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# 1 **Chemico-microstructural changes in earthen building materials containing** 2 **calcium carbide residue and rice husk ash**

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## 10 **Abstract**

11 Clay earthen materials can essentially be stabilized with calcium carbide residue (CCR) and rice husk ash  
12 (RHA) to produce compressed earth block (CEBs) with improved mechanical performances for  
13 application in building construction. Nevertheless, the curing process in mixtures of these materials needs  
14 to be monitored in order to assess the maturation of the reaction among these materials and their  
15 reactivity. This study investigated the curing process in mix solutions and microstructural changes in the  
16 cured mixtures made of kaolinite-rich earthen material, portlandite-rich CCR, and silica (amorphous)-rich  
17 RHA. Dry mixtures were prepared by adding 0-25 % CCR and 10-25 % CCR:RHA (various ratios) to the  
18 earthen material (5 g). The mix solutions were prepared by addition of 100 mL of deionized water to the  
19 dry mixtures. Stabilized CEBs were also produced by manually compressing moisturized mixtures in  
20 295x140x95 mm<sup>3</sup> mold. The curing process was undertaken between 1-90 days at 40±2 °C. Throughout  
21 the curing, the chemical changes in mix solutions were monitored by measuring the pH, electrical  
22 conductivity (EC) and concentration of unconsumed calcium ions [Ca<sup>2+</sup>]. The microstructural changes in  
23 cured mixtures were characterized using X-Ray diffraction (XRD), thermogravimetric analysis (TGA)  
24 and scanning electron microscopy (SEM). The EC and [Ca<sup>2+</sup>] decreased over the curing time mainly due  
25 to the consumption of calcium ions through pozzolanic reaction involving the earthen material with CCR  
26 and CCR with RHA. The minimum values of EC and [Ca<sup>2+</sup>] were reached after 45 days of curing in the  
27 mix solutions containing the earthen material and CCR alone and 28 days in those containing the earthen  
28 material and CCR:RHA. This was related to the end of the reaction and occurrence of optimum maturity  
29 in the respective mixtures. The XRD analyses revealed the consumption of kaolinite and portlandite from  
30 the raw materials and formation of calcium silicate hydrates (CSH) and calcium aluminate hydrates  
31 (CAH) in the cured mixtures. The SEM micrographs showed the formation of porridge-like products  
32 forming an interlocking network which densely cemented the matrix of stabilized CEBs.

33 **Keywords:** Calcium carbide residue; calcium consumption; electrical conductivity; kaolinite;  
34 microstructural change; mix solution; pozzolanic reaction; rice husk ash

## 35 **1. Introduction**

36 Local and non-conventional materials hold potential to cater for the increasing need for  
37 affordable and decent housing in most developing countries, specifically Burkina Faso [1].  
38 Earthen and secondary materials such as calcium carbide residue and rice husk are widely  
39 available. The usage of these materials in building construction can provide several socio-  
40 economic, healthy, environmental and architectural benefits [1-3]. Indeed, many researchers are  
41 currently aiming at reviving the usage of earth-based materials in building construction [3-14].  
42 Compressed earth blocks (CEBs), among many other techniques, are promising for the  
43 construction of modern housing [4, 8-14].

44 The quality of available earthen material usually dictates the need for stabilization in order to  
45 reach the required performances of CEBs. Among many techniques of stabilization, the effects  
46 of mineral binders such as cement, lime, pozzolan and geopolymer on the curing behaviors and  
47 mechanical performances of CEBs are widely studied [4, 9-14]. Cement stabilized CEBs require  
48 around 28 days of curing to reach the optimum maturity of the hydration reaction, while lime  
49 stabilized CEBs require extended curing time to reach satisfactory performances such as strength  
50 and durability, among others [10, 11, 14-19].

51 When lime ( $\text{Ca}(\text{OH})_2$ ) is added to the clayey earthen material, it involves silica, alumina and  
52 eventually iron oxide in pozzolanic reaction for developing cementitious products [15-19]. The  
53 rate of this reaction is influenced by various conditions such as the reactivity of the materials and  
54 the curing temperature of their mixtures, among others [15, 17-18]. Comparative studies revealed  
55 that increasing the curing temperature (20-50 °C) increases the kinetic of the pozzolanic reaction  
56 (by a factor of 6) between the smectite-rich clay soil and industrial-grade lime [17-18].  
57 Additionally, calcium carbide residue (CCR), a lime-rich byproduct from the production of  
58 acetylene gas, was reported to behave similarly to lime for stabilization of clayey soil [20-22].  
59 Moreover, the pozzolanic reaction involving lime or CCR was also reported in the presence of  
60 natural pozzolan, fly ash and rice husk ash (RHA) [11, 23-27].

61 In the recent study [27], the stabilization of earthen material using CCR partially substituted by  
62 RHA (CCR:RHA) improved the compressive strength of CEBs and revealed the possibility to  
63 accelerate their curing process. Nevertheless, this study [27] was only limited to testing the  
64 compressive strength of stabilized CEBs at fixed curing time (45 days) and failed to do so at  
65 various curing time which would allow to determine the appropriate time to reach the optimum

66 strength. Testing the strength of CEBs requires bulk samples of the materials which limits its  
67 usefulness for evaluating the curing process at various curing time and conditions.

68 The present study investigates the curing process at 40 °C by simply measuring the electrical  
69 conductivity and concentration of unconsumed calcium ions on small samples of mix solutions  
70 of earthen material-CCR-RHA. This approach is useful as a simple tool to monitor the  
71 maturation of the reaction in the mix solutions and assess the effect of the reactivity of the  
72 materials on the chemical interactions. The effects of the interactions on the mineral and  
73 microstructural changes in the cured mixtures were analyzed using XRD, TGA and SEM to  
74 explain the improvement, reported in the previous study [27], on the compressive strength of  
75 CEBs stabilized with CCR:RHA. Depending on the reactivity of the materials and curing  
76 conditions of mixtures, this approach can allow to closely assess the appropriate curing time to  
77 reach the optimum maturity of the reaction in the mix solution which could possibly be the same  
78 amount of time for reaching the optimum strength of the stabilized CEBs.

## 79 **2. Materials and Methods**

### 80 **2.1. Characterization and processing of the raw materials**

81 The earthen material used in the present study is red-brown clayey soil collected from the  
82 locality of Kamboinse, Ouagadougou, Burkina Faso (12°29'24.48" N; 1°32'59.28" W; altitude  
83 326 m) (Fig. 1a). After drying, the soil particles were separated by softly crushing the earthen  
84 lumps. It was sieved to eliminate the particle larger than 5 mm. The CCR is white-greyish by-  
85 product collected from local industry which produces acetylene gas in the locality of Kossodo,  
86 Ouagadougou (N12°25.935'; W001°29.374'; alt. 301 m). The CCR was ball milled to obtain fine  
87 powder (Fig. 1b). The rice husk was collected as residue of rice farming from the locality of  
88 Bagre, southeast of Burkina Faso (N11°28.43'; W00°32.12'; alt. 233 m). It was incinerated at  
89 400 °C for 4 hours (maximum heating capacity of the furnace 1200 °C). The incineration yielded  
90 a grey-whitish RHA (Fig. 1c).

