Original article

Alkaline activation as an alternative method for the consolidation of earthen architecture

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ABSTRACT

The majority of historic buildings and archaeological remains made of earth exhibit important conservation problems, which require consolidation. Most conventional consolidation treatments used in the past have not succeeded in providing a long-term solution because they did not tackle the main cause of degradation, the expansion and contraction of constituent clay minerals in response to humidity changes. Clay swelling could be reduced significantly by transforming clay minerals into non-expandable binding materials with cementing capacity using alkaline activation. It is demonstrated that a significant degree of clay mineral dissolution and transformation is achieved upon activation with 5 M NaOH and 5 M KOH solutions. Furthermore, adobe test blocks impregnated with either 5 M NaOH or 5 M KOH solution experience an important improvement in water resistance and mechanical strength. The influence of structural and compositional differences of clay minerals commonly present in earthen structures on their reactivity under high pH conditions and the consolidation efficacy of the various alkaline solutions are discussed. Also addressed are possible side effects of the alkaline treatment such as colour change and the formation of potentially damaging salts.

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1. Introduction

Earth has been used as a building material since ancient times and examples of earthen architecture can be found in many parts of the world. Famous examples include Chan-Chan in Peru, Shiban in Yemen, the Rebkung monastery in Tibet and the Alhambra in Spain. In dry climates, earthen structures are in general well preserved with little maintenance. In more humid regions, however, deterioration is a common problem and consolidation treatments are required to ensure the survival of important monuments or archaeological sites. Especially, the action of water of different sources (rain, condensation, capillary rise) can cause severe damage to earthen architecture including cracks and granular disintegration or may even result in the total loss of the structure [1,2].

The susceptibility of earthen structures towards water is a result of the presence of clays in soils used for construction. Clays act as a binder for other constituents such as sand and silt. However, changes in the structure's moisture content cause swelling and contraction of the clay minerals, which in turn results in the above mentioned damage phenomena. Especially deleterious are expandable clays such as smectites or mixed-layer clays, which are commonly found in earth used for construction [3].

Conventional consolidation treatments using synthetic polymers or alkoxysilanes had, often, only limited success and, occasionally, led to a total failure due to esthetical, chemical or physico-mechanical incompatibility. Sometimes the applied product simply does not penetrate sufficiently into the earthen material and only consolidates a superficial outer layer, which typically detaches and falls off. Apart from limited penetration, conventional consolidation treatments do generally not tackle the cause of the problem, the expansion and contraction of the clay minerals, but rather only diminish the alteration effects, thus being ineffective in the long-term [4].

The above shows the urgent need for the development of an alternative, more effective method that allows the *in situ* consolidation of earthen architecture by reducing the swelling capacity of clays. The swelling capacity could be reduced by transforming clays into non-expandable binding materials such as calcium silicate hydrates or aluminosilicates with cementing capacity, using alkaline activation. Ca(OH)$_2$, NaOH or KOH might be suitable as alkaline activators.

Lime, Ca(OH)$_2$, has been used since ancient times as a stabilizer for earthen architecture. Ca(OH)$_2$ provokes pozzolanic reactions at high pH (> 12) at which clay minerals or other aluminosilicates are partially dissolved and transformed into calcium silicate hydrate

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(CSH), calcium aluminate hydrate (CAH) and/or zeolite-like phases. These phases have been recognized in antique roman mortars [5]. They can act as cementing agents and improve the durability and mechanical strength of earthen architecture. This is demonstrated by the soundness and resistance of ancient lime-amended rammed earth structures such as the Alhambra fortress [6].

NaOH and KOH might also be suitable for the alkaline activation of aluminosilicates. Both have been widely applied in the synthesis of zeolites since the mid-1930s [7]. Al and Si sources for zeolite synthesis include clay minerals and feldspathoids [8]. However, zeolite synthesis takes generally place at relatively high $T (\geq 60\,°C)$ and P (autoclave), reaction conditions which are not applicable in architectural conservation interventions.

More recently the geochemistry that yields the synthesis of zeolites has been applied for the production of alkaline activated cements, which are termed geopolymers [9], low-temperature aluminosilicate glass [10] or hydroceramics [11]. Often comparisons are drawn between zeolite chemistry and geopolymer chemistry due to the similarities between the two systems, and the geopolymeric gel phase is frequently described as a zeolitic precursor [12]. Commonly, alkaline activated cements are cured at T between $60–90\,°C$ [10,11].

The main objective of this study is the evaluation of alkaline activation as an alternative consolidation treatment for clayey material such as rammed earth or adobe. Consolidation treatments for earthen architecture are generally applied at room T. Thus, an important aspect of this study is to determine the extent of mineral transformation under high pH conditions at room T. The evaluation will also have to consider the efficacy of different activator solutions, e.g. $Ca(OH)_2$, NaOH and KOH. In the preparation of alkali-activated cements and in the synthesis of zeolites, clay minerals are directly mixed with the alkaline solution. In contrast, alkaline activation in a conservation treatment has to be performed by impregnation with the alkaline solution, as it is commonly done when applying conventional consolidants. Thus, it has to be determined whether an adequate penetration depth can be achieved using alkaline solutions and whether the alkaline solution concentration is sufficiently high to promote mineral transformation and stabilization. The suitability and performance of this consolidation method as an *in situ* treatment is evaluated here by applying alkaline solutions to adobe test blocks. The ultimate goal of this research is to determine whether alkaline treatments can improve the water resistance and mechanical properties of earthen materials. Furthermore, the damage potential of salts, which might form during alkaline activation will be assessed.

2. Materials and methods

2.1. Materials and sample preparation

For our study we chose the soil from the hills close to the city of Granada (Alhambra Formation), which was historically used as a construction material for rammed earth structures [6,13]. In order to evaluate the reactivity of this soil, 5 g of powdered clay ($< 2\,\mu m$ fraction separated using centrifugation) was subjected to alkaline activation using 100 mL of the following solutions:

- $0.025\,M\ Ca(OH)_2$, this concentration corresponds to a saturated solution at room T;
- 5 M NaOH;
- 5 M KOH.

Two batches were prepared for each alkaline solution. The clay samples were kept in tightly capped polypropylene bottles and stored in the laboratory at $20\,°C$. Bottles were stirred periodically

and samples for analysis were taken at predetermined time intervals (1 week, 1, 2.5, 4, 6 months, 1 year).

