = \text{pH} \quad (7)$$

The average value of  $\text{p}K_{\text{app}}$ ,  $\text{p}K_{\text{app,av}}$ , was calculated as:

$$\text{p}K_{\text{app,av}} = \sum_{i>1}^n \text{p}K_{i,\text{app}} f_i(\text{p}K_{\text{app}}) \quad (8)$$

which is a direct measure of the average energy of the proton binding.

## RESULTS AND DISCUSSION

During the titration (data not presented) acid-treated minerals consumed more base above  $\text{pH} \approx 7.5$  than the untreated minerals. The higher the degree of concentration of the treatment, the greater the effect observed. Acid treatment led to a decrease of base consumption below  $\text{pH} \approx 7$  for bentonite and zeolite and an increase for illite and vermiculite. Slight changes in base consumption were noted for biotite and kaolin. After alkaline treatment, the base consumption in a whole pH range was generally greater than for untreated minerals, which was particularly evident for bentonite, kaolin and zeolite.

The actual charge vs. pH dependence for the studied minerals is illustrated in Figure 1. Acid and alkali treatments led to the decrease of the actual charge of the bentonite developed below  $\text{pH} \approx 7.5$ , which can be due to the decrease of the structural charge. Large amounts of newly-formed variable charge constituents (Si oxides) in acid-treated bentonite causes a sharp increase in the actual charge above  $\text{pH} \approx 7.5$ , tending to exceed the original mineral charge above  $\text{pH} \approx 9$ . Alkali

