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Assessment of surface heterogeneity of lime treated kaolinites: probed by low-pressure argon and nitrogen gas adsorption

Yadeta C. Chemed ^a, Dimitri Deneele ^{b, c, *}, Angelina Razafitianamaharavo ^d, Frédéric Villieras ^d, Guy Ouvrard ^c

^a Adama Science and Technology University, School of Applied Natural Science, Department of Applied Geology, P.O.Box 1888, Adama, Ethiopia

^b IFSTTAR, GERS, EE, F-44344 Bouguenais, France

^c Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France

^d Laboratoire Interdisciplinaire des Environnements Continentaux (LIEC), UMR 7569 CNRS, Ecole Nationale Supérieure de Géologie, BP 40, 54501 Vandoeuvre-lès-Nancy, France

* Corresponding author

Abstract

It is a common practice to alter the undesirable behavior of clayey soils (i.e. swelling-shrinkage and high plasticity) with lime addition. However, the reaction mechanism involved in the early stage (first minute up to 24 hr after mixing) of lime treatment is still not well explored. In the present work, the surface chemistry of lime ([Ca] = 22 mmol/l and pH=12.63) treated kaolinites (Kaol) was studied using argon and nitrogen gas adsorption. The effect of pH ([Ca] = 22 mmol/l and pH=12.63 vs. [Ca] = 22 mmol/l and pH=7) was also examined. The derivative low-pressure adsorption isotherms were analyzed using derivative isotherm summation (DIS), focusing on the analysis of surface heterogeneity. After the treatment with lime, the specific surface area and adsorption energy distribution of Kaol were modified. The adsorption of the calcium cation at both

investigated pH (i.e. pH 7 and pH 12.63) takes place on the basal and lateral face of Kaol, however, the species of adsorbed calcium cation appeared to be different. The treatment also leads to a decrease in basal surface area due to basal face-basal face particle aggregation. The basal surface of Kaol treated with lime exhibited polar sites when probed with nitrogen molecule. These sites may have promoted linkage and flocculation of Kaol particles, which in turn play a role in the short-term modification of the macroscopic behavior of lime treated kaolins.

Keywords: Kaolinite, lime treated, low pressure, argon, nitrogen, surface heterogeneity

1 Introduction

The clayey soils usually exhibit high swelling-shrinkage behavior and compressibility and are generally unsuitable for construction works. These behaviors are mainly governed by the amount and type of clay minerals present in the soil. Hence, it is a common practice to use lime (CaO or $\text{Ca}(\text{OH})_2$) as a chemical additive to alter these undesirable properties and made the clayey soil suitable in construction activities (Bell, 1996; Dang et al., 2016; Emarah and Seleem, 2018, Das et al., 2021). When lime is added to the soil in presence of moisture, the swelling potential and plasticity decrease in the short-term, and mechanical strength increases in the long-term (Bell, 1996).

The long-term stabilization mechanism (i.e. pozzolanic reaction) has been thoroughly studied and well understood (Bell, 1996; Al-Mukhtar et al., 2010; Pomakhina et al., 2012; Eisazadeh et al., 2012; Vitale et al., 2017). It is related to precipitation of cementitious hydrated gels. On the other hand, the short-term reaction mechanisms, which are mainly controlled by surface phenomena (Bell, 1996; Chemedi et al., 2015; Vitale et al., 2016), are less explored. The reaction at this stage is crucial in soil stabilization as it can affect the mixing ability of the soil with lime (Konan et al.,

2009) and retards long-term pozzolanic reaction (Chemed et al., 2018). Hence, a better understanding of the reaction mechanism is central for the optimization of the technique.

