



From the historical sugar refinery of Chichaoua (Morocco) to the lab: a reverse engineering experimentation on the hydration of earthen materials stabilized with lime

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Abstract

In order to explain the good state of conservation and good mechanical characteristics of the lime-stabilized earth of the sugar refinery near Chichaoua (Morocco, XVIth A.C.) XRD, SEM-EDX, TG-DSC, FT-IR analyses were performed on collected samples. Moreover laboratory earth samples were prepared with selected clay minerals (presence of attapulgite) and lime, involving a reverse engineering process in order to investigate the reaction products during curing. The same analyses performed on the historical samples were carried out on lab samples. Moreover, compressive strength was assessed. The results were compared to the ones obtained on the historical samples. The maturation of lime-stabilized rammed earth was due to lime carbonation and to earth drying and consolidation. Furthermore, the formation of mixed CSH phases was evidenced, possibly because of a slow pozzolanic reaction between lime and clays, that took place in long times both in lab and in historical samples.

Keywords: pozzolanic reaction, lime stabilized earth, reverse engineering, hydration

1. Introduction

Recently, the use of earthen materials in modern constructions has become the object of renewed interest not only for developing countries, but also for a new emerging market after a period of complete oblivion due to the wide diffusion of industrial products and the association of earthen buildings with images of poverty, cultural and social relegation. Earth and earth based materials are the ecologic and sustainable material par excellence; they are widely available in nature at an extremely low price, used without the necessity of special transformations, require a reduced energy amount for their processing and show good breathability and thermal insulating properties. Thanks to these characteristics, they have been used since ancient times to build architectural structures in many European, American, Asian and African countries and are bearer of important and significant knowledge, and technological culture (Houben & Guillaud, 2006; Galdieri, 1982; Jaquin, 2008; Guillard, 2012). The only drawback of these architectures is the limited durability of the material against the aggressive action exerted by external agents (rain, capillary rise, erosion due to anthropic action) that makes it necessary a constant maintenance (Guettala et al., 2006; Matthew, 2004; Avrami et al., 2008). The choice of suitable materials for the maintenance and conservation should be based on the knowledge gained through retrieval and study of the traditional building techniques together with new experimentation.

In order to retrieve the ancient technical knowledge regarding lime-stabilized earth constructions, the present research proposes a study of the composition and curing state of historical earthen samples that showed high durability and it adopts a reverse engineering approach for their re-proposition and study as improved materials. The research takes its cue from the study of the earthen building material of a Saadian sugar refinery of the second half of the XVIth century located near Chichaoua, in Morocco. The refinery of Chichaoua consists of a hydraulic part with an aqueduct, mill's rooms and a small room for cooking and processing the juice, and a

large room for the sugar refinement. It was a production plant built exclusively according to the formwork technique, which consists in compressing the earth in a formwork with a pestle realising single building blocks. The earthen material used shows excellent condition of conservation despite the total abandonment lasted for more than four centuries, in particular high mechanical properties were measured (Gamrani et al., 2012; Rovero et al., 2014). The characterization of the Saadian materials highlighted that the local earth used, constituted by inactive clay minerals (illite, chlorite, kaolinite, attapulgite, added with a significant amount of slaked lime, 20–25% of the total). Both the presence of lime and of attapulgite might have played a role in the good conservation state by providing a stabilizing function. Lime, is one of the oldest chemical stabilizers that can improve strength, stiffness, workability of raw earth (Ciancio et al., 2014). Attapulgite might have influenced the curing processes by acting as an hygrometric flywheel, thus stabilizing the earth and promoting the formation of pozzolanic products.

In order to further study the historical production technique of the Saadian samples and to evaluate the behaviour of similar mixtures, the reverse engineering approach used in the present research involved:

- individuation of mixture composition and assessment of the curing state of the historical samples by XRD, SEM-EDX, TG-DSC, FT-IR spectroscopy with the final aim to relate them to the good conservation state;
- in-lab reproduction of lime-stabilized earth mixtures similar to the historical ones. In particular, in order to investigate the effects due to attapulgite, specimens with or without this clay were prepared;
- study of the curing process of the lab specimens over time by XRD, SEM-EDX, TG-DSC, FT-IR spectroscopy. The reaction compounds that develop between slaked lime and clay minerals of the earthen material capable to justify the excellent durability of the material itself, are identified;
- Determination of compressive strength of the lab specimens;
- evaluation of the results in comparison to the properties of the historical mortars.

The presented methodology allowed to investigate different aspects of the curing of lime-stabilized earth, the hydration and hardening mechanism and the properties of the final material; aspects that can be related to the good durability of the historical samples.

2. Materials and methods

2.1 Historical samples

The mineralogical composition of earth and Chichaoua lime-stabilized specimens have been presented in Gamrani et al. (2012). Among the historical samples of rammed earth collected and studied by Gamrani et al. (2012), two significant samples were selected for a further study on the material composition and curing state:

- Sample A7, collected from the refinery's aqueduct (Figure 1), realized according to the rammed earth technique (compacted stabilized earth). This sample (Figure 2) is light brown in colour with the diffuse presence of brighter parts due to lime lumps.
- Sample S3, collected from the earth of the furnace area (Figure 3) in order to evaluate the composition of the local clay alone, not stabilized with lime. This sample (Figure 4) shows flakes and powder of reddish-brown earth.



