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Effect of calcium formate as an accelerator on the physicochemical and mechanical properties of pozzolanic cement pastes

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Abstract

The aim of the present work is to study the effect of calcium formate (CF) as an accelerator on the properties of pozzolanic cement pastes. Three types of cements were used in this investigation. These cements were OPC and pozzolanic cements containing 80 mass% OPC and 20 mass% silica fume (SF) or 20 mass% ground clay bricks (GCB). The dosages of CF were 0.00, 0.25, 0.50, and 0.75 mass% of cement. The compressive strength, total porosity, and hydration kinetics such as free lime and combined water contents were investigated. The results obtained in this study showed that the addition of CF shortens the initial and final setting times and increases the compressive strength and combined water content as well as gel/space ratio at all ages of hydration. On the other hand, it decreases the total porosity. CF activates the liberation of $Ca(OH)_2$ of OPC pastes. The free lime content of pozzolanic cement in the presence of CF increases up to 7 days, then decreases at the later ages of hydration.

Keywords: Pozzolanic cement; Calcium formate; Silica fume; Compressive strength; X-ray diffraction

1. Introduction

Many substances are known to act as accelerators for concrete. They include alkali hydroxides, silicates, fluorosilicates, organic compounds, calcium nitrate, calcium thiosulphate, aluminum chloride, potassium carbonate, sodium chloride, and calcium chloride. Calcium chloride is the most widely used because of its ready availability, low cost, and predictable performance characteristics over several decades [1]. Calcium chloride 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. Hence, there is a continuing attempt to find an alternative to calcium chloride, one equally effective and economically but without its limitations.

Calcium formate (CF) is a by-product produced in the manufacture of the polyhydric alcohol. CF is an accelerator for the hydration of C_3S at equal concentration; however, $CaCl_2$ is more effective in accelerating the hydration of C_3S [2]. At early ages, Bensted [3] found that the cement paste produces more ettringite in the presence of CF than in the presence of $CaCl_2$. However, the amount of C-S-H was higher in the presence of $CaCl_2$.

Condensed silica fume (SF) is a by-product of the manufacture of silicon or silicon alloys, which are produced in the submerged electric arc furnaces. SF particles appear to be formed by the oxidation and condensation of the gaseous silicon suboxide SiO that is formed in the reaction zone.

Ground clay bricks (GCB), known in Egypt as Homra, is a solid waste material (broken and crushed bricks) produced from the manufacture of clay bricks. GCB constitutes mainly of silica quartz, aluminosilicates, anhydrite, anorthite, and hematite [4]. Therefore, it acts as a pozzolanic material. In Egypt, about 5–10% of the product of clay brick is considered as a waste product.

This paper aims to investigate the effect of CF as an accelerator on the hydration characteristics of some

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pozzolanic cement pastes and to explore the physical state of the hydration products of these hardened cement pastes.

2. Materials and experimental work

The materials used in this investigation were ordinary Portland cement (OPC) provided from Helwan Portland Cement, SF from Ferro-Silicon Alloys (Edfo-Aswan), GCB from Misr Brick (Helwan, Egypt), and CF. The chemical analysis of the staring materials is given in Table 1.

Different mixes were made by substituting 20 mass% of SF or GCB as a partial substituent of OPC (Table 2). Each dry mix was homogenized for 1 h in a porcelain ball mill using two balls to assure complete homogeneity. The mixing of cement pastes was carried out with the standard water of consistency as describer by ASTM specifications as well as setting times [5,6]. The required water of standard consistency and setting times were given in Table 2. CF was added to mixing water during the mixing operation. The dosages of CF were 0.00, 0.25, 0.50, and 0.75 mass% of cement. Continuous vigorous mixing for about 3 min completed the mixing. Freshly prepared cement paste was placed in 2-cm cubic moulds into two approximately equal layers. Each layer was compacted and pressed until homogeneous specimen was obtained. After the top layer was compacted, the moulds were then vibrated for a few minutes to remove any air bubbles to give a better compaction of the paste. The surface of the paste was smoothed by spatula. The moulds were cured in a 100% relative humidity at 23 ± 2 °C for 24 h, then demoulded and cured under tap water up to 360 days.

