

HYDRATION CHARACTERISTICS OF PROMPT CEMENT IN THE PRESENCE CITRIC ACID AS RETARDER

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Submitted October 6, 2014; accepted March 20, 2015

Keywords: Prompt cement, Citric acid, Hydration characteristics, Retarder

The aim of the present work is to study the influence of citric acid (CA) as retarder on the properties of prompt cement pastes. The dosages of CA were 0.50, and 0.75, 1.00 and 1.25 mass % of prompt cement. The initial and final setting times, bulk density, compressive strength, total porosity, and hydration kinetics such as free lime, combined water contents and XRD for selected sample were investigated. The results obtained in this study showed that the addition of CA elongates the initial and final setting times and decreases the compressive strength and combined water contents, whereas, it increases the total porosity at all ages of hydration. CA retards the liberation of $\text{Ca}(\text{OH})_2$ of prompt pastes. The free lime contents of prompt cement pastes are slightly increased up to 28 days then sharply increased up to 90 days. Thus, it is suggested that citrate sorbed onto the clinker surface and formed a protective layer around the clinker grains retarding their dissolution. The sharp increase of compressive strength at later ages after 28 days up to 90 days. The presence of 0.75 mass % citric acid achieves the initial and final setting time of the prompt cement according to the ASTM specification.

INTRODUCTION

Natural prompt cement is produced by firing a unique clayey limestone at moderate temperatures. Prompt cement calcined over a wide range of temperatures from 600 - 1200°C, which match the characteristics of nineteenth century Roman cement [1]. This special production process forms constituents such as active dicalcium silicates, alumina rich calcium aluminates and calcium sulphoaluminates of mineralogical composition. Prompt cement shows quick-setting, rapid hardening and resistance to seawater attack. It has been reported that C_3S may be formed in the hottest regions of the kiln. Cements containing high sulphate contents contained small amounts of anhydrite or the calcium sulphoaluminate, ye'elimite and spurrite [1, 2]. Roman cement composition changes significantly as the intensity of the calcination conditions increases. The principal hydraulic phases are aluminates of unknown mineralogy occurring within an amorphous phase as well as crystalline belite. For prompt cements calcined at lower temperatures the dominant belite is $\alpha\text{-C}_2\text{S}$, whereas $\beta\text{-C}_2\text{S}$ is the stable form with the calcination temperature. The strength development of the cements is strongly dependent upon calcination conditions. The hydration

mechanisms responsible for the dormant period remain to be confirmed. Optimal cements are produced at low temperatures, approximately 750°C from measurements within the charge, and contain evidence of incomplete calcination through the presence of quartz and calcite.

Roman cement unlike Portland cement, was produced by calcining a single rock source at a low temperature with the only pre-calcination processing. Roman cement was more expensive and prolonged as being some five times that of Portland cement; the cement was used for renders and cast decorative elements. Roman cements were characterized by a brown colour and a rapid setting. The most rapid setting was a particular asset in hydraulic engineering [3]. The obtained phases are belites and amorphous aluminates. Other components include uncalcined remainants, lime, brownmillerite and gehlenite [4].

Admixture that retards setting is used in hot weather and other purpose including, oil well cementing. Many organic materials, such as sucrose, citrates, lignosulfonate, naphthene and sulphonate are typical retarders. They are effective in low concentration. Ramachandran, et al. [5], discussed the factors affecting the efficiency of retarders with cement. They included dosages of retarders, adding time, temperature and cement composition.

The initial setting time elongates with the retarder content and generally shortens with temperature. Retarders are more effective with cement low aluminate phase because the later, or their hydration products, consume amounts of retarder. Retarders are most effective after delayed addition time (2 - 4 min) after mixing. The retarders are widely used containing hydroxyl and carboxylic groups, such as in citrates, salicylates, tartarates and lignosulfonates.

