Available online at www.sciencedirect.com

ScienceDirect

Applied Clay Science 39 (2008) 122–132

Applied Clay Science

www.elsevier.com/locate/clay

# Alkaline treatment of clay minerals from the Alhambra Formation: Implications for the conservation of earthen architecture

K. Elert [a], E. Sebastián [a], I. Valverde [b], C. Rodriguez-Navarro [a,*]

[a] *Dpto. Mineralogía y Petrología, Universidad de Granada, Fuentenueva S/N, 18002 Granada, Spain*
[b] *Dpto. Construcciones Arquitectónicos, Universidad de Granada, Avda. Severo Ochoa S/N, 18071 Granada, Spain*

Received 22 February 2007; received in revised form 3 May 2007; accepted 10 May 2007
Available online 2 June 2007

## Abstract

Clay–water interactions result in damage and loss of earthen architecture. Natural and artificial additives were traditionally added to earth in order to increase its water resistance and mechanical strength. More recently, portland cement, ethyl silicates and synthetic resins have been applied to consolidate earthen structures, however often with limited success. Here, in an effort to design a more effective procedure for the *in situ* consolidation of earthen architectural remains, the alkaline reaction of clay-rich earth used in the construction of the Alhambra (Spain) was studied. Alhambra Formation clays were treated with diluted $Ca(OH)_2$, NaOH and KOH solutions. The most sensitive smectite fraction was rapidly destroyed after alkaline treatment. Furthermore, NaOH and KOH treatments resulted in the formation of interstratified illite–smectite, the partial destruction of both expandable and non-expandable clays, and their transformation into poorly-crystalline alkali aluminosilicates and calcium silicate hydrates, the latter two exhibiting cementing properties. These preliminary results suggest that alkaline activation might be efficient in stabilizing earthen architecture, as well as other clay-rich building and ornamental materials by reducing the intracrystalline swelling capacity of smectites, limiting osmotic swelling of both expandable and non-expandable clays, and producing gel-like silicate cements. However, further research and field tests will be necessary to study the effectiveness of the treatment *in situ*.

*Keywords:* Clay; Alkaline treatment; Conservation; Earthen architecture

## 1. Introduction

In industrial or engineering applications such as backfill for nuclear waste disposal or waste water barrier, the swelling capacity of clays is a desirable feature (Wilson et al., 2006). However, in the case of earthen architecture clay swelling in the presence of water is one of the most important factors of deterioration (Houben and Guillaud, 1994). Two types of clay swelling can be distinguished: a) intracrystalline swelling which only occurs in expandable clays (e.g., smectite); and b) osmotic or interparticle swelling which takes place in any clay when water saturated, and may eventually lead to total structural failure (Rodriguez-Navarro et al., 1998).

Man has used earth as a primary building material since prehistory. As a result, the volume and significance of earthen architecture is enormous and includes

---

* Corresponding author. Tel.: +34 958 246616; fax: +34 958 243368.
*E-mail address:* carlosrn@ugr.es (C. Rodriguez-Navarro).

0169-1317/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.clay.2007.05.003

invaluable archaeological remains such as Chan Chan in Peru or the Alhambra in Spain. Traditionally, natural and artificial materials such as dung, animal blood, or slaked lime were added to earth in order to increase its water resistance and mechanical strength (Lunt, 1980), and over the last decades many efforts have been undertaken to develop conservation treatments to protect, consolidate and strengthen earthen structures subjected to weathering phenomena. Polyvinyl alcohol, ethyl silicates, epoxy and acrylic resins and Portland cement have been used for the *in situ* consolidation of earthen architectural remains with often limited success (Armbrust and Dickerson, 1971; Chiari, 1990; Houben and Guillaud, 1994). Therefore, the development of an effective conservation treatment for earthen architecture is still an important need as has been also indicated by a recent survey (Palumbo et al., 1999).

Here, in an effort to design an effective procedure for the *in situ* consolidation of earthen structures (e.g., rammed earth and adobe), mineralogical changes of clay-rich materials induced by alkaline treatment were studied. A clay-rich soil used in southern Spain's earthen architecture (i.e., the Alhambra, Granada) was selected as a model material for alkaline treatments.

Reaction products of clays or other reactive aluminosilicates treated with highly alkaline solutions, often referred to as geopolymers, alkali-activated cement or hydroceramics, have been described as zeolite-like poorly-crystalline or amorphous alkali aluminosilicates, with strong cementing properties (Palomo and Glasser, 1992; Davidovits, 1994; Roy, 1999; Palomo et al., 2004; Provis et al., 2005). Their compositional and structural similarities with zeolites make these cements very stable under earth surface conditions (Deer et al., 1963).

NaOH and KOH are commonly used as alkaline activators. Traditionally, $Ca(OH)_2$ has also been used. For instance, the superior resistance of Roman cements is thought to be due to puzzolanic reactions undergone by brick dust or thermally activated clays in the presence of lime (Da Silva and Glasser, 1992; Roy, 1999).

However, the reaction of clays with lime solutions at ambient temperature results in limited formation of calcium silicate hydrates (CSH) (Eades and Grim, 1960), imparting little consolidation effect to soils or earthen materials, as demonstrated by laboratory tests and field applications (Attoh-Okine, 1995; Roger and Glendinning, 1997; Rajasekaran et al., 1997; Kinuthia et al., 1999; Mohamed, 2000; Rao et al., 2001).

Although there is considerable evidence regarding the transformation of clay minerals in highly alkaline NaOH and/or KOH solutions to form zeolite-like poorly-crystalline phases (Mosser-Ruck and Cathelineau, 2004; Viellard et al. 2004; Ramirez et al. 2005), such treatments were typically performed at relatively high *T* (>50 °C), over a short period of time (Drief et al., 2002; Mosser-Ruck and Cathelineau, 2004). Thus, little is known about reactions products formed at low *T*, a crucial factor in the treatment of earthen architecture materials.

We studied the alkaline reactions undergone by clay-rich soil activated with $Ca(OH)_2$, NaOH and KOH at room temperature leading to a partial destruction of clays and the precipitation of new phases including zeolite-like cements. These results suggest that this technology could be a method to efficiently stabilize and, possibly, consolidate earthen architecture *in situ*.

## 2. Methodology

### 2.1. Clay material and alkaline activation

Previous studies on the Alhambra earthen structures enabled the identification of the earth sources in the nearby hills (Alhambra Formation; De la Torre et al., 1996). Samples of this type of earth were collected and carbonates were eliminated using acetic acid (0.2 N). The fraction $\varnothing<2$ μm (i.e., clay fraction) was separated by centrifugation (Kubota KS-8000). Oriented aggregates (OA) were prepared by depositing concentrated clay dispersions on glass slides. Once dried, and prior to X-ray diffraction (XRD) analysis, OA were submitted to ethylene glycol (EG) and dimethyl sulfoxide (DMSO) solvation, as well as to thermal treatment (at 550 °C for 4 h), following standard procedures in clay mineralogy analysis (Moore and Reynolds, 1989). The bulk clay fraction was subjected to alkaline activation at room *T*. 5 g of clay were added to 100 mL solution of: a) 0.024 M $Ca(OH)_2$ (i.e., saturated solution at room *T*; Boynton, 1980); b) 0.382 M NaOH; and c) 0.386 M KOH. Samples of the alkaline-treated clay suspensions were collected at predetermined time intervals, i.e., 1, 3, 7, 14, 45, 60, 150, and 360 days, and deposited on glass slides to prepare OA. Once dry, they were subjected to further analysis (see below).