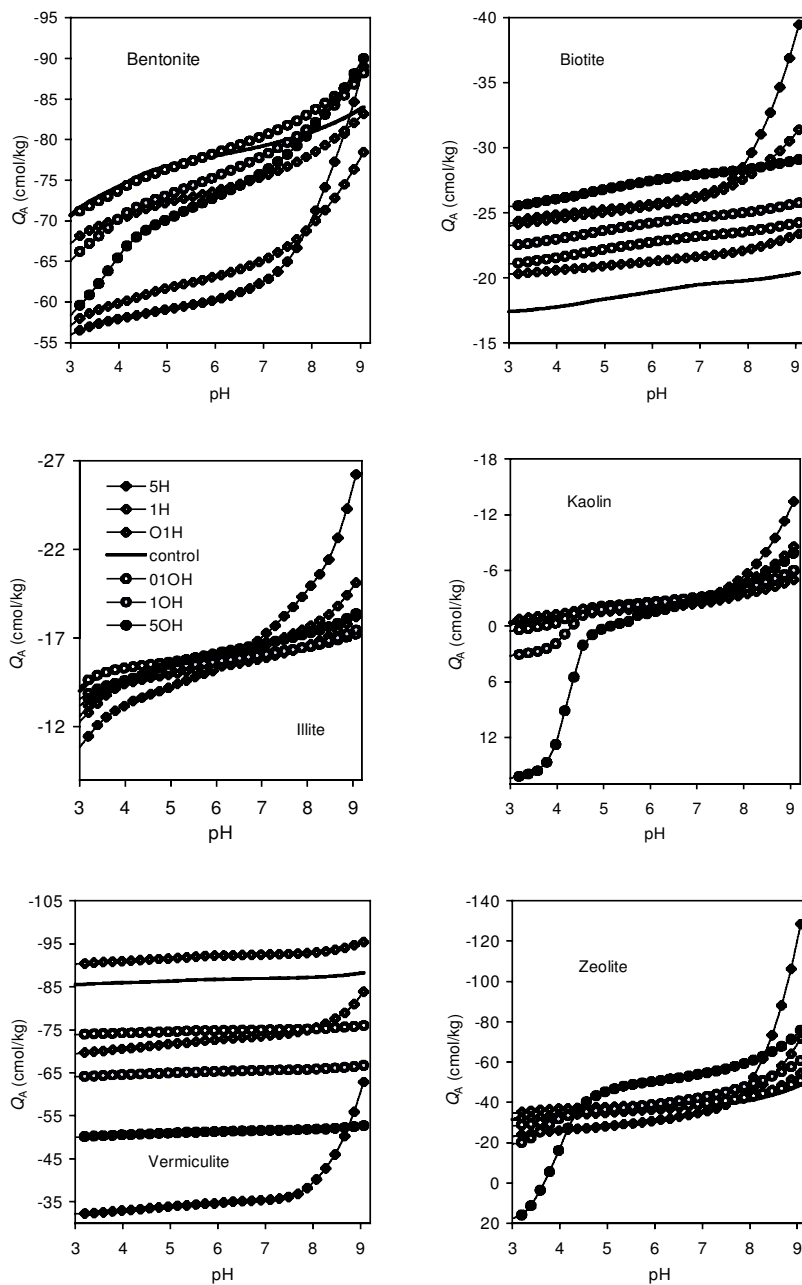


Figure 1. Actual surface charge vs. pH dependencies for the studied minerals as related to acid and alkali treatment.

treatment has less effect on the structural charge of the bentonite, though the input of variable charge surfaces increases the actual charge at high pH values. It is possible that positive charging of these surfaces causes a decrease of the actual charge at lower pH values. For kaolin and zeolite, changes of the actual charge after all but extreme acid and alkali treatments are less pronounced. The illite is markedly affected only by treatment with extremely concentrated acid. For  $1 \text{ mol dm}^{-3}$  and  $5 \text{ mol dm}^{-3}$  NaOH-treated kaolin and  $5 \text{ mol dm}^{-3}$  NaOH-treated zeolite, a positive actual

charge appears below pH of  $\sim 4.3$  and  $\sim 3.7$ , respectively. In the vermiculite studied the structural charge seems to decrease with an increase in the concentration of either treatment with the exception of sample 01H. For the latter sample, acid treatment of the smallest concentration may dissolve some charge-blocking species, e.g. Al polycations present in the interlayers. The variable charge on vermiculite seems to occur only in acid-treated samples, where the actual charge curves of alkali-treated samples are roughly parallel to each other. The lack of the variable charge constituents in destruc-

tion products of the alkali-treated vermiculite may indicate that these products are coarse and the finely dispersed ones were dissolved. Indeed, the visual assessment of the alkali-treated samples revealed no fine particles. The acid-treated vermiculite particles were of similar shape, but whiter in color. Similar size and color of acid and alkali-treatment products were observed for biotite, though the biotite charge behavior was different. A sharp increase of the actual charge was observed after all treatments, opposite to the behavior of the other minerals studied. This should be due to the lattice and not to variable charge increase, because charge-pH curves after treatments are parallel also (ignoring high pH parts for acid-treated samples). The above phenomenon may be caused by the formation of expanded smectite-like (14 Å) structures in the biotite studied, as was seen from the XRD patterns (Jozefaciuk and Bowanko, 2002). The expanded spaces are available for exchange ions.

The actual charge results from the sum of permanent (structural) charge and the variable charge. The amounts of the variable and the permanent charge of the control minerals is given in Table 1. As an estimate of the permanent charge, the actual charge developed at pH = 6.5 was used, because this was least dependent on the pH. The amount of permanent charge is largest in vermiculite and bentonite. In bentonite this is ~5 times greater than the variable charge whereas in vermiculite it is ~30 times larger. Illite and biotite have smaller permanent charge but a similar ratio of both charge types

as found in the bentonite. The low-grade zeolitic material studied has rather low permanent charge, though the amount of variable charge is only half as large. The amount of permanent charge in kaolinite is lowest among the studied minerals, though this is lower than the variable charge which exceeds it in illite, biotite and vermiculite.