Citric acid (CA) retards the hydration of Portland cements or its constituents. Citric acid has a retarding effect on the hydration in the system C_3A -gypsum-portlandite-water and C_3S [6-8]. Citrate forms stable complexes with polyvalent metal cations, which affects on both, the solution and the (ferro-) aluminate surface [9], as well as increases the dissolution rate of the ferrite phase. The effect of CA and citrate on Portland cement showed from the heat evolution rates that the hydration of Portland cement is retarded [9-11]. Other investigations aimed to understand the mechanisms of the retardation. The extent of complex formation of the dissolved ions was determined. CA retards cement hydration not only by complex formation, but also by slowing down the dissolution of the clinker grains. Thermodynamic calculations did not indicate precipitation of a crystalline citrate species. Thus, it is suggested that citrate sorbed onto the clinker surface and formed a protective layer around the clinker grains retarding their dissolution [12]. Electrical conductivity measurements of the paste indicate that in the presence of citric acid, the concentration and the mobility of the charge carriers are decreased. Zeta potential measurements give definite proof regarding the adsorption of citrate ions onto the Portland cement grain surface, and in its presence the values become negative [11].

Prompt cement paste uses in caulking boats, filling cracks, blanking of pipe work and conventional rapid fixing work. Mortar uses in rapid fixing work high early strength. On the other hand shotcrete dry process using prewetting lance used in stabilization of rock slopes or faces, tunnel lining and river-bank erosion protection. The goal of this paper is to provide an idea about the influence of the possible inhibition effect of citric acid on the setting time, physic-chemical and mechanical properties of prompt cement.

This paper aims to a understand the influence of CA as a set retarder on the hydration characteristics of prompt cement pastes. The changes in the physic-chemical and mechanical characteristics as a function of hydration time and CA dosages were studied.

EXPERIMENTAL

The material used in this investigation was Prompt cement provided from Prompt Cement Vicat Company, (Paris, France). The chemical composition of starting materials is shown in Table 1. The specific surface area determination was measured using Blaine apparatus according to ASTM method (ASTM Designation C 204-79). The Blaine surface area of Prompt cement was $7676 \text{ cm}^2 \text{ g}^{-1}$.

Figure 1 shows XRD analysis of prompt cement which are CaCO_3 with appreciable amounts of $\beta\text{-C}_2\text{S}$, $\text{Ca}(\text{OH})_2$ and small amount of gehlenite C_2AS , as well as gypsum. Figure 2 illustrates the DTA thermogram of prompt cement powder. It shows three characteristics endotherms. The broad endotherm at about 90°C is mainly due to the free water. The weak endotherm located at about 162°C is mainly due to dehydrated amorphous C-S-H , the broad endotherm located at 300°C may be due to the formation of aluminate ferrite gel $\text{C}_2(\text{A},\text{f})\text{H}_8$ [16]. On the other side the intense endothermic peak at 457°C is mainly due to the dehydroxylation of $\text{Ca}(\text{OH})_2$. Two other endotherms located at 771 and 859°C are due to the calcination of amorphous and crystalline calcite.

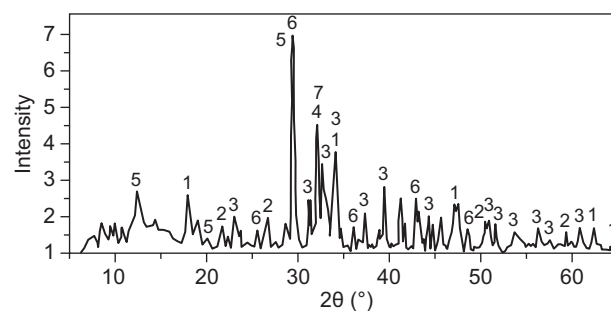


Figure 1. X-ray diffraction pattern of anhydrous prompt cement (1 - $\text{Ca}(\text{OH})_2$; 2 - SiO_2 ; 3 - C_2S ; 4 - C_3A ; 5 - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; 6 - CaCO_3 ; 7 - C_2AS).

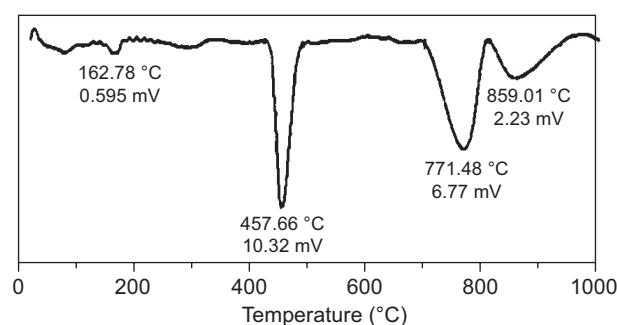


Figure 2. DTA thermogram of prompt cement.

