

# Mineralogy, surface properties and electrokinetic behaviour of kaolin clays derived from naturally occurring pegmatite and granite deposits



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### ABSTRACT

This paper presents research on the surface characteristics, specific surface area (SSA), cation exchange capacity (CEC) and the electrophoretic mobility (EPM) of kaolin clays obtained from different naturally occurring pegmatite and granite deposits worldwide. Particular emphasis was placed on studying the influence of ancillary minerals on these properties, as well as the diversity in morphological and structural characteristics of kaolinite in samples. Mineral composition and the morphology of the kaolin samples were investigated using X-ray diffraction (XRD) and field emission scanning electron microscope (FE-SEM), respectively. The SSA was determined by the BET method, CEC by ammonium selective electrode and surface charge by EPM measurements. Results showed that the surface properties of the kaolin samples were strongly influenced by the presence of ancillary constituents, particularly smectite minerals. Their occurrence, even in trace amounts, significantly increased the SSA and CEC values of the investigated samples. Most importantly, EPM measurements revealed that the character of the amphoteric surfaces of the dominant kaolinite mineral in the samples was rescinded by the permanent pH-independent siloxane basal charge of smectite. The presence of ancillary smectites, characterized by higher surface reactivity, hindered the surface properties of the prevailing kaolinite mineral in the kaolin clay deposits.

**Keywords:** kaolin clays, igneous deposits, ancillary minerals, surface properties

### 1. INTRODUCTION

The term clay minerals refers to the naturally occurring layer-type aluminosilicate minerals, which contain structural hydroxyl groups and belong to the general class of phyllosilicates (GRIM, 1968; BAILEY, 1980). Due to their overwhelming structural and chemical diversities and related unique surface physico-chemical properties, clay minerals attract considerable interest in biogeochemical processes, particularly in chemical binding, transport, transformation

and deposition of organic and inorganic compounds (GRIM, 1968; NEWMAN, 1987; SONDI & PRAVDIĆ, 2002; BERGAYA et al., 2006). They are the omnipresent components of suspended matter, soils and modern sediments that appear mainly in the form of colloids and nanoparticles (THENG & YUAN, 2008). Their role should be considered in simultaneous and complex physico-chemical interactions that involve, besides clay minerals, humic matter and/or iron and manganese oxides/oxyhydroxides as natural surface coatings (CHEKLI et al., 2013). The investigation of clay mine-

ral surfaces and their interactions with organic and inorganic compounds is crucial for understanding their role in geochemical cycles in the natural environment (SONDI et al., 1996a; SONDI & PRAVDIĆ, 2002).

Surfaces of clay minerals are structurally, morphologically and chemically heterogeneous. In general, they exhibit two morphological planes of different structure, chemical composition and consequently, different surface properties (van OLPHEN, 1951; SPOSITO, 1984; ZHOU & GUNTER, 1992). These are the siloxane surface basal layer characterized by a permanent negative charge arising from isomorphous substitutions (mostly of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$ ) in the crystal structure, and the edge surface (broken bonds) characterized by the variable amphoteric charge (MOORE & REYNOLDS, 1997). The contribution of these surfaces to the total external surface area depends on the type of clay minerals. For kaolinite, the edge fraction occupies 12 to 14 % of the total surface area (FERRIS & JEPSON, 1975; JAMES & WILLIAMS, 1982). For smectite clays, it is no more than 1%, and for illite 2–10% (WAN & TOKUNAGA, 2002). Studies on the physical disintegration of clay mineral particles have shown significant alteration of their surface properties governed by the ratio between the siloxane and edge surfaces (SONDI & PRAVDIĆ, 1996b; SONDI et al. 1997a; VDOVIĆ et al., 2010).

