Effect of calcium chloride on the hydration characteristics of ground clay bricks cement pastes

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ABSTRACT
Effect of CaCl₂ on the hydration characteristics of the different cement pastes using ordinary Portland cement (OPC) and blended Portland cement with ground clay bricks (GCB) was studied. Various mixes were prepared using a water/solid ratio (W/S) of 0.25 (by weight). Three percentages of CaCl₂ (0.25, 0.5 and 0.75%) are used; the CaCl₂ used was dissolved in the mixing water. The hydration characteristics were tested via the determination of the combined water content, phase composition, compressive strength, total porosity (P%) and X-ray diffraction analysis (XRD) at different time intervals up to 180 days. The results showed that calcium chloride accelerates cement hydration in all systems studied. Ten % GCB in the presence of 0.50% CaCl₂ is the optimum ratio which has the higher compressive strength.

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1. Introduction
Super-plasticizers are admixtures, which are added to concrete mixture in very small dosages. Their addition results in significant increase of the workability of the mixture, in reduction of water/cement ratio or even of cement quantity. Their performance depends on the type of the superplasticizer, the composition of the concrete mixture, the time of addition and the temperature conditions during mixing and concreting (Papayianni et al., 2005).

The influence of the presence of concrete admixtures on the hydration reaction of cement pastes was studied. Two admixtures (1) an accelerator and (2) a retarder, have been added to the cement pastes at different ages. The presence of such admixtures affects the physicochemical properties of the products. The addition of the accelerator the rate of hydration reaction whereas the retarder delays the reaction rate; the intensity of X-ray increases diffraction peaks characterizing the formed phases during the hydration reaction is generally increased in the presence of the accelerator and reduced with the retarder (Ismail and El-Hemaly, 1991). Calcium chloride is the most widely used because of its ready availability and low cost. CaCl₂ has long been known to accelerate both the setting and hardening of Portland cement concrete, the effect of
strength decreases with time and the final strength can be reduced due to the formation of chloroaluminate hydrates, which is responsible for the concrete softening. One of the limitations to the wider use of calcium chloride in reinforced concrete is that if present in larger amounts, it promotes corrosion of the reinforcement, unless suitable precautions are taken (Heikal, 2004).

The hydration of the system $C_3A-\text{CaCl}_2-\text{CaSO}_4\cdot2\text{H}_2\text{O}$ shows that the calcium chloride primarily accelerates the reaction between $C_3A$ and gypsum. Sulfate reacts first followed by reaction of $C_3A$ and chloride after the gypsum has been used up. $\text{CaCl}_2$ appears to stabilize the formation of trisulfoaluminate hydrate (ettringite) $C_3A\cdot3\text{CaSO}_4\cdot3\text{H}_2\text{O}$. After all $\text{CaSO}_4$ has been used, conversion of trisulfoaluminate to monosulfoaluminate $3\text{Ca}_2\cdot\text{CaSO}_4\cdot12\text{H}_2\text{O}$ occurs (Ramachandran et al., 2002). The results indicate that the addition of 2% calcium chloride significantly increases the direct tensile strength and the dynamic modulus of hardened cement paste. It is concluded that the addition of calcium chloride can partially inhibit the cracking caused by drying and sorption induced microcracking in the concrete system (Haque, 1980). Abdelrazig et al. (1999) concluded that addition of calcium salts has a pronounced effect on the pH value of the concrete, hydroxyl and sulfate ion concentrations. This is in agreement with the results from X-ray diffraction and differential scanning calorimetry, which show rapid precipitation of more gypsum and calcium hydroxide within the first 5 min on adding these salts than in neat OPC pastes.