Table 1. The chemical composition of starting materials.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	TiO_2	Na_2O	K_2O	BaO	SO_3	LOI
Prompt Cement	14.27	5.86	3.31	54.96	3.65	-	0.20	0.24	0.88	0.04	3.08	13.5

The required amount of each dry mix was placed on a smooth, non-absorbent surface and a crater was formed in the center. The required amount of water of consistency was poured into the crater and the cement on the outer edges was turned into the crater by the aid of a trowel. The dry cement around the outside of the crater was slightly troweled over the mixture to absorb the water for about one minute then mixing was completed for three minutes by gauging trowel. CA as a retarder namely 0.5; 0.75; 1.00 and 1.25 mass % of prompt cement in mixing water on these characteristics of cement pastes was evaluated. Freshly prepared cement paste was placed in inch stainless steel cubic moulds into two approximately equal layers. Each layer was manually compacted and pressed until homogeneous specimen was obtained. The moulds were then vibrated for a few minutes to remove any air bubbles to get a better compaction of the pastes then smoothed by trowel. Immediately after moulding, the moulds were cured in humidity chamber at about 100 % RH at room temperature $23 \pm 1^\circ\text{C}$ for 24 hrs then demoulded and cured under tap water up to the time of testing.

The water of consistency, initial and final setting times were determined according to ASTM methods (ASTM Designation: C-191, 2008).

The specimens were cured in a humidity chamber at $25 \pm 1^\circ\text{C}$ for 24 hours, then demolded and immersed in tap water for further investigations.

The bulk density was carried out before the specimens subjected to compressive strength determination. Samples were weighed suspended in water and in air (saturated surface dry). Each measurement was conducted on at least three similar cubes of the same mix composition and age. The following equation was used for calculating the bulk density [13-15].

$$\text{Bulk density (dp)} = \frac{\text{saturated weight}}{\text{volume of sample}} \quad \text{g}\cdot\text{cm}^{-3}$$

$$\text{Volume of sample} = \frac{\text{saturated weight} - \text{suspended weight}}{\text{density of liquid (water)}}$$

$$\text{Bulk density (dp)} = \frac{\text{saturated weight}}{\text{saturated weight} - \text{suspended weight}}$$

The total porosity was determined from the evaporable (We) and total (Wt) water contents and bulk density (dp) of the hardened cement specimen using the following equation [13-15]:

$$\varepsilon = \left(\frac{0.99 We \times dp}{(1 + Wt)} \times 100 \right)$$

The non-evaporable (combined) water content is retained in the sample after the free (evaporable) water is removed by drying the saturated cement paste at 105°C for 24 hours.

A set of three cubes was used for the determination of compressive strength of cement paste (ASTM Designation: C-150, 2007). The compressive strength measurements were done on a compressive strength machine of Seidner, Riedinger, Germany, with maximum capacity of 600 KN force.

The free lime content of cement paste can be thermally determined 0.5 g of the hardened cement pastes was placed in a porcelain crucible and introduced in a cold muffle. The temperature was increased up to 390 then to 550°C at heating rate of $3^\circ\text{C}\cdot\text{min}^{-1}$. The loss of weight occurred in the temperature range $390 - 550^\circ\text{C}$ with soaking time of 15 min is equal to the weight of water of calcium hydroxide, $\text{Ca}(\text{OH})_2$. Therefore, the free lime content can be calculated.

The combined water content is considered as the percent of ignition loss of the dried sample (on the ignited weight basis). Approximately 2 g of the pre-dried sample were gradually ignited up to 1000°C for 1 hour soaking time. The results of combined water were corrected from the water of free lime present in each sample [13-15].

XRD technique was carried out on some selected hardened cement pastes to show the hydration products. The XRD technique was carried out using Philips, Pw 1390 channel control, (Copper target-Nickel filter), 40 kV – 25 mA. The sample was finely ground to pass a 200-mesh sieve. The identification of all samples was confirmed by computer-aided search of the PDF database obtained from the Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data (JCPDSICDD), 2001.