### 2.2. Analysis of clay materials and reaction products

The clay-rich Alhambra Formation soil (whole sample) was analyzed by means of powder XRD. In the case of the clay fraction, before and after alkaline activation, oriented aggregates (OA) were used for analysis. XRD patterns were collected using a Phillips PW 1547 diffractometer with Cu-Kα radiation ($\lambda=1.5418$ Å); exploration range 3° to 60° $2\theta$; steps of 0.028 °$2\theta$; and goniometer speed of 0.01 °$2\theta s^{-1}$. Semi-quantitative XRD analysis of clay minerals was performed following correction of raw intensity values with reference intensity ratios determined using the internal-standard method (Klug and Alexander, 1967). The morphology and composition of both clay-fraction and reaction products of the alkaline treatment were studied by means of field emission scanning electron microscopy (FESEM; Leo Gemini 1530) coupled with EDX microanalysis (INCA-200, Oxford). Prior to FESEM analysis, samples were carbon-coated for compositional (qualitative) analyses and textural studies. Compositional changes were also examined using a transmission electron microscope (TEM, Philips CM20) equipped with an EDAX solid-state ultrathin-window energy dispersive X-ray (EDX) detector. The acceleration voltage of the microscope was 200 kV and a lens aperture of 40 µm was used as a compromise between amplitude and phase contrast for the images. The identification of new phases was facilitated collecting SAED (selected area electron diffraction) patterns. Quantitative analytical electron microscopy (AEM) analyses were performed in scanning TEM mode using a 10 nm diameter beam and 20 × 100 nm scanning area. A low-background condenser aperture and an analytical Be sample holder were employed to improve spectrum quality. Ms, Ab, Bt, Sps, Ol, Ttn, KFds and $CaSO_4$-$MnSO_4$ standards were used to obtain *k*-factors allowing X-ray intensities to be corrected by the thin-film method (Lorimer and Cliff, 1976). Average errors for analyzed elements expressed as a percentage of atomic proportions are 6 (Na), 3 (Mg), 2 (Al), 4 (K), 4 (Ca), 5 (Ti), 3 (Mn), and 3 (Fe). Errors due to K and Na loss during AEM analysis were corrected by determining K and Na at 15–30 and 100 s beam-exposure time and scaling K and Na concentrations back to zero seconds as described by Worden et al. (1987). Prior to TEM analysis samples were dispersed in ethyl alcohol and deposited on Formvar© and carbon-film coated gold grids instead of copper grids to avoid overlapping of the *K* band of Na and the *L* band of Cu (Drief et al., 2001). The pH evolution during the alkaline attack was monitored using a pH-meter Stick Piccolo HI 1280 (Hanna Instruments).

## 3. Results and discussion

### 3.1. Mineralogy of the raw material

Powder XRD analysis of the whole sample shows that the earth from the Alhambra Formation, which was used for the construction of the Alhambra fortress, is composed of quartz and phyllosilicates, with small amounts of feldspars, calcite and iron oxihydroxides (goethite and, possibly, lepidocrocite). The latter are responsible for the red colour of the clay and the Alhambra fortress (al-Hamrá = the red; De la Torre, 1994). XRD analysis of OA shows that the clay fraction includes about 45% illite ($d_{001}$ = 9.98 Å), 30% kaolinite ($d_{001}$ = 7.14 Å), 15% smectites ($d_{001}$ = 12.5–14 Å) with minor amounts (< 10%) of paragonite ($d_{001}$ = 9.60 Å), and possibly a small amount of mixed-layer illite/smectite as evidenced by the shifts of $d_{001}$ reflections following EG, DMSO and heat (550 °C) treatments (Fig. 1).

### 3.2. Analysis of the treated clays

In all cases, XRD analysis of the clay fraction evidences the disappearance of smectites after alkaline treatments for short periods of time (i.e., disappearance of the 12.5–14 Å broad Bragg peak). No further significant mineralogical changes were observed after one year treatment with saturated $Ca(OH)_2$ solution. Following NaOH treatment for 1 year, the intensity of the kaolinite and illite 001 Bragg peaks was significantly

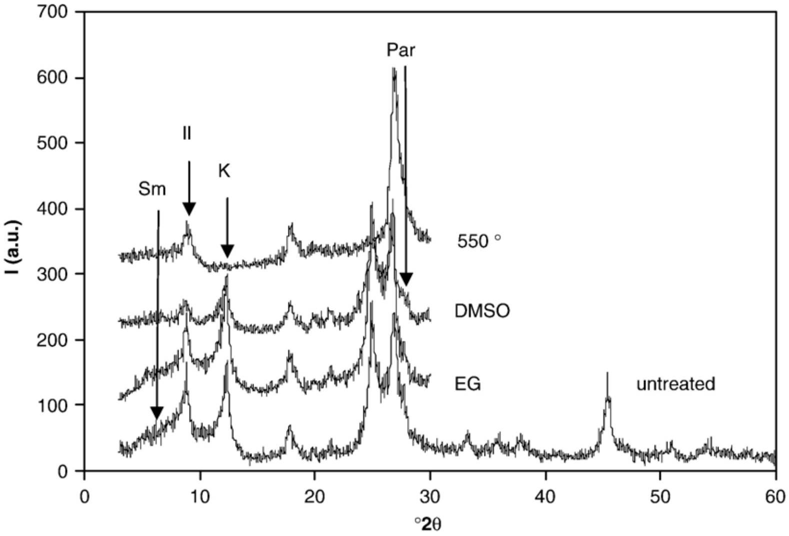

Fig. 1. XRD patterns of Alhambra Formation clays (OA). Legend: Il: illite; K: kaolinite; Sm: smectites; Par: paragonite.