Numerous studies concerning the surface properties of clay mineral particles, mostly kaolinite and montmorillonite, have been reported in the literature (HERRINGTON et al., 1992; SONDI & PRAVDIĆ, 1996b; SONDI et al., 1997a,b; ZHUANG & YU, 2002; TOMBÁČZ & SZEKERES, 2004, 2006). Clay minerals occur in nature mainly in complex mineral assemblages, together with numerous inorganic and organic compounds, mostly in the form of surface coatings. While the effects of organic and inorganic surface coatings on the reactivity of clay mineral particles have been the subject of numerous studies (ZHUANG & YU, 2002; SONDI et al., 1997b), the influence of mineral phases present in minor amounts has been neglected, despite the fact that even commercial clay deposits contain various amounts of different mineral constituents accompanying the dominant clay mineral phase (JEPSON, 1988).

When dealing with natural clay minerals, the main difficulty is their separation from the rest of the mineral and organic constituents. This involves various physical and chemical procedures that are rarely completely efficient in the removal of all impurities and often cause significant changes and modifications of the native physico-chemical

properties of clay mineral surfaces. Therefore, the use of clay minerals from primary igneous deposits appears to be helpful in studying their native surface properties. Their surfaces, unlike those found in pedogenic or sedimentary environments, are free of organic matter and they are not significantly altered by the presence of inorganic surface coatings. This makes them ideal for studying the effect of the presence of ancillary mineral phases on the surface properties of the dominant clay minerals in clay solids.

Kaolin clays are deposits rich in kaolin-group minerals that mainly include kaolinite, halloysite, dickite and nacrite, with kaolinite being the most common (CYGAN & TAZAKI, 2014). Kaolinite is a dioctahedral clay mineral of rather large particle diameter (up to several tens of micrometers), and accordingly, low specific surface area (SSA) and cation exchange capacity (CEC) (MA & EGGLETON, 1999; BERGAYA et al., 2006). Kaolinite usually exhibits low or no permanent charges on the siloxane surfaces on account of the limited isomorphous substitution in its structure (MOORE & REYNOLDS, 1997; BAILEY, 1991), which makes the contribution of the amphoteric edges to their surface properties significant (MA & EGGLETON, 1999).

The main objective of this study was to investigate the surface properties and the electrokinetic behaviour of kaolin samples obtained from different pegmatite and granite deposits worldwide. In particular, this study aims to clarify the influence of ancillary minerals associated with the prevailing kaolinite mineral on the surface properties and the reactivity of kaolin samples. The results obtained should complement existing knowledge on the surface properties of kaolin clays.

## 2. METHODOLOGY

### 2.1. Source of kaolin clays

Five kaolin samples derived from pegmatite and granite deposits, with various content and amounts of ancillary minerals, were investigated (Table 1). Sample S1 (Mamoes, Ecuador) originates from a pegmatite, but it is not clear whether it is an alteration of feldspar by hydrothermal fluids, or by meteoric water. Sample S2 (Jacu, Brazil) originates from a pegmatite but its origin is not yet determined. Samples S3 and S5 (Almas, Parelhas, Brazil) were obtained from a pegmatite, and they were probably formed as a supergene alteration. Sample S4 was obtained from Sierra Leone and formed as an alteration of granite.

**Table 1:** Sample information and qualitative mineralogical composition of the investigated kaolin clays.

Sample	Location	Major component	Minor component
S1	Mamoes, Ecuador	kaolinite	muscovite, quartz
S2	Jacu, Brazil	kaolinite	muscovite, quartz
S3	Almas, Parelhas (2003)	kaolinite	muscovite, quartz, feldspars
S4	Sierra Leone	kaolinite	muscovite, quartz, feldspars, smectites
S5	Almas, Parelhas (2004)	kaolinite	muscovite, quartz, feldspars, smectites

In order to remove the coarser fractions, samples were dispersed in deionized water for 2 weeks and regularly stirred. Prior to separation, kaolin clay dispersions were sonicated in an ultrasonic bath, left to settle for 2 minutes after which the upper 5 cm of the suspension was separated from the residue using a pipette. The suspension was used for particle size measurement and then freeze-dried (FreeZone 2.5, Labconco, USA) for further measurements. Separated kaolin samples were not subjected to any kind of chemical treatment.