Acid treatment leads, in general, to the production of larger amounts of variable surface charge than the alkali treatment of the same concentration (Figure 2). This figure shows the ratio of the variable charge of the treated mineral to that of the control sample. The acid treatment is more aggressive as this forms more variably-charged destruction products. Vermiculite and zeolite produce the largest amounts of variable charge after acid treatment. Zeolite and kaolin are most affected by alkali treatment. The effect of the treatments on the permanent charge is shown in Figure 3, constructed in a similar fashion to Figure 2. Slight changes in permanent charge due to acid and alkali treatments were observed for illite. For the other minerals except biotite, the structural charge generally decreased. For biotite, an increase of the permanent charge after both treatments was observed. The decrease of the structural charge may be connected with the destruction of the crystal structure of the mineral (Rampazzo and Blum, 1991; Warren *et al.*, 1992). This should be a principal process at least under acid attack, as, in contrast to the acidic treatments, the mineral destruction was not shown by XRD patterns of alkali-treated minerals (Jozefaciuk and Bowanko,

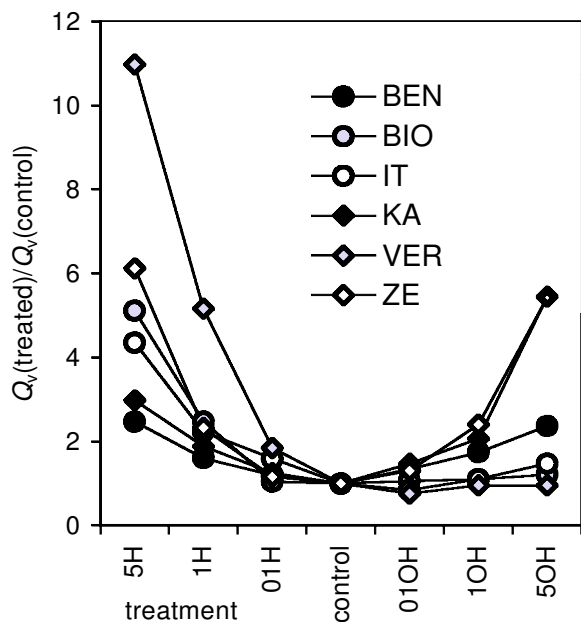


Figure 2. Changes in the amount of variable surface charge of the studied minerals in the treatments applied. On the vertical axis the ratio of variable charge of the treated mineral to that of the untreated one is given. BEN: bentonite; BIO: biotite; IT: illite; KA: kaolin; VER: vermiculite; ZE: zeolite.

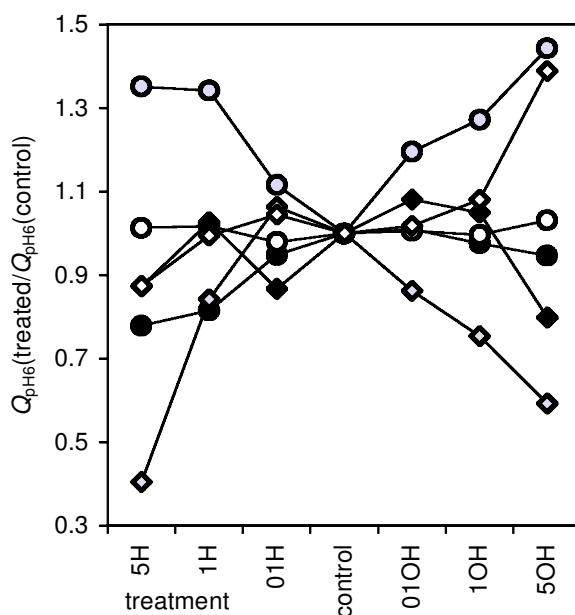


Figure 3. Changes in the amount of permanent surface charge of the studied minerals in the treatments applied. On the vertical axis the ratio of the actual charge measured at pH = 6.5 for the treated mineral to that of the untreated one is given. Symbols as in Figure 1.

2002). The increase of the permanent charge may also be related to a removal of charge-blocking species, *e.g.* positively-charged hydroxy-Al polymers present as surface coatings or located in interlayers (Keren, 1986) or the rearrangement of the mineral structure (in the case of biotite).