Figure 1: The aqueduct

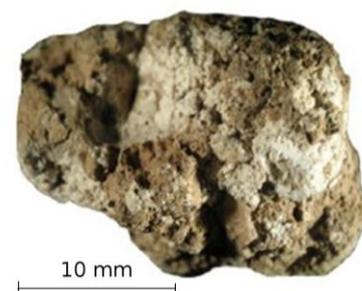


Figure 2: Sample A7, lime stabilized sample collected from the aqueduct



Figure 3 Furnace Area



Figure 4 Sample S3, earth from the furnace area

2.2 Laboratory specimens

After the analysis and characterization of the historical samples the following starting materials were selected for the preparation of laboratory specimens: a reddish-brown earth collected in north-east Italy, pre-alps area (supplied by S. Marco Laterizi S.p.A); a pure attapulgite clay (supplied by CTS); a slaked lime matured for three years under water (supplied by “La bottega del restauro”); and a silicatic-carbonatic sand (size fraction 0/2 μ m).

The selected materials were mixed in different proportion with water and casted in different ways in order to obtain: i) specimens suitable for the study of the lime-earth interaction and ii) specimens suitable for the study of the mechanical properties of newly made lime-stabilized rammed earth with and without attapulgite. The specimens names, the relative mixture composition and the specimens casting are reported in Table 1.

The interaction between clay and lime was investigated by studying mixtures of lime, earth and sand (R or RA) at different curing times.

Specimens with 20% of attapulgite and without this clay were prepared with a low content of sand or by alternating lime and clays in order to evaluate the attapulgite effects and to simplify the investigation of the interactions between lime and clays.

The mechanical properties of lime-stabilized earth were determined on lime-stabilized mixtures (R_sand, RA_sand), obtained by mixing lime, earth, sand in different proportions with or without attapulgite. The amount of sand used is similar to that of the historical samples of Chichaoua to better compare the physical properties measured. The starting materials were roughly mixed to prepare workable earth specimens with the presence of lime lumps inside in order to simulate the composition and structure of the historical samples.

Table 1: Mix design of laboratory specimens

<i>name</i>	<i>Starting materials</i>	<i>Mixture composition % by volume</i>				<i>Specimens casting</i>
		<i>Reddish earth</i>	<i>Attapulgite</i>	<i>lime</i>	<i>sand</i>	
R	Reddish-brown clay, sand and lime	60%	none	20%	20%	Starting materials mixed roughly with water and compacted in polystyrene moulds (4x4x16 cm ³); drying and curing at 24°C and 60% HR till 1 year
RA	Reddish-brown clay, attapulgite sand and lime	48%	12%	20%	20%	
R_sand	Reddish-brown clay, sand and lime	40%	none	20%	40%	Mixture roughly mixed to maintain lime lumps; cast in polystyrene moulds (4x4x16 cm ³) and stored at 24°C and 60% HR for 3 months
RA_sand	Reddish-brown clay, attapulgite sand and lime	32%	8%	20%	40%	

2.3 Investigation techniques

The curing and hydration state was assessed on the historical samples in order to relate them to the good conservation state and durability of the historical samples. Then, samples collected from the specimens R and

RA were analyzed with similar techniques in order to evaluate the possible formation of interaction compounds over time and to compare them with the composition of the historical samples. Different samples were collected from the specimens at 2, 7, 14, 28 day, 3, 6, 12, months and grinded with acetone, dried in oven at 40°C and stored under N₂ atmosphere to stop the curing process.

The following investigation techniques were used both on the historical sample and on the laboratory specimens at different ageing times:

- a JEOL JSM- 5600 LV Scanning electron microscope equipped with an energy dispersive x-ray probe (OXFORD-Link Isis series 300) was used in order to observe the samples microstructure on previously golden sample in secondary electron mode (20KeV);
- a Nicolet Nexus 670/870 FT-IR spectrometer was employed in the mid-infrared region (4000-400 cm⁻¹) at 4 cm⁻¹ resolution on KBr pellets (1:100-wt% sample/KBr) to evaluate the specimens composition and the presence of functional groups significant of the presence of silicates hydrates;
- differential scanning calorimetry/thermogravimetric analysis was used to determine the specimens composition and the thermal stability of the compounds present, in particular the linked water and the calcium hydroxide and carbonate content. 25 mg of dried and crushed samples were put in Pt/RH crucibles and analysed with as Netzsch STA 409/c instrument with a heating program of 10°C/min from 30°C to 1000°C in air;
- X ray diffraction (X'Pert PRO diffractometer by PANalytical equipped with X'Celerator detector and HighScore software for acquisition and interpretation of the data, Cu Kα1= 1.545 Å radiation, 40 KV, 30 mA, 2θ = 3-70°) was used to investigate the mineralogical compositions of slaked lime, earth and earth with slaked lime, in particular the presence of phases indicative of hydration-pozzolan reactions. The analysis of the clay minerals was carried out with a PHILIPS PW 1729 diffractometer according to the following operative conditions: Cu Kα1= 1.545Å radiation, 40 KV, 20 mA, 2θ = 3-20°).