The kinetics of hydration was followed by the determination of free lime [7], as well as combined water contents. The combined water content was determined by the ignition loss of the dried paste on ignited weight basis minus the amount of water held by free lime and the loss of the anhydrous blend. The compressive strength was determined up to 360 days. The total porosity, ε, was calculated by the determination of bulk density, d_p, the total water, W_t, and the evaporable water content, W_e, of hardened cement paste as expressed in the following equation:

$$\varepsilon = \frac{0.99 \times W_e \times d_p}{1 + W_t}$$

The gel/space ratio (X) is represented by the following equation [8]:

$$X = \frac{2.06 V_c \alpha}{V_c \alpha + W_o/C}$$

where C = weight of the cement; V_c = specific volume of cement = 3.19 cm^3/g; W_o = volume of mixing water; and α = the fraction of the cement that has been hydrated (degree of hydration), as calculated from the following equation:

$$\alpha = \frac{W_n}{W_n^\infty}$$

where W_n^∞ is the chemically combined water content after complete hydration and W_n is the combined water content at any time of hydration.

The gel space ratio is then expressed as:

$$X = \frac{0.647\alpha}{0.319\alpha + W_o/C}$$

X-ray diffraction patterns of the hydration products were performed using a Philips diffractometer (PW 1050170). The patterns were run with nickel-filtered copper radiation at 40 kV and 20 mA with a scanning speed 2θ of °2 min^{-1}.

Table 1
The chemical analyses of the starting materials (mass%)

Oxide	OPC	SF	GCB
SiO_2	20.50	96.10	74.80
Al_2O_3	5.50	0.52	14.03
Fe_2O_3	3.75	0.70	5.04
CaO	65.05	0.21	1.25
MgO	0.78	0.48	1.30
SO_3	2.13	0.10	0.80
Na_2O	0.48	0.31	–
K_2O	0.09	0.49	–
L. O. I	2.19	1.14	–
Surface area	3250 cm^2/g	19.5 m^2/g	3100 cm^2/g

Table 2
Mix composition, CF dosages, standard water of consistency, and setting times

Mix No.	OPC (mass%)	SF (mass%)	GCB (mass%)	CF (mass%)	W/C ratio	Setting times (min)	
						Initial	Final
I.0	100	00	00	0.00	0.245	100	270
I.1	100	00	00	0.25	0.245	80	210
I.2	100	00	00	0.50	0.245	70	200
I.3	100	00	00	0.75	0.245	70	180
II.0	80	20	00	0.00	0.325	140	330
II.1	80	20	00	0.25	0.325	90	240
II.2	80	20	00	0.50	0.320	80	190
II.3	80	20	00	0.75	0.315	70	170
III.0	80	00	20	0.00	0.260	145	290
III.2	80	00	20	0.50	0.265	70	170

3. Results and discussion

3.1. Initial and final setting times

The setting times of OPC and pozzolanic cement pastes containing 20 mass% of GCB or SF are shown in Table 2.

The initial and final setting times are accelerated with the addition of CF. The setting is associated with the formation of calcium sulphoaluminate hydrates. The formation of these tri- and mono-sulphoaluminate hydrates (AFt and AFm) depends on the amount of aluminate compounds, reaction velocity, rate of solution of calcium sulphate retarder, and calcium hydroxide liberated during the hydration of OPC phases (C_3S and β-C_2S). Addition of CF reduces the setting times. CF intensified the formation of ettringite; either pure C_3A or the one present in cement is considered [9] not only because it accelerates the ettringite formation, but also increases the hydration of the reaction rates of C_3S and β-C_2S. The rapid setting of cement pastes in the presence of CF may be attributed to the crystalline shape of ettringite, which during precipitation would produce a felt of fine needles. In addition, the formate ions can form analogues of AFt and AFm phases, i.e., $C_3A \cdot 3Ca(HCO_2)_2 \cdot 30H_2O$ and $C_3A \cdot Ca(HCO_2)_2 \cdot 10H_2O$, respectively [10].