Additionally, adobe test blocks (size: $4 \times 4 \times 4$ cm) were prepared from the < 1 mm fraction of the Alhambra Formation soil (soil/water mass ratio = 3/1) using wooden molds. The blocks were treated by impregnation with the various alkaline solutions (6 blocks per solution) during 20 minutes and cured in sealed plastic bags for 50 days as a proxy to an in situ treatment. Afterwards, the bags were opened to facilitate slow drying at $\sim 20\,°C$ and $\sim 45\%$ RH until a stable weight was reached after ~ 40 days. Note that during the drying phase, adobe blocks were exposed to atmospheric CO_2. Subsequently, they were submitted to further testing in order to evaluate the efficiency of the treatment.

The interactions of highly concentrated alkaline solutions with clay minerals are manifold and may include:

- the exchange of cations in the clay minerals for the dominant cation in the alkaline solution [14,15];
- flocculation induced by highly concentrated alkaline solution which results in decreased osmotic and intracrystalline swelling of clays, depending on the electrolyte concentration [16];
- clay mineral dissolution and transformation [17].

In order to determine the main causes leading to modifications in the blocks water resistance and mechanical strength upon alkaline activation, additional adobe samples were treated with saturated (4.65 M) KCl solution following the same protocol as in the case of the alkaline solution. Whereas cation exchange and flocculation are facilitated by a treatment with KCl, mineral dissolution and transformation will not occur due to the neutral pH of the KCl solution.

Furthermore, a salt crystallization study was performed in order to obtain a ranking of the damage potential of salts, which might form during alkaline activation. For this test, calcarenite blocks ($3 \times 3 \times 25$ cm) from Santa Pudia, a quarry in the province of Granada, were used. This limestone has a known high susceptibility to salt damage. Adobe blocks could not be used in this test due to their poor water resistance. The porosity of the limestone ($27.7 \pm 0.1\%$) is practically identical to the one of the treated adobe blocks ($27.6 \pm 0.9\%$). However, the volume of pores with a diameter $< 1\,\mu m$, which is decisive in producing salt damage [18], is slightly higher in the treated adobe blocks ($\sim 79\%$) than in the limestone ($\sim 63\%$). Thus, the damage patterns observed in the limestone might not be identical in adobe which is assumed to have a higher susceptibility to salt damage as a result of the lower mechanical resistance and the higher volume of small pores. However, the ranking of the salts damage potential is not likely being influenced by differences between both porous materials.

The stone blocks were partially immersed in saturated salt solution. The surface of the salt solutions was covered with paraffin in order to promote the migration of the salt solution through the pore system of the stone and to avoid creeping and excessive solution evaporation. The salt solutions included here were Na_2CO_3, K_2CO_3 and $KHCO_3$. These carbonates might form upon alkaline activation. Their damaging potential was evaluated by visual observations and by the determination of material loss as well as of the amount of salt crystallized as efflorescence and/or subflorescence.

2.2. Analytical methods

The chemical composition of the clay fraction and the < 1 mm fraction of the untreated soil was determined using a commercial wavelength dispersive X-ray fluorescence spectrometer (BRUKER S4 Pioneer).

The mineralogical evolution was studied with X-ray diffraction (XRD) using a X'Pert PRO (PANalytical B.V.) equipped with

Table 1
XRF results of Alhambra Formation soil (wt%).

Material	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	Na$_2$O	MnO	TiO$_2$	MgO	K$_2$O	CaO	LOI[a]	Total
<2 μm	38.8	25.9	16.17	0.52	0.00	0.71	1.01	3.43	0.74	12.25	100.08
<1 mm	49.1	23.3	8.85	0.54	0.05	0.86	0.95	2.76	0.91	12.25	99.69

[a] Loss on ignition.

Cu-Kα radiation; Ni filter; 45 kV voltage; 40 mA intensity; exploration range of 3° to 60° 2θ and goniometer speed of 0.05° 2θ s^{-1}.

Morphology and composition of mineral phases were studied using 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) equipped with an EDAX solid-state ultra-thin window energy dispersive X-ray (EDS) detector.

Thermogravimetric analysis (TG) was performed on a Shimadzu TGA-50H under flowing air and a constant heating rate of 20 °C min^{-1} (25–950 °C).

The pH evolution during the alkaline attack was monitored using a pH-meter Stick Piccolo HI 1280 (Hanna Instruments).

In order to evaluate the efficiency of the consolidation treatment, the penetration depth of the alkaline solution in adobe blocks was determined using a pH indicator (alizarin red). Treated adobe blocks were split in half and the indicator solution was applied by brushing. The pH of the freshly broken, humid adobe blocks was determined using pH indicator paper (pH 1–14, Filter-Lab, Spain). Indicator paper strips (7 × 10 mm in size) were directly applied to the surface at different positions in order to determine a pH profile. Colour changes were compared to the chart provided by the manufacturer. The reliability of the indicator strip was verified using standard solutions (pH 4–9).

Changes in the porosity of adobe blocks upon treatment were determined with mercury intrusion porosimetry (Micromeritics Autopore III 9410 porosimeter). Water resistance and mechanical properties of untreated and treated adobe blocks were evaluated using a standard water absorption test [19] and a drilling resistance measurement system (Sint Technology, Italy) [20]. Drilling parameters: 15 mm maximum depth, 20 mm/min penetration rate, 200 rpm revolution speed and a diamond-tip 5 mm diameter drill bit. Furthermore, spectrophotometric measurements (CM-700d, Konika Minolta) were performed to determine color change due to alkaline activation. Color change (ΔE) was determined using the CIE-LAB system [21].

3. Results

3.1. Chemical and mineralogical characterization of the starting material

X-ray fluorescence analysis (Table 1) of the <2 μm fraction of the untreated Alhambra Formation soil showed a high silica and aluminium content. This is not surprising because the material contains mainly phyllosilicates and trace amounts of quartz and feldspars (see XRD results below). The relatively high amount of Fe can be explained considering the presence of iron oxihydroxides, which are responsible for the red color of the Alhambra Formation soil.

Compared to the clay fraction, the SiO$_2$ concentration is higher in the <1 mm fraction due to the higher amount of quartz. The concentration of iron compounds, on the other hand, was lower, indicating that iron oxihydroxides are mainly associated with the clay fraction.

Semi-quantitative powder XRD of the <1 mm fraction of the Alhambra Formation soil revealed that the sample was composed of 53 ± 5% quartz and 44 ± 5% phyllosilicates together with small amounts of feldspars (2 ± 5%), calcite/dolomite (1 ± 5%) and iron oxihydroxides.

XRD of the oriented aggregates of the clay fraction showed the following composition: 45 ± 5% illite (d_{001} = 9.98 Å), 30 ± 5% kaolinite (d_{001} = 7.14 Å), 15 ± 5% smectites (d_{001} = 12.5–14 Å) with minor amounts (<10%) of paragonite (d_{001} = 9.60 Å) and chlorite (d_{004} = 3.53 Å).