The mechanical properties were assessed through compression tests after three month curing at 20 °C and 80% HR on R and RA specimens of 4x4x4 cm³, by using a press with a pre-load of 10 N and a loading rate of 10N/min. The mechanical properties of the specimens were assessed (EN 12390-3:2009).

3. Results and discussion

3.1 The historical samples from Chichaoua

The SEM-EDX observation of sample A7, carried out on lime-stabilized rammed earth, and of sample S3, composed only by the local earth, allowed to observe a different microstructure (Figures 5, 6). Both the samples have a inhomogeneous microstructure with fine round shaped grains and laminated grains and the EDX microanalysis showed the presence of Ca, Si, Al, Mg, Cl, Fe (Figure 7). However, in sample A7, the matrix is more coherent and the presence of acicular and amorphous structures binding the grains is visible at the interfaces between white lumps and clay (Figure 5).

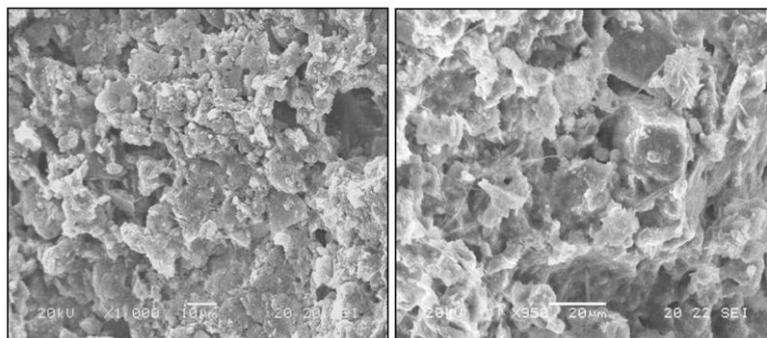


Figure 5: SEM image of sample S3 (without slaked lime) (left); SEM observation of sample A7 at the interface between lime lumps and clay (right). It is possible to notice fine acicular structure of CSH, not visible in the earth alone

The SEM images of the white lumps of A7 showed both rhombohedral and hexagonal crystals and the presence of a high percentage of calcium, detected by EDX probe, to be referred to calcite and calcium hydroxide,

respectively. The contemporary presence of calcium hydroxide inside small lumps (ranging from 8 mm³ to 1 cm³) confirms the use of lime to stabilize the rammed earth furthermore evidencing an incomplete carbonation inside the earth material. The interfacial zones between the lime lumps and the clay in A7 (Figure 5-right) show the presence of fine acicular structures containing Ca and Si. These structures seem similar to typical CSH phases Type I visible in hydraulic binders (such as pozzolana-lime pastes) (Falchi et al,2013; Falchi et al.,2015). The presence of hexagonal crystals containing Ca, Si, Al was also observed, probably related to the presence of aluminosilicate hydrates (Figure 6). Both the acicular and the hexagonal structures were present only at these lime lumps- earth interfaces and only in lime-stabilized specimens; S3 did not show the presence of similar structures.

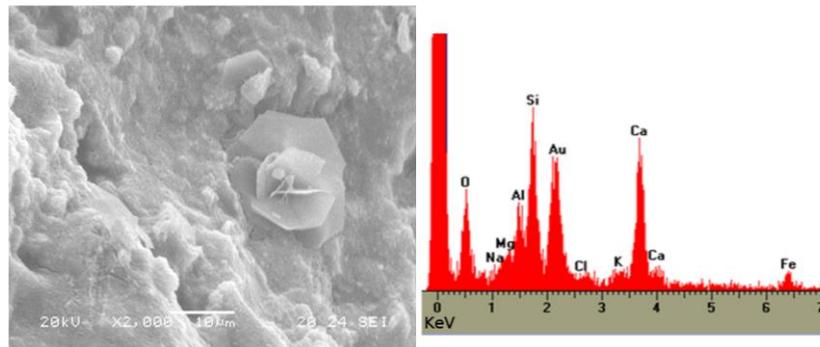


Figure 6: SEM observation of sampleA7 at an interface lump-clay (left). It is possible to see the layered structure of an aluminosilicate crystal; EDX spectrum of sample A7 evidencing the presence of Ca, Fe, Si, Mg, Na, Al (right).

The FT-IR analysis of Sample A7 (Figure 7), carried out on powder collected from lumps and clay, confirmed the presence of calcium carbonate in the lumps (typical stretching absorption at 1433 cm⁻¹, bending at 874 cm⁻¹ and 713 cm⁻¹), while the typical -OH stretching absorption of the calcium hydroxide at 3640 cm⁻¹ was not observed. The presence of different silicates and aluminosilicates compounds was testified by the broad absorption of hydroxyl groups due to not-linked water at 3440 cm⁻¹ and the high peaks in the 1000-1100 cm⁻¹ range due to silicates. In particular the peak of Si-O-Si stretching at 1027 cm⁻¹ and bending at 780 cm⁻¹, 527 cm⁻¹, 473 cm⁻¹ are probably due to hydrated silicates, too.