91 The geotechnical and physical properties of the earthen material were characterized in  
92 accordance with standards NF P 18-056 [43], NF P 94-057 [44], NF P 94-051 [45], and NF P 94-  
93 093 [46]. The particle size distribution of CCR and RHA was analyzed by laser diffraction  
94 technique using the Mastersizer analyser machine. The chemical compositions were determined  
95 by X-ray fluorescence (XRF) technique using the ARL Perform'X Sequential XRF equipment.  
96 After determination of loss on ignition on the sample materials calcined at 1000 °C for 2 hours,

97 340-450 mg (Ms) of the sample was fused in (11xMs) of lithium borate flux to form pellet for  
98 XRF analyses. Mineral compositions were determined by X-ray diffraction (XRD) technique  
99 performed using Bruker D8-Advance Eco 1.5 kW diffractometer equipped with copper  
100 anticathode (Cu K $\alpha$   $\lambda$ = 1.54060 Å, 40 kV, 25 mA) and Lynxeye xe detector in coupled  
101 2 $\theta$ / $\theta$  mode. The XRD patterns were acquired from 2 to 70° 2 $\theta$  at step sizes of 0.02° 2 $\theta$  and scan  
102 time of 2 s per step. The qualitative and semi-quantitative analyses were carried out using  
103 Diffrac.Eva V4.11 software of the Bruker. The specific surface area was determined according to  
104 Brunauer-Emmett-Teller (BET) methods by Nitrogen adsorption using micrometrics Gemini  
105 V1.01 instrument.

106 The earthen material contains 50 % of particles smaller than 30  $\mu$ m ( $D_{50}$  < 30  $\mu$ m), 90 % of  
107 particles smaller than 3000  $\mu$ m ( $D_{90}$  < 3000  $\mu$ m) and 30 % of clay particles (< 2  $\mu$ m) (Table 1).  
108 Table 2 presents the predominance of silica (51.0 %), alumina (23.7 %), iron (III) oxide (12.7 %)  
109 and traces of alkali and alkaline earth oxides (Na<sub>2</sub>O, K<sub>2</sub>O and CaO) in the earthen material. The  
110 mineral composition contains predominantly kaolinite clay (76 %), quartz (11 %) and goethite  
111 (9 %), the latter explaining the red-brown color of the earthen material.



112  
113 **Fig. 1.** Raw (top) and processed (bottom) materials: (a) earthen material, (b) calcium carbide  
114 residue, (c) rice husk/ash.

115 The physical properties of CCR are summarized in Table 1. The CCR has  $D_{50}$  < 20.5  $\mu$ m,  
116  $D_{90}$  < 125  $\mu$ m) and BET specific surface area of 14 m<sup>2</sup>/g. CCR contains predominantly CaO  
117 (67.4 %) and loss on ignition at 1000 °C of 26.7 %. The CCR contains mainly 43 % portlandite  
118 (Ca(OH)<sub>2</sub>), aragonite (21 %), calcite (16 %) and rapidcreekite (13 %) (Table 2).

119  
120

121 **Table 1**

122 Geotechnical and physical properties of the raw and processed materials.

| Geotechnical properties of the earthen material |      | Physical properties of the materials     |      |       |        |
|---|------|--|------|-------|--------|
|   |      | Earth                                    | CCR  | RHA   |        |
| Gravel (%)                                      | 11.2 | Specific density (-)                     | 2.75 | 2.49  | 2.24   |
| Sand (%)  | 22.2 | Blaine surface area (cm <sup>2</sup> /g) | -    | 8 286 | 26 114 |
| Silt (%)  | 36.5 | BET surface area (m <sup>2</sup> /g)     | -    | 14    | 115    |
| Clay (%)  | 30.1 | D <sub>10</sub> (μm)                     | <2   | 3     | 4      |
| Optimum water content (%)                       | 17.4 | D <sub>50</sub> (μm)                     | 30   | 20.5  | 11     |
| Maximum dry density (g/cm <sup>3</sup> )        | 1.76 | D <sub>90</sub> (μm)                     | 3000 | 100   | 50     |
| Limit of liquidity (%)                          | 45   |  |      |       |        |
| Plasticity index (%)                            | 16   |  |      |       |        |

123 The RHA was ground into the fine powder to reach D<sub>50</sub> of 11μm, D<sub>90</sub> of 50 μm and BET surface  
 124 area of 115 m<sup>2</sup>/g which is higher than that of CCR (Table 1). The chemical composition  
 125 (Table 2) shows that RHA contains 90 % of silica, with the reactive (amorphous) fraction of  
 126 68 % according to the test proposed by Mehta [28]. This fraction is in agreement with that  
 127 previously reported by Muthadhi [24].

128 **Table 2**

129 Chemical and mineral compositions of the raw and processed materials.

| Chemical compositions (%)      |       |      |      | Mineral composition (%)    |       |     |                  |
|--------------------------------|-------|------|------|----------------------------|-------|-----|------------------|
| Oxides                         | Earth | CCR  | RHA  | Minerals                   | Earth | CCR | RHA              |
| SiO <sub>2</sub>               | 51.3  | 4.7  | 91.2 | Kaolinite                  | 76    | 4   | Mainly amorphous |
| Al <sub>2</sub> O <sub>3</sub> | 24.1  | 1.7  | 1.6  | Portlandite                | -     | 43  |                  |
| Fe <sub>2</sub> O <sub>3</sub> | 12.8  | 0.7  | 0.6  | Aragonite                  | -     | 21  |                  |
| CaO                            | 0.2   | 66.3 | 0.8  | Calcite                    | -     | 16  |                  |
| TiO <sub>2</sub>               | 0.9   | 0.0  | 0.1  | Rapidcreekite              | -     | 13  |                  |
| MnO                            | 0.1   | 0.0  | 0.2  | Quartz                     | 11    | 3   |                  |
| MgO                            | 0.1   | 0.3  | 0.2  | Goethite                   | 9     | -   |                  |
| Na <sub>2</sub> O              | 0.0   | 0.0  | 0.0  | Traces (Mica, K-Feldspars) | 4     | -   |                  |
| K <sub>2</sub> O               | 0.3   | 0.1  | 1.8  |                            |       |     |                  |
| P <sub>2</sub> O <sub>5</sub>  | 0.1   | 0.0  | 0.6  |                            |       |     |                  |
| LOI (1000 °C)                  | 10.2  | 26.2 | 2.9  |                            |       |     |                  |
| Total                          | 100   | 100  | 100  | Total                      | 100   | 100 |                  |

130 **2.2. Preparation and curing of the mixtures**

131 Some dry mixtures were prepared using the earthen material and 0-25 wt % CCR with respect to  
 132 the dry mass of the earthen material. Others were prepared using the same amount of earthen

133 material and 10 to 25 wt % CCR:RHA in various ratios, i.e. 10 to 25 wt % CCR from which 10  
 134 to 40 wt % was partially substituted by RHA (Table 3). About 5 g of the dry mixtures were kept  
 135 in plastic bottles, filled with 100 mL of deionized water and rigorously shaken for preparing the  
 136 mix solutions. The pH of these solutions was measured after 1 hour to evaluate the change in the  
 137 basicity as described by Eades and Grim [29]. The bottles were tightly closed to minimize the  
 138 carbonation, cured in oven at  $40\pm 2$  °C and regularly shaken before the measurements which were  
 139 made after different periods of curing: 1, 7, 28, 45, and 90 days. Five samples of each mixture  
 140 were prepared for testing each one after every curing period.

141 Similarly, the appropriate amount of water, equivalent to the proctor optimum water content, was  
 142 added to the dry mixtures for preparing the stabilized CEBs. The CEBs were produced by  
 143 manually compressing appropriate amount of moisturized mixtures in the mold  
 144 ( $295\times 140\times 95$  mm<sup>3</sup>) of terstaram press. The compression capacity of the machine is estimated at  
 145 35 bars. The CEBs were covered to prevent the loss of humidity and minimize the carbonation  
 146 during the curing process which took place for 45 days at  $40\pm 2$  °C.