## 2.2. Laboratory Methods and Techniques

The mineral composition was determined by the X-ray diffraction method using an X-ray powder diffractometer Philips PW 3040/60 X'Pert PRO (PANalytical, B.V., the Netherlands) with Cu-tube accelerated by 40 kV and a current of 40 mA. The X-ray diffraction patterns were analyzed using HighScore Plus software (Panalytical, 2004) and the mineral components were identified according to the JCPDS powder diffraction files. Clay minerals were identified according to their basal peaks after standard preparation procedures and sample treatments proposed by STARKEY et al. (1984). The diffraction peaks on the XRD patterns were coded as follows: K – kaolinite, S – smectite, M – muscovite, F – feldspars, Q – quartz.

The cation exchange capacity (CEC) was determined using an ammonia selective electrode based on the method described by BUSENBERG & CLEMENCY (1973). The specific surface area measurements (SSA) were performed by a single-point nitrogen adsorption, using a FlowSorb II 2300 instrument (Micromeritics, USA). Particle size was determined using a laser diffraction particle size analyzer LS 13 320 (Beckman Coulter, USA). Electrophoretic mobility was measured using a Zetasizer Nano ZS (Malvern, UK). The software automatically calculated the zeta-potential from electrophoretic mobility using the Henry equation. Samples were prepared in a  $1 \times 10^{-3}$  mol dm<sup>-3</sup> NaCl solution and the pH range (2–10) was adjusted with a 0.1 mol dm<sup>-3</sup> solution of HCl and NaOH.

## 3. RESULTS AND DISCUSSION

### 3.1. Mineralogy and surface properties of kaolin clay samples

According to XRD analyses, kaolinite was identified as a primary mineral phase in all the investigated samples (Fig. 1). However, a significant difference in the content of ancillary minerals in the kaolin clays was determined. The associated minor mineral phases in samples S1 and S2 were muscovite and quartz, in sample S3 muscovite, quartz and feldspars while in samples S4 and S5 muscovite, quartz, feldspars and smectites occurred (Table 1). The presence of smectite clays in samples S4 and S5 could be the result of similar weathering processes. However, the X-ray diffraction results (Fig. 1) show different patterns that could arise from the origin of samples S4 and S5. Smectite in sample S4 was developed

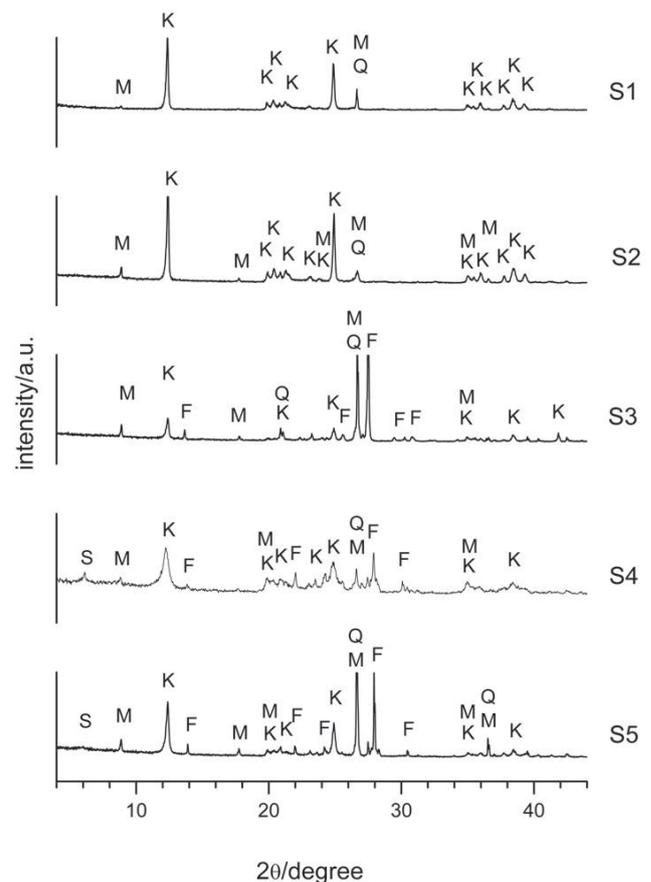


Figure 1: XRD patterns of the investigated kaolin clays.