The addition of $\text{CaCl}_2$ reduces retarding effect (lead wastes) but was associated with a decrease in the overall extent of cement hydration, particularly at high $\text{CaCl}_2$ concentrations. The acceleration effect that caused by $\text{CaCl}_2$ is associated with lower concentrations of hydroxyl ions in solution. This reduction in the pH value causes a reduce in dissolution and subsequent reduce in adsorption of $\text{Pb(OH)}_2$ ions onto $\text{C-S-H}$ surfaces forming around hydrating cement particles (Cheeseman and Asavapis, 1999). Juenger et al. (2005) suggested that $\text{CaCl}_2$ accelerates the formation of “inner product” calcium silicate hydrate (C–S–H) with a low-density microstructure. The addition of $\text{CaCl}_2$ increased the pH of white Portland cement (WPC) in the immediate period and at 24 h. The addition of $\text{CaCl}_2$ reduced the setting times and solubility and increased the pH of cements in the initial periods (Bortoluzzi et al., 2009). Addition of calcium chloride accelerates the rate hydration of white Portland cement, resulting a decrease in setting time and an increase in early strength of the pastes. The compressive strength of all cement pastes containing calcium chloride was higher than that of the pure cement paste; white Portland cement paste with added 3% $\text{CaCl}_2$ exhibited the best bioactivity (Torkittikul and Chaipanich, 2012).

Homra (crushed clay bricks), is a pozzolanic material that can react with lime liberated from the hydration of ordinary Portland cement produce additional amounts of calcium silicate hydrates (CSH). This reaction improves the microstructure of cement pastes. Partially replacing cement by ground brick or heat-treated brick clay gives early strengths that are lower than that of the control. At 90 days, however, the strengths are the same as or are greater than that of the control (Heikal, 2000; O’Farrell et al., 2006). The effect of substitution of Portland cement by homra on the physicochemical properties of cement pastes. The results revealed that the water of consistency increases with homra content, the initial and final setting times are elongated. The free lime contents increase up to 7 days then decrease up to 90 days in homra blended cements whereas increase up to 90 days in OPC pastes (El-Didamony et al., 2000).

The presence of ground brick (GB) alters significantly the compressive strength of mortar and this is attributed to both the dilution effect and production of additional C–S–H gel from reaction of GB with CH. The additional C–S–H gel refines the pore size distribution of the mortar (O’Farrell et al., 2001). The 10% and 20% clay brick replacements had no negative effect on the mortar compressive strength and very limited effect on the mortar shrinkage. The freeze–thaw resistance of the mortar was improved by the brick replacement. However, the use of crushed brick as aggregate appeared not to reduce potential alkali–silica reaction (Bektas et al., 2009).

The aim of this study is to investigate the effect of calcium chloride on the hydration characteristics of some blended cement pastes, blended containing GCB as well as Portland cement for comparison.

### Table 1 – Chemical composition of the used Portland cement, metakaolinite and ground clay bricks.

<table>
<thead>
<tr>
<th>Oxide (%)</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>Cl$^-$</th>
<th>MgO</th>
<th>SO$_3$</th>
<th>CaO-free</th>
<th>Ignition loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>22.12</td>
<td>5.78</td>
<td>4.69</td>
<td>62.87</td>
<td>0.29</td>
<td>0.11</td>
<td>0.02</td>
<td>2.36</td>
<td>0.91</td>
<td>0.92</td>
<td>–</td>
</tr>
<tr>
<td>GCB</td>
<td>74.80</td>
<td>14.03</td>
<td>5.04</td>
<td>1.25</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.30</td>
<td>0.80</td>
<td>–</td>
<td>2.58</td>
</tr>
</tbody>
</table>