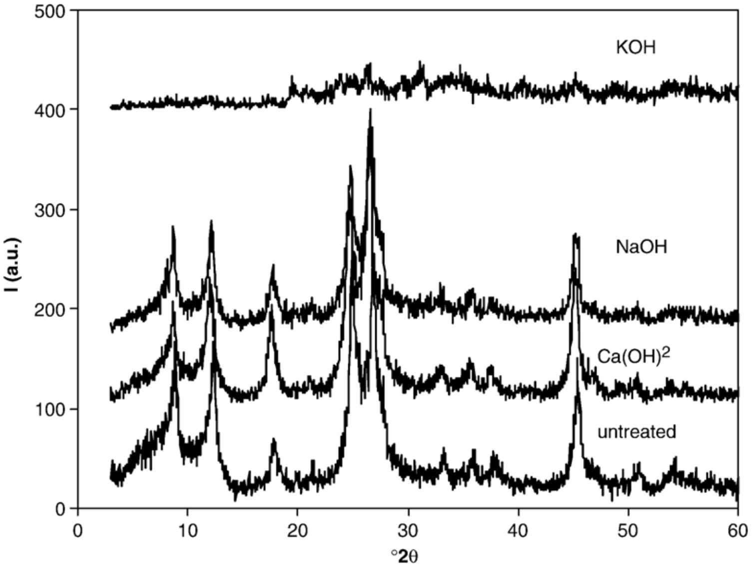

Fig. 2. XRD patterns of Alhambra Formation clays (OA) treated with $Ca(OH)_2$, NaOH and KOH for one year.

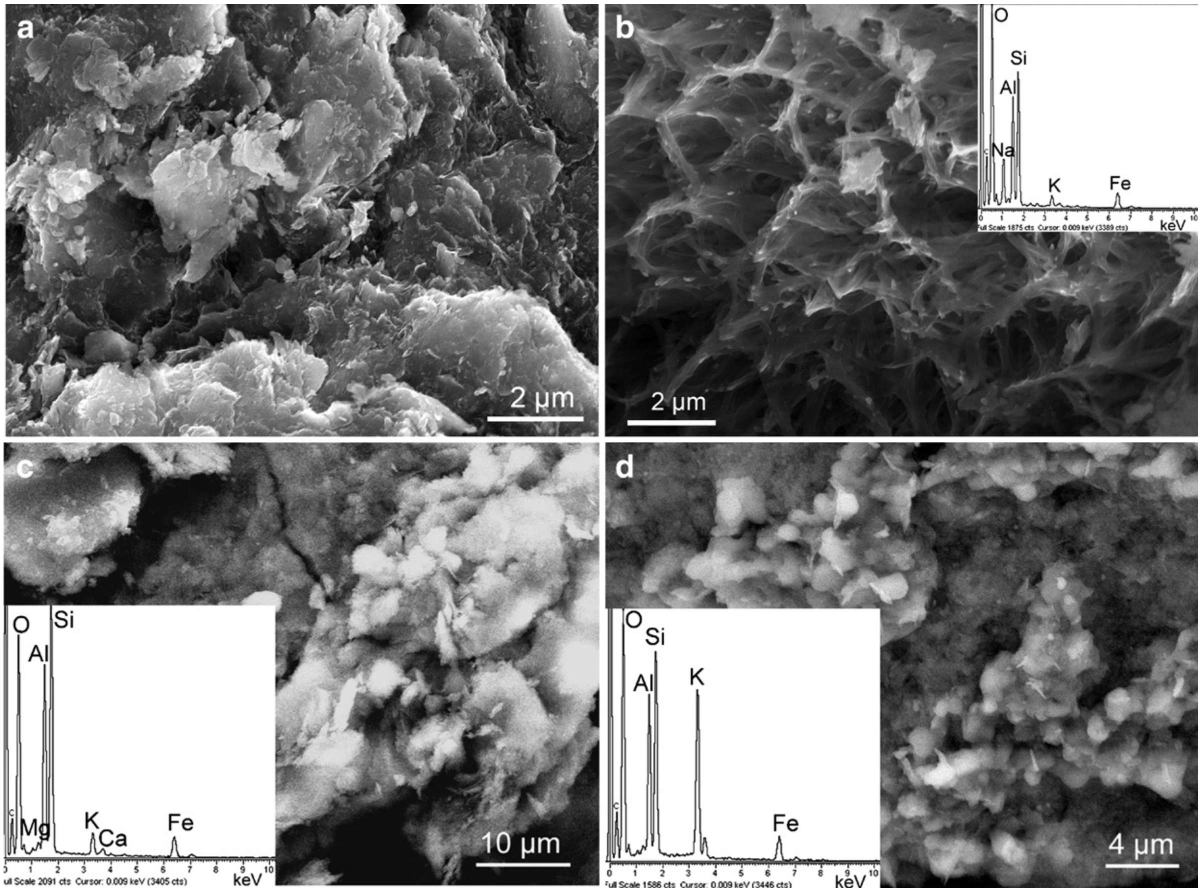

Fig. 3. FESEM photomicrographs of: a) untreated clays; b) clays treated (one year) with $Ca(OH)_2$; c) newly formed Na-zeolite-like phases after one year NaOH treatment; and d) newly formed K-Al-silicate phases after one year KOH treatment. Insets show EDX spectra.