3.2. Mineralogical changes in powdered clays upon alkaline activation

X-ray diffraction revealed that significant mineralogical changes occurred in the powdered clay samples treated with 5 M NaOH or 5 M KOH, whereas saturated Ca(OH)$_2$ solutions did not result in any important modifications after 1 year of treatment (Fig. 1a). In the case of the 5 M NaOH or 5 M KOH treatment, the 001 Bragg peak of kaolinite decreased after 2.5 months and was only detectable as a trace after 1 year, indicating the almost complete destruction of this clay mineral (Fig. 1b and c). The intensity of the illite 001 Bragg peak only showed a significant reduction in samples treated with 5 M NaOH. The shoulder corresponding to smectites was reduced after 2.5 months of treatment with 5 M NaOH or 5 M KOH, indicating a partial destruction of this clay mineral. Furthermore, in samples treated with NaOH or KOH, new zeolitic phases were detected. The sodic environment favoured the formation of faujasite and hydroxysodalite after 6 months and 1 year, respectively (Fig. 2). The potassic environment, on the other hand, led to the formation of zeolite K-I and chabazite after 4 months and 1 year, respectively (Fig. 3).

3.3. Mineralogical changes in adobe blocks upon alkaline activation

XRD analysis did not reveal any important mineralogical changes in adobe blocks treated with different alkaline solutions. Note that no sodium or potassium carbonates were detected in treated adobe blocks, neither right after treatment, nor after the adobe blocks had been stored under laboratory conditions (air exposure, ∼20 °C and ∼45% RH) for 2 years. FESEM provided evidence for clay mineral dissolution and formation of amorphous phases. Fig. 4b (dashed arrow) reveals drying cracks in adobe blocks treated with 5 M NaOH typical for a gel-like structure, showing a slightly increased Na concentration if compared to the untreated adobe block. In blocks treated with 5 M KOH a gel-like structure covering the clay particles was also observed which had an increased K concentration (Fig. 4c). Furthermore, TG curves of adobe blocks treated with 5 M NaOH, and especially those treated with 5 M KOH, showed a smaller weight loss between 50–300 °C than the untreated adobe samples (Fig. 5a and b). Clay minerals, especially smectites [22], loose absorbed water in this temperature range and the observed smaller weight loss is interpreted as evidence for the partial destruction of these minerals. The higher weight loss difference in the case of the adobe block treated with KOH if compared to the sample treated with NaOH suggests a more extensive dissolution of clay minerals and is in agreement with the higher water resistance observed in these blocks (see below).
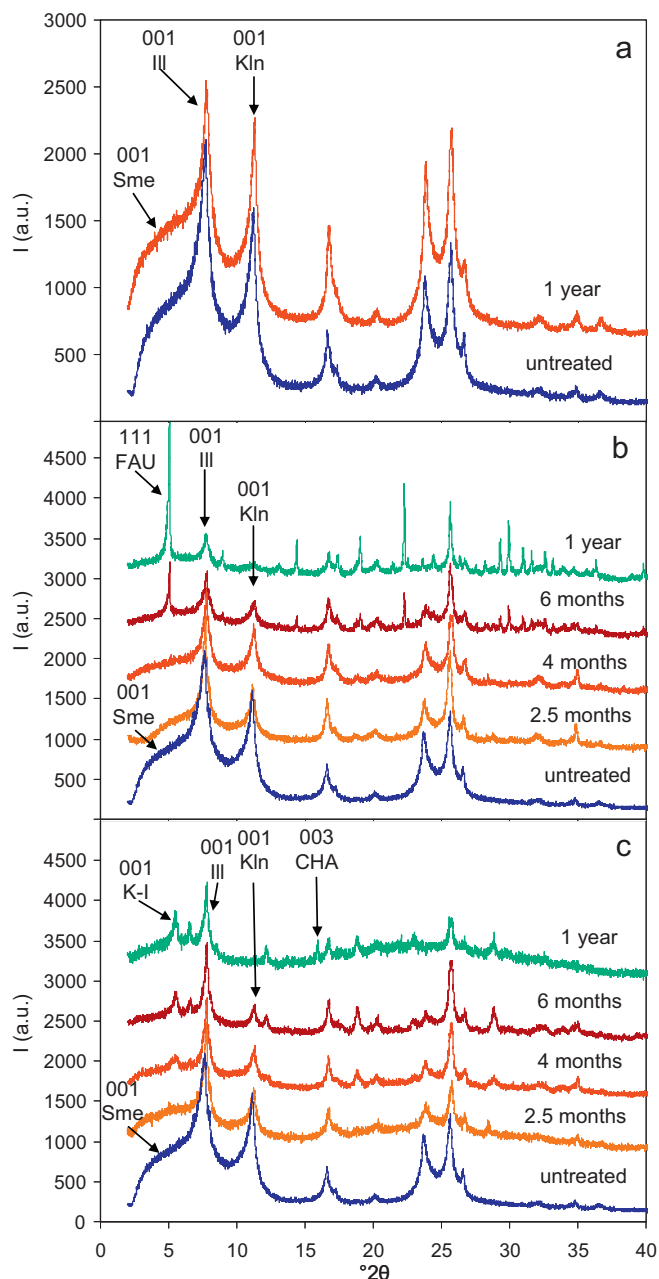
Fig. 1. X-ray diffraction patterns of untreated powdered clay sample (< 2 μm fraction) and samples treated for up to 1 year with: a: saturated Ca(OH)₂ solution; b: 5 M NaOH; c: 5 M KOH solutions (Sme: smectite; Ill: illite; Kln: kaolinite; FAU: faujasite; K-I: zeolite K-I; CHA: chabazite).

Fig. 2. Field emission scanning electron microscopy (FESEM) image of zeolitic phases formed in the < 2 μm fraction of the Alhambra Formation soil treated with 5 M NaOH for 1 year (FAU: faujasite; SOD: hydroxysodalite). Energy dispersive X-ray spectrum of FAU crystal in inset.

Fig. 3. Field emission scanning electron microscopy (FESEM) image of zeolitic phases formed in the < 2 μm fraction of the Alhambra Formation soil treated with 5 M KOH for 1 year. Energy dispersive X-ray spectrum of chabazite (CHA) in upper inset. Transmission electron microscopy image of zeolite K-I (K-I) after 6 months of treatment with 5 M KOH in lower inset.

3.4. pH evolution during alkaline activation

During the alkaline activation of powdered clay samples (< 2 μm fraction), a drop in pH was detected which was more severe in the case of saturated Ca(OH)₂ solution if compared to 5 M NaOH or 5 M KOH (Fig. 6).