### Table 2 – The composition and designation of the prepared mixes.

<table>
<thead>
<tr>
<th>Mixes</th>
<th>Composition</th>
<th>% OPC</th>
<th>% GCB</th>
<th>% CaCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI</td>
<td>100%</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MIA</td>
<td>100%</td>
<td>–</td>
<td>0.25</td>
<td>–</td>
</tr>
<tr>
<td>MIB</td>
<td>100%</td>
<td>–</td>
<td>0.50</td>
<td>–</td>
</tr>
<tr>
<td>MIC</td>
<td>100%</td>
<td>–</td>
<td>0.75</td>
<td>–</td>
</tr>
<tr>
<td>MII</td>
<td>90%</td>
<td>10%</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MIIA</td>
<td>90%</td>
<td>10%</td>
<td>0.25</td>
<td>–</td>
</tr>
<tr>
<td>MIIIB</td>
<td>90%</td>
<td>10%</td>
<td>0.50</td>
<td>–</td>
</tr>
<tr>
<td>MIIC</td>
<td>90%</td>
<td>10%</td>
<td>0.75</td>
<td>–</td>
</tr>
<tr>
<td>MIIIB</td>
<td>80%</td>
<td>20%</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MIIB</td>
<td>80%</td>
<td>20%</td>
<td>0.25</td>
<td>–</td>
</tr>
<tr>
<td>MIIIB</td>
<td>80%</td>
<td>20%</td>
<td>0.50</td>
<td>–</td>
</tr>
<tr>
<td>MIV</td>
<td>70%</td>
<td>30%</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MIVA</td>
<td>70%</td>
<td>30%</td>
<td>0.25</td>
<td>–</td>
</tr>
<tr>
<td>MIVB</td>
<td>70%</td>
<td>30%</td>
<td>0.50</td>
<td>–</td>
</tr>
<tr>
<td>MIVC</td>
<td>70%</td>
<td>30%</td>
<td>0.75</td>
<td>–</td>
</tr>
</tbody>
</table>

OPC: ordinary Portland cement; GCB: ground clay bricks.
2. **Materials and methods**

2.1. **Materials**

The materials used in this investigation were; ordinary Portland cements (OPC), ground clay bricks (GCB), calcium chloride (CaCl₂) and naphthalene formaldehyde sulfonic acid (NFS) as a water-reducing agent (super-plasticizer). Chemical composition of the used Portland cement and GCB is given in Table 1.

2.2. **Methods**

Different series of blended cement pastes were prepared in presence and absence of different ratio (0.25, 0.5 and 0.75% by weight of the solid binder) of calcium chloride. The composition and designation of the different mixes are given in Table 2. The water/solid ratio used was 0.25 for all mixes. The pastes were molded in the form of one cubic inch and cured at about 100% relative humidity for the first 7 days. Then the samples were immersed in distilled water for the rest of hydration times which extended up to 180 days.

2.3. **Investigations technique**

The hydration characteristics of the different cement mixes were investigated via;

1. The determination of chemically combined water content

   Two representative samples of each dried hardened plain and blended cement pastes, exactly about one gram of each, were weighed in silica crucibles and ignited for 1 h at 950 °C in an adjusted muffle furnace, cooled in a desiccator then weighed. The chemically combined water \( W_n \%) was calculated using the following equation:

   \[
   W_n \% = \left( \frac{W_2 - W_3}{W_1 - W_1} \right) \times 100
   \]

   where, \( W_1 \): the weight of the empty crucible (g), \( W_2 \): the weight of the crucible + sample before ignition (g), \( W_3 \): the weight of the crucible + sample after ignition.

2. X-ray diffraction analysis

   The material containing crystalline phases is bombarded with X-ray using Cu target under working conditions of 40 kV and 25 mA by using Nickel filter. Some of the X-rays are diffracted by the crystal surfaces and can be represented in the form of diffraction pattern.

3. Compressive strength

   A set of three cubes, representing the same mix and same age, were used for the determination of the compressive strength of the hardened cement pastes. The average of the three results was considered expressed in kg/cm². The strength test machine used in this work was of Point load taster (D550-C-trols type, Milano-Italy) having a maximum load of 60 tons.

4. The determination of total porosity

   Two representative cubes of each mix after 28 days were used for porosity measurement; the average of the two results was considered.

   \[
   P(\%) = \frac{(W_1 - W_3)}{(W_1 - W_2)} \times 100
   \]

   where; \( W_1 \): weight in air of the saturated surface-dry cube, \( W_2 \): weight of the cube suspended in water and \( W_3 \): weight of the cube (in air) after drying (100–105 °C) for 24 h.