The distribution functions of apparent surface dissociation constants of the original and the treated minerals are presented in Figure 4. This function for original bentonite is u-shaped and contains a peak developed at  $\sim$ pH 4.3. A similar shape is observed for

kaolin, though the relative numbers of weakly acidic sites (high  $pK_{app}$  values) is greater than that of strongly acidic sites (low  $pK_{app}$  values). The u-shaped function with a larger number of strongly acidic sites is also observed for original illite, though the peak at  $pK_{app} \approx 4$  is lacking. Original vermiculite and zeolite appear to have a small number of strongly acidic surface sites. The  $pK_{app} \approx 4$  peak does occur for zeolite. Original biotite seems to have the most heterogeneous surface, though for this mineral, and also for the vermiculite, the highest variations in  $pK_{app}$  distribution functions were calcu-

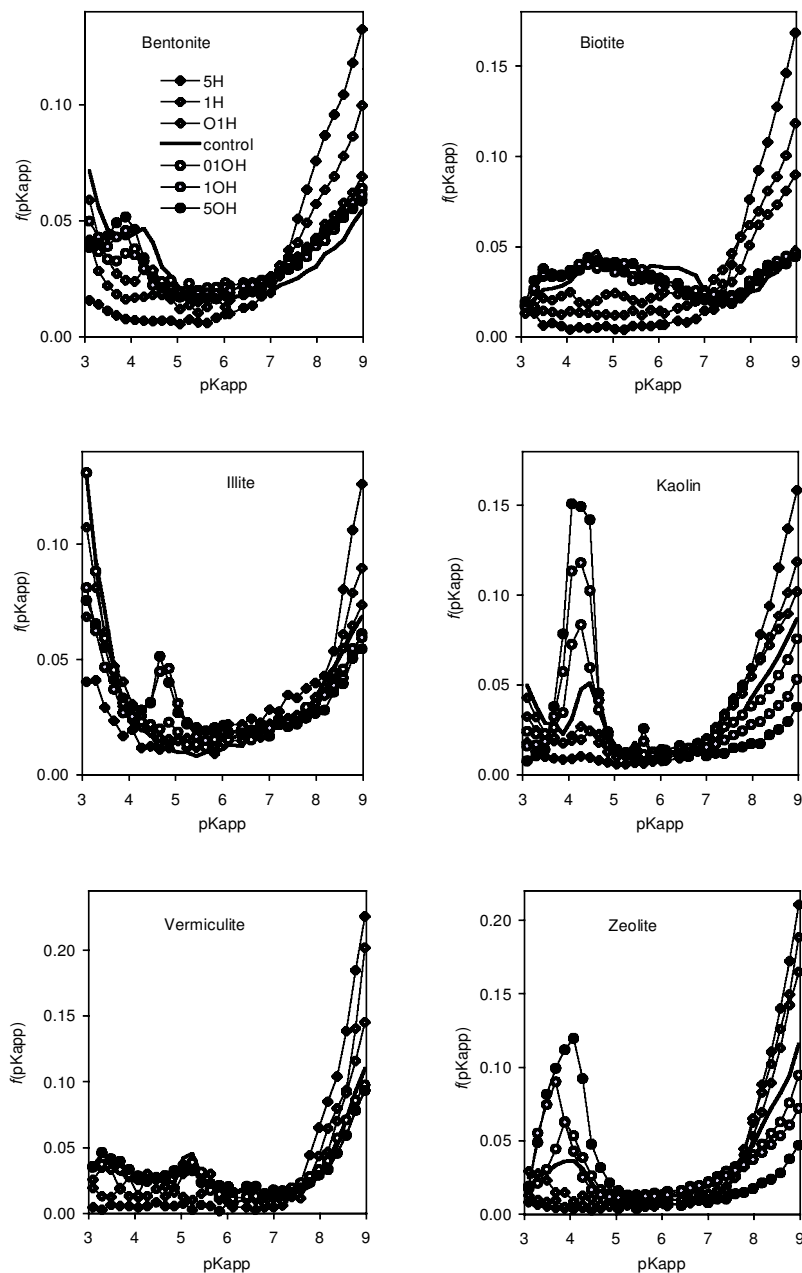


Figure 4. Distribution functions of apparent surface dissociation constants for the studied minerals as related to acid and alkali treatment.