The true surface interaction of clay minerals with a solution, which is difficult to look at directly, is usually inferred from adsorption at solid-liquid interface or characterization of surface chemistry of the treated sample. In the previous works (Konan et al., 2009; Chemed et al., 2018), adsorption at solid-liquid interface were used to assess lime solution-Kaol interfacial phenomenon. Their findings revealed that adsorption of calcium cation mainly takes place on a permanent charge and Si-O⁻ sites at neutral pH, whereas adsorption on pH-dependent charge site is dominant at alkaline pH. In addition, the adsorbed species of calcium cation at pH 7 and pH 12.63 found to be different. However, using this technic, it is impossible to identify the adsorption sites due to difficulty in isolation of the different faces (basal and lateral faces). Thus, a study on surface characteristics with techniques that can distinguish the different crystallographic surfaces is indispensable.

The different crystallographic surfaces of clay minerals can be probed using high-resolution gas adsorption coupled with DIS (Michot et al., 1990; Bardot et al., 1998). The technique, particularly low-pressure argon gas adsorption was successfully applied in previous works (Villieras et al., 1992; 1997; Bardot et al., 1998; Hassan et al., 2005; Mbey et al., 2019) for a quantitative estimation of surface heterogeneity in terms of lateral and basal surfaces of different clay minerals. Furthermore, it has been demonstrated that the presence and nature of surface cation viz. size, electronegativity and polarizability influences the normal interaction energy between the probe gas (argon and nitrogen) and the probed surface (Villieras et al., 1992; Bardot et al., 1998; Hassan et al., 2005). These advantages can be utilized to indirectly probe the nature (species) of the surface cations and adsorption sites.

In the present work, the surface chemistry of four Kaol samples treated with lime (Ca(OH)_2) was characterized using low-pressure quasi-equilibrium argon gas adsorption in order to identify calcium cation adsorption sites. For this purpose, the derivative gas adsorption isotherms of lime treated and Na-exchanged Kaol samples were analyzed using derivative isotherm summation (DIS), focusing on the analysis of surface heterogeneity. The effect of pH value was also investigated by comparing isotherms of lime ($[\text{Ca}] = 22 \text{ mmol/l}$ and $\text{pH}=12.63$) and calcium chloride ($[\text{Ca}] = 22 \text{ mmol/l}$ and $\text{pH}=7$) treated samples. Polar/nonpolar surface characteristics of Kaol samples were examined using nitrogen gas adsorption.

2 Materials and experimental procedures

2.1 Materials

Four Kaols of different properties and origins, namely KGa-2 (high defect), KGa-1b (low defect), SPwt (low defect) and B24 (high defect), were selected for this investigation. Kaol KGa-1b and KGa-2 were purchased from the Source Clay Repository of the Clay Minerals Society. Kaol SPwt and B24 were collected from Cornwall, UK and Charente basin, France, respectively. Chemical analysis and X-ray diffraction pattern showed the mineralogical purity of the Kaol samples is > 95% ([Chemedda et al., 2018](#)). Minor phases in the samples include muscovite (in B24 and SPwt), quartz and anatase. Hydrated lime, Ca(OH)_2 (Merck, analytical grade, purity above 97%) and $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (analytical grade, Merck, Germany) were utilized for preparation of hydrated lime and calcium chloride solution, respectively. High purity argon gas (> 99.9996%) and nitrogen gas (> 99.999%) provided by Alphagas were used for gas adsorption experiment.

2.2 Chemical treatment

The Kaol samples were first purified (i.e. the samples were de-carbonated, organic matters were removed and clay sizes were fractionated) and then exchanged with sodium at pH 7. Na-Kaol was prepared by sodium exchange in 1M NaCl solution. The samples were then washed with distilled water repeatedly until the supernatant was chloride free and had lower conductivity ($< 5 \mu\text{S/cm}$). Lime and calcium chloride treated Kaol were prepared by suspending Na-exchanged Kaol samples in freshly prepared calcium hydroxide ($[\text{Ca}] = 22 \text{ mmol/l}$ and $\text{pH}=12.63$) and calcium chloride ($[\text{Ca}] = 22 \text{ mmol/l}$ and $\text{pH}=7$) solution, respectively. For this purpose, 6 g sample were kept in contact with calcium chloride and lime solutions (30 ml) in centrifuge tubes and shaken mechanically. This was followed by centrifugation for 15 min at 8000 rpm to separate the solid from solution. The preparations (weighting and mixing) were performed under argon atmosphere in a nitrogen glove box.