3.5. Penetration depth of alkaline solutions in adobe blocks

The penetration depth of the different alkaline solutions in adobe blocks immersed during 20 minutes was determined to be about 1 cm. After 50 days of curing in sealed plastic bags, the alkaline solution had penetrated the entire block (Fig. 7). Furthermore, pH indicator strips showed that the pH was ∼ 12 in the case of
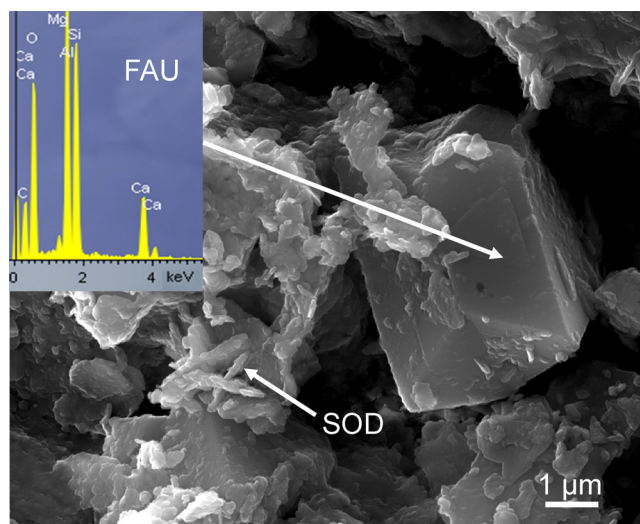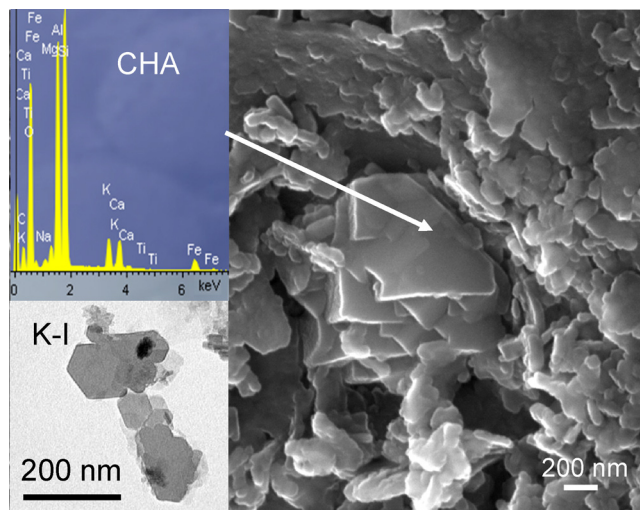
blocks treated with 5 M NaOH or 5 M KOH, whereas, the pH of blocks treated with saturated Ca(OH)₂ solution was only 7–8.

3.6. Porosity of untreated and treated adobe blocks

Mercury intrusion porosimetry revealed that the porosity of the adobe blocks increased by about 7–16% upon treatment and subsequent drying-induced shrinking (Table 2). This increase was caused by fracturing during clay mineral expansion upon immersion in water or alkaline solutions. Fracturing resulted in an increase in the volume of pores between 2–80 μm diameter, whereas the volume of pores below 1 μm diameter remained unchanged (Fig. 8). As we will see below, this increase in porosity did not result in a reduction in water resistance or mechanical strength.
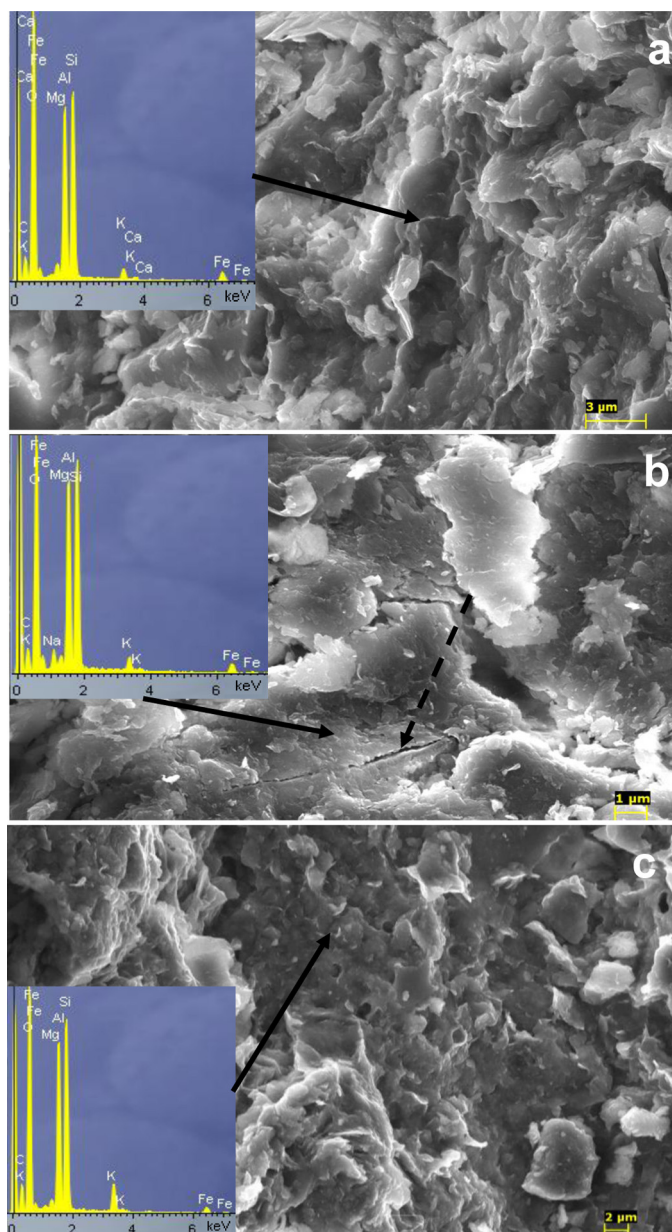
Fig. 4. Field emission scanning electron microscopy (FESEM) images of: a: an untreated adobe block and adobe blocks treated with; b: 5 M NaOH; dashed arrow in b: shows drying cracks; c: 5 M KOH (energy dispersive X-ray spectra in insets).

3.7. Water resistance of treated and untreated adobe blocks

The water resistance of adobe blocks treated with the different alkaline solutions was evaluated by immersion in water over

Table 2
Porosity (average value of 4 samples per treatment) of untreated and treated adobe blocks [immersed in water or treated with 0.025 M Ca(OH)$_2$, 5 M NaOH and 5 M KOH for 20 min].