Table 1. Apparent surface dissociation constants ( $pK_{app,av}$ ), amounts of variable ( $Q_v$ ) and permanent ( $Q_p$ ) charge, and surface densities of variable ( $SCD_v$ ) and permanent charge ( $SCD_p$ ) for untreated minerals.

	Bentonite	Biotite	Illite	Kaolin	Vermiculite	Zeolite
$Q_v$ , cmol kg <sup>-1</sup>	13.4	2.99	3.53	4.46	2.80	17.2
$Q_p$ , cmol kg <sup>-1</sup>	-78.6	-19.2	-15.9	-2.6	-86.9	-37.6
$pK_{app,av}$	5.82	6.07	5.85	6.41	6.44	6.86
$SCD_v$ , C m <sup>-2</sup>	0.041	0.110	0.090	0.089	0.008	0.124
$SCD_p$ , C m <sup>-2</sup>	0.24	0.71	0.40	0.05	0.24	0.27

lated from the replicates of the experimental data. The peaks observed at  $pK_{app} \approx 4$  may come from positively-charged Al hydroxyls of mineral edges having a PZC of  $\sim 7.5$  (Parks, 1965) as well as from metal oxide impurities. The Al and Fe oxides (especially hydrated ones) have high isoelectric points, up to 10 for Al and 9 for Fe species (Parks, 1965). A few pH units below the isoelectric point, such surfaces can be almost totally charged, thus developing most of the charge in a rather narrow pH range, which leads to the occurrence of the peak on the distribution function. A peak from negative surface charging should occur symmetrically above PZC, though this range is outside the experimental window applied.

After acid treatment, the amount of slightly acidic surface functional groups increases for all minerals while the amount of stronger acidic groups decreases. However, Srasra and Trabelsi-Ayedi (2000) suggested the generation of the strong acidic sites due to 3 M HCl boiling solution treatment of a glauconite. The partial dissolution of Al layers of the minerals (thus changing the character of the edges) or Al and Fe oxide surface coatings, or impurities, can be responsible for the decrease in the number of surface groups of stronger acidic character. Note the decrease of the  $pK_{app} \approx 4$  peak in acid-treated samples. The newly-formed amorphous silica from the mineral destruction may lead to an increase in the number of slightly acidic surface groups after acid treatment. The isoelectric point of all kinds of Si oxides is not  $>3$  (Parks, 1965). Its surface hydroxyls are not very reactive (Goates and Anderson, 1956) and so these compounds can develop large amounts of negative surface charge at high pH values (*i.e.*  $>7.5$  as observed in the present experiments).

The opposite tendencies of  $f(pK_{app})$  were found after alkaline treatment. A fraction of weakly acidic surface functional groups decreases in most of the minerals (silica dissolution) or increases only slightly. The amount of surface groups of intermediate acidity, and particularly these forming  $pK_{app} = 4$  peaks, rises sharply with increasing concentration of alkali treatment. The mineral dissolution patterns (Jozefaciuk and Bowanko, 2002), and especially high Si dissolution in alkaline media, can indicate that strong alkali action removes outer silica sheets from mineral structures leading to an exposure of Al (hydroxylated) layers thus increasing the positive surface charging at low pH values. A possibility

that the rise of  $pK_{app} \approx 4$  peak reflects accumulation of Fe oxides precipitated after destruction of mineral structures due to low Fe solubility in alkaline media seems less probable because of a lack of evidence of structural degradation from XRD patterns. However, these patterns may remain unchanged if congruent dissolution of the structure takes place. Iron oxides can also accumulate if the finest mineral particles are dissolved. The disappearance of the finest particles after alkali (and acid) treatment was observed in vermiculite and biotite which have the largest particles.