RESULTS AND DISCUSSION

The required water of standard consistency and setting times

The required water of consistency, initial and final setting time of prompt cement with and without CA as a retarder are graphically represented in Figure 3. The results show that the water of consistency increases gradually with CA dosages, this increasing is consumed in the hydrolysis of CA. The setting times in absence of CA is a few minutes (3 - 4 min), there is no appreciable difference between the initial and final setting times of prompt cement pastes. This means that this paste can be demoulded after four hours, whereas, in the presence of CA the initial and final setting times are elongated. CA delays the flash setting reactions of prompt cement pastes. The COOH and OH groups containing CA coat the grains of the prompt cement, hence they delay the initial and final setting times. Bishop and Barron [16], discussed the mechanisms of set retarder fall into four steps; complex formation preventing the precipitation of portlandite, formation of a semipermeable film broken down by osmotic pressure gradients, surface adsorption of retarders directly on anhydrous surface cement grains, nucleation and growth poisoning of hydrates.

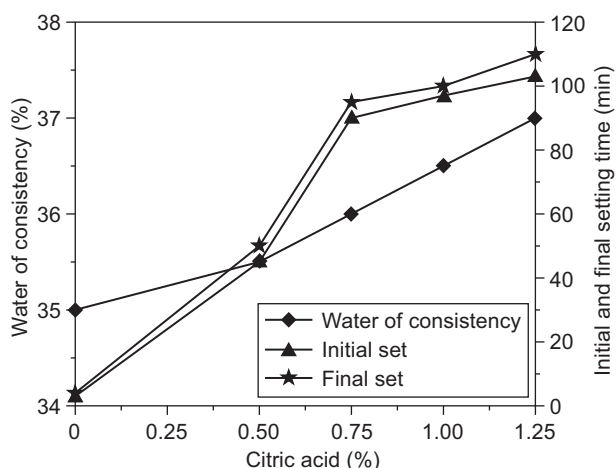


Figure 3. The required water of standard consistency, initial and final setting times of prompt cement with and without citric acid as a retarder up to 90 days.

CA decreases the dissolution and hydrolysis of prompt cement grains, this is due to CA getting adsorbed on the prompt cement grains forming acid complex mostly by Ca^{2+} ions and poisoned the calcium complex nucleating sites [17], as well as formation of citrate complexes with different cations such as Ca^{2+} , Al^{3+} and Fe^{3+} . These citrate complexes are more stable with three valent cations (Al^{3+} and Fe^{3+}) than divalent Ca^{2+} or monovalent cations [12, 18]. The formation of these complexes formed in the pore solution, could retard the formed hydrated products. CA retards the dissolution of gypsum, which restrict the dissolution of aluminate and/or ferrite phases as well as the formation of ettringite was slowed down [18].

The presence of 0.75 mass % CA achieves the initial and final setting time of the prompt cement according to the ASTM specification. The mineralogical compositions of prompt cement are active dicalcium silicate, alumina-rich calcium aluminate and calcium sulphoaluminates. This composition is responsible for quick-setting (few minutes), rapid hardening, and high range water of consistency.

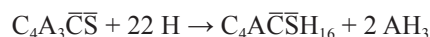
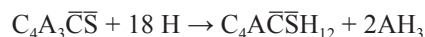
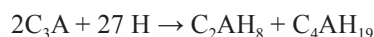
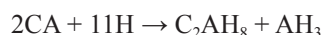
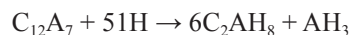
Table 2. The chemical composition of starting materials.

Symbol	Prompt %	Citric acid
M0	100	–
M1	100	0.50
M2	100	0.75
M3	100	1.00
M4	100	1.25

Chemically combined water content

The chemically combined water contents of prompt cement pastes with and without CA as a retarder are graphically represented as a function of curing time

up to 90 days in Figure 4. The chemically combined water content increases with curing time for all cement pastes. Prompt cement without CA as a retarder gives the higher values of combined water than those with CA. The combined water content decreases with the CA content. These results attributed to the role of CA as a retarder which delays the hydration reactions of prompt cement minerals (dicalcium silicate, alumina-rich phases). As the amount of CA content increases the chemically combined water content decreases, this is due to the retardation of the hydration of prompt cement pastes. Chemically combined water content of all cement pastes increases sharply after 28 days. This is mainly due to the increase of the rate of hydration of β - C_2S at later ages, which affects the values of chemically combined water of cement pastes. The increase in the chemically combined water content after 28 days, may be due to the carbonation of cement paste. The hydration reactions take a place at early age in prompt cement causes flash set as shown [19]:



CA delays these hydration reactions and causes a lowering in the chemically combined water contents till the lowest values in the presence of 1.25 mass % CA.