147 **Table 3**

148 Weight percentage of CCR and CCR:RHA (ratios) added to the earthen material.

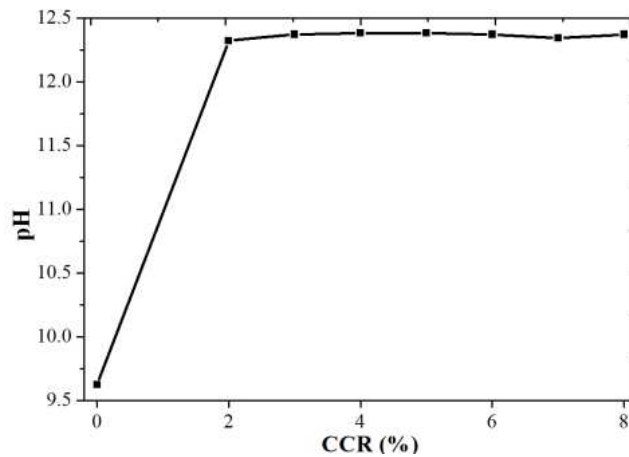
| Binder              | Fraction of binder added to the earthen material (wt %) |   |   |   |             |              |                  |
|---------------------|---|---|---|---|-------------|--------------|------------------|
| CCR                 | 2   | 4 | 5 | 8 | 10          | 20           | 25               |
| CCR:RHA<br>(ratios) | -   | - | - | - | 10<br>(9:1) | 20<br>(18:2) | 25<br>(22.5:2.5) |
|                     |   |   |   |   | (8:2)       | (16:4)       | (20:5)           |
|                     |   |   |   |   | (7:3)       | (14:6)       | (17.5:7.5)       |
|                     |   |   |   |   | (6:4)       | (12:8)       | (15:10)          |

149 **2.3. Measurements of electrical conductivity and concentration of calcium ion**

150 The electrical conductivity (EC) and concentration of unconsumed calcium [ $Ca^{2+}$ ] were  
 151 monitored in mix solutions of earth-CCR and earth-CCR:RHA systems. After each curing period  
 152 (1, 7, 28, 45 and 90 days), 60 ml of the solution were filtered and used for the measurements of  
 153 the EC and [ $Ca^{2+}$ ]. The EC was measured using pHenomenal CO 3100 lab conductimeter,  
 154 equipped with conductivity probe CO 11. The [ $Ca^{2+}$ ] was titrated by potentiometric method with  
 155 0.05 M EDTA (Ethylenediaminetetraacetic acid), using 905 titrado equipped with  
 156 polymer-calcium membrane electrode. This method was similarly used by Al-Mukhtar et al.  
 157 [17, 18] for monitoring the behavior and mineralogy changes in lime-treated clayey soils.

## 158 2.4. Microstructural characterization of the cured mixtures

159 X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were carried out on dried  
160 ( $40\pm 2$  °C) cured mixtures, previously used for measurements of the EC and  $\text{Ca}^{2+}$ , to identify the  
161 mineral changes induced throughout the curing process. The scanning electron microscopy  
162 (SEM) was performed on crushed CEBs to characterize the microstructural changes in cured  
163 CEBs. The XRD was performed as described in section 2.1. The TGA was carried out using  
164 automatic Multiple Sample Thermogravimetric Analyzer TGA-2000 of the Las Navas  
165 Instruments. The analysis was carried out in the range of 25-1000 °C at heating rate of 5 °C/min  
166 in dry air environment. The SEM was performed using the ZEISS GeminiSEM (Sigma 300)  
167 equipped with two energy dispersive spectrometers (EDS, Silicon Drift Detector XFlash of  
168 Bruker, 30 mm<sup>2</sup>). The operating conditions of the SEM were set at 20 keV, ~200  $\mu\text{A}$  and  
169 distance of 8.5 mm.



170

171 **Fig. 2.** Evolution of the pH in earth-CCR mix solution after 1 hour.

## 172 3. Results and discussion

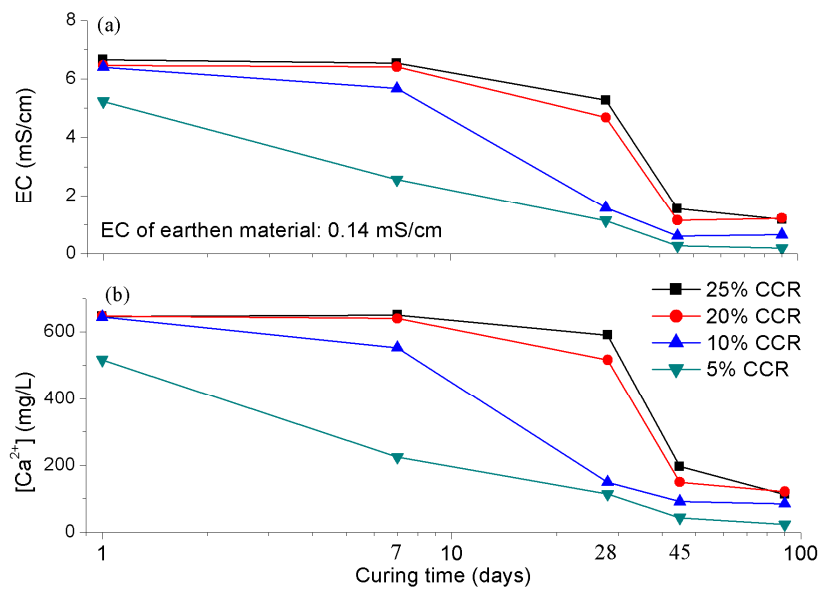
### 173 3.1. Change of the pH in the mix solutions

174 The pH of the mix solutions immediately reached the maximum value of 12.4 after 1 hour of  
175 addition of only 2 % CCR from a pH of 9.6 of the earthen material (Fig. 2). This is explained by  
176 the fact that CCR contains good amount of portlandite (43 % of  $\text{Ca}(\text{OH})_2$ ) which dissolves to  
177 give hydroxyl ions ( $\text{OH}^-$ ) and calcium ions ( $\text{Ca}^{2+}$ ),  $\text{OH}^-$  being responsible for the increase of the  
178 basicity. According to Eades and Grim [29], the 2 % CCR basically corresponds to the fraction  
179 of CCR necessary for affinity saturation of clayey earthen material used in the present study. It is  
180 the fraction of CCR responsible for the short term modification of the clay material through  
181 cation exchange and flocculation-agglomeration [17-19]. Beyond this fraction, the CCR must

182 contribute in time dependent pozzolanic reaction, with the aluminosilicates, responsible for the  
183 mineral changes in the mixtures [17-19, 29]. The low cation exchange capacity of the  
184 kaolinite-rich earthen material can be related to the limited occurrence of oxides of alkali and  
185 alkaline earth in its chemical composition (Table 2).

### 186 3.2 Evolution of the electrical conductivity and unconsumed calcium ions in mix solutions

187 Fig. 3a shows that the electrical conductivity (EC) of the mix solutions reached  
188 ~5.5 millisiemens/cm (mS/cm) and ~6.5 mS/cm respectively after one day of addition of  
189 5 % CCR and  $\geq 10$  % CCR from 0.14 mS/cm of the earthen material. The elevated EC in solution  
190 containing CCR is related to  $\text{Ca}^{2+}$  and  $\text{OH}^-$  from the dissolution of portlandite in the CCR. The  
191 low EC in the solution of the earthen materials (0.14 mS/cm) is again explained by the limited  
192 content of alkali and alkaline earth elements. The EC in mix solutions of earthen material and  
193 CCR decreased over time, as the curing proceeds, but at different rate depending on the mix  
194 composition (Fig. 3a). Moreover, the concentration of unconsumed calcium ions [ $\text{Ca}^{2+}$ ] in the  
195 mix solutions similarly decreased over the curing time (Fig. 3b). The EC and [ $\text{Ca}^{2+}$ ] reached the  
196 apparent minimum values after 45 days of curing in all mix solutions containing earthen material  
197 and CCR alone. Nevertheless, the EC and [ $\text{Ca}^{2+}$ ] continuously decreased at the highest rate  
198 between the 7<sup>th</sup> and 45<sup>th</sup> day for the mix solution containing 10 % CCR while the highest rates  
199 were recorded between the 28<sup>th</sup> and 45<sup>th</sup> day for the mix containing more than 10 % CCR  
200 (Fig. 3).