Average values of  $pK_{app}$  calculated from the distribution functions for the control minerals are included in Table 1. Small differences in these values are noted. The highest surface acidity is found for original bentonite and illite and the lowest for zeolite. Figure 5 shows changes of average  $pK_{app}$  values under acid and alkali treatments. An increase in  $pK_{app}$  after acid treatment indicates the weakening of overall surface acidity (or increase in proton binding forces). The

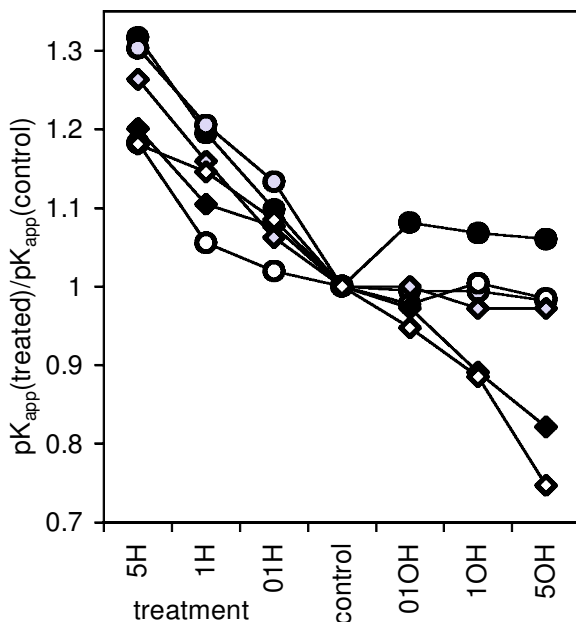


Figure 5. Changes in average values of apparent surface dissociation constants of the studied minerals in the treatments applied. On the vertical axis the ratio of  $pK_{app,av}$  of the treated mineral to that of the untreated one is given. Symbols as in Figure 1.

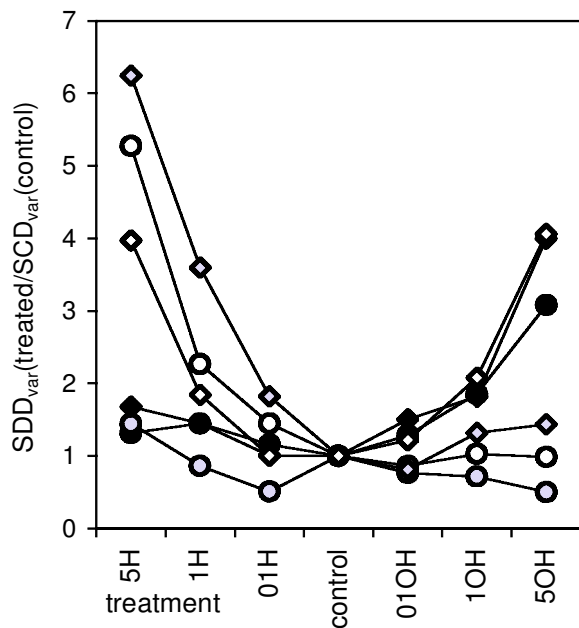


Figure 6. Changes in variable surface charge density of the studied minerals in the treatments applied. On the vertical axis the ratio of surface charge density of the treated mineral to that of the untreated one is given. For the calculations the surface areas calculated from water vapor desorption isotherms and the variable charge were taken. Symbols as in Figure 1.

decrease in surface acidity indicates that the minerals become less reactive towards charged and polar compounds and that the reaction products become more hydrophobic, which was also frequently observed from the decrease in water vapor adsorption energy (Jozefaciuk and Bowanko, 2002). The opposite phenomena occur after alkali treatment. Generally, the surfaces of the reaction products bind protons with less force; thus more polar surfaces are formed.