The FT-IR spectrum of sample S3 (Figure 7) showed a lower presence of carbonates with respect to silicates, and the peaks of different aluminosilicates were clearly visible, in particular the stretching due to linked hydroxyls at 3167, 3581, 3545, 3421 cm⁻¹. The shoulder at 1092 cm⁻¹ and the peaks at 1193 cm⁻¹ and at 994 cm⁻¹ are typical of attapulgite.

The TG-DSC analysis of the sample gave further information of the thermal stability of the lime-stabilized earth of Chichaoua (Figure 7). The analysis of sample S3 showed the mass losses and relative endothermic peaks in the 80 °C-200°C range due to the loss of absorbed water and to the loss of interlayer water of clay minerals. The peaks at 194 °C, 411° C , at 484 °C and 851 °C are typical of attapulgite and its transformations (e.g. into enstatite at 851° C). The endothermic peak at 570 °C is probably related to the polymorphic transformation of α -quartz into β -quartz. The mass losses between 625° C and 760°C, due to de-carbonation reactions, indicates the presence of a small amount of dolomite and a significant amount of calcite. The TG-DSC analysis of the lumps in sample A7 highlights an important mass loss between 380-470 °C typical of the dehydration reaction of calcium hydroxide and the mass loss between 650-750 °C is due to the de-carbonation of calcium carbonate. This confirms again the presence of not well carbonated lime inside the sample. The analysis of the powder at the interfaces lumps-clay in sample A7 put in evidence the presence of calcium hydroxide and calcium carbonates, too.

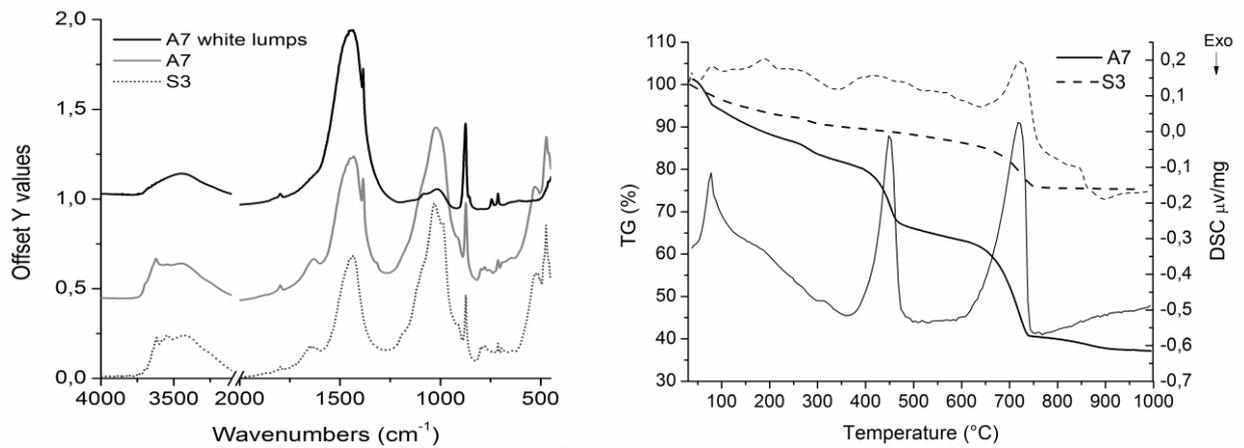


Figure 7: FT-IR spectra of the historical samples A7 and S3 (left); TG-DSC curves of the historical samples A7 and S3 (right)

3.2 Study of the interactions between lime and rammed earth on laboratory specimens

The composition of the starting materials for laboratory specimens preparation is described in Table 2. Furthermore, XRD analysis of the reddish earth evidenced the presence of quartz, calcite, dolomite, feldspars and clay minerals (illite 25%, kaolinite 20%, chlorite 10%, illite-smectite 20% and smectite 25%).

Table 2: Composition of the starting materials

Material	Compounds and FT-IR peaks	Compounds and TG mass losses
Reddish earth	calcite and dolomite (1435 cm^{-1} , 876 cm^{-1}); silicates, in particular the large band at $1000\text{--}1100\text{ cm}^{-1}$, due to the convolution of peaks related to Si-O-Si, Si-O, Al-O-Si absorptions, is centred at 1029 cm^{-1} and shows main shoulders at 1166 , 1088 , 900 cm^{-1}	calcium carbonate and dolomite ($650\text{--}800^\circ\text{C}$)
Attapulgit	peaks at 3616 , 3551 , 3408 cm^{-1} due to linked water molecules in the interlayer; 1654 cm^{-1} due to water; peaks at 1200 , 1097 , 1035 , 984 , 912 cm^{-1} due to Si-O-Si and Al-OH stretching typical of ribbon silicates of the smectite-palygorskite group; at 860 cm^{-1} due to Al-Mg-OH stretching	not linked water (till 80°C), interlayer zeolitic water (till 100°C), coordination water (till 900°C)
Sand	carbonates (1476 cm^{-1} , 1417 cm^{-1}) and silicates (1167 , 1086 , 1028 cm^{-1}).	calcium carbonate and dolomite ($650\text{--}800^\circ\text{C}$)
Lime	Calcium hydroxide ($-\text{OH}$ v 3643 cm^{-1}); calcium carbonate (1476 cm^{-1} , 1417 cm^{-1})	calcium hydroxide ($350\text{--}450^\circ\text{C}$)

XRD, FT-IR, SEM-EDX, and TG-DSC analysis of R and RA at different curing times allowed highlighting the chemical and mineralogical modification of the mixture over time.