Table 2: Specific surface area (SSA), cation exchange capacity (CEC) and the mean size (Mz) of the investigated kaolin clay samples.

Sample	SSA (m <sup>2</sup> g <sup>-1</sup> )	CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	Mz (μm)
S1	6.9	3.4	28.0
S2	9.6	4.2	20.5
S3	14.4	7.6	17.8
S4	19.4	8.5	16.7
S5	18.1	15.5	18.8

through the weathering of finer grains of feldspar from a granite rock in a tropical climate in Sierra Leone, while that in sample S5 derived from a pegmatite.

The grain size distribution spectra of the kaolin samples are shown in Figure 2. All spectra exhibit a similar granulometric distribution pattern, with a mean particle size ranging from 17 to 28 μm (Table 2). The relatively large particle size of the kaolin clays indicates the presence of kaolinite “booklets”, the micron-sized morphological structures built up of numerous platelets that are typical for the kaolinite mineral (BERGAYA et al., 2006; BALAN et al., 2014). The appearance of these morphological features was confirmed by the FE-SEM images displayed in Figure 3A-D. These are characterized by stacked pseudo-hexagonal platelets with diameters

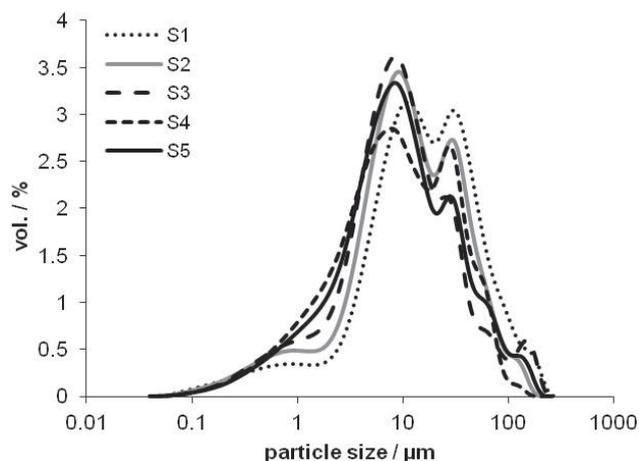


Figure 2: Particle size distribution of the investigated kaolin clays.

0.1–1.5  $\mu\text{m}$  and a thickness in the range of approximately 30–100 nm. The stacking of platelets produced “booklets” of several tens of micrometres which is especially evident in sample S2 where a high degree of stacking led to the exposure of edge surfaces (Fig. 3B,C).

The CEC and SSA of kaolin clay samples are shown in Figure 4. The obtained CEC and SSA values were in the range of 3.4–15.5  $\text{cmol}_+\text{kg}^{-1}$  and 6.9–19.4  $\text{m}^2\text{g}^{-1}$ , respectively (Table 2). The results obtained have shown that kaolin solids with a greater content of ancillary smectite (samples S4 and S5) displayed higher CEC and SSA values. Smectites are characterized by high CEC and external SSA values, up to 120  $\text{cmol}_+\text{kg}^{-1}$  and 78  $\text{m}^2\text{g}^{-1}$ , respectively (BERGAYA et al., 2006; SONDI et al., 1996a). Thus, the high SSA values of 19.4 and 18.1  $\text{m}^2\text{g}^{-1}$  obtained for samples S4 and S5, should be ascribed to their presence in the investigated kaolin solids. Smectites are also characterized by small particle diameters (ZHUANG & YU, 2002) and their presence in samples should lower the mean particle size of the kaolin samples. Indeed, the obtained mean particle size for samples S4 and S5 is in accordance with these observations (Table 2). A relatively high SSA of 14.4  $\text{m}^2\text{g}^{-1}$  was also measured for sample S3. Since this sample did not contain smectites, relatively high SSA values could be the consequence of the smaller grain size of the kaolin clay samples (17.8  $\mu\text{m}$ ).

