



Research paper

Influence of organic matter on the reactivity of clay minerals in highly alkaline environments



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ABSTRACT

Soil organic matter has important implications in dissolution reactions of clay minerals and their transformation. Under acidic conditions increased dissolution rates are generally reported. However, in high pH environments, organic matter (OM) might have a passivation effect on the mineral surface, thereby hindering dissolution and transformation substantially. The reduced reactivity of clay minerals is an important consideration when clays are used as backfill materials in nuclear waste disposals or when lime is used for soil stabilization. Here the outcome of a comparative study is presented using soil, containing common clay minerals such as smectite, interstratified illite–smectite, illite and kaolinite, that was treated with highly concentrated alkaline solutions in the presence and absence of naturally occurring organic matter. The results clearly show that clay mineral dissolution and the formation of new zeolitic phases at room *T* are delayed in the presence of OM. The soils' OM content is, thus, an important parameter to be considered in systems where clay minerals are exposed to highly alkaline environments.

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1. Introduction

The interaction of organic matter (OM) with clay minerals has been studied extensively in the past and it has been established that OM stabilization occurs through the formation of organo-mineral complexes (Allison, 1973; Mayer, 1994; Leinweber et al., 1999). Especially, expandable clays and allophanic materials have been found to be responsible for the reduction in bioavailability of organic molecules (Mayer, 1994). However, little attention has been paid to the fact that the presence of OM might, to a significant degree, influence reactions between clay minerals and pore waters, in particular in high pH environments. Wattel-Koekkoek (2002) stated that the sorption of OM would render the clay surface hydrophobic, resulting in its passivation. Reduced reactivity modifies clay minerals stability and their transformation into new phases. This aspect needs to be considered not only when clay is used as a backfill material for nuclear waste disposal or as waste water barrier where clay minerals are in direct contact with high-pH alkali-rich solutions generated by water-induced concrete alteration (Wilson et al., 2006), but also in the case of soil stabilization using lime or cement (Lunt, 1980). Reduced mineral reactivity in the presence of OM might also have implications in the alkaline treatment of clays at high pH, a novel treatment method proposed by the authors for the consolidation of earthen architecture (Elert et al., 2008).

According to Cornejo and Hermosin (1996) humic substances are the main components of soil OM interacting with the soil inorganic

components (i.e., clays) and forming organo-mineral complexes. Conventionally, humic substances are divided according to their solubility characteristics: (i) humic acid is not soluble under acidic conditions but is soluble in alkali; (ii) fulvic acid is soluble in acid and alkali; (iii) humin is not soluble in acid and alkali.

The chemical weathering of minerals, including clay minerals, at low pH by organic acids has been studied extensively and increased mineral dissolution is often reported as a result of the formation of metal-organic complexes or the catalytic effect of organic acids on proton promoted mineral dissolution (Huang and Keller, 1971; Ganor et al., 2009). However, interactions depend on the organic acid species. Chin and Mills (1991) determined that low molecular weight organic ligands increased kaolinite dissolution rate, whereas humic acid inhibited dissolution. The inhibiting effect of humic acid is not surprising, considering its insolubility under acidic conditions. At high pH, some humic substances, especially those being insoluble in alkaline solutions, might exert a similar dissolution inhibiting effect by causing the passivation of the mineral surface. Claret et al. (2002) studied the reactivity of clay minerals from the Callovo-Oxfordian formation which is considered a potential host for nuclear waste storage. The authors detected very limited mineral transformation of these clays under high pH conditions which they associated with the presence of OM. Furthermore, Lunt (1980) suggested that the presence of OM inhibited the setting of cement or impaired pozzolanic reactions when lime was used for the stabilization of soils. Thompson (1967) also observed a retardation of pozzolanic reactions in lime-stabilized soils containing more than 1 wt.% OM which he attributed to a “masking effect” of OM and/or an organic matter chelation reaction. Despite the previous studies, information on the

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inhibiting effect of OM on the dissolution of clay minerals is very limited and no attempt has been made so far to directly compare the mineralogical evolution (i.e. dissolution and transformation) of clay minerals in contact with highly alkaline solutions in the presence and absence of OM.

Here, the outcome of a laboratory study is presented which was conducted in order to evaluate the suitability of an alkaline treatment for the consolidation of earthen architecture by reducing the soils swelling capacity. In contact with highly alkaline solutions clay minerals dissolve and transform into non-expandable reaction products (i.e., zeolites) which have cementing properties and improve water resistance and mechanical strength of the earthen material (Elert et al., *in press*). However, a preliminary study showed that transformation was very limited, possibly as a result of the presence of OM (Elert et al., 2008). In order to determine the effect of OM on the clay minerals reactivity one batch of soil was treated with H₂O₂ to remove OM prior to the alkaline treatment and its mineralogical evolution was compared to that of a batch of the same soil containing OM. The direct comparison of the mineralogical evolution of soil from the Alhambra Formation with and without OM exposed to high pH conditions is presented here which allows the determination of a global retardation effect on the dissolution and transformation of clay minerals exerted by OM.

The soil chosen in this study was collected from the Alhambra Formation in Granada, Spain. This soil was used historically for the construction of earthen architecture such as the historic city walls and the Alhambra fortress (de la Torre et al., 1996; Ontiveros et al., 1999). It contains illite, kaolinite and interstratified illite–smectite as main clay minerals, with minor amounts of paragonite and chlorite. A bibliographic review of the mineralogical composition of earthen constructions revealed that these minerals, maybe with the exception of paragonite which is a mineral of rather rare occurrence, are the most common in the majority of earthen structures around the world (Houben and Guillaud, 1994). This is not surprising since they are also the most common clay minerals in soils (Velde, 1992). Thus, the results of this study will be relevant to many applications using common clayey soils in contact with alkaline solutions.

