



Research Paper

Impact of the substitution distribution and the interlayer distance on both the surface energy and the hydration energy for Pb-montmorillonite

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ABSTRACT

The understanding of the adsorption of charged species in swelling clays is of primary importance to optimise the capture of heavy metal ions in soils. Adsorption is expected to depend on the microscopic structure of the clay, which varies strongly with the origin and history (hydration–desorption cycles, temperature ...) of the sample. Then it is necessary to evaluate the distinct interaction energies between water molecules, interlayer cations and clay surfaces, taking into account the position of the substitutions in the clay layer. Here we propose an investigation of plausible structures of some Pb-montmorillonites differing by their interlayer distances, their layer charges and the distribution of substitutions in octahedral sheet from a modelling approach, looking at the evolution of the partial charges in these structures. Using a methodology previously developed in the simpler case of alkali cations, we also estimate the surface energy in the dry state and then the details of the hydration energy for the cation and for the clay layer to interpret the capacity of ion adsorption in swelling clays to capture heavy metals. We conclude from our calculations that a cell structure with intermediate layer charge (close to 0.5 per unit cell) is probably the best candidate to allow the capture of the Pb^{2+} as interlayer cations considering the electrostatic effect. The hydration process of the cation appears as the most energetic part of the hydration of swelling clays compared to the interactions with the layer, but the cation mobility is limited since the hydration process is not complete. This means that the heavy metal ions, present in the interlayer space, will be unable to diffuse and will be captured in the case of a low layer charge.

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1. Introduction

Scientific progress has improved human life in various domains (Serrano et al., 2005; Chaturvedi et al., 2006; Yot and Méar, 2009). However, natural systems have been strongly modified, which affects both health and environment (Sen Gupta and Bhattacharyya, 2008; Babel and Kurniawan, 2003). In particular, the presence of metallic ions in the environment is responsible for the contamination of living organisms (Chaturvedi et al., 2006). This is why the reduction of the quantity of metal present in water or in soil represents a big challenge in order to avoid harmful effects to humans (Volzone, 2004). Moreover, the understanding of both their diffusion and adsorption properties is essential in order to foresee the risks for the ecosystem (Chaturvedi et al., 2006). Heavy metals are the high-density metallic elements of the periodic classification. Some metals are extremely harmful (mercury, lead, cadmium, and chromium (VI)). It is therefore necessary to propose adequate procedures in order to avoid (i)

possible bio-accumulation and redissolution of metals in the ecosystem and (ii) reaching the critical metal concentration that is dangerous for some living organisms.

The research for the purification of water contaminated with heavy metals has led to the development of new processes, such as co-precipitation, coagulation and extraction in solvents in the case of liquid or ionic mercury (Lima and Araujo, 1994; Blanchard et al., 1984). The immobilisation of metals by precipitation or sorption is considered as the most efficient way to reduce the quantity of metal in contaminated soils (Vega et al., 2009; Pavlovic et al., 2009; Bhattacharyya and Sen Gupta, 2008; Sen Gupta and Bhattacharyya, 2008; Sipos et al., 2008; Singh et al., 2001). Different solids, such as zeolites, activated carbons, silicas (specially the natural, modified or pillared clays) are potential candidates for metal retention (Lantenois et al., 2007; Singh et al., 2001; Matthes et al., 1999; Pinnavaia et al., 1985). In waste storage sites, compacted natural clays are present in great quantity and their properties for cationic exchange capacity or hydraulic conductivity make them efficient adsorbents. The adsorption capacity for metallic cations has already been studied and the following order has been found: $Cr > Ni > Zn > Cu > Co > Pb$ for a Na-montmorillonite (Abollino et al., 2003). Due to their large specific

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surface areas and high cation exchange capacity, the swelling clays display a strong capacity to capture metallic cations. To elucidate the role of the clay framework and predict the capacity of adsorption for ions, the molecular approach is a powerful tool. Moreover molecular simulation can allow determination of the important structural parameters that have to be considered to improve the adsorption capacity for ions. In addition, the hydration state of the sample strongly influences the mobility and the interaction of the cation in the interlayer space. The understanding of the hydration process in these solids is therefore a crucial step to completely elucidate the mechanism of heavy metal capture in swelling clays.

This paper focuses on the determination of the surface energy in the dry state which is linked to the cohesion energy between clay layers. This energy has to be counterbalanced during the clay hydration (Salles et al., 2006; Douillard et al., 2007a,b). It follows that the knowledge of the surface energy is the initial step to estimate the hydration capacity of a solid. The calculation of the hydration energy for the interlayer cation and the surface layer completes the description of the hydration and allows the elucidation of the driving force for the hydration in swelling clays (Salles et al., 2007). Such a method has been successfully compared with a recent interpretation of the conductivity measurements (Salles et al., 2008) and calorimetry data (Salles et al., 2009). For this complete description, we have to build a consistent structure for ideal montmorillonites saturated with Pb^{2+} cations. Then we propose to study the influence of both the layer charge and the opening of the interlayer space using electrostatic calculations. Since no structural data is available today for montmorillonite saturated with the Pb^{2+} cation at the dry state, we have to propose, as a first step, a “plausible” structure, before having a microscopic view of the adsorption of heavy metal ions. This is why the influence of the layer charge by imposing different substitution positions in different surface charge structures is studied. The impact of these substitutions on the surface energy and the chemical reactivity are also discussed.