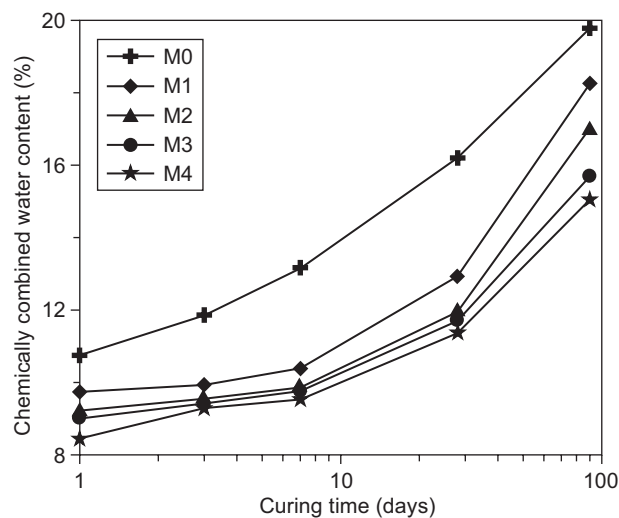


Figure 4. Chemically combined water contents of prompt cement with and without citric acid as a retarder up to 90 days.

XRD diffraction patterns

The XRD diffraction patterns of the hardened prompt cement pastes in the presence of CA as a retarder are shown in Figure 5. The results indicate that the

intensity of CH peaks increases with curing time as a result of β -C₂S hydration process, also the intensity of peaks corresponding to C-S-H increases with curing time as well as the unhydrated β -C₂S decreases with curing time. The peak areas corresponding to Ca(OH)₂ increase rapidly between 28-90 days. At 28 days, some amorphous Ca(OH)₂ is formed, which is not detected by XRD technique. XRD technique determines only crystalline Ca(OH)₂. Figure 5 also shows the presence of calcium carbonate and calcium carboaluminate phases.

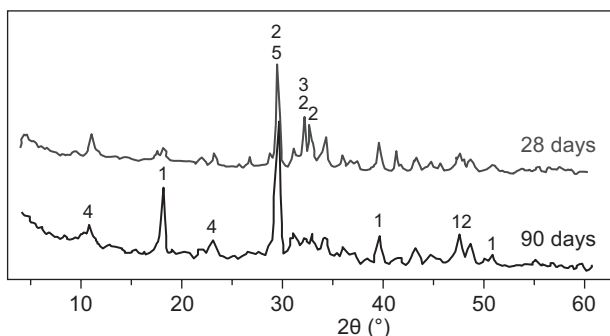


Figure 5. XRD diffraction patterns of prompt cement at 28 and 90 days (1 – CH, 2 – C-S-H; 3 – C₂S; 4 – C₃A·CC₂H₁₂; 5 – CC)

Free lime

The free lime contents of prompt cement with and without CA retarder with curing time up to 90 days is shown in Figure 6. Free lime content of prompt cement pastes increases with curing time up to 90 days, this is due to the continuous hydration of β -C₂S which liberates free lime. On the other hand, the free lime contents of the prompt cement pastes in the presence of CA retarder are lower than those of neat prompt cement pastes. This is due to the role of retarder, which delays the hydration reaction. As the amount of CA retarder increases the free lime content decreases due to the retardation of the hydration of cement paste.