2. Materials and methods

2.1. Materials

Soil samples were taken from the Alhambra Formation in close proximity to the Alhambra Fortress, Granada (Spain). The Alhambra Formation outcrops at the east margin of the Granada Basin and constitutes a good example of a fluvial (delta-fan) debris-flow deposit from the Pleistocene–Early Pliocene age (Martin, 2000). The clay-rich soil samples were taken from the upper horizon of the Alhambra Formation and constitute a typical example of Mediterranean red soils (Martin-Garcia et al., 1998). Carbonates were eliminated using acetic acid (0.2 N) and the clay fraction (<2 μm) was separated by centrifugation (Kubota KS-8000). Semiquantitative X-ray analysis of oriented aggregates showed that the <2 μm fraction was composed of 45 ± 5% illite, 30 ± 5% kaolinite, 15 ± 5% smectite/interstratified illite–smectite and <10% paragonite and chlorite. TEM-AEM data revealed the beidellitic character of smectites. Deconvolution of the diffractogram of the oriented aggregate after an ethylene glycol treatment suggested the presence of an illite–smectite interstratification of variable proportions, dominated by smectite-rich phases. For a complete mineralogical characterization of the Alhambra Formation soil see Elert et al. (2008).

Prior to alkaline treatment, the OM of one batch of the clay was eliminated using hydrogen peroxide. The clay dispersion (10 g/10 ml H₂O) was mixed at room T (20 °C) with 50 ml of 20% H₂O₂ (wt/wt) solution and stirred until frothing subsided. The treatment was repeated twice. Afterwards the sample was washed with deionised water.

Note that we will refer to samples treated with H₂O₂ prior to alkaline activation as samples without OM, while samples not treated with H₂O₂ prior to alkaline activation will be referred to as samples with OM.

For the alkaline treatment, 5 g of the clay fraction was mixed with 100 ml of 5 M NaOH or 5 M KOH solution. The starting pH of the NaOH and KOH solutions was >13. Samples of the alkaline-treated clay suspensions were kept in air-tight polyethylene bottles at room T. The bottles were shaken periodically and aliquots were collected after 1 day, 2 weeks, 4, 6 months, 1 and 6 years. Dispersed clay samples (3 ml) were washed with deionised water until a pH of 7 was reached. After decanting excess water, oriented aggregates (OA) were prepared and dried at room T.

2.2. Methods

The amount of OM was determined using thermogravimetric analysis (TG) on a Shimadzu TGA-50H coupled with Fourier transform infrared spectroscopy (FTIR; Nicolet 550) for evolved gas analysis. Analyses were performed in flowing air (100 ml/min) and at a constant heating rate of 20 °C min⁻¹ (25–950 °C). One analysis per sample was performed.

Elemental analysis of nitrogen, carbon and hydrogen was performed to verify the organic carbon content using a Fisons Carlo Erba EA 1108 CHNS-O equipped with TCD detection system. The samples were heated to 1020 °C during 800 s and calculations were carried out employing Eager 200 software. One analysis per sample was performed.

The mineralogical evolution of the clay fraction of the Alhambra Formation soil upon alkaline treatment was determined by means of X-ray diffraction (XRD). XRD patterns of oriented aggregates (OA) were collected using a X'Pert PRO diffractometer (PANalytical B.V.) equipped with Cu-Kα radiation; Ni filter; 45 kV voltage; 40 mA intensity; spinner; exploration range of 3° to 60° 2θ and goniometer speed of 0.05° 2θ s⁻¹.

The morphology and composition of the clay fraction and the new phases formed during the alkaline treatment were studied by means of field emission scanning electron microscopy (FESEM, AURIGA, Carl Zeiss SMT) coupled with EDS microanalysis (INCA-200, Oxford) as well as transmission electron microscopy (TEM, Philips CM20, CIC-UGR) operated at 200 kV and equipped with an EDAX solid-state ultra-thin window energy dispersive X-ray (EDS) detector.

Nitrogen sorption isotherms of powdered clay samples before and after alkaline treatment were obtained at 77 K on a TriStar 3000 (Micromeritics). About 0.2 g of sample was degassed at 150 °C for 3 h prior to analysis using a sample degas system (VacPrep 061, Micromeritics). Two analyses per sample were performed.

3. Results

3.1. Determination of OM content in Alhambra Formation soil (<2 μm fraction) using TG coupled with FTIR for evolved gases and elemental analysis

The major weight loss observed during TG analysis in the H₂O₂-treated and in the untreated soil samples can be attributed to adsorbed and structural water of clay minerals (Fig. 1). The sample with OM showed a more pronounced weight loss between 300 and 500 °C, the temperature range commonly associated with the thermal decomposition of OM (Boyle, 2004). The difference in weight loss between the untreated samples and the samples treated with H₂O₂ was 1.1 wt.%, which is attributed to the OM content.

The evolved gas spectrum taken at 356 °C of the clay sample treated with H₂O₂ did not show any detectable amounts of CO and only a small amount of CO₂, whereas the spectrum of the untreated clay sample revealed the presence of CO in addition to a much larger amount of CO₂ (Fig. 2). These results suggest that the H₂O₂ treatment was effective in destroying OM. The release of a small amount of CO₂ in the sample

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