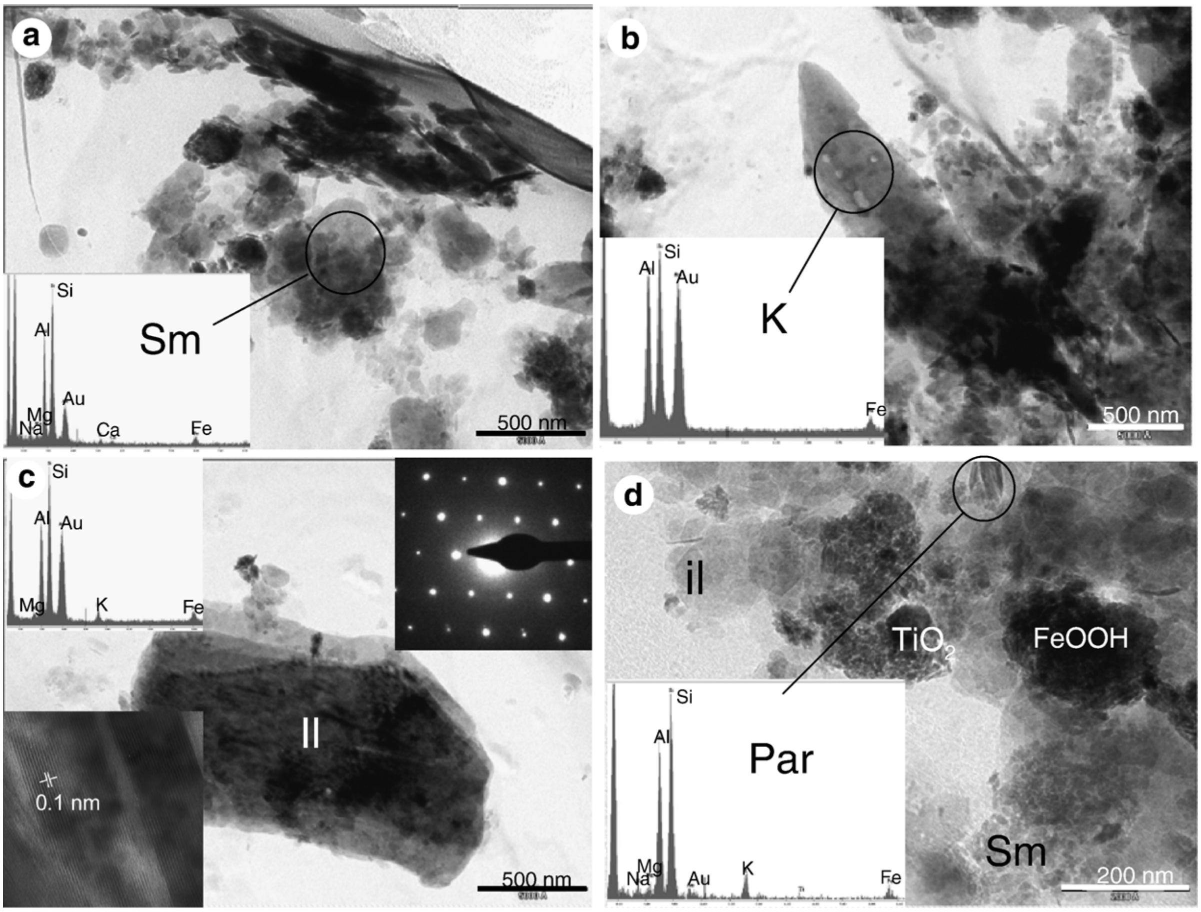

Fig. 4. TEM images of untreated Alhambra Formation clays: a) smectites (Sm) (EDX spectrum in inset); b) kaolinite (K) identified by EDS (inset); c) illite (Il), identified by SAED (inset, upper-right corner), EDX spectrum (inset, upper-left) and TEM high-resolution lattice-finger image showing $d_{001}=0.1$ nm (inset, lower-left); and d) paragonite (Par; see EDX in inset), along with Il, Sm, goethite (α-FeOOH) and rutile ($TiO_2$).

reduced, evidencing the partial destruction of these phases. Similar peak intensity reduction upon alkaline treatment has been reported elsewhere (Ferrage et al., 2005). In the case of KOH solution, one year treatment caused an almost complete destruction of the phyllosilicates, resulting in a poorly-crystalline material. Although some peaks not corresponding to the clay minerals were detected, XRD analysis did not allow unambiguous identification of newly formed phases due to the high background noise (Fig. 2). Formation of poorly-crystalline or amorphous phases upon high pH treatment of clays as indicated by the high background noise has been reported previously (Drief et al., 2001). Provis et al. (2005) relate a featureless broad hump at 27–29° 2$\theta$, a characteristic which can be observed in the case of clays treated with KOH (Fig. 2), to the presence of nanocrystalline zeolite precursors immersed in an amorphous aluminosilicate gel phase. The hump at 27–29 °2$\theta$ appears to correspond to short-range order in Si–Si bonds (ca. 3.2 Å).

FESEM analyses yielded a high magnification picture of the transformation undergone by the clay minerals following alkaline treatments for one year (Fig. 3). Furthermore, EDX microanalyses helped us to disclose the composition of the newly formed phases that were not clearly identified by XRD. FESEM analyses confirmed that $Ca(OH)_2$ produces little morphological or chemical changes in the clays, although a few granular or flake-like Ca-aluminosilicates were detected (Fig. 3b). This newly formed phase is assumed to be a tobermorite-type CSH gel. CSH gels typically form upon $Ca(OH)_2$ treatment of clays (Diamond et al., 1964). Traditionally, hydrated lime has been used as an additive for soils and earthen structures stabilization (Houben and Guillaud, 1994) for two reasons: a) $Ca(OH)_2$ carbonation results in the precipitation of $CaCO_3$;

Table 1
Representative structural formulae of clay minerals of the Alhambra Formation calculated from TEM-AEM data

| Analysis | Si | $^{IV}Al$ | $^{VI}Al$ | Mg | Fe | Σ Oct. cat.[a] | K | Ca | Na | Σ Int. cha.[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| Structural formulae of illite based on 11 oxygens | | | | | | | | | | |
| 1 | 3.01 | 0.99 | 1.52 | 0.17 | 0.57 | 2.27 | 0.57 | – | – | 0.57 |
| 2 | 3.02 | 0.98 | 1.79 | 0.08 | 0.36 | 2.24 | 0.33 | – | – | 0.33 |
| 3 | 3.27 | 0.74 | 1.84 | 0.29 | 0.04 | 2.17 | 0.48 | – | – | 0.48 |
| 4 | 3.13 | 0.86 | 1.93 | 0.15 | 0.14 | 2.22 | 0.42 | – | – | 0.42 |
| Structural formulae of smectite based on 11 oxygens | | | | | | | | | | |
| 1 | 3.60 | 0.40 | 1.60 | 0.17 | 0.02 | 2.03 | 0.13 | 0.06 | – | 0.25 |
| 2 | 3.60 | 0.40 | 1.57 | 0.24 | – | 1.98 | 0.39 | – | 0.16 | 0.55 |
| 3 | 3.83 | 0.17 | 1.82 | 0.12 | – | 2.06 | 0.05 | – | 0.13 | 0.18 |
| 4 | 3.68 | 0.32 | 1.48 | 0.24 | – | 2.14 | 0.29 | – | – | 0.29 |
| 5 | 3.56 | 0.44 | 1.52 | 0.63 | – | 2.34 | 0.14 | – | – | 0.14 |
| Structural formulae of paragonite based on 11 oxygens | | | | | | | | | | |
| 1 | 3.17 | 0.83 | 1.89 | 0.12 | – | 2.10 | 0.07 | – | 0.63 | 0.70 |
| 2 | 3.33 | 0.67 | 1.76 | 0.21 | – | 2.11 | 0.07 | 0.05 | 0.44 | 0.61 |

Structural formulae of kaolinite based on 7 oxygens

| | Si | Al | Mg | Fe |
|---|---|---|---|---|
| 1 | 2.02 | 1.75 | – | 0.23 |
| 2 | 2.09 | 1.78 | – | 0.11 |
| 3 | 2.15 | 1.65 | 0.14 | 0.06 |
| 4 | 2.23 | 1.60 | 0.07 | 0.06 |
| 5 | 2.08 | 1.78 | 0.11 | 0.06 |
| 6 | 2.10 | 1.59 | 0.10 | 0.24 |
| 7 | 1.99 | 1.94 | – | 0.06 |

–Below detection limit.

[a] Sum of octahedral cations.

[b] Sum of interlayer charge.

and b) puzzolanic reactions between clay minerals and $Ca(OH)_2$ can result in the formation of Ca-silicate hydrates (Eades and Grim, 1960), both phases having cementing properties. However, our results show that puzzolanic reactions are very limited at room temperature. This is most probably due to the very low solubility of calcium hydroxide (Boynton, 1980) and the comparatively low pH achieved during treatment (see below), which may explain why the application of $Ca(OH)_2$ solutions has a limited effect on the *in situ* consolidation of earthen structures or clay-rich soils (Rao et al., 2001).