2.3 Low-pressure gas adsorption at 77K

The low-pressure adsorption isotherms were recorded with lab-built quasi-equilibrium device (at LIEC (Laboratoire Interdisciplinaire des Environnements Continentaux), Nancy) equipped with three high accuracy differential pressure sensors (0 – 10 Pa, 0 – 103 Pa and 0 – 105 Pa). A full review of the technique and the setup of the apparatus could be found in previous works ([Michot et al., 1990](#); [Bardot, 1998](#)). The principle of the measurement is based on introduction of adsorbate through a calibrated microleak continuously at a constant and slow flow rate ([Michot et al., 1990](#); [Villieras et al., 1992; 1997](#)).

About 1 g of samples were put in the adsorption cell and outgassed for 18 hr under a residual pressure of 10^{-4} Pa. The outgassing was carried out at three different temperatures in successive steps (110°C, 150°C and 200°C) on the same sample. More than 3000 data points were obtained from recording of quasi-equilibrium pressures as a function of time. To obtain derivative

adsorption isotherm, the data points were plotted as first derivative of adsorbed quantity vs. logarithm of relative pressure ($\ln(P/P_0)$), with P_0 being the saturated vapor pressure (Michot et al., 1990; Villieras et al., 1992; 1997). The derivative adsorption isotherm represents the adsorption energy distribution for the used gaseous probe (Michot et al., 1990; Bardot, 1998). The experimental derivative adsorption isotherms are then modeled with the sum of “local” theoretical isotherms derived from Brunauer, Emmett and Teller (BET) formalism using DIS procedure (Villieras et al. 1992). The lateral interaction parameter (ω) was kept constant (± 0.2) during the modeling of isotherms. For each “local” adsorption isotherm, three parameters were then obtained: the position of the peak ($\ln P/P_0$), which depends on solid-gas and gas-gas interaction energies; the lateral interaction parameter between adjacent adsorbed gas molecules (ω), and a monolayer capacity (V_m). The specific surface area was calculated from monolayer capacity of each domain of local isotherm by applying BET derived formalism.

3. Results and discussion

3.1. Effect of outgassing temperature

The effect of outgassing temperature on the argon adsorption energy distribution were analysed first to identify cations on charged and neutral surface. An example of experimental derivative argon adsorption isotherm for different outgassing temperatures of Na-KGa-2 (high defect) and Na-KGa-1b (low defect) samples are presented in Figure 1. Irrespective of the outgassing temperature, all the derivative adsorption isotherms show the same shapes with a main peak located at low and medium energy ($\ln(p/p_0) > -5$) representing the adsorption on the basal surfaces. While the shoulder and tail at high energy, located at $\ln(p/p_0) < -6$, attributed to the adsorption on lateral surfaces. At $\ln(p/p_0) > -3$, low energy domain represent adsorption on basal surface and multilayer adsorption (Villieras et al., 1992; 2002; Bardot et al., 1998; Hassan et al., 2005). With

increasing outgassing temperature, the major lower energy peak shifted to lower energy and the peak become narrow, i.e. the low energy surfaces become energetically less heterogeneous (Villieras et al., 1992; 2002).