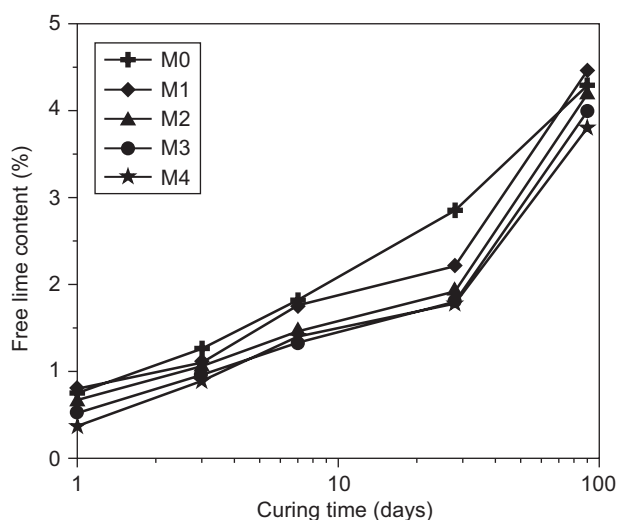


Figure 6. Free lime contents of prompt cement pastes with and without citric acid as a retarder up to 90 days.

The crystallization of Ca(OH)₂ and hydration degrees decrease in the presence of CA retarder [11]. CA retarder adsorbed onto the surface of prompt cement grains reduce the dissolution of anhydrous cement grains forming slightly soluble precipitate, this leads to lower in Ca(OH)₂ as shown in the obtained values of free lime contents as shown in Figure 6.

The free lime contents of all cement pastes increase sharply from 28 up to 90 days, this is mainly due to the slow rate of hydration of β -C₂S at early ages, which liberate free lime during its hydration. The free lime content of cement pastes are slightly increased up to 28 days then sharply increased up to 90 days due to the high reactivity of β -C₂S at later ages.

Bulk density

The bulk density of hardened prompt cement pastes with and without retarder is graphically represented up to 90 days in Figure 7. The bulk density is one of the most important factors in the determination of porosity, assessment of durability and strength in the hydrated cement. The bulk density of cement pastes depends on the degree of hydration. As the hydration progresses, the hydration products fill a part of the pore volume because the volume of hydration products is more twice than that of anhydrous cement; this decreases the porosity and increases the bulk density. The bulk density of prompt cement pastes increases with curing time. As the amount of CA increases the bulk density decreases due to the retardation of the prompt cement phases at all curing times.

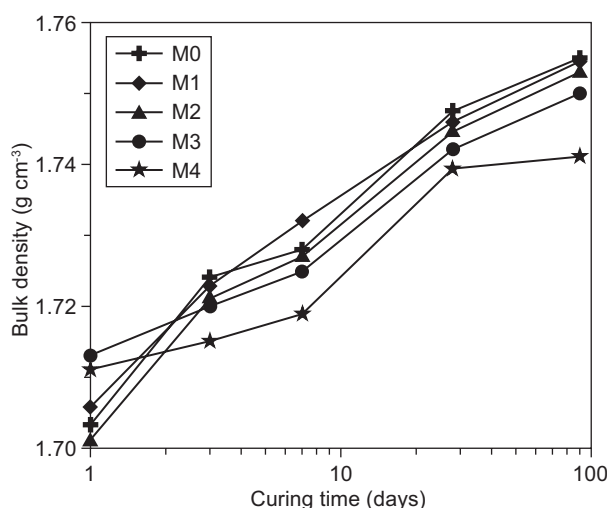


Figure 7. Bulk density of hardened prompt cement pastes with and without citric acid up to 90 days.

At early ages (one day) the cement pastes with 1.0 mass % (M3) and 1.25 mass % (M4) of CA give the higher of bulk density than that containing lower amounts. This is mainly due to that this prompt cement expands; i.e. the expansion decreases the bulk density. At higher

contents of CA the expansion delays, therefore, the bulk density increases. On prolong hydration the retarder dissolves and the cement behaves as an expanding cement then the bulk density decreases with the of CA dose from 3 up to 90 days

Total Porosity

The values of total porosity of hardened prompt cement pastes with and without retarder are given in Figure 8. The total porosity is an intrinsic property of cement pastes, the porosity of the pastes depends on many factors and typically increases with the ratio and decreases with the curing period. The addition of CA increases the water of consistency, therefore, the total porosity increases with the amount of CA. CA adsorbed onto the surface of prompt cement grains to form slightly soluble precipitate. Precipitation of dissolved species produces a more porous structure. The interesting features are relationship between porosity and compressive strength in the presence of CA [17]. As the mixing water increases the free water and the total porosity are gradually inc