NaOH treatment resulted in the formation of Na-aluminosilicate phases, showing morphologies quite different from those of untreated clays (Fig. 3c). The fractal-like porous structure of these newly formed Na-aluminosilicates closely resembles poorly-crystalline CSH gels formed after $Ca(OH)_2$ treatment of thermally activated kaolinite and montmorillonite (Liebig and Althaus, 1997). Qualitative microanalyses reveals a chemical similarity with hydroxysodalite ($Na_6Al_6Si_6O_{24}\cdot H_2O$). Palomo and Glasser (1992) and Baccouche et al. (1998) reported hydroxysodalite formation following NaOH treatment of metakaolin and interstratified illite–smectite, respectively. Hydroxysodalite has also been detected following NaOH treatment of fly ashes (Querol et al., 2001).

KOH treatment led to the formation of micronsized potassium aluminosilicate phases with a spherulitic morphology (Fig. 3d). It is assumed that such newly formed phases include K-rich zeolites as well as amorphous phases. Potassium aluminosilicates with similar composition and morphology have been observed in fly ash samples activated with KOH (Palomo et al., 2004).

TEM analyses confirmed XRD and FESEM results regarding the mineralogy of the Alhambra Formation clays. Smectites (Fig. 4a), kaolinite (Fig. 4b), illite (Fig. 4c) and small amounts of paragonite (Fig. 4d) were observed. Table 1 shows selected structural formulae (determined form AEM results) of the main clay minerals in the Alhambra Formation. Small amounts of goethite and rutile were also observed (Fig. 4d). In addition, TEM analyses allowed the identification of phases formed after one year alkaline treatment (Fig. 5).

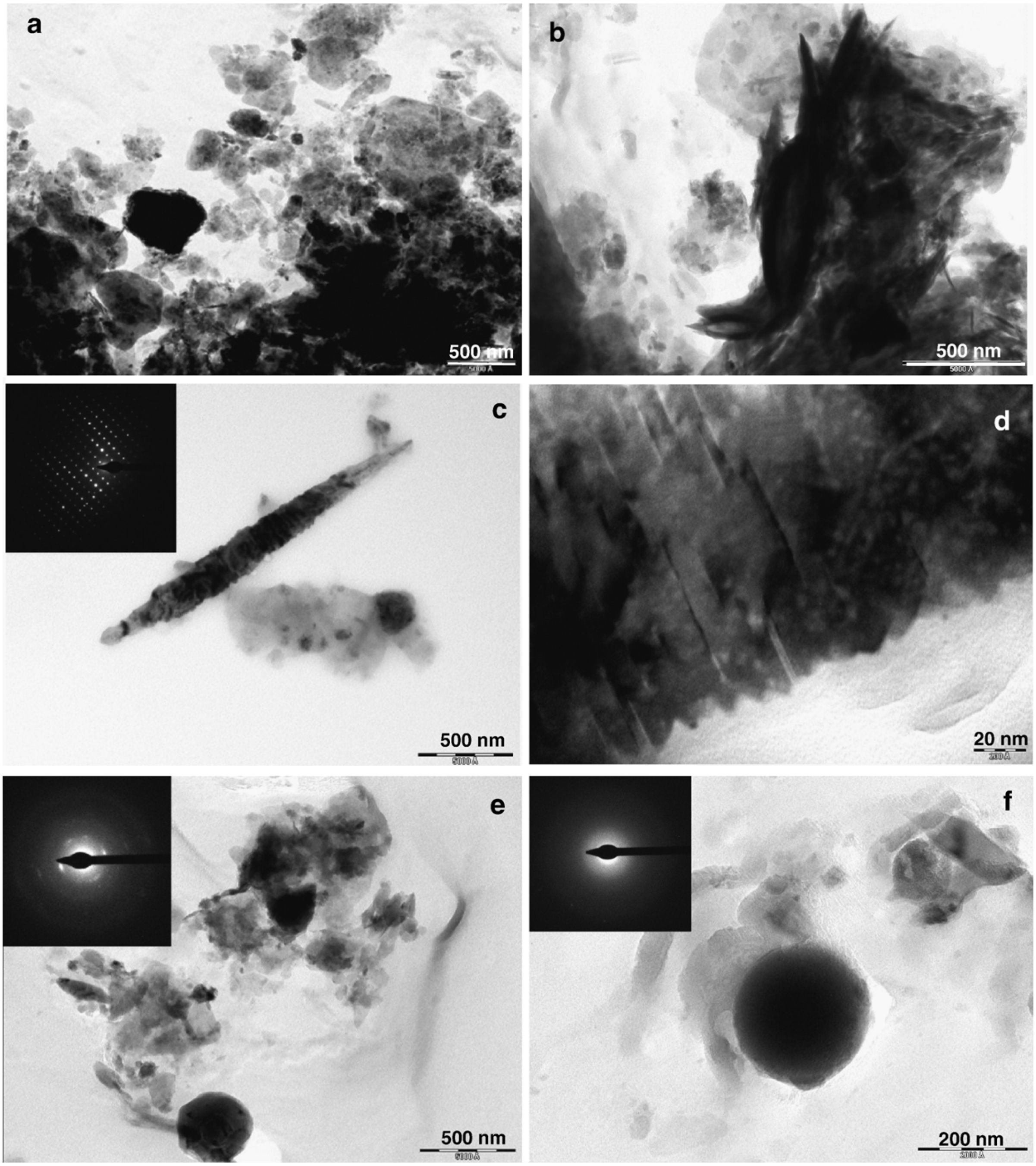

Fig. 5. TEM images of clay after 1 year treatment: a) with $Ca(OH)_2$, showing reduction of smectite particles with size <100 nm; b) with NaOH showing newly formed Na-aluminosilicates composed of fibrous aggregates; c) with NaOH, newly formed crystalline, fibrous phase similar to foshagite (see SAED in inset showing reflections at: $d_{311} = 0.27$ nm, and $d_{004} = 0.33$ nm); d) detail of (c) showing an oriented aggregate of prismatic foshagite nanocrystals; e) treated with KOH, newly formed interstratified illite–smectite and a sphere-shaped, poorly-crystalline phase (see SAED in inset) chemically similar to magnesium smectite; and f) with KOH, sphere-shaped, amorphous phase rich in Si (see diffuse halos in SAED pattern, inset).

The $Ca(OH)_2$ treatment caused little changes in clay mineralogy and the presence of newly formed granular or flake-like Ca-aluminosilicates detected with FESEM could not be unambiguously confirmed using TEM. However, a reduction of the amount of smectite particles <100 nm could be detected (Fig. 5a).

Table 2
Structural formulae based on 11 oxygens of a newly formed fibrous phase (similar to foshagite) after NaOH treatment for one year (see Fig. 5c)

| Analysis | Si | Al | Mg | Ca | Na |
|---|---|---|---|---|---|
| 1 | 1.13 | 0.05 | 0.23 | 2.95 | – |
| 2 | 1.10 | 0.05 | 0.18 | 3.05 | – |
| 3 | 1.28 | 0.03 | 0.15 | 2.74 | – |
| 4 | 1.07 | 0.04 | 0.30 | 2.98 | – |
| 5 | 0.96 | 0.03 | 0.11 | 3.29 | 0.28 |

– Below detection limit.