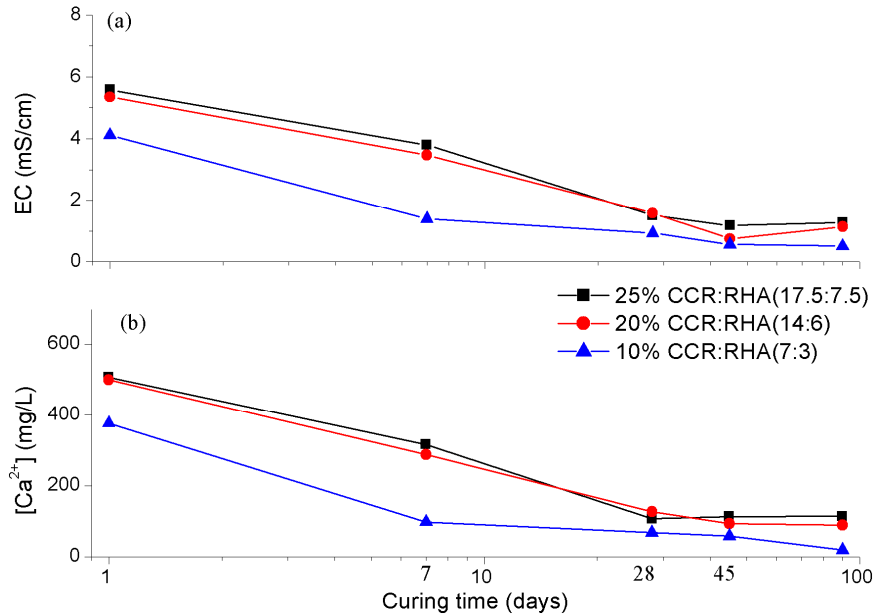
201  
202 **Fig. 3.** Evolution of (a) electrical conductivity (EC) and (b) concentration of unconsumed  
203 calcium ions [ $\text{Ca}^{2+}$ ] in mix solutions of earthen material and 5-25 % CCR.

204 Fig. 3 shows that the decrease of the EC is related to the consumption of free calcium ions which  
205 initially dissolved from the CCR. At early age of curing (1-28 days depending on the mix  
206 composition), this consumption is counteracted by more calcium ions dissolving from the excess  
207 CCR. This partly explains the delayed decrease of the EC and  $[Ca^{2+}]$  for the mix solution  
208 containing more than 10 % CCR, which remained practically constant until the 7<sup>th</sup> day.  
209 Additionally, the delayed decrease of the EC and  $[Ca^{2+}]$  can be explained by the presence of low  
210 affinity kaolinite clay in the earthen material whose low cation exchange capacity results in  
211 limited short term consumption of  $Ca^{2+}$ . The effect of the pozzolanic reaction, responsible for  
212 consumption of good amount of  $Ca^{2+}$  as well as  $OH^-$ , was essentially noticeable after the 7<sup>th</sup> day  
213 of curing. The pozzolanic reaction between  $Ca(OH)_2$  in the CCR and aluminosilicates in the  
214 earthen material results in consumption of  $Ca^{2+}$  which is also accompanied by the consumption  
215 of  $OH^-$  [17, 18]. For mixtures containing 10 % CCR and less, the EC and  $[Ca^{2+}]$  immediately  
216 started decreasing from the first day of curing given that a fraction of it (2 % CCR) contribute to  
217 the immediate satisfaction of the affinity of the earthen material and the remaining fraction to the  
218 beginning of the pozzolanic reaction. This leaves only limited fraction of excess CCR for further  
219 dissolving and replenishing these mixtures with  $Ca^{2+}$  and  $OH^-$ .

220 The change in the evolution of the EC and  $[Ca^{2+}]$  can suggest that 10 % is the amount of CCR  
221 which initially dissolves to saturation for effective contribution to the pozzolanic reaction with  
222 the earthen material used in the present study. The excess content ( $> 10$  % CCR) may result in  
223 occurrence of residual CCR in the mixture which, in addition to not reacting efficiently, may  
224 compromise the physico-mechanical stability of the mixtures. Indeed, the compressive strength  
225 of earthen materials was previously reported to reach the maximum value after addition of  
226 8-10 % CCR, beyond which the strength either remained constant or decreased [20, 21, 27].  
227 Therefore, there was need for effective consumption of the residual CCR which justify the partial  
228 substitution of the CCR with the pozzolanic material such as RHA locally available.

229 Fig. 4 shows that the EC and  $[Ca^{2+}]$  decreased even faster for mix solutions containing the  
230 earthen material and CCR:RHA, thus faster reaction in mixes containing RHA. Fig. 4b obviously  
231 shows that the consumption of  $Ca^{2+}$  is faster in the mix solution containing the earthen material  
232 and 10 % CCR:RHA (7:3 ratio), i.e. 7 % CCR and 3 % RHA, than it was in the solution  
233 containing the earthen material and only 5 % CCR in Fig. 3b. This implies that the CCR is  
234 simultaneously consumed by the earthen materials and the RHA in mixes containing the earth  
235 and CCR:RHA; while it is only consumed by the earthen material in the mixes containing earth  
236 and CCR alone. Moreover, while the mix solution containing 10 % CCR required 45 days to

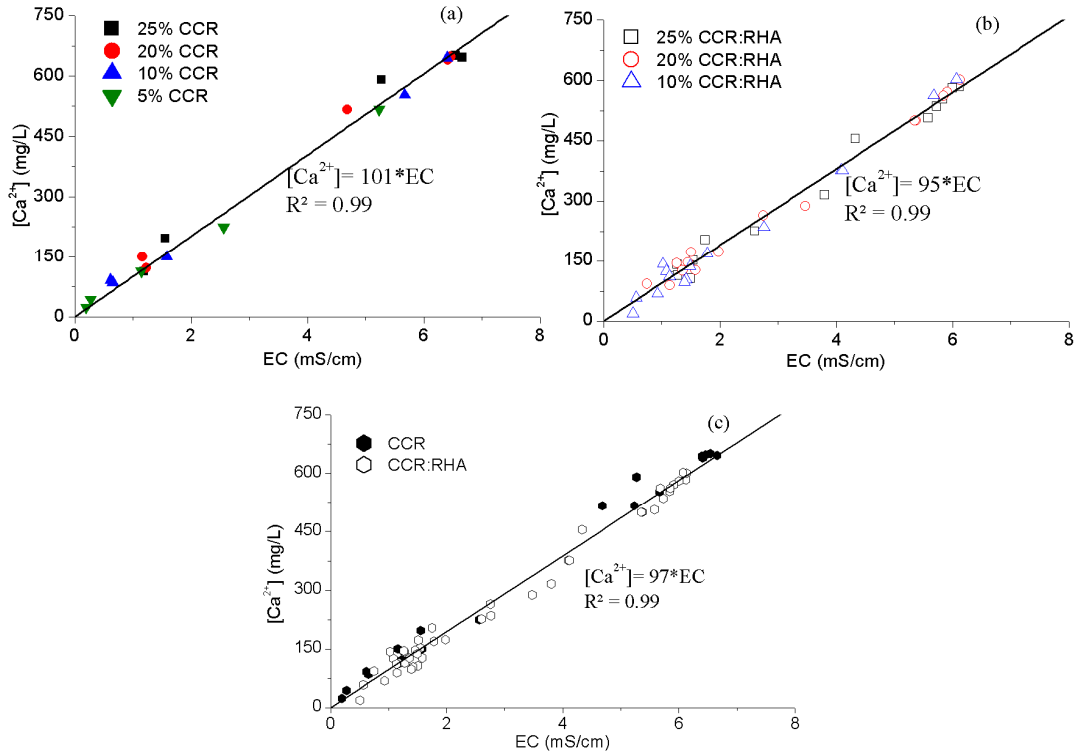
237 reach the minimum EC and  $[Ca^{2+}]$  (Fig. 3); the solution containing 20 % CCR:RHA in (14:6  
 238 ratio), i.e. 14 % CCR and 6 % RHA, reached the minimum values in only 28 days (Fig. 4). The  
 239 minimum EC and  $[Ca^{2+}]$  basically correspond to the end of the reaction. Therefore, it can be  
 240 deduced that RHA accelerated the reaction in the earth-CCR-RHA mixtures and considerably  
 241 reduced the time pending for the reaction to take place and reach the optimum maturity. This  
 242 implies that curing time of earth-based mixtures can potentially be reduced from 45 to 28 days  
 243 when they are stabilized with CCR:RHA instead of CCR alone.