Concerning the mineralogical modification of R and RA specimens, induced by the addition of the slaked lime to earth, over 5 months of curing, it mainly consisted in a decreasing intensity of the portlandite peaks evidenced by XRD analysis. This is not in relation with a corresponding intensification of the peak of calcite, indicating that the slaked lime is not only suffering carbonating process but is also involved into a pozzolanic reaction with the clay minerals, giving rise to others compounds. These compounds are not identifiable through XRD diffraction probably due to their low crystallinity. The XRD exam repeated after 28 days and 5 months, does not show the presence of crystalline reaction products between the slaked lime and the clay fraction of the earth. Nevertheless, a decrease of intensity of the peaks of the clay minerals in the more aged specimens, can be noticed (Figure 8).

FT-IR spectra of RG and RGA samples, cured for 2, 7, 14, 28 days, 3, 6, 12 months (Figure 9), allowed to observe the reduction of calcium hydroxide (peak at 3643 cm^{-1}) and the contemporary increase of carbonates

stretching and bending peaks (1440 cm^{-1} , 875 cm^{-1}). In particular calcium carbonate in the form of calcite is produced since the beginning, as indicated by the peak at 1432 cm^{-1} and the bands at 875 cm^{-1} and 712 cm^{-1} of symmetric carbonate stretching (ν_1 mode) and in-plane bending modes (ν_4 mode). After 6 months, a second peak is visible at 1448 cm^{-1} and 1084 cm^{-1} , 858 cm^{-1} , 729 cm^{-1} due probably to the presence of calcium carbonates polymorphs. In particular, the bands at 1080 cm^{-1} (symmetric carbonate stretching ν_1 mode), 858 cm^{-1} (carbonate out-of-plane bending ν_2 mode), are typical of aragonite and at 729 cm^{-1} (ν_4 mode) of vaterite (Zhaodong et al., 2008). The peaks at 1448 cm^{-1} and 1084 cm^{-1} could be also attributed to mixed phases of alumino-carbonates hydrates.

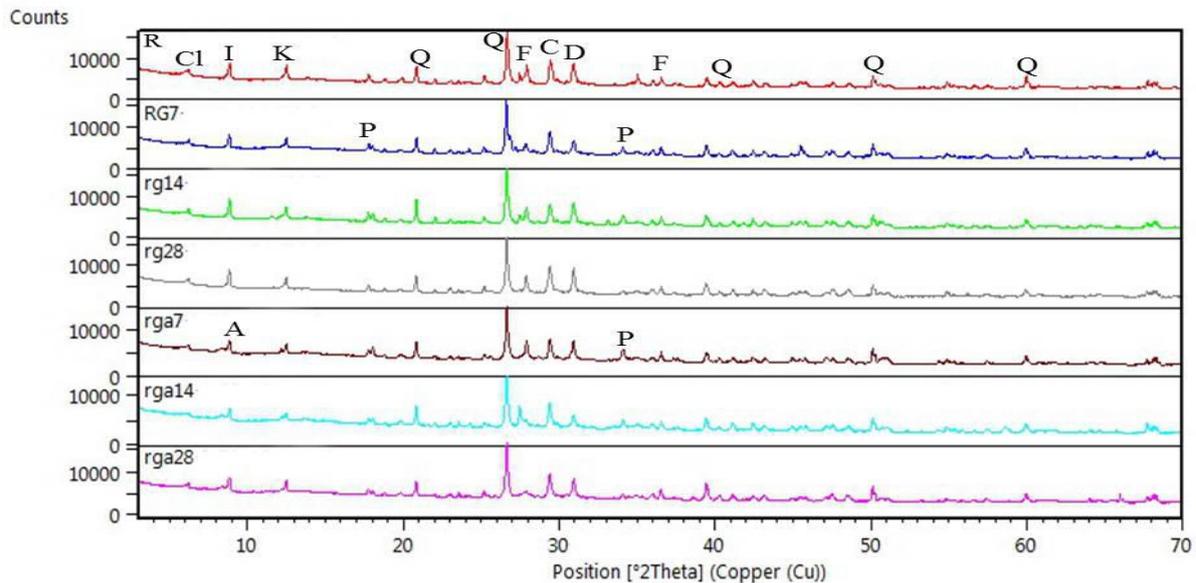


Figure 8: XRD spectra, comparison among reddish earth (R), reddish earth with lime (RG) and reddish earth with lime and Attapulgitite (RGA) in different curing time (7, 14 e 28 days). Q=Quartz, F=Feldspars, C=Calcite, D=Dolomite, P=Portlandite, I=Illite, K=Kaolinite, Cl=Chlorite, A=Attapulgitite.