In the case of the NaOH treatment, several newly formed fibrous phases were observed with the TEM. Fig. 5b shows a Na-aluminosilicate composed of fibrous aggregates. Textural and compositional similarities with the newly formed phase observed using FESEM (Fig. 5c) are evident. SAED patterns (see inset in Fig. 5c) and AEM microanalyses (Table 2) enabled the identification of another fibrous phase as CSH, with a Ca/Si ratio similar to that of foshagite ($Ca_5Si_3O_{11}{\cdot}3H_2O$). A detail (Fig. 5d) of this fibrous phase revealed a palisade structure formed by an aggregate of isooriented nanoparticles. Formation of micronsized crystals by oriented aggregation of nanoparticles (Penn and Banfield, 1998) appears to be a dominant growth mechanism in colloidal systems (Penn et al., 1991) as well as in microbial biomineralization (Rodriguez-Navarro et al., 2007). Such a mechanism is an efficient alternative for classical crystal growth which takes place via incorporation of grow units (atoms or molecules) on crystal faces. In contrast, in far-from-equilibrium highly supersaturated systems, a high nucleation density may result in the formation of numerous nanocrystals that eventually may aggregate in an oriented fashion (Penn et al., 1991; Rodriguez-Navarro et al., 2007), as observed here. Recently, Davis et al. (2006) have shown that zeolite phases can form via oriented aggregation of nanosized aluminosilicate precursors.

Table 3
Structural formulae based on 11 oxygens of newly formed phase (similar to interstratified illite-smectite) after KOH treatment for one year (see Fig. 5e)

| Analysis | Si | $^{IV}$Al | $^{VI}$Al | Mg | Fe | Σ Oct. cat. [a] | K | Na | Σ Int. cha. [b] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 3.55 | 0.45 | 1.51 | 0.25 | 0.30 | 1.77 | 0.47 | 0.23 | 0.70 |
| 2 | 3.59 | 0.41 | 1.74 | 0.12 | 0.23 | 2.09 | 0.33 | 0.09 | 0.42 |
| 3 | 3.45 | 0.55 | 1.59 | 0.20 | 0.28 | 2.07 | 0.58 | 0.09 | 0.67 |
| 4 | 3.26 | 0.74 | 1.30 | 0.16 | 0.58 | 2.04 | 0.72 | 0.20 | 0.92 |

– Bellow detection limit.

[a] Sum of octahedral cation.

[b] Sum of interlayer charge.

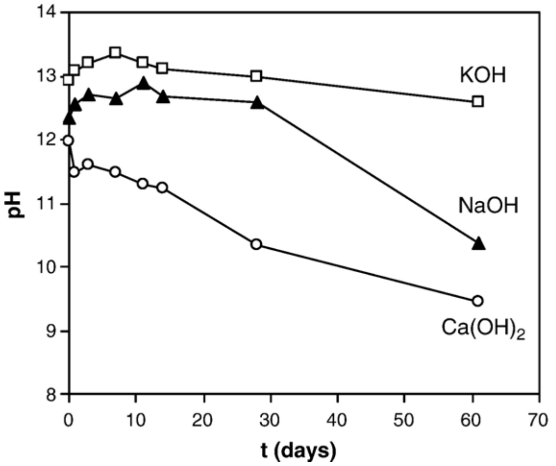

Fig. 6. pH evolution during alkaline treatments.

TEM analyses also showed that the KOH treatment caused important mineralogical changes in the clay fraction. A massive presence of K-aluminosilicates of planar shape was detected (Fig. 5e). Their structural formula calculated using AEM data (Table 3) show that they have a composition similar to that of mixed-layer illite–smectite observed by Drief et al. (2002) after KOH treatment of smectite. Illitization of smectites treated with KOH solution has also been reported by other authors (Bauer and Velde, 1999). Together with the interstratified clays, a spherical-shaped phase rich in Si and Mg with small amounts of K, Al and Fe was observed. Compositionally, this phase is similar to saponite, ($(Mg, Al, Fe)_3(Al, Si)_4O_{10}(OH)_2$), but with an excess in potassium. This newly formed phase is poorly crystalline (see SAED inset in Fig. 5e) and has been described as well by Ramirez et al. (2002) in the case of alkaline treated bentonite. Finally, another spherical-shapes phase, rich in Si and of amorphous structure (Fig. 5f) has been detected after KOH treatment. The composition of the amorphous structures seems to depend on the elements in solution that have not been incorporated into the surrounding crystalline phases (e.g. mixed-layer illite–smectite) after the alkaline attack. They are precipitation products of a gel formed after the dissolution of the most reactive phyllosilicates (e.g., smectites) in the clay fraction of the Alhambra Formation.

The pH evolution (Fig. 6) shows a similar trend for all three alkaline treatments. In the case of $Ca(OH)_2$, however, the pH dropped from 12 to about 10 after only 4 weeks, and further decreased to 9.5 after 2 months of treatment. NaOH and KOH solutions had a significantly higher starting pH of ~13, that was maintained over the first 4 weeks and remained above pH 10 after 2 months. The degree of alteration caused in the clay fraction of the Alhambra Formation seems to be directly related to the pH, solutions with higher pH resulting in more significant mineralogical changes. Our results are in agreement with findings by Ramirez et al. (2005) who did not observe significant changes in Callovo-Oxfordian clay treated with $Ca(OH)_2$, NaOH and KOH at pH below 12.

With respect to the pH decrease in the alkaline solutions over time, the same behaviour has been described by numerous researchers (Martinez-Ramirez et al., 1996; Ramirez et al., 2002; Mosser-Ruck and Cathelineau, 2004). It can be concluded that the alkaline solutions induce the hydrolysis and partial dissolution of clay minerals, resulting in the release of Si, Al, Mg and Fe. The increase in Al and Si concentration in solution leads to the formation of aluminol and silanol groups and thus to the acidification of the solution (Martinez-Ramirez et al., 1996; Taubald et al., 2000; Mosser-Ruck and Cathelineau, 2004; Rozalén Astudillo, 2006). Such drop in pH might lead to the eventual stop of the alkaline attack of the clay minerals.

## 4. Conclusions

Our results show that the clays from the Alhambra Formation undergo significant mineralogical and textural changes following long-term treatment with diluted alkaline solutions at room temperature. All treatments resulted in the early destruction of the expandable clays (smectites). However, NaOH and KOH solutions were more efficient than $Ca(OH)_2$ solution in promoting the destruction of other clay minerals such as kaolinite, illite and paragonite. The higher efficiency can be explained by the pH dependency of these reactions; the solubility of Si and Al being higher as pH increases (Nagy, 1995).