244  
 245 **Fig. 4.** Evolution of (a) electrical conductivity (EC) and (b) concentration of unconsumed  
 246 calcium ions  $[Ca^{2+}]$  in mix solutions of earthen material and 10-25 % CCR:RHA in 7:3 ratio.

247 The optimum dosage of CCR:RHA can effectively act similar to cement for stabilization of  
 248 earth-based materials, such as CEBs, in term of curing time and possibly improve the mechanical  
 249 performances of CEBs at early age [3, 13, 27]. In fact, the previous study reported that the  
 250 compressive strength improves threefold from 2.2 to 6.6 MPa when the CEBs were respectively  
 251 stabilized with 15 % CCR and 15 % CCR:RHA (10.5:4.5) after 45 days of curing in ambient  
 252 conditions of the laboratory ( $30 \pm 5$  °C) [27]. Note that this improvement does not only depend on  
 253 the reactivity of materials, i.e. CCR reacting with earth and RHA, but also on the conditions in  
 254 which the mixtures were produced and cured. The reactivity of lime ( $Ca(OH)_2$ ) in the CCR  
 255 should have improved if the temperature were increased and maintained at  $40 \pm 2$  °C as in the  
 256 present study. The effect of curing temperature was shown in the studies carried out by  
 257 Al-Mukhtar et al. [17, 18], where the soil showed accelerated consumption of lime at curing  
 258 temperature of 50 °C compared to 20 °C. In the same studies, the unconfined compressive  
 259 strength of the soil treated with 10 % lime cured at 50 °C ( $\sim 4$  MPa) improved almost twice

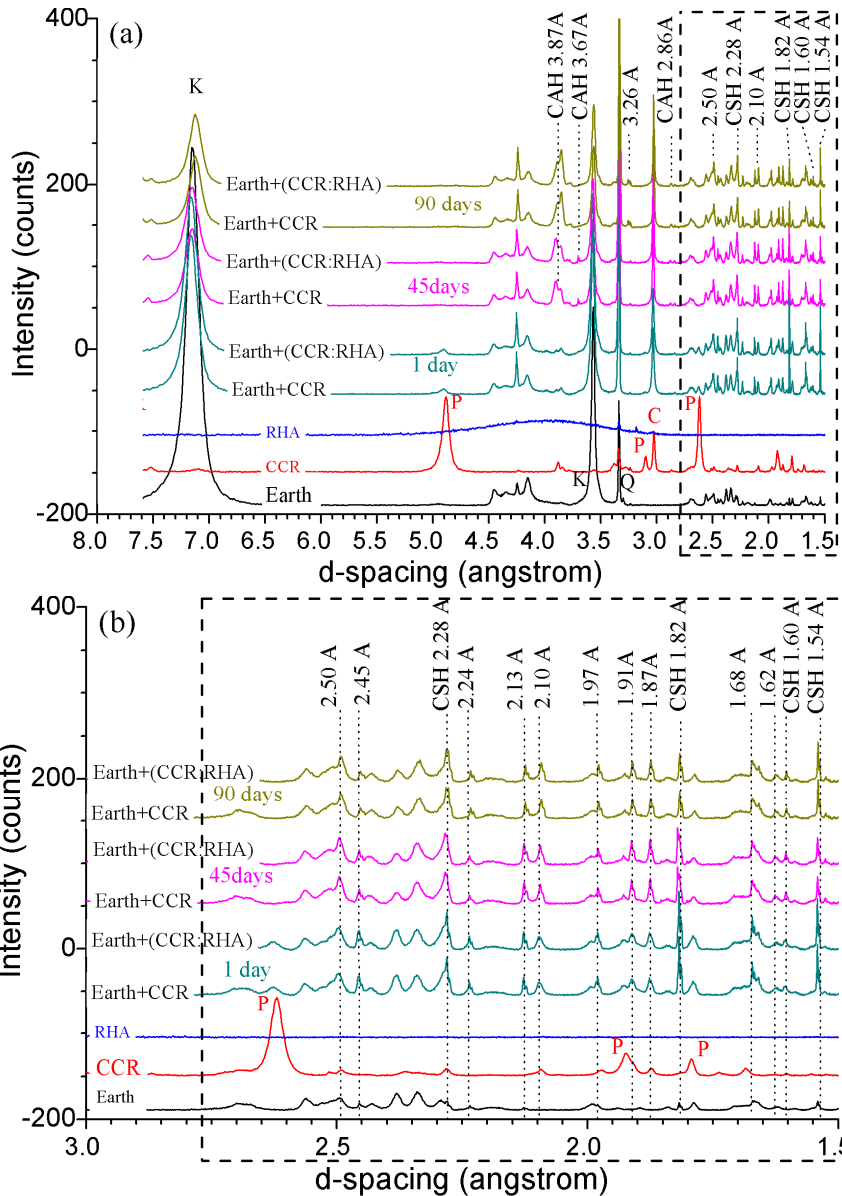
260 compared to the strength recorded at 20 °C (~2 MPa) after 45 days of curing [17, 18]. More  
 261 studies should investigate the effect of the aforementioned reduction of curing time on the  
 262 evolution of the mechanical performances of earth based-materials, particularly CEBs, stabilized  
 263 with CCR and CCR:RHA.



264  
 265 **Fig. 5.** Correlation between the EC and  $[Ca^{2+}]$  in the mix solutions cured for various time  
 266 (1, 7, 28, 45, 90 days) containing the earthen material and (a) 5-25 % CCR, (b) 10-25 %  
 267 CCR:RHA in various ratios, (c) combination of all data.

268 Furthermore, Fig. 5 shows linear correlations between EC and  $[Ca^{2+}]$  with regression coefficients  
 269 ( $R^2$ ) greater than 0.95. These correlations are presented in Fig. 5a for mix containing the earthen  
 270 material and 5-25 % CCR, Fig. 5b for those containing the earthen material and 10-25 %  
 271 CCR:RHA in various ratios and all data are compiled in Fig. 5c. The equation relating the EC  
 272 and  $[Ca^{2+}]$  was proposed to be of type  $[Ca^{2+}] = k * EC$ ; with  $[Ca^{2+}]$ , concentration of unconsumed  
 273 calcium ion; EC, electrical conductivity of the mix solution; and k, correlation coefficient  
 274 considered to vary around 97. This coefficient can reach a value of 101 for CCR-rich mix  
 275 solutions (Fig. 5a) and value of 95 for RHA (i.e. CCR:RHA)-rich solutions (Fig. 5b). This  
 276 implies that  $[Ca^{2+}]$  can simply be deduced from the measurement of the EC in the mix solutions  
 277 and vice versa, rather than having to carry out series of titrations of calcium ions. Therefore, it is  
 278 possible to monitor the extent of curing and rate of consumption of calcium in stabilized earth  
 279 based-materials. This correlation between the EC and  $[Ca^{2+}]$  is mostly useful for mixtures where  
 280 the consumption of  $Ca^{2+}$  through the pozzolanic reaction is the main phenomena controlling

281 concentration of ions in the solutions such as in kaolinite-rich earthen material. If other ions such  
 282 as sodium and potassium existed in the solution, for instance from the exchangeable cations in  
 283 smectite-rich soil where EC=2.7 mS/cm [17, 18], the EC and its correlation with  $[Ca^{2+}]$  would  
 284 have to take into account the contribution of these ions. Additionally, the approach used in the  
 285 present study can be extended to compare the reactivity of various earthen materials before  
 286 selecting the most appropriate for production of stabilized CEBs without prior testing of the  
 287 mechanical performances of the bulk samples.