The CEC of 15.5  $\text{cmol}_+\text{kg}^{-1}$  in sample S5, was the highest of all the investigated samples, which is in accordance with the presence of smectites in this sample. A similar conclusion was proposed by MA & EGGLETON (1999) who

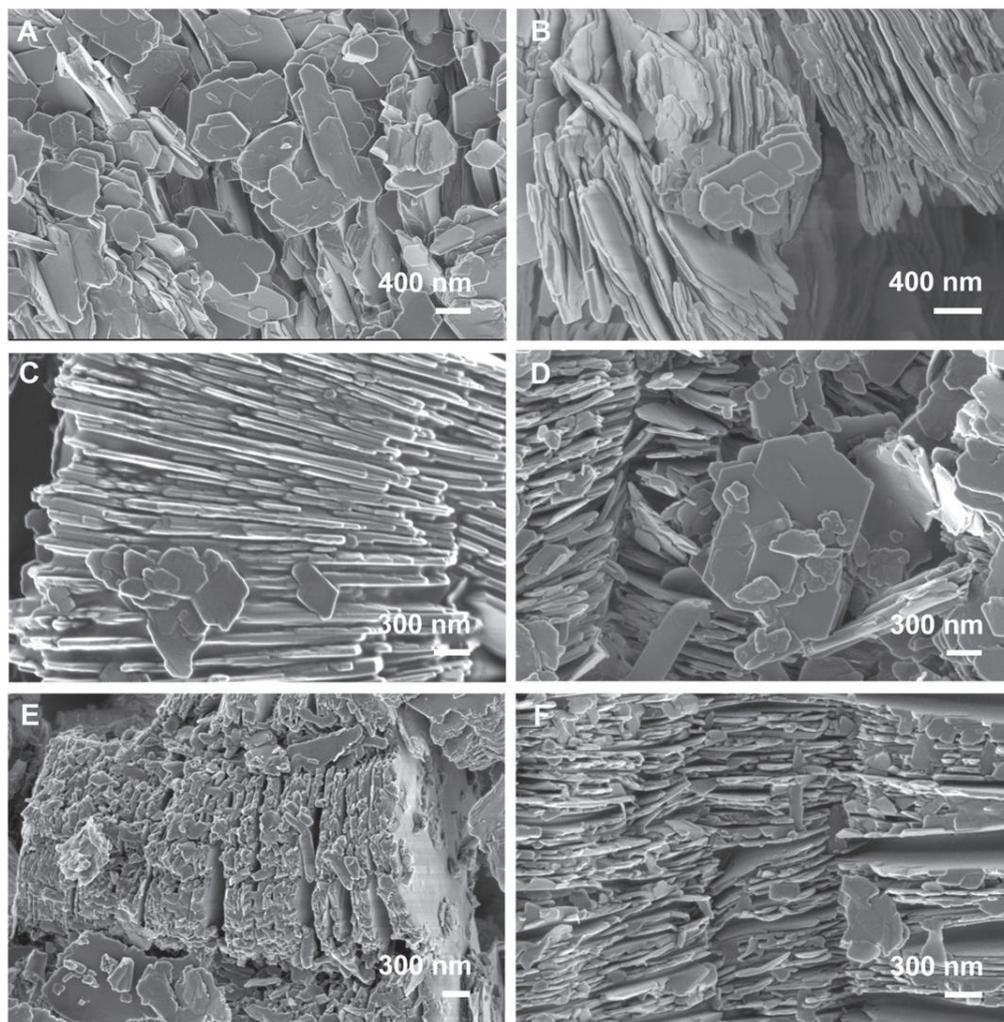
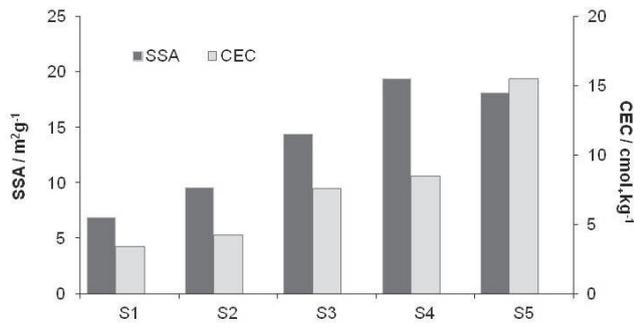
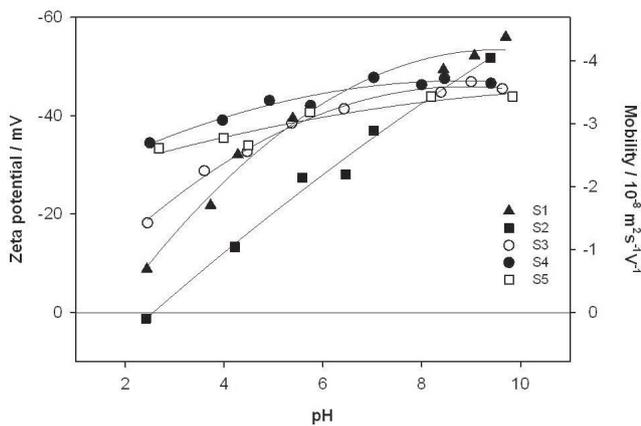