The derivative argon adsorption isotherms were modelled using six local isotherms assigned to local derivative adsorption isotherms (Hassan et al., 2005) following DIS techniques. The three highest energy domains (1, 2 and 3) attributed to adsorption on lateral faces whereas the three low energy domains (4, 5 and 6) represent adsorption on basal faces (Bardot et al., 1998; Hassan et al., 2005). The obtained modelling parameters (i.e. $\ln(P/P_0)$ which represents the normal interaction energy of the argon molecule with surface (Villieras et al., 1992;1997;2002), volume adsorbed (V_m) and lateral interaction (ω)) after different outgassing temperature are presented in Table 1, for Na-KGa-2 and Na-KGa-1b. Irrespective of the outgassing temperature, the total specific surface area remains nearly constant. It means that the modification of the derivative adsorption features is mainly related to variation in the argon adsorption energy distribution rather than the variation of amount of gas adsorbed. Concerning local isotherms, the position of domains 1, 2, 3 and 4 appeared to be unaffected by outgassing temperature suggesting charged lateral (domain 1, 2 and 3) and basal (domain 4) surfaces. On these sites, the surface cations bound tightly (Hassan, 2005). On the other hand, domain 5 shows relatively greater sensitivity to outgassing temperature (i.e. the peak position shifts to lower energy after outgassing at 200°C) implying the elimination of physisorbed compounds and/or loosely bound cations from uncharged surface (Hassan, 2005). Since the purpose of using this technique is to identify the calcium adsorbed on charged surface (not neutral compound), domain 3 (charged lateral surface) and 4 (charged basal surface) were considered for further analysis (next section). The isotherms after outgassing at 200°C were also

considered to minimize the effect of physisorbed compounds on the gas adsorption energy distribution.

3.2. Effect of chemical treatment

3.2.1. Derivative adsorption isotherms

The derivative argon adsorption isotherms of the Na-exchanged, lime treated and calcium chloride treated samples are compared in [Figure 2](#), for an outgassing temperature at 200°C. After treatment, major differences are noted in the shape of the derivative adsorption isotherms, particularly for the low energy peak, due to change both in intensity and position of the peak. In both cases, the intensity of the major peak attributed to basal face decreases and becomes wider. However, the change is more pronounced for lime treated sample. This finding is consistent with more calcium adsorption and surface modification in the presence of lime than with calcium chloride solution ([Chemedá et al., 2015](#)). In the case of lateral faces, additional argon molecules are adsorbed at high energy range resulting in a well-developed high energy peak which could corresponds to a new adsorption site generated by flocculated structure ([Bardot et al., 1998](#)). The intensity of the peak is relatively higher for lime treated sample in accordance with higher flocculation in the presence of hydrated lime than calcium chloride solution ([Chemedá et al., 2015](#)). Generally, the major modification on the lower energy peak suggests the interactions of the two solutions (lime and calcium chloride solutions) with Kaol dominantly takes place on the basal surface. However, with this technique, it is impossible to know exactly whether the reaction is on silica or alumina basal faces.

An example of the derivative adsorption isotherms together with their decompositions before and after treatment with lime and calcium chloride solutions are presented in [Figure 3](#), for KGa-1b and KGa-2. The numerical DIS results for the four studied Kaol are summarized in [Table 2 & 3](#).

3.2.2. Textural parameters

The total specific surface area deduced from the sum of monolayer capacity of each domain of local isotherm by applying BET derived formalism decreased after lime and calcium chloride treatments as evidenced from the decrease in the intensity of low energy peak. Nevertheless, in some cases (KGa1b, KGa-2), the adsorption of additional argon in high energy region obscured this change ([Table 2](#)). The change is more evident in the low energy peak, particularly for domains 4 and 5 ([Figure 4](#)). The extent of the change is different for the four studied Kaol samples, which appears to be depend on the degree of defect and cation exchange capacity. Indeed, there is an approximate linear relationship between the amounts of calcium adsorbed ([Chemeda et al., 2018](#)) and the change (decreased) in basal specific surface area derived from domains 4 and 5 ([Figure 5](#)). The more the amount of calcium adsorbed, the more the basal specific surface area decreased. This phenomena can be interpreted in two ways: 1) involvement of exchangeable cation, in the present case calcium, in the first mono-layer adsorption site of argon molecule and/or 2) the aggregation of Kaol particles.