3.2. Compressive strength

The variations of compressive strength values of OPC and pozzolanic cement pastes containing 20 mass% of GCB or SF are represented in Fig. 1. The results show that the addition of different dosages of CF, namely, 0.0, 0.25, 0.5, and 0.75 mass%, results in an increase in the compressive strength values due to the acceleration effect of CF. CF increases early and later strength and accelerates C-S-H formation, but it does not decrease 28 days compressive strength and presents no risk of reinforcement corrosion, whereas $CaCl_2$ decreases 28 days compressive strength and promotes the corrosion of reinforcement [11].

The effect on calcium silicate phases is mainly attributed to the fact that the diffusion rate of $HCOO^-$ ions is much higher than the Ca^{2+}. Formate ions ($HCOO^-$) can penetrate into the hydrated layers covering C_3S and β-C_2S grains. As a consequence, the precipitation of $Ca(OH)_2$ is accelerated as well as the decomposition of calcium silicates [12]. The influence of CF on strength of cement pastes may depend on the C_3A content [13]. The acceleration of strength development is more significance in low C_3A content.

The formate ion has attached itself chemically to the silicon atom (or aluminium or iron), the formate group can undergo further reactions with the hydroxyl ions present in solution, thus cross linking or binding adjacent silicate groups. The removal of hydroxyl groups from the pore system could further encourage the dissolution of the unhydrated cement grains [10,14]. The cross linking of formate ions would lead to formation of a much more C-S-H, as a result of this the compressive strength enhances.

3.3. Total porosity

The total porosity of hardened OPC and pozzolanic cement pastes containing 20 mass% SF or GCB is illustrated in Fig. 2. The total porosity decreases with curing

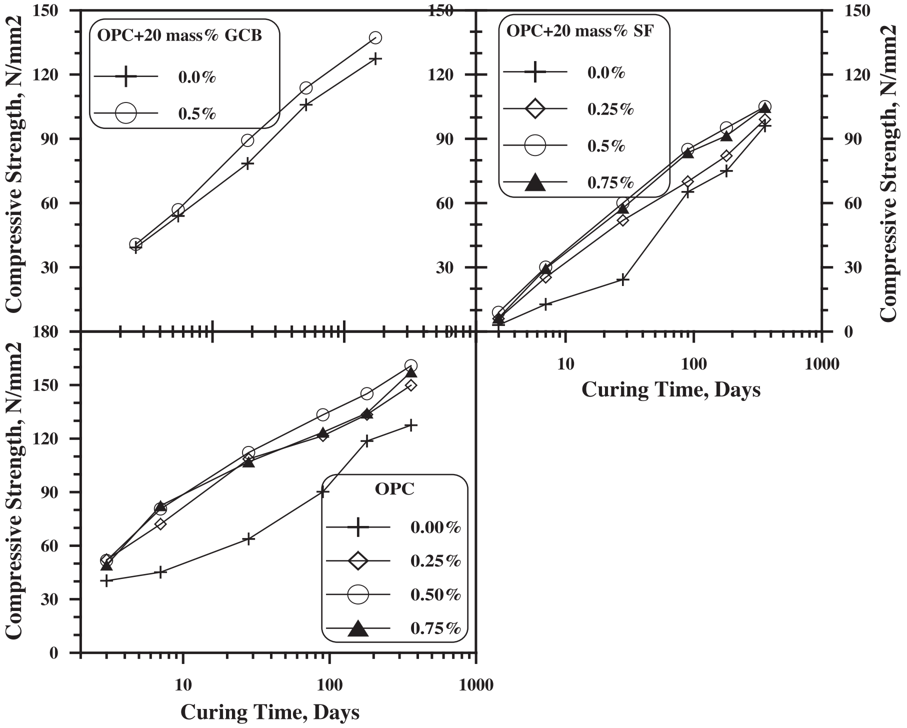

Fig. 1. Effect of CF on compressive strength of OPC pastes made with and without GCB or SF (20 mass%).