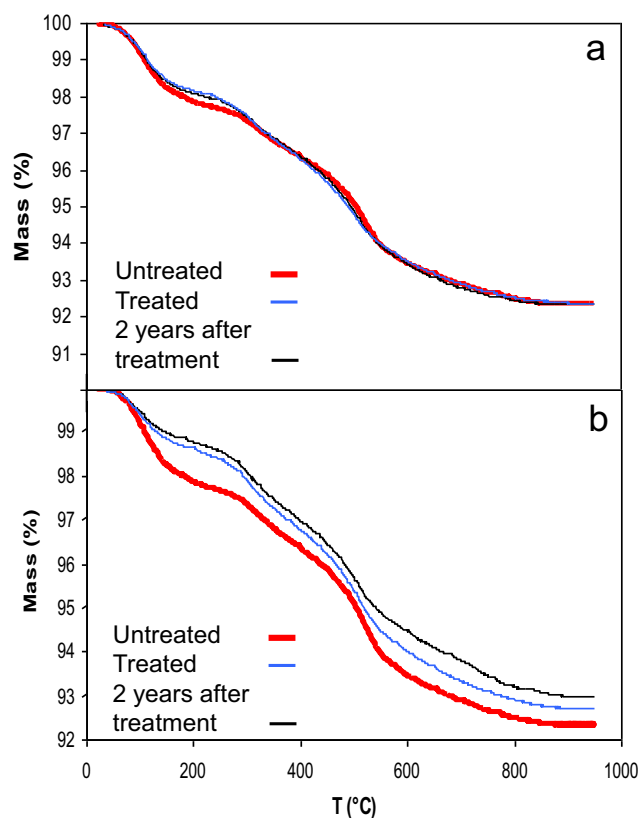| Sample	Porosity (%)
Untreated	24.7 ± 0.7
Water	27.2 ± 1.3
Ca(OH)$_2$	27.8 ± 0.9
NaOH	28.7 ± 0.4
KOH	26.5 ± 1.2

Fig. 5. Thermogravimetric analysis curves of untreated adobe blocks and blocks treated with: a: 5 M NaOH; b: 5 M KOH solutions.

prolonged periods of time. Note that tests were performed in duplicate in order to verify the results. The Ca(OH)$_2$ treatment did not improve water resistance if compared with the untreated samples. Both samples experienced severe material loss (Fig. 9) and a complete disintegration after 2.5 h. Samples treated with NaOH and, especially the ones treated with KOH showed better water resistance. The latter withstood the action of water for almost 48 h.

Test results further showed that the treatment with saturated KCl solution did not result in improved water resistance. The blocks treated with KCl experienced significant material loss after immersion in water for 2 h (Table 3).
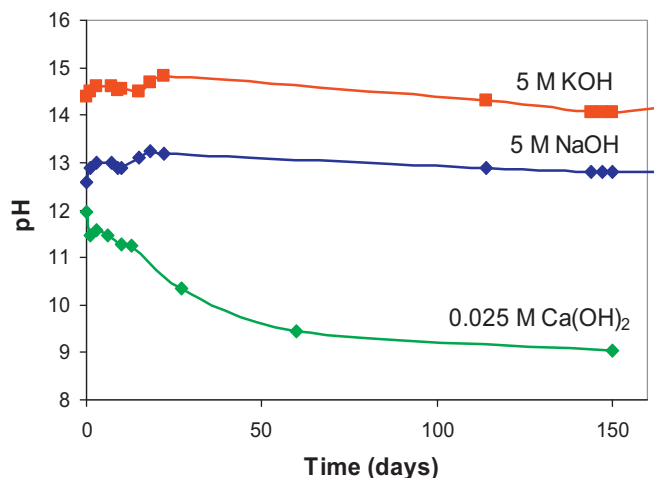

Fig. 6. pH evolution of powdered clay samples (< 2 μm fraction) during activation with various alkaline solutions.
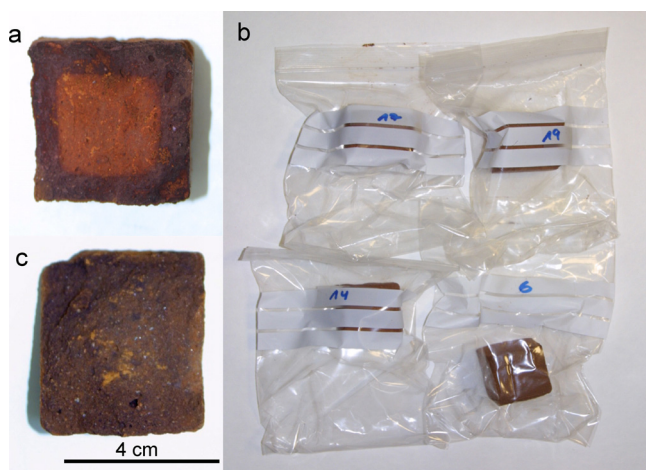
Fig. 7. a: penetration depth in adobe blocks immersed for 20 minutes in alkaline solution is evidenced by a color change towards violet (blocks were split in half and treated with a pH indicator); b: curing of treated adobe blocks in sealed plastic bags for 50 days; c: penetration depth in adobe blocks after curing for 50 days.
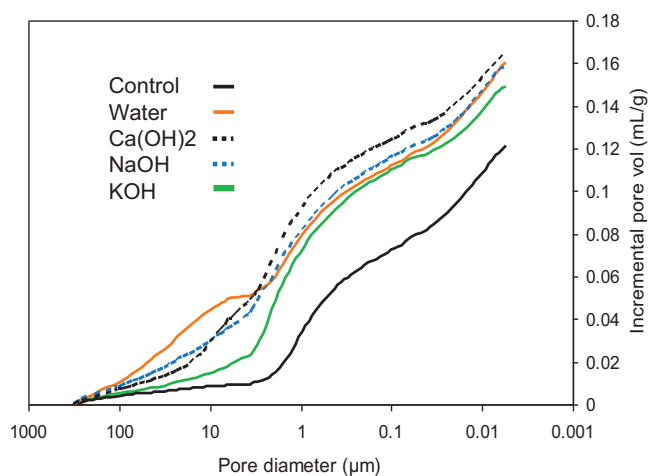

Fig. 8. Pore size distribution of untreated adobe blocks (control) and blocks which have been immersed for 20 min in water, saturated Ca(OH)$_2$ solution, 5 M NaOH and 5 M KOH solutions.
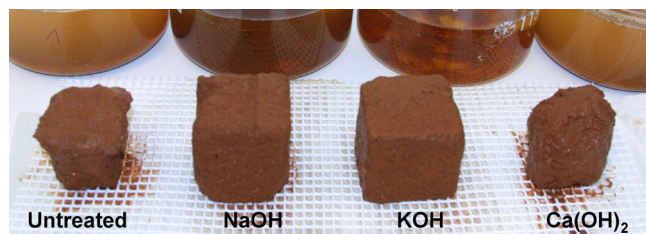

Fig. 9. Untreated and treated adobe blocks after immersion in water for 1 h.