5. Thermal analysis (DTA technique)

   The thermal analysis (DTA techniques) was carried out using differential thermal analyzer of the type Shimadzu.
DTA-50 thermal analyzer (Co-Kyoto, Japan). A sample of 30 mg was placed in a crucible at heating rate of 10 °C/min using α-Al₂O₃ as a reference material.

3. Results and discussion

3.1. Combined water content (Wn %)

The results of chemically combined water are shown in Fig. 1 for all mixes in absence and presence of calcium chloride. It is obvious that there is a continuous and gradual increase in the combined water for all mixes up to 180 days. It is clear that the presence of CaCl₂ causes increase in the combined water content at all hydration ages comparing with control mixes (without CaCl₂). Increasing the ratio of CaCl₂ (from 0.25 to 0.5 or 0.75) leads to more increase in the values of combined water content. This increase in combined water content of these pastes is due to the progress of hydration of various components of the used mixes. The main hydration products for all mixes are calcium silicate hydrate (CSH) and calcium hydroxide (CH) in addition to the hydrates of the aluminates phases. The presence of CaCl₂ is supposed to accelerate the formation of “inner product” calcium silicate hydrate (CSH) with high water content according to Juenger et al. (2005). Hence, it can be concluded that the liberated calcium hydroxide react with active silica and alumina containing the GCB, to produce more calcium silicate (CSH) and alumino-silicate hydrates, which is considered the main binding agent. These finding agree well with those reported by O’Farrell et al. (2001) and Badogiannis et al. (2005).

3.2. Compressive strength

All mixes show an increase in the values of compressive strength with increasing hydration time according to Fig. 2. This increase is due to progress of the cement hydration. The compressive strength values of all the mixes containing CaCl₂ are higher than those of hardened blended cement pastes without CaCl₂ at all hydration ages. Also, increasing the ratio of CaCl₂ (from 0.25 to 0.75) causes an increase in the compressive strength values of the different mixes. This increase is clear at the hydration ages from 90 to 180 days, where a sharp increase in the compressive strength is noticed at these hydration times especially in case of the mixes containing 10 and 20% ground clay bricks (MIIA,B,C and MIIB,MIIC).

This result is an indication for the acceleration effect caused by calcium chloride and reduction in the porosity of the pastes due to formation of more hydration products. The results indicate that the ratio of 0.50 CaCl₂ can be considered the...
Fig. 3 – X-ray diffraction patterns for (a) MI 0% CaCl₂; (b) MIA 0.25% CaCl₂; (c) MIC 0.75% CaCl₂.
Fig. 4 – X-ray diffraction patterns for (a) MII 0% CaCl\textsubscript{2}; (b) MIIA 0.25% CaCl\textsubscript{2}; (c) MIIC 0.75% CaCl\textsubscript{2}.
Fig. 5 – X-ray diffraction patterns for (a) MIII 0% CaCl$_2$; (b) MIIIA 0.25% CaCl$_2$; (c) MIIIC 0.75% CaCl$_2$. 
Fig. 6 – X-ray diffraction patterns for (a) MIV 0% CaCl₂; (b) MIVA 0.25% CaCl₂; (c) MIVC 0.75% CaCl₂.
optimum ratio for the highest compressive strength. Finally, we also noticed (Fig. 2) that the values of the compressive strength of the mixes containing either 10 or 20% GCB in absence or presence of CaCl₂ are nearly the same, yet the values in case of 10% GCB are slightly higher than those obtained with 20% GCB. This means that 10% GCB is the best ratio concerning the increase of the compressive strength and no need to use higher ratios of GCB. On the other hand, in case of hardened cement pastes blended with 30% GCB, the values of the compressive strength are lower than those of the mixes containing 0, 10 or 20% GCB at all hydration ages. This result may be attributed to the decrease in the amount of Portland cement on increasing the ratio of GCB.