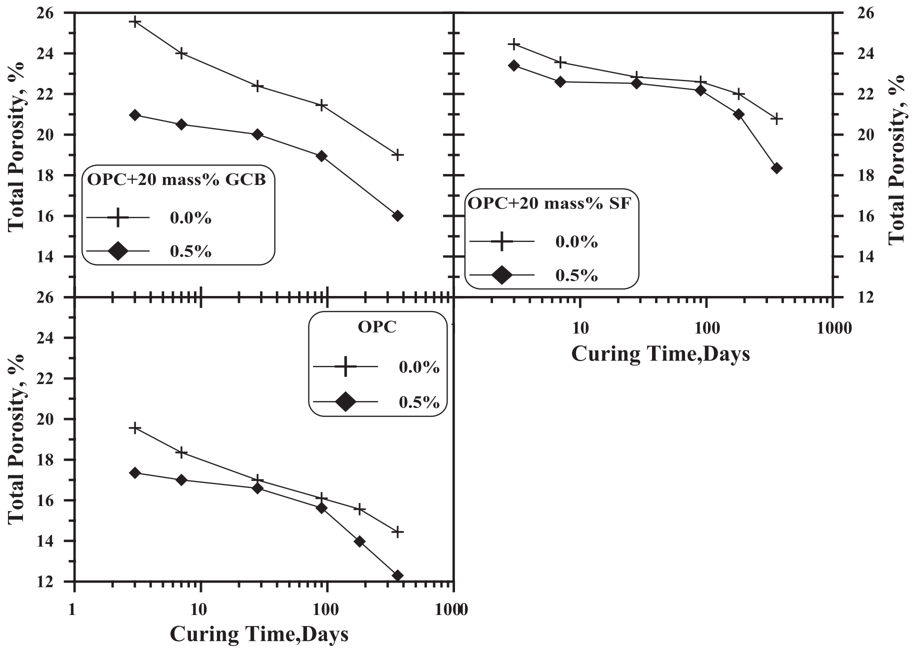

Fig. 2. Variations of total porosity of OPC pastes made with and without GCB or SF (20 mass%).

time due to the progress of hydration, which leads to fill a part of the pores. It was shown also that the total porosity of pozzolanic cement pastes increases than OPC pastes. This is mainly due to the increase of the standard water of consistency from 24.5 for OPC pastes to 26.5 and 32.5 for pozzolanic cement pastes containing GCB and SF, respectively. At early ages, the total porosity of pozzolanic cement pastes containing GCB is higher than that of SF due to the higher surface area and the pozzolanic activity of SF.

Addition of 0.5 mass% CF decreases the total porosity from 19.56, 24.46, and 25.57 to 17.35, 23.40, and 20.96 for OPC, OPC + 20 mass% SF, and OPC + 20 mass% GCB at 3 days, respectively; while the total porosity decreases at 360 days from 14.44, 20.78, and 19.00 to 12.29, 18.35, and 17.00 for OPC, OPC + 20 mass% SF, and OPC + 20 mass% GCB, respectively. Calcium formate activates the hydration of the aluminosilicate including GCB forming more hydration products especially at later ages.

3.4. Gel/space ratio

The gel/space ratios (*X*) of the hardened OPC and pozzolanic cement pastes were calculated on the basis of the degrees of hydration and their W/C ratios; the *X* values are given in Table 3. On increasing the gel/space ratio, the amount of hydration products increases; consequently, the synergistic effect of hydration products formed in the pores of the cement pastes enhances the compressive strength. The presence of 0.5 mass% CF increases the gel/space ratio and also the degree of hydration (higher combined water contents). The production of more dense and close-textured structure of cement pastes including CF leads to an increase in the rate of hydration of cement particles.