288  
 289  
 290 **Fig. 6.** XRD patterns of the earthen material, CCR, RHA and mixtures cured for 1, 45, 90 days:  
 291 earth+20 % CCR; earth+20 % CCR:RHA (16:4 ratio); (a) full view, (b) detailed view;  
 292 k= Kaolinite, P= Portlandite, C= Calcite, Q= Quartz, CSH= Calcium Silicate Hydrates, CAH=  
 293 calcium aluminate hydrates.

### 294 3.3. Mineral changes in the cured mixtures

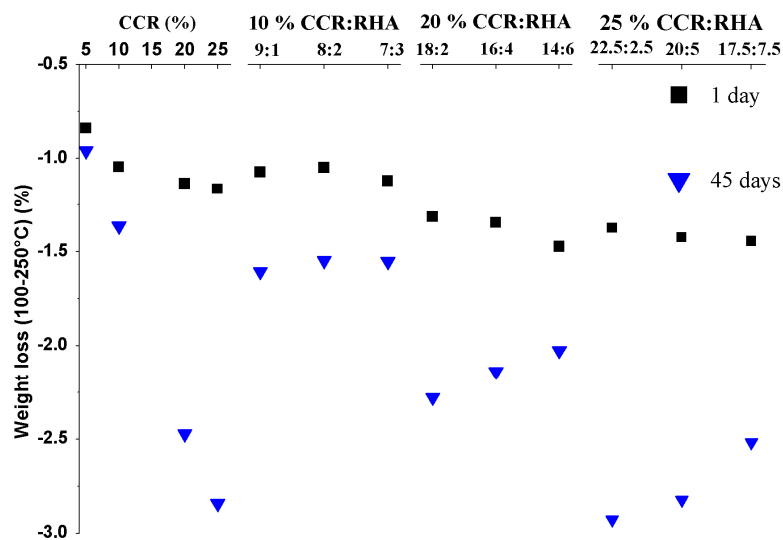
295 The change of the mineralogy from the raw materials to the cured mixtures was characterized  
296 using XRD and TGA. The XRD patterns of selected cured mixtures are presented in Fig. 6. It  
297 reveals that the specific reflection of portlandite at 2.62 Å in CCR disappears after one day of  
298 curing, while that of kaolinite at 7.15 Å significantly reduced over time (Fig. 6a). This reveals  
299 the mineral changes in the cured mixtures resulting from the reaction of the constituent materials.  
300 Secondary peaks can be observed at 3.87, 3.67, 3.26, 2.86, 2.28, 1.82, 1.60, and 1.54 Å (Fig. 6a).  
301 These peaks confirm the formation of crystalline products in the cured mixtures, which were  
302 identified as calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH). Prior  
303 studies similarly reported the formation of CSH and CAH from the reaction between kaolinite  
304 clay and  $\text{Ca}(\text{OH})_2$  [14,19,30]. Moreover, the XRD spectra of cured mixtures significantly  
305 changed between 3.0-1.5 Å (Fig. 6b). There was appearance of new peaks and increase in the  
306 intensity of some peaks existing in the raw earthen material, mainly corresponding to quartz  
307 mineral. Although the peaks in Fig. 6b are not fully identified, they are possibly related to the  
308 CSH products of reaction involving silica and  $\text{Ca}(\text{OH})_2$ .

309 Fig. 2 showed the increase of the pH in the mix solutions, containing only 2 % CCR, up to the  
310 initial value of 12.4 due to the dissociation of the  $\text{Ca}(\text{OH})_2$  from the CCR into  $\text{Ca}^{2+}$  and  $\text{OH}^-$ .  
311 This increase of the basicity in the mix solutions was responsible for the dissolution of fine  
312 aluminosilicates, kaolinite clay and silica among others [30]. In the presence of  $\text{Ca}^{2+}$ , this results  
313 in the precipitation into CSH and CAH cementitious products [15, 18]. This agrees with the  
314 previous study that only the fraction of CCR as small as 5 % can impact permanent structure  
315 changes in kaolinitic earthen material and improve the compressive strength of stabilized CEBs  
316 thereof formed [27].

317 Fig. 6a additionally shows that only 50 % of the intensity of the peak of kaolinite (7.15 Å)  
318 remained after 45 days of curing compare to 1 day of curing for mixtures containing either the  
319 earthen material and CCR or earthen material and CCR:RHA. The remaining intensity of this  
320 peak (7.15 Å) reached 40 % after 90 days of curing which shows that the reaction involving  
321 kaolinite substantially took place in 45 days. This agrees with the concentration of unconsumed  
322 calcium which reached the apparent minimum after 45 days of curing in mix solution containing  
323 the earthen material and CCR (Fig. 3b). Therefore; the consumption of portlandite from CCR  
324 and kaolinite from the earthen material is responsible for the reaction between the earthen  
325 material and CCR, which reached the optimum after 45 days of curing. Additionally, this  
326 suggests that RHA basically interact with the CCR not the earthen material given that the

327 intensity of the peak of kaolinite remains practically the same for mixtures containing either  
 328 CCR or CCR:RHA at a given curing time (Fig. 6a). Besides, the intensity of the reflection peak  
 329 of calcite ( $\sim 3.01 \text{ \AA}$ ) slightly increased in the mixtures cured for 45 and 90 days compared to the  
 330 mixtures cured for 1 day (Fig. 6a). This reveals that carbonation may have taken place possibly  
 331 during the drying and testing of the mixtures, though the precautions were taken by carefully  
 332 covering the samples during curing.

333 The loss of weight of cured mixtures was tentatively determined from the TGA between 100 and  
 334  $250^\circ\text{C}$  (Fig. 7). It shows that the loss of weight in this temperature range generally increases with  
 335 the binder (CCR or CCR:RHA) content from 1 day to 45 days of curing. It indeed agrees with  
 336 prior reports that CSH mainly losses the gel water in this range of temperature [15, 30, 31]. This  
 337 complies with the XRD results of the cured mixtures (Fig. 6a) and compressive strength of  
 338 stabilized CEBs [27], confirming the formation of more CSH products with the curing time and  
 339 binder content.