The convolution band of the silicates and aluminates ($900\text{--}1100\text{ cm}^{-1}$) showed the increase of the shoulder at 1091 cm^{-1} in comparison to the peak centred at 1016 cm^{-1} and their shift to lower wave numbers, till 1083 cm^{-1} and 1033 cm^{-1} after 6 months. This indicates the formation over times of hydrated silicates phases due to a pozzolanic reaction between slaked lime and the clay giving rise to amorphous CSH products. Similar peaks and trends over times were observed also for RS samples (collected from the interfaces between clay and lime) with the presence of calcium carbonate polymorphs at 3 and 6 months and the broadening and shifting to lower wave numbers of the silicates convolution band around 1090 cm^{-1} , thus suggesting the formation of hydrated CSH compounds at the interface lime-earth.

In presence of Attapulgitite (Figure 9), it is still possible to observe the production of calcite taking place over the first 6 months, but not peaks related to other calcium carbonate polymorphs. Furthermore, the $900\text{--}1100\text{ cm}^{-1}$ zone is quite completely covered by the absorptions due to the Attapulgitite in particular at 1090 cm^{-1} .

The SEM-EDX images and analysis gave different hints of the production of hydrated phases and calcium carbonation formation after 3 months. In comparison to 7-days cured specimens, the presence of acicular structures ascribable to CSH phases, rhombohedral grains of calcite and a more compact matrix in specimens cured 3 months are visible at high magnifications (3000X) (Figures 10,11).

The TG-DSC analysis after 28 and 365 days curing allowed to observe the carbonation of the calcium hydroxide over time (Figure 12). After 1 year, no calcium hydroxide ($400\text{--}450\text{ }^\circ\text{C}$) was detected and both the TG and DSC curves of R and RA became similar. In particular, it is possible to individuate higher mass losses and the increase of the DSC curve due to de-hydration of newly formed hydrated phases in the $90\text{ }^\circ\text{C}\text{--}300\text{ }^\circ\text{C}$ range. The mechanical properties indicate that both R_sand and RA_sand specimens have a comparable compressive strength around 1.15 MPa ($1.14 \pm 0.19\text{ MPa}$ for R_sand and $1.21 \pm 0.22\text{ MPa}$ for RA_sand), due to the pozzolanic reaction slightly improving the final compressive strength.

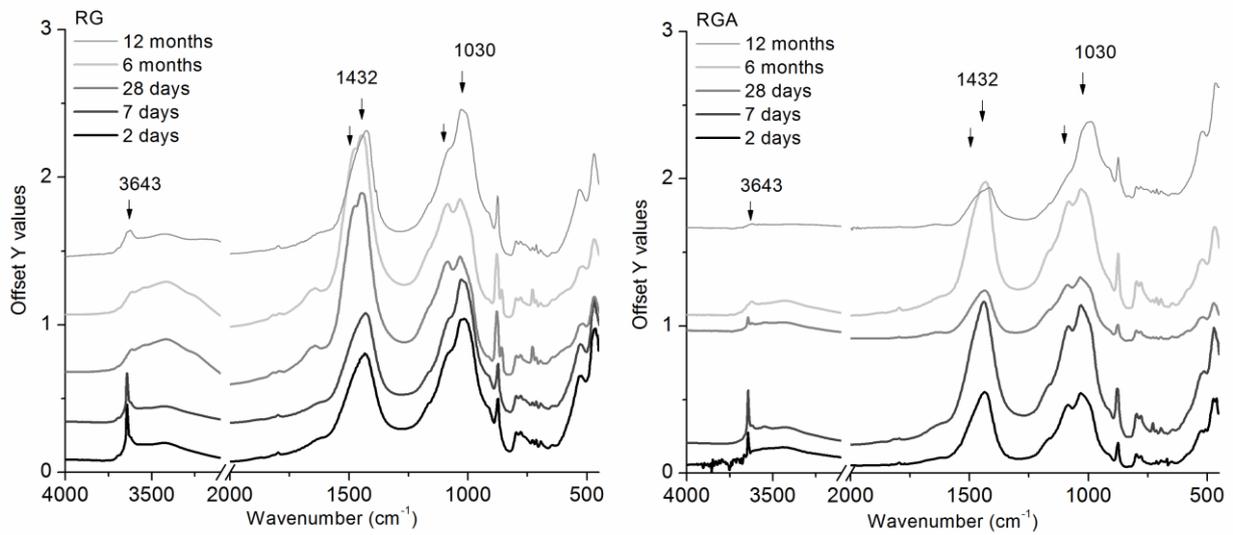


Figure 9: FT-IR spectra of RG and RGA mixtures at different curing times.