3.5. Free lime contents

A graphical representation of free lime contents for various hardened cement pastes as a function of curing time up to 360 days is shown in Fig. 3. The free lime content of hardened OPC pastes increases with curing time up to 360 days; whereas in the OPC + 20 mass% GCB pastes, it increases up to 7 days then decreases up to 1 year. The free lime content of OPC + 20 mass% SF pastes decreases with curing time and CF due to highly pozzolanic activity and surface area of SF as shown in a previous work [15]. However, CF accelerates the formation of $Ca(OH)_2$ of OPC and OPC + 20 mass% GCB up to 360 days. Under the influence of CF as an accelerator, $Ca(OH)_2$ goes into the solution and forms with the aluminates and silicates of

Table 3
Gel/space ratios of hardened OPC and pozzolanic cement pastes cured up to 360 days in presence or absence of CF

Curing time	OPC		OPC + 20% SF		OPC + 20% GCB	
	0.0% CF	0.5% CF	0.0% CF	0.5% CF	0.0% CF	0.5% CF
3	1.9950	1.9990	1.9870	1.9900	1.9830	1.9950
7	2.0010	2.0020	1.9920	1.9930	1.9880	1.9996
28	2.0035	2.0040	1.9940	1.9950	1.9960	2.0014
90	2.0044	2.0055	1.9967	1.9977	1.9985	2.0050
180	2.0057	2.0076	1.9973	1.9980	–	–
360	2.0079	2.0090	1.9980	2.0020	2.0020	2.0080

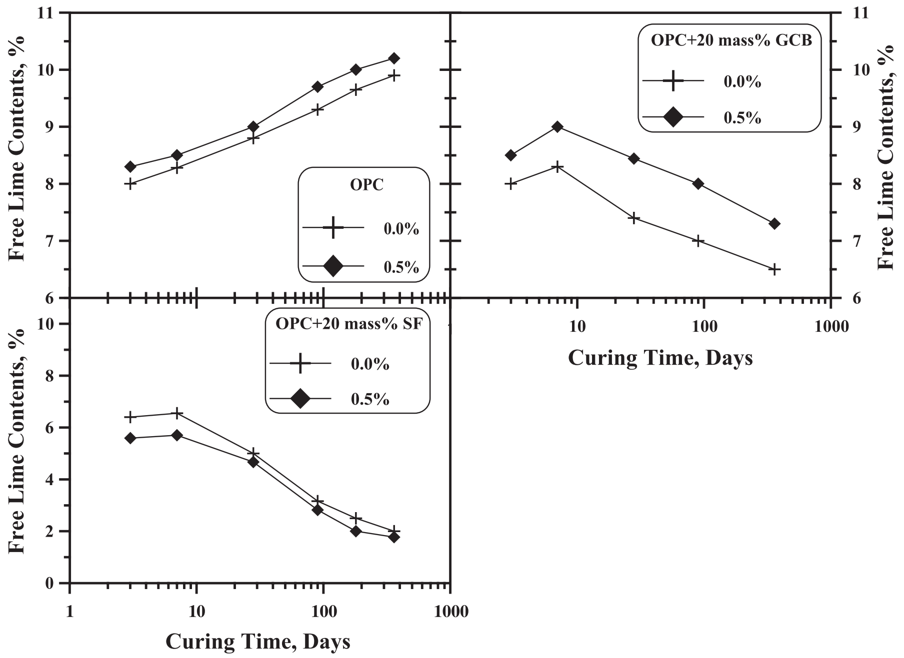

Fig. 3. Free lime contents of OPC pastes made with and without 20 mass% GCB or SF

GCB new hydrated calcium silicate and aluminate hydrates. As a result of this effect, the free lime of OPC + 20 mass% GCB decreases after 7 days and up to 1 year.