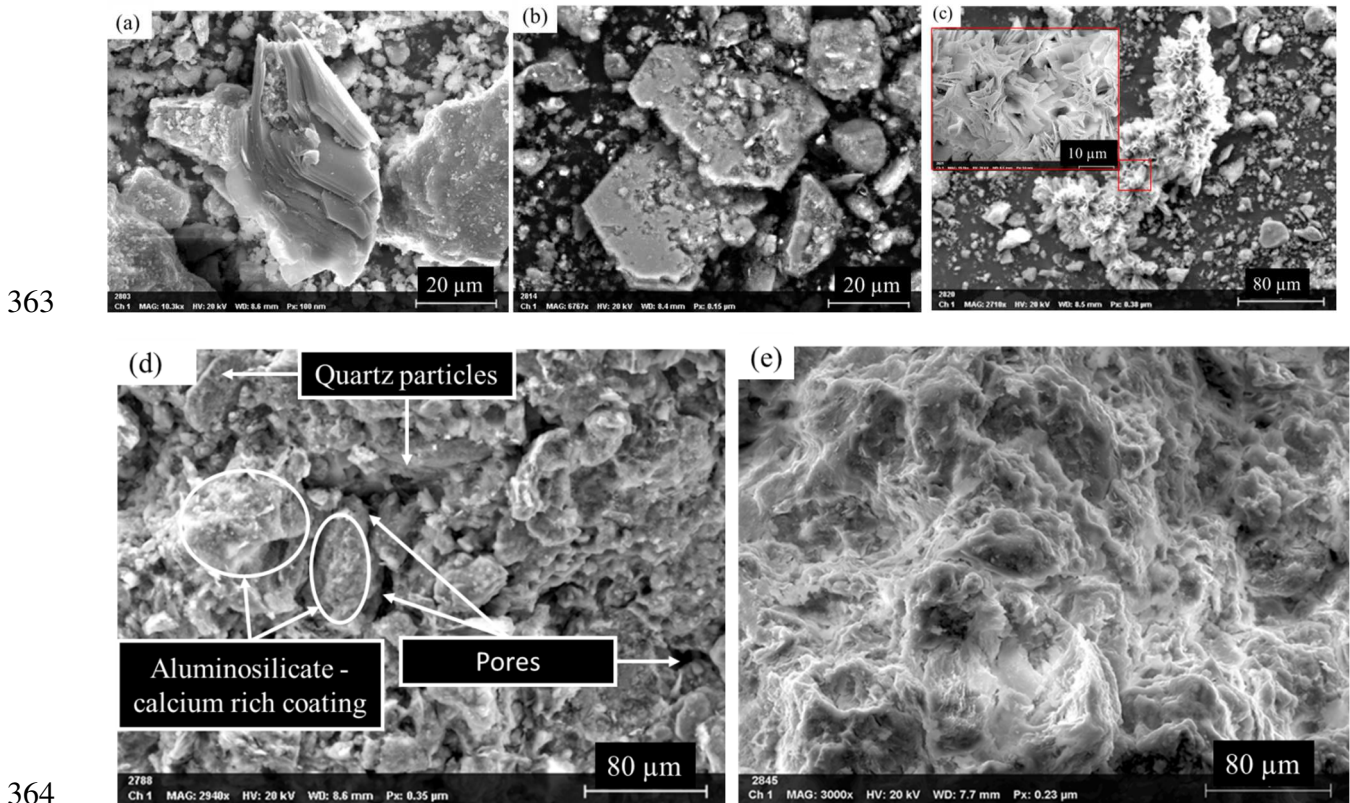
340

341 **Fig. 7.** Loss of weight in 100-250 °C range for various mixtures cured for 1 and 45 days.

### 342 3.4. Microstructural changes in cured mixtures

343 SEM was performed to further confirm the chemical interactions and microstructural changes  
 344 which took place in cured mixtures (Fig. 8). Fig. 8a shows portlandite-rich particles in the raw  
 345 CCR, which dissolved in the cured mixtures (Fig. 8b). This results in formation of new products  
 346 rich in calcium-silica, in plate-like shape, which grow into an interlocking network in cured  
 347 mixtures containing CCR:RHA (Fig. 8c). The formation of similar products was previously  
 348 reported in cured soil-lime mixtures, which were identified as CSH phases [30].

349 The SEM micrographs of stabilized CEBs show the formation of “porridge-like” cementing  
350 products. The microstructure of CEBs stabilized with 20 % CCR shows the earthen particles  
351 coated by aluminosilicate-calcium rich products and appearance of no-cemented pores in the  
352 inter-particle zones (Fig. 8d). By contrary, the microstructure of CEBs stabilized with  
353 20 % CCR:RHA (14:6 ratio) shows that the particles and inter-particle zones are cemented  
354 (Fig. 8e). For CEBs containing CCR alone, the cementing products are only limited to the  
355 earthen particles, leaving some open inter-particle pores. The RHA, in CEBs containing  
356 CCR:RHA, improves the formation of more products for the cementation of the particles and the  
357 inter-particle pores. The densification of the microstructure of CEBs stabilized with CCR:RHA  
358 compared to that of CEBs stabilized with CCR alone essentially explains the improvement of the  
359 compressive strength previously reported for the CEBs stabilized with CCR:RHA [27].  
360 Nevertheless, it would be interesting to confirm the evolution of the percentage and size of pore  
361 in stabilized CEBs through specialized testing such as mercury intrusion porosimetry or X-ray  
362 tomography.



365 **Fig. 8.** SEM micrographs (a) raw CCR, (b) cured mixtures containing 20 % CCR, (c) cured  
366 mixtures containing 20 % CCR:RHA (14:6 ratio); (d) CEBs stabilized with 20 % CCR, (e) CEBs  
367 stabilized with 20 % CCR:RHA (14:6 ratio).

## 368 4. Conclusions

369 The chemical interactions took place between CCR and earthen material, and CCR and RHA  
370 which were evidenced by the consumption of portlandite from the CCR by the kaolinite from the  
371 earthen material and amorphous silica from the RHA. These interactions were responsible for the  
372 decrease of the electrical conductivity and concentration of unconsumed calcium, and permanent  
373 change of the mineralogy and microstructure in the cured mixtures. The following conclusions  
374 are reached from this study:

- 375 1. The measurement of the electrical conductivity (EC) and concentration of unconsumed  
376 calcium [ $\text{Ca}^{2+}$ ] allowed to monitor the curing process and establish the linear correlation  
377 between EC and [ $\text{Ca}^{2+}$ ] ( $[\text{Ca}^{2+}] = 97 * \text{EC}$ ; with  $R^2 > 0.95$ ) in the mix solutions of kaolinitic  
378 earthen material-CCR-RHA. The curing process of earthen building materials containing  
379 CCR or CCR:RHA in various ratios can possibly be monitored by measuring the electrical  
380 conductivity and predicting the concentration of unconsumed calcium and vice versa. This  
381 can be useful for selecting the most reactive, among different earthen materials, with  
382 portlandite-rich material based on the rate of the consumption of calcium;
- 383 2. The curing process of mixtures containing kaolinitic earthen material and CCR requires at  
384 least 45 days to reach the optimum maturity of the pozzolanic reaction in mix solutions,  
385 while those containing the earth and CCR:RHA require only 28 days at  $40 \pm 2$  °C. The  
386 RHA accelerates the curing process in the mix solutions of earth and CCR:RHA and had  
387 previously improved the compressive strength of stabilized CEBs. This implies that  
388 CCR:RHA in optimum ratio could possibly act like cement for stabilization of CEBs to  
389 reach the optimum compressive strength after only 28 days of curing rather than 45 days;
- 390 3. The chemical interactions, responsible for the consumption of calcium ions, during the  
391 curing of mixtures containing the earthen material and CCR or CCR:RHA results in the  
392 formation of calcium silicate hydrates and calcium aluminate hydrates. These hydrates are  
393 responsible for the cementation and densification of the microstructure of stabilized  
394 CEBs.

395 Further study should elucidate the curing process of CEBs stabilized with CCR and/or  
396 CCR:RHA. This can be done by investigating the improvement of the physico-mechanical and  
397 hygro-thermal performances of stabilized CEBs at various curing time in order to confirm the  
398 possibility of reduction of curing time observed in the present study. This may allow to correlate  
399 the consumption of calcium ions in mix solutions of earth-CCR-RHA with the compressive  
400 strength of stabilized CEBs thereof produced.