Table 3
Material loss of adobe blocks after immersion in water for 2 hours.

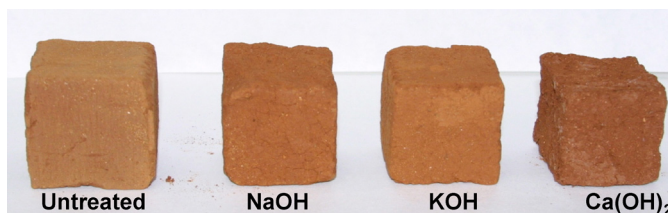| Treatment	Material loss (wt%)
4.65 M KCl	74
5 M KOH	0.1
Untreated	90

Fig. 10. Color change in treated adobe blocks upon alkaline activation.

3.8. Mechanical strength of untreated and treated adobe blocks

Drilling resistance measurements revealed that 5 M NaOH and 5 M KOH treatments resulted in a significant strength increase, whereas the Ca(OH)$_2$ treatment did not induce any improvement if compared with the untreated samples (Table 4). Drilling resistance curves showed some fluctuation as a result of the materials inhomogenity. However, no significant changes in drilling resistance along depth profiles were detected, which would have suggested the formation of superficial hard crusts in treated samples.

The drilling resistance of the adobe block treated with KOH was compared to that of a block treated with saturated KCl. Results showed that the KCl treatment did not improve drilling resistance significantly.

3.9. Color change upon treatment

Generally, changes in color are thought to be acceptable when ΔE is ≤ 5 [23]. Considering the experimental ΔE values, it is evident that KOH and NaOH caused a color change, which was only slightly above the acceptable limit. Samples treated with Ca(OH)$_2$, on the other hand, experienced a more severe colour change as a result of a darkening of the adobe block (Fig. 10, Table 5).

3.10. Formation of salts upon alkaline activation

During the treatment of soils with alkaline solutions, unreacted alkalis might react with atmospheric CO$_2$ to form carbonates. Actually, in a few cases the formation of carbonates, namely CaCO$_3$, Na$_2$CO$_3$ and KHCO$_3$, was observed upon activation of powdered clay samples as a result of an improper seal. Calcium carbonate is the reaction product of lime mortar and generally improves mechanical properties of the soil. Sodium carbonate and potassium carbonate, in contrast, are soluble salts, which may produce serious

Table 4
Average drilling resistance of adobe blocks before and after alkaline activation (based on a minimum of 10 drill tests, using 3 samples per treatment).

Sample	Drilling resistance (N)
Untreated	4.36 ± 0.48
Ca(OH)$_2$ treatment	4.66 ± 0.50
NaOH treatment	7.29 ± 0.57
KOH treatment	6.92 ± 0.78
KCl treatment	4.60 ± 0.23

Table 5
Average colour change (ΔE) of treated samples (average value of 6 measurements, using 2 samples per treatment).

Sample	ΔE
KOH	5.14 ± 0.55
NaOH	5.81 ± 0.72
Ca(OH)$_2$	10.25 ± 0.81

Table 6
Material loss, salt retained in the stone prisms and salt efflorescence (wt%).

	Na_2CO_3	K_2CO_3[a]	$KHCO_3$
Material loss[b]	57.2	0	0
Salt retained	55.7	17.8	37.9
Efflorescence	44.3	28.2	62.1

[a] Only 46 wt% K_2CO_3 solution had evaporated after 7.5 months.
[b] With respect to the initial weight of the stone prisms.

damage during cycles of crystallization in porous building materials [24]. Note, that XRD analysis did not reveal the presence of sodium or potassium carbonates in any of the treated adobe blocks, not even 2 years after storage under laboratory conditions.

Their absence can be explained considering the much higher clay/alkali molar ratio in the case of the adobe blocks (2.17) if compared to the powdered clay samples (0.014). Gaucher and Blanc [15] reported that 1 mol montmorillonite would consume 4.68 moles of OH^- during dissolution under alkaline conditions. We calculated that each adobe block contained about 0.1 mol of reactive clay (kaolinite and smectite) to which 0.046 mol OH^- was added during the alkaline impregnation treatment. Thus, the OH^- concentration was 1 order of magnitude lower than that required for the dissolution of the total amount of reactive clay and a significant amount of clay should still be present after all OH^- is consumed during mineral dissolution. In the case of the powdered clay samples, the reactive clay content in each batch was 0.0072 mol, to which 0.5 mol OH^- was added. Considering the results by Gaucher and Blanc [15], 0.466 mol OH^- would still be available after all reactive powdered clay has dissolved. This excess in alkali explains the formation of carbonates, which has been observed in a few powdered clay samples.

The salt crystallization test performed using calcarenite allowed the ranking of the damage potential of the carbonates detected in this study during the alkaline activation: $Na_2CO_3 > K_2CO_3 > KHCO_3$. Limestone blocks partially immersed in Na_2CO_3 solution showed severe damage including scaling and fracturing, which affected the whole stone block. Note that efflorescence was very limited, suggesting that in-pore crystallization of this salt was dominant. Samples treated with K_2CO_3 and $KHCO_3$ revealed some efflorescence but very limited damage and no material loss (Table 6).

4. Discussion

4.1. Mineralogical changes in clays upon activation using different alkaline solutions

XRD data showed that smectites and kaolinite dissolved readily, while illite showed a higher resistance towards the action of the alkaline treatment. Variations in clay reactivity can be explained by structural and chemical differences of the clay minerals. According to Schoonheydt and Johnston [25] surface properties of clay minerals depend on their chemical composition, the nature of the surface atoms, the extent and type of defect sites, the layer charge and the type of exchangeable cations. The higher reactivity of smectites if compared to illites, especially, in samples treated with KOH is a result of compositional differences (Fig. 1c). Smectites and illites are 2:1 clays and general agreement exists that the contribution of the basal layer to the reactivity of these clay minerals is limited and dissolution takes mainly place at hydroxyl groups located at broken edges, steps and defect sites [25,26]. Differences in the chemical composition between illite and smectites result in a more stable structure in the case of illite, which does not experience intracrystalline swelling, whereas smectites swell readily in polar solvents and offer a much greater surface area for reaction. Kaolinite, a 1:1

clay, has generally a lower surface area compared with other clay minerals [27]. However, the extensive dissolution shown by this clay mineral (Fig. 1b and c), can be explained by the presence of hydroxyl groups at the gibbsite layer which offer additional reactive sites for dissolution and contribute to the clays overall reactivity [28].