Figure 3: FE-SEM photomicrographs of kaolinite in the kaolin clay samples: S1 (A), S2 (B, C), S3 (D), S4 (E) and S5 (F).



**Figure 4:** The specific surface area (SSA) and the cation exchange capacity (CEC) of the investigated samples.



**Figure 5:** Electrophoretic mobility and zeta-potential of the kaolin clay samples dispersed in  $1 \times 10^{-3}$  mol dm<sup>-3</sup> NaCl solution, as a function of pH.

discovered that the presence of smectites coincided with the high CEC occurring in some kaolin clays. However, the CEC in sample S4, which also contains ancillary smectites, was not as high as expected ( $8.5 \text{ cmol} \cdot \text{kg}^{-1}$ ) probably due to dilution with other minerals of low surface reactivity (quartz, muscovite and feldspars).

Despite their common origin, samples S3 and S5 exhibit different compositions of ancillary minerals (Table 1), with the main variation being the presence of smectite in sample S5, and consequently the disparity in CEC values,  $7.6 \text{ cmol} \cdot \text{kg}^{-1}$  (S3) and  $15 \text{ cmol} \cdot \text{kg}^{-1}$  (S5).

The absence of smectites and the presence of quartz and muscovite in samples S1 and S2 resulted in the lowest CEC and SSA values of all the investigated samples. These results were in accordance with the surface properties of the pure kaolinite clay minerals that usually exhibit relatively large particle diameters and low SSA and CEC values (van OLPHEN, 1977; MA & EGGLETON, 1999; WILKINSON & REINHARDT, 2005; BERGAYA et al., 2006). Accordingly, the surface properties of ancillary minerals in these kaolin samples have not rescinded the native surface properties of the dominant kaolinite mineral. The presence of smectites, even in small amounts, significantly changes surface properties and raises the CEC and SSA values of the kaolin clay

samples. In our previous study (SONDI et al., 1996a) it was shown that a natural clay mixture of illite (30%), chlorite (55%) and montmorillonite (15%) exhibited the surface properties of montmorillonite, regardless its relatively low content in the clay fraction.