2. Computational section

2.1. Theoretical approach

2.1.1. Lattice energy

The first step of the calculation is the classical computation of the lattice energy in a crystal using the Madelung matrix, corresponding to the summation of the electrostatic influence relative to the different positions of the atoms constituting the crystal. For this, the crystal structure, including H atoms, the relationships defined by the space group of the crystal and the formal charges have to be known. Details of such calculations giving the Madelung constant M and the Madelung tensor M_{ij} are given elsewhere (Quane, 1970). One result obtained from our calculations is the value of the electrostatic part for the lattice energy, i.e. the actual attractive part of this energy, when considering ionic solids (Douillard and Henry, 2003; Huheey et al., 1993).

$$U_e = -\frac{N_a M e^2}{r_e} \quad (1)$$

where U_e , N_a , M , e and r_e correspond to the lattice energy, the Avogadro number, the Madelung constant, the electron charge and the internuclear distance respectively. The choice of r_e is detailed in Quane (1970). It must be emphasized that the preliminary calculation of the lattice energy considers that the crystal is fully ionic.

2.1.2. Atomic charge

Pauling suggested that the effective electrical charge located on a chemical species interacting in a chemical bond is related to the electronegativity of the atom, which represents its capacity to attract

electrons. Another concept is necessary in order to interpret the chemical bonds quantitatively in such a way: the hardness corresponding to the measure of resistance of a chemical species to change its electronic configuration (Pauling, 1932). The formalization of electronegativity and hardness concepts has been carried out in the framework of density functional theory (Parr and Yang, 1994). In this theory the chemical potential μ of the electrons of the studied system is the derivative of the energy, E , with respect to the number of electrons, N , at constant external potential, ν . It is also defined as a definition of the electronegativity χ :

$$\mu = (\partial E / \partial N)_\nu = -\chi. \quad (2)$$

The hardness η is then

$$\eta = \left(\frac{\partial^2 E}{\partial N^2} \right)_\nu = \left(\frac{\partial \mu}{\partial N} \right)_\nu. \quad (3)$$

Practically, it is possible to determine the global distribution of the electron density around atoms in a molecule or a crystal using scales for electronegativity and hardness. For this, it is necessary to compute the equalization of the chemical potentials of the different atomic charge clouds upon bond formation, and then to determine atomic charges. It is very simple for diatomic molecules A–B: for any electron transfer dN from B to A at the internuclear distance r , the change in energy is the following using the same notations:

$$dE = \left[\left(\frac{\partial E}{\partial N_A} \right)_{N_B, r} - \left(\frac{\partial E}{\partial N_B} \right)_{N_A, r} \right] dN + \left(\frac{\partial E}{\partial r} \right)_{N_A, N_B} dr. \quad (4)$$

In this case, the equilibrium imposes $dr = 0$ (i.e. $r = r_e$, where r_e is the internucleus equilibrium distance) and $dE = 0$. It follows that the equation is simplified into:

$$0 = \left[\left(\frac{\partial E}{\partial N_A} \right)_{N_B, r_e} - \left(\frac{\partial E}{\partial N_B} \right)_{N_A, r_e} \right] dN. \quad (5)$$

There is an equalization of the effective electronegativities of A and B (denoted χ_A and χ_B), ensured by the change dN of the effective atomic charges q_i . Then, using the previously mentioned definition of the hardness, one gets a relation between the atomic electronegativities χ_i^0 of pure/single isolated species, the charges q_i , the hardnesses η_i and the resulting mean electronegativity $\bar{\chi}$ which corresponds to the value obtained at equilibrium:

$$\chi_A = \chi_A^0 + \eta_A q_A = \chi_B^0 + \eta_B q_B = \chi_B = \bar{\chi} \quad (6)$$

which gives for the charge, since $q_A = q_B$: $q_A = \frac{\chi_B^0 - \chi_A^0}{\eta_A + \eta_B}$.

From this equation, the difference of electronegativities can be considered as driving the electron transfer, in contrast with the sum of hardnesses which is opposed to this transfer.

However, this calculation, simple in the case of diatomic molecules, becomes more complex in the case of crystals, where long-range forces act and a spatial summation is performed. It is therefore necessary to know equilibrium distances for all atoms in the crystal. We will discuss this in the next paragraph.

In the calculation, the Allen electronegativity scale, which is related to spectroscopic characteristics of the atom, is used (Huheey et al., 1993; Allen, 1989).

In addition, the model supports the hardness scale linked to the radius of the atom considered as a sphere with a uniformly distributed electric charge q (Henry, 1997). The radius is taken here as the size of the diffuse orbital of the element (this hardness scale is detailed in Henry, 1997). The calculation is then independent from the assumptions or relative scales but depends only on physical values that can be

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