The observed difference between saturated $Ca(OH)_2$ solution and 5 M NaOH or 5 M KOH solutions in promoting clay mineral dissolution and zeolite formation can be associated with the low solubility of $Ca(OH)_2$ in water which results in a low OH^- concentration. During clay mineral dissolution, OH^- is consumed, leading to a decrease in pH [15]. This decrease was more severe in the case of the saturated $Ca(OH)_2$ solution which reached an equilibrium pH of < 10 after 60 days of treatment. It has been shown experimentally that dissolution rates of clay minerals as well as the formation of zeolites increase significantly at a pH well above 10 [8,29], which explains the higher efficiency observed in the case of 5 M NaOH or 5 M KOH, both resulting in a pH > 12 over the course of the treatment.which explains the higher efficiency observed in the case of 5 M NaOH or 5 M KOH, both resulting in a pH

General agreement exists that the type of zeolite formed during treatment depends on the dominant cation in the activator solution. The zeolitic phases identified in the Alhambra Formation soil treated with 5 M NaOH or 5 M KOH are in agreement with observations made by Barrer [8] who discussed the structure-directing role of cations and concluded that sodic environments would favor the formation of faujasite and sodalite hydrates, whereas chabazite forms in potassic environments.

4.2. Changes in adobe blocks upon alkaline activation

From the evaluation of the penetration depth it can be concluded that a good penetration can be achieved using alkaline solutions. Furthermore, it is demonstrated that a high enough pH is maintained during treatments with 5 M NaOH or 5 M KOH, facilitating mineral dissolution and transformation. In contrast, the buffering effect of the clay minerals caused a drastic pH decrease in the case of saturated $Ca(OH)_2$ solution, rendering this treatment inefficient.

Water resistance and mechanical strength were significantly improved after treatment with 5 M NaOH and 5 M KOH. Comparison of blocks treated with KOH and KCl gave clear evidence that mineral dissolution and transformation at high pH must have been the main factors leading to this improvement. FESEM and TG analyses confirmed the dissolution of clay minerals in adobe blocks treated with NaOH or KOH. However, XRD and FESEM did not allow the identification of crystalline zeolitic phases and it is concluded that the mineralogical changes must have been limited to the transformation of clay minerals into amorphous phases, possibly zeolite precursors. Indirect evidence for the formation of amorphous phases with cementing properties is also provided by drilling resistance measurements, which revealed increased mechanical strength in adobe blocks treated with 5 M NaOH or KOH. Criado et al. [30] acknowledged the fact that the formation of well-crystallised zeolites would require very long periods of time, whereas amorphous zeolite precursors are expected to form at ambient conditions within a short reaction time. The fact that we did not observe crystalline zeolitic phases in treated adobe blocks indicates that the formation of amorphous phases must have been sufficient in promoting improvements in water resistance and mechanical strength. Xu and van Deventer [31] also reported improvements in the mechanical strength in alkali-activated cements due to the formation of amorphous phases (zeolite precursors). A few researchers even question whether the formation of crystalline zeolitic phases is desirable for achieving improved mechanical strength [32,33]. Grutzeck et al. [33] suggested that the formation of crystalline zeolites, depending

on their morphology, might disrupt the alkali-activated cement matrix.

The spectrophotometric measurements suggest that treatments with NaOH or KOH caused color changes only slightly above the permissible threshold whereas saturated $Ca(OH)_2$ solution resulted and a more severe darkening of the adobe block. Thus, NaOH and KOH solutions would be preferable in conservation treatments.

4.3. Formation of salts upon alkaline activation

During alkaline activation a competition between the dissolution reaction of clay minerals and the carbonation of excess alkalis might exist, the later resulting in the formation of carbonates. Cizer et al. [34] studied the competing pozzolanic and carbonation reactions in the case of lime-metakaolin mortars and found that carbonation would be favoured at 60% RH where mortar pores were only partially filled, facilitating the diffusion and dissolution of atmospheric CO_2. At higher RH (93%) pozzolanic reactions were enhanced and carbonation reaction was hindered as a result of the mortars high moisture content, which reduces CO_2 diffusion drastically. They concluded that in order to improve pozzolanic reactions and ensure a sufficient strength development, lime-metakaolin mortars should be kept moist for at least 28 days. A similar recommendation would be applicable in the case of alkaline treatments for the consolidation of earthen architecture, hindering carbonate formation and enhancing the dissolution and transformation of clay minerals.

In any case, the risk of salt induced damage can be reduced by using KOH instead of NaOH. The salt crystallization test demonstrated a much lower damage potential of potassium carbonates if compared with sodium carbonate. The ranking of the damage potential of the carbonates in this study is in general agreement with published data for stone materials with varying porosity, always identifying Na_2CO_3 as one of the most damaging salts [24]. Note, that the risk of the formation of damaging carbonates might be further reduced by an addition of $Ca(OH)_2$ to the alkaline activation solution. Upon carbonation the formation of the less soluble $CaCO_3$ will be favored, consuming CO_2 that might have dissolved in the alkaline treatment solution, and, thereby, preventing the formation of more soluble Na_2CO_3 or K_2CO_3.

5. Conclusions

Our research results prove that the application of alkaline solutions for the consolidation of earthen structures can be regarded as a valuable alternative to conventional consolidation treatments. Adobe test blocks showed a significant improvement in water resistance and mechanical strength after impregnation with 5 M NaOH or 5 M KOH and curing for 50 days at room T. These improvements are thought to be the result of the dissolution of clay minerals and their transformation into amorphous phases with cementing properties. However, the use of KOH solution is preferable because any potassium carbonates, which might form during alkaline activation, are generally found to have a lower damage potential than sodium carbonates.

Some aspects were identified which deserve further research. These include the possible use of less concentrated alkaline solutions to control the risk of carbonate formation due to excess alkali as well as to reduce treatment cost and environmental impact; or the preparation of conservation mortars using a mixture of soil and KOH solution.

Finally, the positive outcome of the laboratory study should be confirmed by an in situ application in the field. The evaluation of the risk of salt formation upon alkaline treatments should be an important consideration during field-testing. For this purpose adobe test walls or, ideally, pilot areas in historic earthen structures could be treated with alkaline solutions and their performance monitored over extended periods of time. Alkaline solutions should be applied repeatedly and the earthen structure should be kept humid over an extended period of time to facilitate mineral dissolution and transformation and to hinder salt formation. This could be achieved by periodical wetting using water and by covering the structure during treatment with impermeable plastic.