The first possibility can be checked by comparing the surface area occupied by the two cations (sodium and calcium) knowing their amount on the surface (from [Chemeda et al., 2018](#)). For this purpose, surface area occupied by Na and Ca-cations were compared for the raw (Na-Kaol) and calcium chloride treated samples ([Table 4](#)). The area occupied by Ca-cation is either equal or lower than the area occupied by Na-cation, which is not surprising as the size of the two cations are nearly the same ($\text{Ca} = 0.99 \text{ \AA}$, $\text{Na} = 0.97 \text{ \AA}$) and the former neutralizes two charge sites per cation.

It means that the area should increase when Na-cation is replaced by Ca-cation contrary to our observation. The other possibility is aggregation of Kaol particles. The replacement of monovalent cations by high order valency cations can change the particle arrangement from dispersed to flocculated structure (Mpofu et al., 2003, 2005; Chemedi et al., 2015). The decrease in basal specific surface area could be thus linked to the aggregation (probably basal face-basal face) of the clay particle that makes inaccessible a part of basal surface for argon adsorption. A similar phenomenon between monovalent and divalent cation (Na vs. Ca, Li vs. Mg and K vs. Ba) was observed for illite by Bardot (1998), although the change is more pronounced in the case of illite. However, the observed modification cannot solely be accounted to change in texture (aggregation) of Kaol particles as there is also a shift in peak position in addition to decrease in the intensity. The observed difference could also be linked to the effect of the treatments on surface chemistry (this point addressed in next section).

3.2.4. Surface energetic parameters

The energetic parameters ($\ln(P/P_0)$) of domain 3 and 4 varied depending on the nature of the treatment (i.e. shifted to higher energy after lime treatment), revealing the modification of surface chemistry of lateral and basal surfaces (i.e. different surface cations) (Figure 6). This hypothesis is furthermore supported by the fact that the obtained peak position in the case of raw sample (Na-Kaol) and calcium chloride treated sample (Ca-Kaol) compared well with the peak position of Na-illite (for domain 4, $\ln(P/P_0) = -4.53$ and for domain 3, $\ln(P/P_0) = -6.95$) and Ca-illite (for domain 4, $\ln(P/P_0) = -4.56$ and for domain 3, $\ln(P/P_0) = -7.05$), respectively (Bardot et al., 1998). On the other hand, the peak positions of both domains in the case of lime treated sample are higher than the calcium chloride treated samples. The only difference between the two solutions (i.e. calcium hydroxide and chloride solution) is the initial pH. The observed difference could be then attributed

to the effect of pH on surface charge density and the nature of calcium available for adsorption. However, as it has been demonstrated for the case of synthetic saponites with different layer charge (Michot and Villieras, 2002), the normal adsorption energy of argon on basal face is much more sensitive to the nature of surface cation than to the origin and the density of charge. One can then suppose that the nature of the charge compensating cations in the two cases are different. Indeed, CaOH^+ and Ca^{2+} are the dominant species of calcium available for adsorption at pH= 12.6 and 7, respectively (Mpofu et al., 2005; Chemedi et al., 2015). Hence, in the case of lime treated sample (i.e. CaOH^+ as a surface cation), the argon molecule interacts with OH-ion in addition to calcium and the size is also larger than calcium cation. Therefore, the interaction energy is expected to be higher than the case of the calcium chloride treated sample (i.e. Ca^{2+} as surface cation).