The higher resistance towards alkaline attack of illite compared with kaolinite and smectite has been observed by other researchers as well (Mashal et al., 2004; Ramirez et al., 2005), and has its origin in differences in the chemical composition, the nature of the surface atoms (mainly oxygen and hydrogen), the extent and type of defect sites, the layer charge and the type of exchangeable cations (Schoonheydt and Johnston, 2006). It should also be noted that the reactivity of clay particles is inversely proportional to their size (i.e., proportional to their surface area). Being the smectites the smallest phyllosilicates in the clay fraction of the Alhambra Formation, their fast and quite extensive destruction is not unexpected.

It should be emphasized that the generally low crystallinity of the newly formed phases complicates their study by standard crystallographic techniques such as XRD (Provis et al., 2005). This explains why, in general, newly formed phases were not unambiguously detected by XRD in our experiments, while FESEM and TEM analyses enabled the recognition of newly formed aluminosilicates.

These preliminary results serve as a basis for further research where alkaline solutions will be applied on actual rammed earth samples by immersion in the laboratory, and later on, *in situ*, on earthen architectural remains by spraying or brushing. This will allow us to evaluate whether the alkaline treatment could be a feasible way to stabilize the most water-sensitive components of earthen structures (i.e., the clay minerals) and to increase cementation. The laboratory results showed that all treatments led to the early destruction of the expandable clays (smectites), that are recognized to be a major contributor to the decay of earthen materials subjected to wetting/drying cycles (Houben and Guillaud, 1994). The alkaline treatments also contributed to the partial transformation of non-expandable clays. While the here proposed treatment might thus be effective in reducing damage due to intracrystalline swelling, osmotic swelling might still occur unless complete destruction/transformation of all clays (expandable and non-expandable) is achieved. Therefore, additional strategies such as sheltering or capping with a sacrificial layer to prevent water infiltrations will be required in conservation interventions (Chiari, 1990).

Our tests showed that $Ca(OH)_2$ solution had a very limited effectiveness, most probably due to the low solubility of $Ca(OH)_2$ and the resulting relatively low pH. Conversely, NaOH and KOH treatments seem to be more efficient in transforming clays into stable poorly-crystalline alkali aluminosilicates, calcium silicate hydrates or interstratified illite–smectite. The well documented cementing properties of zeolite-like phases and CSH precipitated as secondary phases in our laboratory experiments are thought to contribute to the stabilization of earthen structures (Liebig and Althaus, 1997; Van Jaarsveld et al., 1997). Such treatments might also be effective to stabilize clay-rich stones prone to decay under wet/dry cycles (Rodriguez-Navarro et al., 1998). Nonetheless, further research and field tests will be necessary to study not only the effectiveness but also possible interactions between alkaline solutions and other minerals in earthen architectural remains (e.g., carbonates, gypsum), as well as the practicality of the treatment (i.e., penetration capacity or adverse effects of the aqueous alkaline solution). Research should also be performed to evaluate potential drawbacks of the alkaline treatment due to uncompleted reaction of the alkali activators and/or formation of detrimental soluble salts such as alkali carbonates or sulfates (e.g., in polluted environments), before actual implementation of such technology in the conservation of earthen structures or ornamental stone.

## Acknowledgements

This research has been financed by the Spanish Government under contract no. MAT2003-02723, and by the research group RNM-179 (Junta de Andalucía, Spain). We thank the Centro de Instrumentación Científica of the University of Granada for their help during FESEM and TEM analyses. We would also like to thank Dr. G. Chiari y Dr. F.J. Huertas for the constructive review of our paper.

## References

Armbrust, D.V., Dickerson, J.D., 1971. Temporary wind erosion control: cost and effectiveness of 34 commercial materials. J. Soil Water Conserv. 26, 154–157.

Attoh-Okine, N.O., 1995. Lime treatment of laterite soils and gravels-revisited. Constr. Build. Mater. 9, 283–287.

Baccouche, A., Srasra, E., El Maaoui, M., 1998. Preparation of Na-P1 and sodalite octahydrate zeolites from interstratified illite-smectite. Appl. Clay Sci. 13, 255–273.

Bauer, A., Velde, B., 1999. Smectite transformation in high molar KOH solutions. Clay Miner. 34, 259–273.

Boynton, R.S., 1980. Chemistry and Technology of Lime and Limestone. John Wiley and Sons, New York.

Chiari, G., 1990. Chemical surface treatments and capping technique of earthen structures: a long-term evaluation. 6th International Conference on the Conservation of Earthen Architecture: Adobe 90 Preprints, Las Cruces, New Mexico, USA, Oct. 14–19, pp. 267–273.

Da Silva, P.S., Glasser, F.P., 1992. Pozzolanic activation of metakaolin. Adv. Cem. Res. 167–178.

Davidovits, J., 1994. Geopolymers: inorganic polymeric new materials. J. Mater. Educ. 16, 91–139.

Davis, T.M., Drews, T.O., Ramanan, H., He, C., Dong, J.S., Schnablegger, H., Katsoulakis, M.A., Kokkoli, E., McCormick, A.V., Penn, R.L., Tsapatsis, M., 2006. Mechanistic principles of nanoparticle evolution to zeolite crystals. Nat. Mater. 5, 400–408.

Deer, W.A., Howie, R.A., Zussman, J., 1963. Rock-Forming Minerals. Framework Silicates, vol. 4. Longmans, London.

M.J. De la Torre, 1994. Estudio de los materiales de construcción en la Alhambra, Doctoral Thesis, Universidad de Granada. 211 pp.

De la Torre, M.J., Sebastián, E., Rodríguez, J., 1996. A study of the wall material in the Alhambra (Granada, Spain). Cem. Concr. Res. 26, 825–839.

Diamond, S., White, J.L., Dolch, W.L., 1964. Transformation of clay minerals by calcium hydroxide attack. In: Bradley, W.F. (Ed.), Proc. 12th Int. Conf. Clays and Clay Minerals. Pergamon Press, New York, pp. 359–379.

Drief, A., Nieto, F., Sanchez-Navas, A., 2001. Experimental clay-mineral formation from a subvolcanic rock by interaction with 1M NaOH solution at room temperature. Clays Clay Miner. 49, 92–106.

Drief, A., Martinez-Ruiz, F., Nieto, F., Sanchez-Navas, A., 2002. Transmission electron microscopy evidence for experimental illitization of smectite in K-riched seawater solution at 50 °C and basic pH. Clays Clay Miner. 50, 746–756.

Eades, J., Grim, R., 1960. Reactions of hydrated lime with pure clay minerals in soil stabilization. Highways Res. Board, Bull. 262, 51–63.

Ferrage, E., Tournassat, C., Rinnert, E., Lanson, B., 2005. Influence of pH on the interlayer cationic composition and hydration state of Ca-montmorillonite: analytical chemistry, chemical modelling and XRD profile modelling study. Geochim. Cosmochim. Acta 69, 2797–2812.

Houben, H., Guillaud, H., 1994. Earth Construction: A Comprehensive Guide. Intermediate Technology Publication, London.