References

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

[2] H. Houben, H. Guillaud, Earth Construction: a Comprehensive Guide, CRA Terre-EAG, Intermediate Technology Publication, London, 1994.

[3] R. Coffman, N. Agnew, G. Austin, E. Doehne, Adobe mineralogy: characterization of adobes from around the world, in: K. Grimstad (Ed.), Proceedings of the 6th International Conference on the Conservation of Earthen Architecture: Adobe 90 preprints: October 14–19, Las Cruces, New Mexico, The Getty Conservation Institute, Marina del Rey, California, 1990, pp. 424–429.

[4] E. Doehne, C.A. Price, Stone Conservation - An Overview of Current Research, The Getty Conservation Institute, Los Angeles, 2010.

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

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

[7] E.M. Flanigen, F.A. Mumpton, Commercial properties of natural zeolites, Mineral. Geol. Nat. Zeol. 4 (1977) 165–175 (Mineralogical Society of America Short Course Notes).

[8] R.M. Barrer, Hydrothermal Chemistry of Zeolites, Academic Press, London, 1982.

[9] J. Davidovits, Geopolymers: man-made rock geosynthesis and the resulting development of very early high strength cement, J. Mater. Educ. 16 (1994) 91–139.

[10] H. Rahier, B. Van Mele, M. Biesemans, J. Wastiels, X. Wu, Low-temperature synthesized aluminosilicate glasses, part I. Low-temperature reaction stoichiometry and structure of a model, J. Mater. Sci. 31 (1996) 71–79.

[11] A. Palomo, M.T. Blanco-Varela, M.L. Granizo, F. Puertas, T. Vazquez, M.W. Grutzeck, Chemical stability of cementitious materials based on metakaolin, Cem. Concr. Res. 29 (1999) 997–1004.

[12] C.A. Rees, J.L. Provis, G.C. Lukey, J.S.J. van Deventer, The mechanism of geopolymer gel formation investigated through seeded nucleation, Colloids Surf., A 318 (2008) 97–105.

[13] E. Ontiveros Ortega, E. Sebastián Pardo, I. Valverde Espinosa, Deterioration in XI–XIV century Arab ramparts (Granada, Spain), Mater. Struct. 32 (1999) 45–51.

[14] R. Fernandez, J. Cuevas, L. Sanchez, R. Vigil de la Villa, S. Leguey, Reactivity of the cement-bentonite interface with alkaline solution using transport cells, Appl. Geochem. 21 (2006) 977–992.

[15] E.C. Gaucher, P. Blanc, Cement/clay interactions-a review: experiments, natural analogues, and modeling, Waste Manage. 26 (2006) 776–788.

[16] O. Karnland, S. Olsson, U. Nilsson, P. Sellin, Experimental determined swelling pressures and geochemical interactions of compacted Wyoming bentonite with highly alkaline solutions, Phys. Chem. Earth 32 (2007) 275–286.

[17] K. Elert, E. Sebastian, I. Valverde, C. Rodriguez-Navarro, Alkaline treatment of clay minerals from the Alhambra Formation: implications for the conservation of earthen architecture, Appl. Clay Sci. 39 (2008) 122–132.

[18] C. Rodriguez-Navarro, E. Doehne, Salt weathering: influence of evaporation rate, supersaturation and crystallization pattern, Earth Surf. Processes Landform 24 (1999) 191–209.

[19] UNI EN 13755, Natural Stone Test Methods - Determination of Water Absorption at Atmospheric Pressure, CNR-ICR, Rome, 2008.

[20] M. Pamplona, M. Kocher, R. Snethlage, L. Aires Barros, Drilling resistance: overview and outlook, Z. Dtsch. Ges. Geowiss. 158 (2007) 665–676.

[21] International Organization for Standardization/CIE, ISO/CIE 11664-6:2014, Colorimetry - Part 6: CIEDE2000 Colour-Difference Formula, International Organization for Standardization/CIE, Geneva, Switzerland, 2014.

[22] R.C. Mielenz, N.C. Schieltz, M.E. King, Thermogravimetric analysis of clay and clay-like minerals, Clays Clay Miner. 2 (1954) 285–314.

[23] H.R. Sasse, R. Snethlage, in: N.S. Baer, R. Snethlage (Eds.), Methods for the Evaluation of Stone Consolidation Treatments, Saving our Architectural Heritage. The

Conservation of Historic Stone Structures, John Wiley & Sons, Ltd., Chichester, 1997, pp. 223–243.

[24] A. Goudie, H. Viles, Salt Weathering Hazards, John Wiley & Sons, New York, 1997.

[25] R.A. Schoonheydt, C.F. Johnston, Chapter 5. Surface and interface chemistry of clay minerals, in: F. Bergaya, B.K.G. Theng, G. Lagaly (Eds.), Handbook of Clay Science, Elsevier, Oxford, 2006, pp. 139–172.

[26] G. Sposito, The Surface Chemistry of Soils, Oxford University Press, New York, 1984.

[27] A. Umran Dogan, M. Dogan, M. Onal, Y. Sarikaya, A. Aburub, D.E. Wurster, Baseline studies of the Clay Minerals Society source clays: specific surface area by Brunauer Emmett Teller (BET) method, Clays Clay Miner. 54 (2006) 62–66.

[28] F.J. Huertas, L. Chou, R. Wollast, Mechanism of kaolinite dissolution at room temperature and pressure: part II. Kinetic study, Geochim. Cosmochim. Acta 63 (1999) 3261–3275.

[29] S.J. Köhler, D. Bosbach, E.H. Oelkers, Do clay mineral dissolution rates reach steady state? Geochim. Cosmochim. Acta 69 (2005) 1997–2006.

[30] M. Criado, A. Palomo, A. Fernández-Jiménez, Alkali activation of fly ashes. Part 1: effect of curing conditions on the carbonation of the reaction products, Fuel 84 (2005) 2048–2054.

[31] H. Xu, J.S.J. van Deventer, The geopolymerisation of aluminosilicate minerals, Int. J. Miner. Process. 59 (2000) 247–266.

[32] A. Fernandez-Jimenez, M. Monzo, M. Vicent, A. Barba, A. Palomo, Alkaline activation of metakaolin-fly ash mixtures: obtain of zeoceramics and zeocements, Microporous Mesoporous Mater. 108 (2008) 41–49.

[33] M. Grutzeck, S. Kwan, M. DiCola, Zeolite formation in alkali-activated cementitious systems, Cem. Concr. Res. 34 (2004) 949–955.

[34] Ö. Cizer, K. Van Balen, D. Van Gemert, Competition between hydration and carbonation in hydraulic lime and lime-pozzolana mortars, Adv. Mater. Res. 133–134 (2010) 241–246.