The acceleration action was also attributed to other causes, such as the alkalinity reduction of the liquid phase and the consequent increase in the dissolution rate of

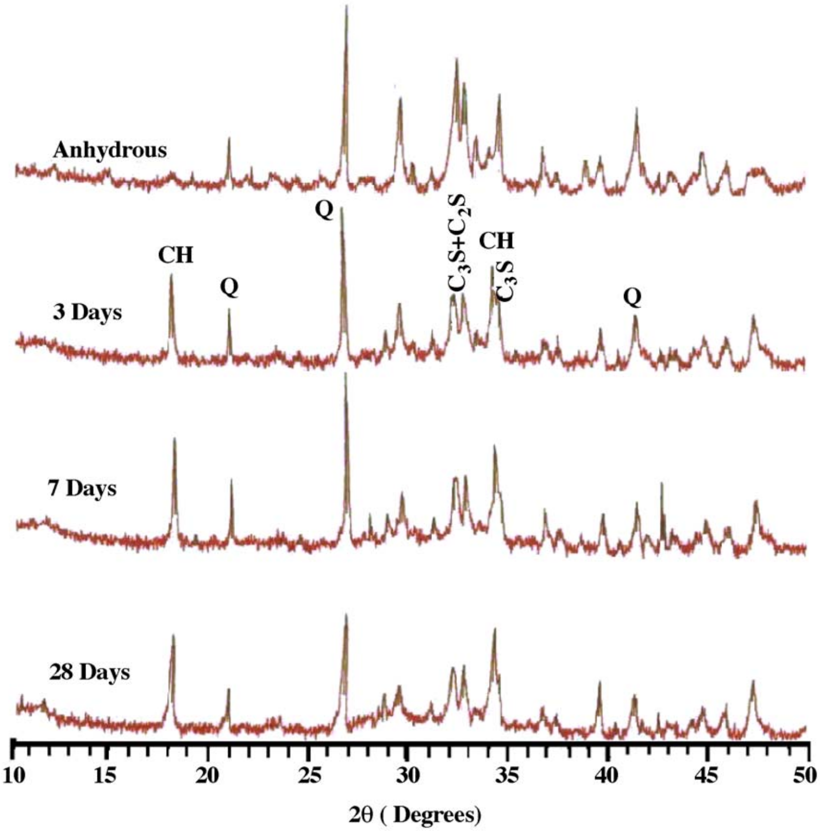

Fig. 4. XRD diffraction patterns of OPC + 20 mass% GCB in presence of 0.5 mass% CF as an accelerator.

hydrolyzed lime. CF adsorption on the surface of the cement grains would facilitate the attachment of H_2O and finally leads to an increase in the concentration of calcium ions in the solution [16].

3.6. Phase compositions

Fig. 4 shows the XRD patterns of hardened OPC + 20 mass% GCB in presence of 0.5% CF cured at 3, 7, and 28 days. It was found that the peaks of $Ca(OH)_2$ and quartz silica decrease with curing time. The free lime reacts with silica forming C-S-H, calcium aluminate hydrates, and calcium sulphoaluminate hydrates. Also, the peaks of unhydrated phases of β-C_2S and C_3S decreases with curing time due to the continuous hydration of these phases.

4. Conclusions

From the above findings it can be concluded that

1. Initial and final setting times are accelerated with the addition of CF.
2. CF increases the early and later strength values and accelerates C-S-H formation. Its effect on calcium silicate phases is mainly attributed to the fact that the diffusion rate of $HCOO^-$ ions is much higher than the Ca^{2+}.
3. At early ages, the total porosity of pozzolanic cement pastes containing GCB is higher values, whereas it is lower than that of pozzolanic cement containing SF at later ages, this is due to the higher surface area and pozzolanic activity of SF. CF activates the aluminosilicate including GCB forming more hydration products especially at later ages.
4. CF increases the gel/space ratio and also the degree of hydration (higher combined water contents).
5. The free lime content of OPC + 20 mass% SF decreases with curing time and CF due to the relatively high pozzolanic activity and surface area of SF. However, CF accelerates the formation of $Ca(OH)_2$ of OPC and OPC + 20 mass% GCB up to 360 days.

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