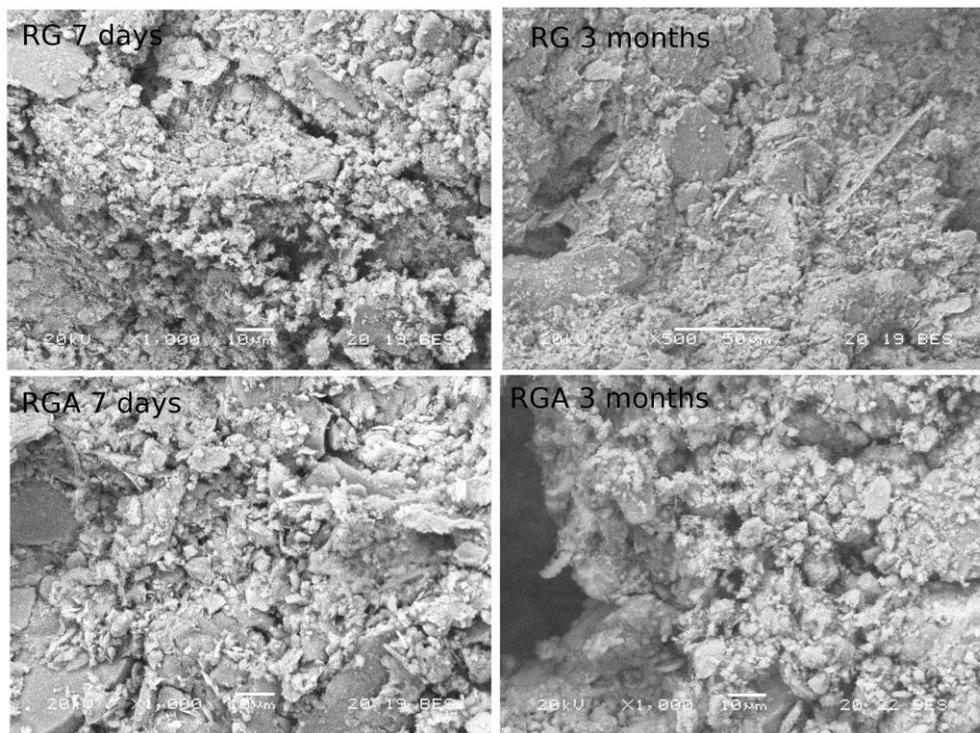


Figure 10 SEM images of RG and RGA after 7 days and 3 months of curing (1000X and 500X)

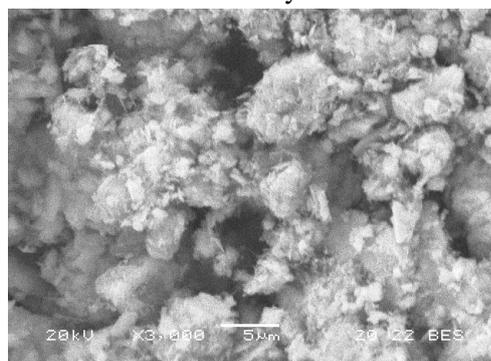


Figure 11 SEM images of RGA after 3 months of curing (3000X)

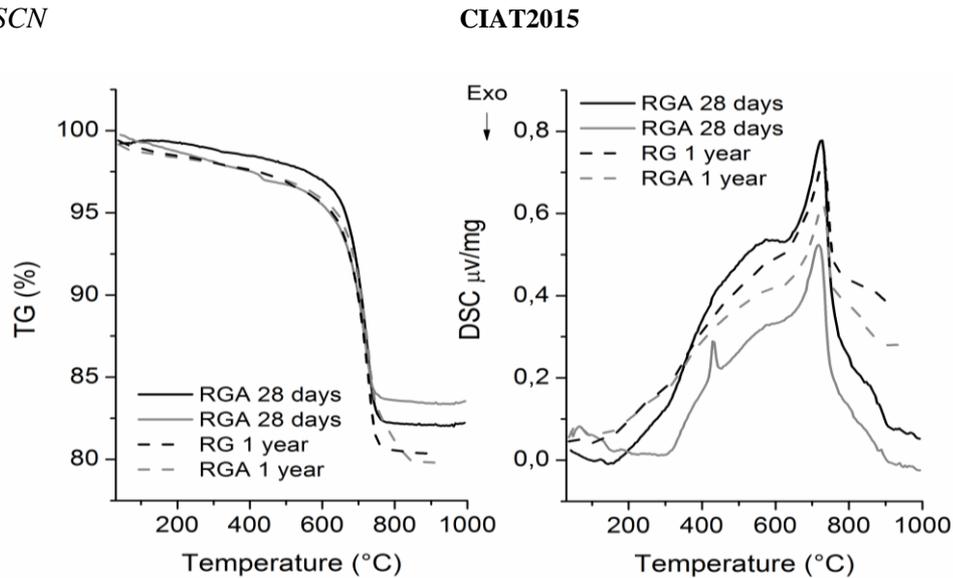


Figure 12 TG-DSC of specimens after 28 and 365 days curing

3.3 Discussion on the interaction lime/earth

The results obtained by the analysis of historical and laboratory samples, prepared to study the first phases of curing, evidence not only the presence of compounds due to the direct carbonation of lime, such as calcium carbonates polymorphs, but also of amorphous CSH and CAH. This indicates that the curing of lime-stabilized rammed earth proceeds by drying and hardening of the mixture, carbonation and pozzolanic reactions that start to take place since the very beginning also with clays not having high pozzolanic activity

The chemical stabilization of earth with lime improving strength and stiffness of the final earthen product, implies therefore, three main phenomena from the chemical point of view: cation exchange, pozzolanic reaction and carbonation (Ciancio et al., 2014). Carbonation is the reaction that occurs when the lime reacts with the carbon dioxide producing a solid calcium carbonate, enhancing the solely earth strength. The cation exchange, in presence of water, begins as soon as the lime is added to the earth. This reaction releases Ca^{++} ions from $\text{Ca}(\text{OH})_2$ and leads to an increase of the pH of the lime-earth mixture. The pH, higher than 12.4 (the pH of a saturated solution of lime-water) favours the solubilisation of silica and alumina present in clay minerals and quartz (pozzolanic reaction). Then, the silica and alumina released react with Ca^{++} ions to form silico-calcium aluminates. From here onwards, in presence of water, the reaction is very similar to the process of hydration of Portland cement: the calcium silicates hydrate to form cementitious compounds.