Kinuthia, J.M., Wild, S., Jones, G.I., 1999. Effects of monovalent and divalent metal sulphates on consistency and compaction time of lime-stabilised kaolinite. Appl. Clay Sci. 14, 27–45.

Klug, H.P., Alexander, L.E., 1967. X-ray Diffraction Procedures for Polycrystaline and Amorphous Materials. John Wiley & Sons, New York.

Liebig, E., Althaus, E., 1997. Kaolinit und montmorillonit als puzzolanische komponenten in kalkmörteln-unbehandelt und nach thermischer aktivierung. ZKG Int. 50, 282–290.

Lorimer, G.W., Cliff, G., 1976. Analytical electron microscopy of minerals. In: Wenk, H.R. (Ed.), Electron Microscopy in Mineralogy. Springer Verlag, New York, pp. 506–519.

Lunt, M.G., 1980. Stabilised soil blocks for building. Building research establishment. Overseas Build. Notes 184, 127–144.

Mashal, K., Harsh, J.B., Flury, M., Felmy, A.R., Zhao, H., 2004. Colloid formation in Hanford sediments reacted with simulated tank waste. Environ. Sci. Technol. 38, 5750–5756.

Martinez-Ramirez, S., Puertas, F., Blanco-Varela, M.T., 1996. Stability of sepiolite in neutral and alcaline media at room temperature. Clay Miner. 31, 225–232.

Mohamed, A.M.O., 2000. The role of clay minerals in marly soils on its stability. Eng. Geol. 57, 193–203.

Moore, D.M., Reynolds, R.C., 1989. X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford Univ. Press, New York.

Mosser-Ruck, R., Cathelineau, M., 2004. Experimental transformation of Na, Ca-smectite under basic conditions at 150 °C. Appl. Clay Sci. 26, 259–273.

Nagy, K.L., 1995. Dissolution and precipitation kinetics of sheet silicates. In: White, A.F., Brantley, S.L. (Eds.), Reviews in Mineralogy 31. Mineralogical Society of America, Washington D.C., pp. 173–233.

Palomo, A., Glasser, P., 1992. Chemically-bonded cementitious materials based on metakaolin. Br. Ceram., Trans. J. 91, 107–112.

Palomo, A., Fernandez-Jimenez, A., Criado, M., 2004. Geopolymers: some basic chemistry, different microstructures. Mater. Constr. 54, 77–91.

Palumbo, G., Ginell, W.S., Rodríguez-Navarro, C., 1999. Earthen Architecture Research Survey: Analysis Report. Getty Conservation Institute, Los Angeles.

Penn, R.L., Banfield, J.F., 1998. Imperfect oriented attachment: dislocation generation in defect-free nanocrystals. Science 281, 969–971.

Penn, R.L., Oskam, G., Strathmann, T.J., Searson, P.C., Stone, A.T., Veblen, D.R., 1991. Epitaxial assembly in aged colloids. J. Phys. Chem., B 105, 2177–2182.

Provis, J.L., Lukey, G.C., Van Deventer, J.S.J., 2005. Do geopolymers actually contain nanocrystalline zeolites? A reexamination of existing results. Chem. Mater. 17, 3075–3085.

Querol, X., Umaña, J.C., Plana, F., Alastuey, A., Lopez-Soler, A., Medinaceli, A., Valero, A., Domingo, M.J., García-Rojo, E., 2001. Synthesis of zeolites from fly ash at pilot plant scale. Examples of potential applications. Fuel 80, 857–865.

Rajasekaran, G., Murali, K., Srinivasaraghavan, R., 1997. Fabric and mineralogical studies on lime treated marine clays. Ocean Eng. 24, 227–234.

Ramirez, S., Cuevas, J., Vigil, R., Leguey, S., 2002. Hydrothermal alteration of "La Serrata" bentonite (Ameria, Spain) by alkaline solutions. Appl. Clay Sci. 21, 257–269.

Ramirez, S., Vieillard, P., Bouchet, A., Cassagnabère, A., Meunier, A., Jacquot, E., 2005. Alteration of Callovo-Oxfordian clay from Meuse-Haute Marne underground laboratory (France) by alkaline solution. I. A XRD and CEC study. Appl. Geochem. 20, 89–99.

Rao, S.M., Reddy, B.V.V., Muttharam, M., 2001. The impact of cyclic wetting and drying on the swelling behaviour of stabilized expansive soils. Eng. Geol. 60, 223–233.

Rodriguez-Navarro, C., Sebastian, E., Doehne, E., Ginell, W.S., 1998. The role of sepiolite-palygorskite in the decay of ancient Egyptian limestone sculptures. Clays Clay Miner. 46, 414–422.

Rodriguez-Navarro, C., Jiménez-López, C., Rodriguez-Navarro, A., Gonzalez-Muñoz, M.T., Rodriguez-Gallego, M., 2007. Bacterially mediated mineralization of vaterite. Geochim. Cosmochim. Acta 71, 1197–1213.

Roger, C.D.F., Glendinning, S., 1997. Improvement of clay soils in situ using lime piles in the UK. Eng. Geol. 47, 243–257.

Rozalén Astudillo, M.L. 2006. Mecanismo y velocidad de disolución de la montmorillonita en soluciones de electrolitos inertes. Influencia del pH y la temperatura. Doctoral Thesis, Universidad de Granada. 234 pp.

Roy, D.M., 1999. Alkali-activated cements. Opportunities and challenges. Cem. Concr. Res. 29, 249–254.

Schoonheydt, R.A., Johnston, C.T., 2006. Surface and interface chemistry of clay minerals. In: Bergaya, F., Theng, B.K.G., Lagaly, G. (Eds.), Handbook of Clay Science. Elsevier, Amsterdam, pp. 87–113.

Taubald, H., Bauer, A., Schäfer, T., Geckeis, H., Satir, M., Kim, J.I., 2000. Experimental investigation of the effect of high-pH solutions on the Opalinus Shale and Hammerschmiede smectite. Clay Miner. 35, 515–524.

Van Jaarsveld, J.G.S., Van Deventer, J.S.J., Lorenzen, L., 1997. The potencial use of geopolymeric materials to immobilise toxic metals: Part I. Theory and applications. Miner. Eng. 10, 659–669.

Viellard, P., Ramirez, S., Bouchet, A., Cassagnabère, A., Meunier, A., Jacquot, E., 2004. Alteration of the Callovo-Oxfordian clay from Meuse-Haute Marne underground laboratory (France) by alkaline solution: II. Modelling of mineral reactions. Appl. Geochem. 19, 1699–1709.

Wilson, J., Savage, D., Cuadros, J., Shibata, M., Vala Ragnarsdottir, K., 2006. The effect of iron on montmorillonite stability. (I) Background and thermodynamic considerations. Geochim. Cosmochim. Acta 70, 306–322.

Worden, R.H., Champness, P.E., Droop, G.T.R., 1987. Transmission electron microscopy of pyrometamorphic breakdown of phengite and chlorite. Mineral. Mag. 51, 107–121.