Based on surface areas measured from water vapor adsorption isotherms (Jozefaciuk and Bowanko, 2002) and the present data, variable and permanent surface charge densities of the minerals studied were calculated. These values for the control minerals are shown in Table 1. The highest surface density of the permanent charge is observed for natural biotite. For bentonite, vermiculite and zeolite, this is >2 times less and for illite ~1.5 times less. The lowest permanent charge density is found for the kaolin. The highest variable-charge density characterizes the surface of the zeolitic material. Slightly lower values are noted for biotite, illite and kaolin. Due to its high surface area, rather low variable charge density occurs on bentonite and this is the smallest for vermiculite.

As compared to the original minerals, the variable charge density (Figure 6) increases in general after both treatments. This may be due to the formation of amorphous phases of high variable charge as well as to hydration of mineral surfaces via breaking of Al–O–Al

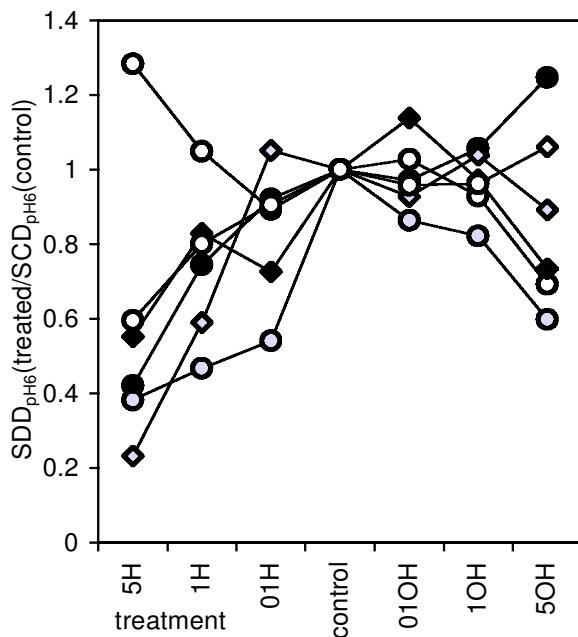


Figure 7. Changes in permanent surface charge density of the studied minerals in the treatments applied. On the vertical axis the ratio of surface charge density of the treated mineral to that of the untreated one is given. For the calculations the surface areas calculated from water vapor desorption isotherms and the actual surface charge measured at pH = 6.5 were taken. Symbols as in Figure 1.

or Si–O–Si bonds and production of ionizable hydroxyls. Changes of external surface build-up from silica to alumina in alkali treatments may also be responsible for the increase in surface charge density, as occurring principally on the same geometrical surface. However, the permanent surface charge density (net charge at pH = 6.5 divided by the surface area) generally decreases, indicating apparently, that newly-formed surfaces have no structural charge (Figure 7). A simultaneous decrease in the structural charge makes the above effect more pronounced.

From the data presented, one can see that various minerals have different susceptibility to changes in environment, as is also observed under natural conditions (Frank and Gebhard, 1991; Righi *et al.*, 1995).

## CONCLUSIONS

Both acid and alkali treatments seriously affect the surface charge properties of minerals and lead to different products. Various minerals react to acids and alkalis with different intensities. After acid attack, the formation of amorphous silica from the destruction of the mineral structure and/or dissolution of Al layers (or coatings) seem to be responsible for the increase in the variable charge of weak acidity in the reaction products. The occurrence of a larger number of variable charges of stronger acidity in alkali-treated minerals was probably



related to a depletion of outer silica sheets from mineral structures exposing alumina sheets or leaving them with an accumulation of Fe (hydr)oxides. Weakly acidic surfaces of the acid-treated minerals might catalyze the reaction of non-polar compounds in non-polar media better whereas polar reactions can be catalyzed better by alkali-treated minerals. The production of larger amounts of variable charge in soil mineral phases may partially counteract the decrease in soil CEC due to changes in soil reaction.

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