Usually, the carbonation reaction occurs in hot-dry climates, where control of curing is difficult, to the detriment of the pozzolanic reaction. This phenomenon should be avoided because it inhibits the formation of cementitious products, and thus reduces the strength of the material (Ciancio et al., 2014). The presence of CSH in the historical samples and their slight hydraulicity, proofs of the occurrence of pozzolanic reaction, could be the explanation of the good durability and good mechanical properties of the Saadian lime-stabilized earth. The pozzolanic reaction can be promoted by a proper mix design and the control of stabilisation regime and curing conditions. In this case, the use of attapulgitite might have influenced the curing processes by acting as an hygrometric flywheel, thus stabilizing the earth and promoting the formation of pozzolanic products in a quite arid climate.

The compressive strength of the laboratory specimens after three month of curing is significantly lower than the compressive strength of the historical samples of Chicahoua (Gamrani et al., 2012), which was quite high for a rammed earth (around 3.5 MPa as average) (Middleton & Schneider, 1987; Walker, 2002; Walker et al., 2005). The observation done on the cured specimens suggests that the curing time is too short in comparison to the longer curing times of the historical samples and that not enough hydraulic compounds have been formed, due to the slow rate of the pozzolanic reaction.

Conclusion

The analytical data of historical and laboratory samples evidence not only the presence of compounds due to the direct carbonation of lime, such as calcium carbonates polymorphs, but also of amorphous CSH and CAH. The formation of these CSH phases let us suppose the starting of a slow pozzolanic reaction between lime and

clay minerals. The presence of attapulgite in the historical samples and in those realized in laboratory might have influenced the curing processes by acting as an hygrometric flywheel, thus stabilizing the earth and promoting the formation of pozzolanic products.

Further research would be carried out to individuate suitable consolidation and protection method for lime-stabilized earth material.

Author Contributions -

To be noted: all the authors should be considered as principal authors.

References

1. Avrami E., Guillaud H., Hardy M., Terra literature review – An overview of research in earthen architecture conservation, *The Getty conservation institute* (2008) 44-47.
2. Ciancio D., Beckett C.T.S., Carraro J.A.H., Optimum lime content identification for lime-stabilised rammed earth, *Construction and Building Materials*, 53 (2014) 59–65.
3. Falchi L., Müller U, Fontana P, Izzo F.C, Zendri E., Influence and effectiveness of water-repellent admixtures on pozzolana–lime mortars for restoration application. *Construction and Building Materials*, 49 (2013) 272–280.
4. Falchi L., Zendri E., Müller U., Fontana P., The influence of water-repellent admixtures on the behaviour and the effectiveness of Portland limestone cement mortars, *Cement and Concrete Composites*, 59 (2015) 107-118.
5. Galdieri E., *Le meraviglie dell'architettura in terra cruda*, Bari, Italia, Laterza (1982).
6. Gamrani N., R'kha Chaham K., Ibnoussina M., Fratini F., Rovero L., Tonietti U., Mansori M., Daoudi L., Favotto C., N. Youbi, The particular "rammed earth" of the Saadian sugar refinery of Chichaoua (IVth century, Morocco): mineralogical, chemical and mechanical characteristics, *Environmental Earth Science*, 66 (1) (2012) 129-140.
7. Guettala A., Abibsi A., Houari H., Durability study of stabilized earth concrete under both laboratory and climatic conditions exposure, *Construction and Building Materials*, 20 (3) (2006) 119-127.
8. Guillard H., Evolution, Innovations, resistances and future directions” in *Rammed Earth Conservation*, Mileto, Vegas & Cristini (eds), *Taylor & Francis Group*, (2012) London.
9. Houben, H., H. Guillaud., “*Traité de construction en terre*” Marseille (2006), *Éditions Parenthèses*.
10. Jaquin P.A., Analysis of Historic rammed earth construction, Durham Thesis, (2008) Durham University.
11. Middleton GF, Schneider LM, Earth-wall construction 4th ed. Bulletin 5, *CSIRO* (1987), Sydney
12. Nan Z., Chen X., Yang Q., Wang X., Shi Z., Hou W., Structure transition from aragonite to vaterite and calcite by the assistance of SDBS, *Journal of Colloid and Interface Science*, 325/2 (2008) 331-336.
13. Rovero L., Tonietti U., Fratini F., Gamrani N., The saadian sugar refinery of Chichaoua (morocco): constructive and structural investigations for conservation, *Restauro Archeologico*, 2, (2014), 65-82
14. Walker P. Standards Australia, HB 195 The Australian earth building handbook, *Standards Australia International Ltd* (2002) Sydney.
15. Walker P, Keable R, Martin J, Maniatidis V. Rammed earth: design and construction guidelines, *BRE Bookshop* (2005) United Kingdom.

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