3.3. Total porosity (P%)

The total porosity of OPC and blended cement pastes containing ground clay bricks in absence and presence of CaCl₂ at 28 days of hydration is given in Table 3. It is obvious that the total porosity of the pastes MIA, MIB and MIC, in presence of 0.25, 0.50 and 0.75% CaCl₂, respectively, is lower than that of the control mix (100% OPC). Increasing the amount of CaCl₂ from 0.25 to 0.75% decreases the total porosity of the pastes. This can be attributed to the acceleration effect caused by calcium chloride.

The cement pastes blended with GCB both with the ratios 10 and 20% (MII and MIII, respectively) show a decrease in the
total porosity (with a slight difference between them) compared with the control mix MI. This may be due to the pozzolana-lime reaction which causes formation of more hydration products that fill up the available pores leading to a decrease in the porosity of the cement pastes. The acceleration effect of CaCl₂ causes a decrease in the total porosity. On the other hand, the total porosity of the blended cement pastes with 30% GCB (MIV) is higher than those mixes (MII–MIII). This can be attributed to slower rate of hydration on increasing the amount of pozzolana.

3.4. Phase composition

The phase composition of the various hardened Portland cement pastes, in absence and presence of CaCl₂, is examined at different hydration ages (1, 3, 7, 28, 90 and 180 days) using X-ray diffraction technique and are shown in Figs. 3–6. The hydration of the cement components results in conversion of C₃S (alite phase) and β-C₂S (belite phase) into the hydration products, calcium silicate hydrate (CSH) and calcium hydroxide (CH). Accordingly, the intensity of the characteristic

![Picture of DTA curves](image)

**Fig. 8** – DTA curves for (a) MII 0% CaCl₂; (b) MIIA 0.25% CaCl₂; (c) MIIC 0.75% CaCl₂ at 180 days.
peaks of CH as one of the more crystallized hydration products, gradually increases with increasing hydration age, due to the progress of hydration of Portland cement constituents. On the other hand, the intensity of the peaks characteristic of the reactants such as alite and belite phases decreases with increasing the hydration age. It can be noticed that the intensity of CH peaks in presence of CaCl₂ is higher than those in absence of the salt at all hydration ages for all mixes. This indicates that CaCl₂ accelerates the hydration of Portland cement components.

3.5. Thermal analysis

Figs. 7 and 8 show the DTA curves of the control mixes (MI, MII) in absence and presence of 0.25 and 0.75% CaCl₂ (w/w) hydrated for 180 days. The endothermic peaks in the DTA curves at 50–120 °C can be attributed to the evaporation of the physically and chemically combined water in CSH (Dweck and Buchler, 2000; Dweck et al., 2003). While as, the endothermic peaks at about 450 °C may be due to the decomposition of calcium hydroxide (CH). Obviously, the endothermic peaks of the decomposition of CSH and CH in presence of CaCl₂ are higher than those of the control mixes. This indicates that the presence of CaCl₂ causes acceleration of the hydration reaction of Portland cement (formation of CH). The intensity endothermic peak located at 450 °C increases in with increasing the amount of CaCl₂. Such observation supports the results obtained from the X-ray diffraction analysis.

4. Conclusions

The main points that could be derived from this study are summarized in the following:

1. The combined water contents increase with calcium chloride at all the hydration ages. This may be attributed to the acceleration effect of CaCl₂.
2. All the investigated cement pastes containing CaCl₂ showed higher values of compressive strength than those of the control samples.
3. The porosity of cement pastes containing CaCl₂ is lower than those in the control samples (without CaCl₂). This may be due to the formation of more hydration products which fill the pores of the hardened cement pastes.
4. The results of X-ray diffraction analysis indicate that the degree of hydration of samples with calcium chloride is higher than that of samples without calcium chloride, which proves the acceleration effect of CaCl₂.
5. The results of thermal analysis of some selected samples indicate that the degree of hydration of samples containing calcium chloride is more than that of the samples without calcium chloride. This indicates that the presence of CaCl₂ favors the formation of CSH with high water content.

REFERENCES