3.2.5. Argon vs. nitrogen isotherms

Nitrogen and argon have different characteristics: argon molecule gives rise to only non-specific interactions, while due to its inducible quadrupolar momentum, nitrogen molecule interacts also with specific sites (Rouquerol et al., 1989; Villieras et al., 2002; Garnier et al., 2005), provided that the surface of the particle carries localized polar groups or positive charges. For the assessment of polar or non-polar surface characteristics before and after treatment, the adsorption energy distributions of the first monolayer as a function of natural logarithm of pressure ($\ln P$) for nitrogen and argon were compared for selected samples (Figure 7). As usually observed for clay minerals, there is difference between the isotherms of the two gases at the higher energy range for the three samples irrespective of the treatment. It mainly corresponds to specific interaction of nitrogen with surface polar sites (Villieras et al., 1992; 2002; Bardot et al., 1998) and will not be further discussed here as it is not related to the effect of the treatment.

Concerning the basal face, the shape of the peak of the argon and nitrogen derivative adsorption isotherms appeared nearly identical (i.e. narrow and sharp) for Na-exchanged and calcium chloride treated sample. Furthermore, the main peak in both cases located at the same position (the values of $\ln P$ around 6 to 7) suggesting non-polar nature of the basal surface. For the case of lime treated sample, the shape of the two gas isotherms are different as the peak of nitrogen isotherm is relatively wider due to additional shoulder at high energy side. The major peak, which located on the same position for the two gases ($\ln P$ around 6) similar to Na-exchanged and calcium chloride treated samples, can be attributed to non-polar surface site. On this site, both nitrogen and argon adsorbed through low energy interaction (Villieras et al., 2002; Garnier et al., 2005). A shoulder at higher energy side (indicated by arrow) in the case of nitrogen isotherm, could be attributed to the interaction of nitrogen molecules with some polar/ electropositive sites (Villieras et al., 2002; Garnier et al., 2005) on the basal faces. The chemical nature of this site is not known exactly in the present study, hence, a deeper understanding of the surface chemistry of lime treated sample (at microscopic level) would be necessary to interpret this observation. It is tentatively attributed to CaOH^+ or electropositive sites generated by adsorption of hydrolysis species of calcium as indicated by negative to positive surface charge reversal of Kaol particle in the presence of calcium rich alkaline ($[\text{Ca}] = 22 \text{ mmol/l}$ and $\text{pH}=12.63$) solution (Chemeda et al., 2015). These sites may promote linkage and aggregation of Kaol particles.

4. Conclusion

The results of this work revealed that the adsorption of calcium cation from lime ($[\text{Ca}] = 22 \text{ mmol/l}$ and $\text{pH}=12.63$) and calcium chloride ($[\text{Ca}] = 22 \text{ mmol/l}$ and $\text{pH}=7$) solution takes place both on the basal and lateral faces. These sites can be attributed to Si-O^- (lateral face) and local charge defect (i.e. Al^{+3} for Si^{+4} substitution) in tetrahedral sheet at pH 7, and additional charge sites

generated by dissociation of Al_2OH and Al-OH functional groups on octahedral basal and lateral faces, respectively, at pH 12.6. The species of calcium cation available for adsorption at the two pH conditions are different as evidenced by the variation of the adsorption energy ($\ln(P/P_0)$) corresponds to charged surface on the basal and lateral faces depending on the source of the cation (calcium chloride or lime solution). The data indirectly validates the results obtained in previous works (i.e. Ca^{2+} and CaOH^+ at pH 7 and 12.6, respectively) from adsorption at solid-liquid interface (Chemeda et al., 2015) and calculation of pH-dependent calcium cation hydrolysis (Mpofu et al., 2003; 2005). The face-to-face aggregation of Kaol particles, owing to compression of electrical double layer in the presence of calcium cation, mainly accounts for the decrease of basal specific surface area or adsorbed gas volume after lime and calcium chloride treatment. The basal surface of Na-exchanged and calcium chloride treated Kaol samples exhibits mainly non-polar characteristics, whereas lime treatment induces additional polar surface sites. These sites could be CaOH^+ or electropositive sites emerged on Kaol surface in the presence of calcium rich alkaline solution, which in turn induced particle linkage and short-term modification of macroscopic behavior of kaolins.

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