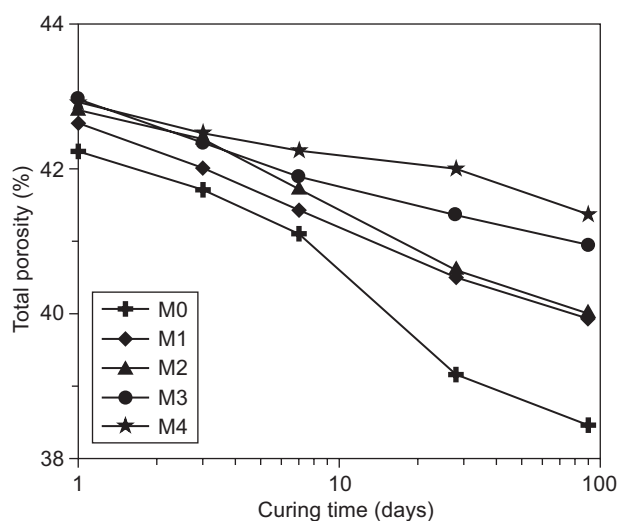


Figure 8. The porosity of prompt cement pastes with citric acid up to 90 days.

Compressive strength

The compressive strength of hardened prompt cement pastes in the presence of CA retarder is graphically represented in Figure 9. The most common formulation of belite sulphoaluminate cement is C_2S , C_3A_3 CS and C_4AF are characteristic by rapid hardening, excellent durability, and self-stressing and volume stability. The hydration products are; C_2AH_8 , C_3AH_12 and C-S-H [16]. It is clear that the compressive strength increases with curing time for all cement pastes but decreases with the dose of CA due to the retardation of hydration of cement paste. Therefore, the formation of C-S-H, which is the

main source of strength delays and then the strength decreases. The higher compressive strength values are of prompt cement free CA.

It is clear that the compressive strength increases with curing time for all prompt cement pastes with and without CA up to 90 days. This is mainly due to the increase of the amount of hydration products and later accumulation of cementing materials within the available pores giving higher strength [20]. The sharp increase of compressive strength at later ages after 28 days up to 90 days is mainly due the slow hydration of β - C_2S at early ages up to 28 days and the higher hydration rate at later ages [21].

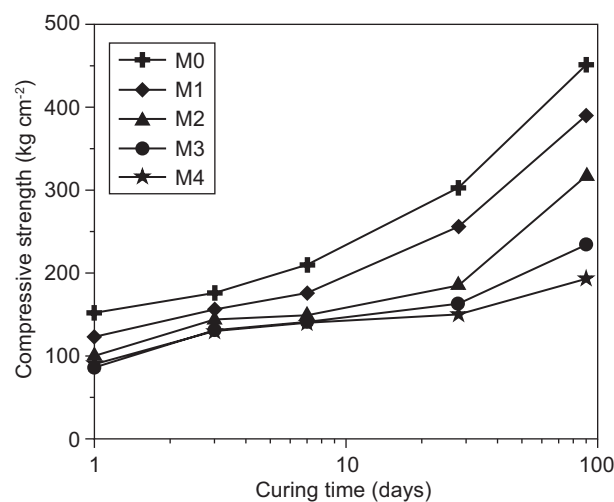


Figure 9. The compressive strength of prompt cement pastes with and without citric acid up to 90 days.

CONCLUSIONS

From the above results it can be concluded that:

- CA elongates the initial as well as final setting times and increases the water of consistency.
- In the presence of 0.75 mass % citric acid achieves the initial and final setting time of the prompt cement according to the ASTM specification.
- CA retards the liberation of $Ca(OH)_2$ of prompt pastes. The free lime contents of prompt cement pastes are slightly increased up to 28 days then sharply increased up to 90 days.
- CA delays the hydration reaction and lowers the values of chemically combined water contents.
- The peak areas corresponding to $Ca(OH)_2$ increase rapidly between 28 - 90 days.
- At early ages (one day) the cement pastes with 1.0 mass % (M3) and 1.25 mass % (M4) of CA give the higher of bulk density than that containing lower amounts.
- The sharp increase of compressive strength was

achieved at later ages after 28 days up to 90.

- The sharp increase of compressive strength at later ages after 28 days up to 90.

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