### 3.2. Electrokinetic behaviour of kaolin clay samples

The EPM and zeta-potential curves as a function of pH for the kaolin clay samples are displayed in Figure 5. For most samples, negative EPM values were measured across the whole pH range investigated. A significant decrease of negative EPM and zeta-potential values with decreasing pH was also determined. This effect was more pronounced in samples S1-S3 than in samples S4 and S5. The strongest effect of pH on EPM was observed in sample S2 where an isoelectric point (IEP) was reached at  $\text{pH} \sim 2.5$ . It leaves no doubt that the structural and the morphological properties of the kaolinite mineral and the presence of ancillary smectite govern the electrokinetic properties of the investigated kaolin clay samples.

The kaolinite mineral usually appears in the form of stacked platelets where the edges represent a larger fraction of the total surface area (BERGAYA et al., 2006). These structures limit the accessibility of the basal siloxane surfaces and expose the amphoteric edge surfaces to the aqueous solution. These surfaces are structurally and chemically heterogeneous and characterized by different charging mechanisms. As a consequence, their ratio will affect the electrokinetic behaviour of the bulk sample (SONDI et al., 1997b; TOMBÁČZ & SZEKERES, 2006).

The morphology of kaolinite minerals investigated in this study was also characterized by the exposed edge surfaces (Fig. 3B,C). Therefore, a significant decrease in their negative charge under acidic conditions is expected, since a part of their charge originates from the amphoteric edge sites which are protonized under low pH conditions. A decrease in EPM with the decrease in pH was more pronounced for kaolin samples that contain kaolinite characterized by more abundant edge surfaces. The obtained EPM values for samples S1-S3 were in accordance with the results previously obtained by SONDI et al. (1997b) who investigated a pure kaolinite solid.

Samples S4 and S5 showed significantly smaller changes of EPM values over the investigated pH range (Fig. 5). This could be explained by the presence of ancillary smectites in these solids. Previous investigations have shown that the portion of edge surfaces in smectites is negligible in comparison to the basal siloxane surfaces (SONDI et al., 1997b; SONDI & PRAVDIĆ, 2002; WAN & TOKUNAGA, 2002). The permanent negative surface charge of smectites exposed at the basal siloxane surfaces is pH independent and described by the Constant Basal Surface Charge (CBSC) model (SONDI et al., 1997b; MA & EGGLETON, 1999). Therefore, charge occurring at the basal surfaces is responsible for the total charge of the smectites while the edge charges are less pronounced. In comparison with samples S1-S3, for

which EPM was pH-dependent and determined by the presence of the amphoteric edge surfaces, samples S4 and S5 exhibited almost no pH-dependency. The prevalence of the negative siloxane surfaces of ancillary smectites over the total surface charge of kaolinite show their overwhelming influence on the electrokinetic behavior of kaolin clays. This study undoubtedly demonstrates that the presence of ancillary smectites hindered the surface charge properties of the prevailing kaolinite mineral in the kaolin clays.

#### 4. CONCLUSION

This study describes the influence of ancillary minerals on the surface properties (SSA, CEC, EPM) of kaolin solids of igneous origin. It was shown that the presence of ancillary minerals with low surface reactivity (quartz, feldspars, and muscovite) exhibit no effect on the surface properties of the prevailing kaolinite and such clays revealed the same behaviour as a pure kaolinite mineral.

The presence of ancillary smectite minerals in kaolin clay samples resulted in a significant increase of their CEC and SSA values. In addition, their presence changed the ratio between the basal siloxane and the amphoteric edge surfaces of kaolin clays resulting in their limited response to the changes in the EPM with the variation of pH.

The results of this study imply that kaolin clays will retain the behaviour of the prevailing kaolinite mineral when they contain ancillary minerals characterized by low surface reactivity. In contrast, the kaolinite surface properties will be rescinded by surface properties of ancillary smectites characterized by higher surface reactivity, even when they are present in trace amounts.

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