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## 412 **References**

- 413 [1] Wyss, Urs. (2005) “La Construction En « matériaux Locaux » Etat d’un Secteur à Potentiel Multiple.” Report  
414 DDCICI Burkina Faso.
- 415 [2] UNESCO (2012) ‘Earthen architecture in today’s world’, in Proceedings of the UNESCO International  
416 Colloquium on the Conservation of World Heritage Earthen Architecture 17-18 December, Paris-France.
- 417 [3] Houben H and Guillaud H (2006) CRATerre: Traité de Construction en Terre: L’encyclopédie de la construction  
418 en terre, Vol I. Editions Parathèses, Marseille.
- 419 [4] Sore SO, Messan A, Prud’homme E, Escadeillas G, and Tsobnang F (2018) Stabilization of Compressed Earth  
420 Blocks (CEBs) by geopolymer binder based on local materials from Burkina Faso. *Constr. Build. Mater.* 165:  
421 333-345. <https://doi.org/10.1016/j.conbuildmat.2018.01.051>.
- 422 [5] Hema CM, Van Moeseke G, Evrad A, Courard L, and Messan A (2017) Vernacular housing practices in Burkina  
423 Faso: Representative models of construction in Ouagadougou and walls hygrothermal efficiency. *Energy*  
424 *Procedia* 122: 535–540. <https://doi.org/10.1016/j.egypro.2017.07.398>.
- 425 [6] Azeko ST, Mustapha K, Annan E, Odusanya OS, and Soboyejo WO (2015) Recycling of Polyethylene into  
426 Strong and Tough Earth-Based Composite Building Materials. *J Mater Civ Eng* 28:1–10.  
427 [10.1061/\(ASCE\)MT.1943-5533.0001385](https://doi.org/10.1061/(ASCE)MT.1943-5533.0001385).
- 428 [7] Laborel-Préneron A, Aubert JE, Magniont C, Tribout C, and Bertron A (2016) Plant aggregates and fibers in  
429 earth construction materials: A review. *Constr Build Mater* 111:719–734.  
430 <https://doi.org/10.1016/j.conbuildmat.2016.02.119>.
- 431 [8] Bruno AW, Gallipoli D, Perlot C, and Mendes J (2017) Mechanical behaviour of hypercompacted earth for  
432 building construction. *Mater Struct* 50:1–15. <http://link.springer.com/10.1617/s11527-017-1027-5>.
- 433 [9] Masuka, S., Gwenzi, W., & Rukuni, T. (2018). Development, engineering properties and potential applications  
434 of unfired earth bricks reinforced by coal fly ash, lime and wood aggregates. *Journal of Building Engineering*,  
435 18: 312–320. <https://doi.org/10.1016/j.jobe.2018.03.010>
- 436 [10] Ouedraogo E, Coulibaly O, Ouedraogo A, and Messan A (2015) Mechanical and Thermophysical Properties of  
437 Cement and/or Paper (Cellulose) Stabilized Compressed Clay Bricks. *J Mater Eng Struct* 2 2:68–76.
- 438 [11] Izemmouren O, Guettala A, and Guettala S (2015) Mechanical Properties and Durability of Lime and Natural  
439 Pozzolana Stabilized Steam-Cured Compressed Earth Block Bricks. *Geotech Geol Eng* 33:1321–1333. DOI  
440 [10.1007/s10706-015-9904-6](https://doi.org/10.1007/s10706-015-9904-6).
- 441 [12] Ronoh V, Kaluli JW, and Too JK (2015) Characteristics of Earth Blocks Stabilized With Rice Husk Ash and  
442 Cement. *J Sustain Res Eng* 2:121–126.
- 443 [13] Walker P and Stace T (1997) Properties of some cement stabilised compressed earth blocks and mortars. *Mater*  
444 *Struct Constr* 30:545–551.
- 445 [14] Reddy BVV and Hubli SR (2002) Properties of lime stabilised steam-cured blocks for masonry. *Mater Struct*  
446 35:293–300.

- 447 [15] Diamond S (1963) Transformation of Clay Minerals by Calcium Hydroxide Attack. *Clays Clay Miner* 12:359–  
448 379.
- 449 [16] Bell FG (1996) Lime stabilization of clay minerals and soils. *Eng Geol* 42:223–237.
- 450 [17] Al-Mukhtar M, Lasledj A, and Alcover JF (2010) Behaviour and mineralogy changes in lime-treated expansive  
451 soil at 20°C. *Appl Clay Sci* 50:191–198. <http://dx.doi.org/10.1016/j.clay.2010.07.023>
- 452 [18] Al-Mukhtar M, Lasledj A, and Alcover JF (2010) Behaviour and mineralogy changes in lime-treated expansive  
453 soil at 50°C. *Appl Clay Sci* 50:199–203. <http://dx.doi.org/10.1016/j.clay.2010.07.022>
- 454 [19] Al-Mukhtar M, Khattab S, and Alcover JF (2012) Microstructure and geotechnical properties of lime-treated  
455 expansive clayey soil. *Eng Geol* 139–140:17–27. 10.1016/j.enggeo.2012.04.004.
- 456 [20] Horpibulsuk S, Phetchuay C, Chinkulkijniwat A, and Cholaphatsorn A (2013) Strength development in silty  
457 clay stabilized with calcium carbide residue and fly ash. *Soils Found* 53:477–486. 10.1016/j.sandf.2013.06.001.
- 458 [21] Kampala A, Horpibulsuk S, Chinkulkijniwat A, and Shen SL (2013) Engineering properties of recycled  
459 Calcium Carbide Residue stabilized clay as fill and pavement materials. *Constr Build Mater* 46:203–210.  
460 10.1016/j.conbuildmat.2013.04.037.
- 461 [22] Vichan S and Rachan R (2013) Chemical stabilization of soft Bangkok clay using the blend of calcium carbide  
462 residue and biomass ash. *Soils Found* 53:272–281. 10.1016/j.sandf.2013.02.007.
- 463 [23] Ganesan K, Rajagopal K, and Thangavel K (2008) Rice husk ash blended cement: assessment of optimal  
464 replacement for strength and permeability properties of concrete. *Constr Build Mater* 22:1675–1683.  
465 10.1016/j.conbuildmat.2007.06.011.
- 466 [24] Muthadhi A and Kothandaraman S (2010) Optimum production conditions for reactive rice husk ash. *Mater*  
467 *Struct* 43:1303–1315. 10.1617/s11527-010-9581-0.
- 468 [25] Ugheoke IB and Mamat O (2012) Review: A critical assessment and new research directions of rice husk silica  
469 processing methods and properties. *Maejo Int J Sci Technol* 6:430–448.
- 470 [26] Hwang C and Huynh T (2015) Investigation into the use of unground rice husk ash to produce eco-friendly  
471 construction bricks. *Constr Build Mater* 93:335–341. 10.1016/j.conbuildmat.2015.04.061.
- 472 [27] Nshimiyimana P, Miracourt D, Messan A, and Courard L (2018) Calcium Carbide Residue and Rice Husk  
473 Ash for improving the Compressive Strength of Compressed Earth Blocks. *MRS Adv* 3:2009-2014.  
474 <http://dx.doi.org/10.1557/adv.2018.147>.
- 475 [28] Mehta PK (1978) Siliceous ashes and hydraulic cements prepared therefrom. US Patent, US4105459 A.
- 476 [29] Eades JL and Grim RE (1996) A Quick Test to Determine Lime Requirements for Lime Stabilization. *Highw*  
477 *Res Rec* 3:61–72.
- 478 [30] Arabi M and Wild S (1986) Microstructural development in cured soil-lime composites. *J Mater Sci* 21:497–  
479 503.
- 480 [31] Arrigoni A, Pelosato R, Dolelli G, Beckett CTS, and Ciancio D (2017) Weathering's beneficial effect on waste-  
481 stabilised rammed earth: a chemical and microstructural investigation. *Constr Build Mater* 140:157–166.  
482 10.1016/j.conbuildmat.2017.02.009.
- 483