Stability and adhesion of calcite/montmorillonite assembly

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ABSTRACT

We analyze here the technical connection between the (104) calcite and (001) montmorillonite surfaces at the atomic level, as well as the conditions to obtain a stable assembly. To this end, the appropriate force field is used to describe the bonding character at the interface. Results show that, in the x direction, the elastic energy provided by calcite to ensure good adhesion at the interface is lower than the one of clay. While in the y direction, it is rather the clay’s atoms that provide energy for the accommodation to calcite. Furthermore, we have evaluated, additionally, the adhesion energy, the interfacial distance and the work of separation. We also show that the presence of water molecules at the interface absorb the excess energy and thus contribute to the stabilization of the interface.

Keywords: Clay mineral, adhesion energy, interface, calcite

INTRODUCTION

The alkaline earth carbonates have been a subject of considerable interest in the Earth sciences because they are the most abundant C-bearing species in the crust, and they represent a major reservoir for C within the Earth’s mantle carbonates (Berg 1986; Canil 1990; Katsura and Ito 1990; Kraft et al. 1991; Bakri and Zouiti 2011; Ayoub et al. 2011; Bouibes et al. 2013; Bouibes and Zouiti 2014; Zouiti and Shahrou 2010). We can find them in aquatic systems forming huge amounts of scale and ocean sediment (Morse and Mackenzie 1990), in the atmosphere (Usher et al. 2003), and as part of the sediment and rock record (Morse et al. 2007). These minerals affect the chemistry of aquatic systems by regulating pH and alkalinity through dissolution/precipitation equilibrium. Moreover, they can govern the mobility and cycling of metal contaminants and radionuclides via ion exchange, adsorption, and co-precipitation reactions (Van Cappellen et al. 1993). Calcite (CaCO₃) is one of the most abundant mineral species on the surface of this planet and is stable at ambient conditions. It is one of the constituents of argillite, a mineral rock used for the wastes disposal.

On the other hand, swelling clays are one of the important components of engineered barriers around underground storage sites of high-activity radioactive waste due to their properties of low permeability and high-retention capacity of cations. Many theoretical and experimental works have been paid for describing the behavior of diffusion of water and some cations in smectite clay (Nye 1979; Cebula et al. 1981; Sposito 1981; Chang et al. 1995, 1997, 1998; Van Der Spoel et al. 1998; Sutton and Sposito 2001; Marry and Turq 2003; Kosakowski et al. 2008; Yang and Zouiti 2013a, 2013b; Benazzouz et al. 2013; Zheng and Zouiti 2011, 2013, 2014; Benazzouz and Zouiti 2012a, 2012b, 2012c, 2012d; Zheng et al. 2010, 2011; Berghout et al. 2010; Tunega et al. 2012).

The study of calcite/montmorillonite interface is particularly of great importance since it helps to clarify many issues on the nuclear waste disposal. In fact, in the Underground Research Laboratory in France, an excavation damaged zone (EDZ) is observed around galleries in the Callovo-Oxfordian argillite (ANDRA 2005). It is characterized by the appearance of micro-fissures whose density decreases as the distance from the wall increases. Argillite is a mineral rock used for the isolation of the high-level radioactive wastes. It is mainly constituted of clay (20–60%) and calcite (10–75%). The analysis of this mineral especially the interaction between calcite and clays at the atomic level will give a clear picture about the strength of the bonds and the mechanical behavior of such rock at the storage conditions.

In this paper, we focus on the structural and energetic properties of the interface between the calcite (104) and montmorillonite (001) surfaces using nanoscale tools. We will discuss the conditions to obtain a stable interface of the assembly. Our first goal is to describe the interatomic bonding between the atomic constituents of calcite and clay at the interface. Then, we will evaluate some thermodynamic properties of CaCO₃ and montmorillonite, taken separately. Finally, we will study the adhesion energy, the work of separation, as well as the elastic energy at the interface.

DESCRIPTION OF THE POTENTIAL MODEL AND CONSTRUCTION OF THE SUPERCELL

Several force fields have been developed to describe the interactions in CaCO₃ to mainly reproduce the structural and thermodynamic properties of carbonates (Pavese et al. 1992, 1996; De Leeuw and Parker 1998; Archer et al. 2003; Raiteri and Gale 2010; Raiteri et al. 2010; Fisler et al. 2000). On the other hand, empirical potential models have been proposed to explore the bulk properties and surface of CaCO₃ (Sekkal and Zouiti 2013; Sekkal et al. 2008; Pavese et al. 1996; Dove and