INVESTIGATION INTO THE ADMIXTURE PROPERTIES OF BONE ASH: A FOCUS ON SETTING TIME OF ORDINARY PORTLAND CEMENT

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ABSTRACT

This paper reports the findings of an investigation into the admixture potential of bone ash (BA) with a focus on the setting time of ordinary Portland cement (OPC). Cow bones are agricultural waste and constitute a sizeable proportion of solid waste in many cities of the world. Heaps of cow bones constitute aesthetic problem to the environment, unnecessary occupation of space and exude unpleasant odour that pollutes the environment. Cow bones need to be properly disposed to check the nuisance they constitute to the society. In the ever increasing endeavours to convert waste to wealth, investigation into the potentials of converting cow bones to beneficial applications in concrete becomes relevant. Bone vis-à-vis cow bone is mainly composed of compounds of calcium. The presence of calcium compounds in bone as well as in cement warrants effects of bone ash on cement to be envisaged. Cow bones were air-dried and incinerated to ash. The resulting ash was sieved through 75µm sieve. Based on weight of cement, 0%, 0.1%, 0.15%, 0.25%, 0.5, 1.0, 1.5%, 2.0%, and 2.5% of the ash were separately mixed with OPC to produce cement-bone ash (CBA). The required quantity of water determined from consistency test was added to the CBA mixture and mixed thoroughly to obtain CBA paste. The CBA paste was tested for setting time. Results show that BA decreases the setting time of OPC; the higher the content of BA, the faster is the reduction in the setting time of OPC. Reaction mechanisms are articulated and developed to explain reasons for the decrease in the setting time of OPC due to the addition of BA. It is concluded that BA is an accelerator; hence BA is recommended for use as an accelerator in concrete.

Keywords: *Admixture, Accelerator, Bone ash, Concrete, Economic disposal, Ordinary Portland cement, Properties, Safe disposal, Setting time, Solid waste.*

INTRODUCTION

Cement, aggregates, and water are the primary components of concrete. The properties of concrete both in the fresh and hardened states are largely dependent on the cement used. The commonest type of cement in use is the ordinary Portland cement (OPC). Sometimes, the properties desired of a given concrete in the fresh and/or hardened states are not achievable by using only the primary components of concrete. In such circumstances, admixture could be added to modify the properties of concrete in the fresh and/or hardened states. One of the properties of concrete that could be modified in the fresh state through the use of admixture is the setting time.

When water is added to cement, the process of setting of cement is initiated by chemical reaction of the cement and water. The chemical reaction that takes place between cement and water is referred to as hydration. Hydration of the cement results in the stiffening of the cement paste. The stiffening of the cement paste as it changes from fluid state to solid state is known as setting. The time it takes the cement paste to set is the setting time. Two types of setting times exist – the initial setting time and final setting time. The initial setting time is the period that elapses between when water is added to the cement and when stiffening of the cement paste becomes noticeable. The initial setting time of OPC should not be less than 45 minutes (BS EN 196-3: 2005+A1: 2008). The final setting time is the period that elapses between when water is added to the cement and when stiffening of the cement paste is completed. The final setting time of OPC should not be more than 10 hours (BS EN 196-3: 2005+A1: 2008). The setting of cement controls the setting of concrete. Therefore, the setting time of concrete can be modified through the modification of the setting time of cement by the addition of admixture.

Regular generation and dumping of solid wastes on authorized dumpsites, such as landfills, and on unauthorized dump places, such as roadsides, side drains, and undeveloped plots of land in residential areas lead to accumulation of solid waste in the environment. The resultant effects of the accumulated solid waste include unsightly surroundings, obstruction to pedestrians and traffic flow, air pollution, and ground water pollution due to leachates from the accumulated solid waste. Safe and economic disposal of solid waste in order to free the environment and the society of the menace constituted by accumulated solid waste have been issues of serious concern to individual countries and the entire world. Efforts have been made through researches to explore the possibilities of converting solid waste to advantageous applications in construction with a high level of success as a way of reducing solid waste accumulation in the environment. Numerous numbers of these researches (Tiamiyu, 1997; Al-Akhras and Samadi, 2004; Zain *et al.*, 2004; Osinubi and Ijimdiya, 2005; Jimoh, 2006; Gbemisola, 2007), to cite but a few, have been undertaken to apply solid waste in soil and concrete to enhance their performances as construction materials. Specifically, the effects of solid waste on the hydration of OPC have also been investigated with beneficial results. Examples exist in

Hwang and Sheen (1991), de Rojas and Frias (1996), Hsiu-Liag *et al*. (2004), and Wang *et al*. (2004).

Generally speaking, bones are rigid organs that form part of the endoskeleton of vertebrates. They function to move, support and protect the various organs of the body, produce red and white blood cells and store minerals. While bone is essentially brittle, it does have significant degree of elasticity, contributed chiefly by collagen (Wikipedia). According to Encyclopedia Britannica (1981) and Wikipedia, the majority of bone is made of the bone matrix which has inorganic and organic parts.

The organic part of the bone matrix is mainly composed of type 1 collagen. Collagen is a fibrous protein. The organic part is also composed of various growth factors that include glycosaminoglycans, osleocalcin, bone sialo, protein, osteopontin and cell attachment factor (Wikipedia). Encyclopedia Britannica (1981) and Dunn Jr. (2009) present that the organic material makes up 30 to 35% of the bone. Of this amount collagen is about 95% (http://www.thepetcentre.com/xtra/bone.comp.html,2007; Dunn Jr., 2009). The other 5% of organic substances is composed of chondroithin sulphate, keratin sulphate and phospholipids. The collagen holds together calcium tetraoxophosphate (V) [$Ca_3(PO_4)_2$] and other calcium minerals in the bone (Encyclopedia Britannica, 1981).

The inorganic part amounts to 65 to 70% of the bone (Encyclopedia Britannica, 1981; Dunn Jr., 2009; Wikipedia). This inorganic part is composed of substances which are mainly of crystalline mineral salts and calcium present in a chemical arrangement called hydroxyapatite (HA) (Encyclopedia Britannica, 1981; Dunn Jr. 2009; Wikipedia). Hydroxyapatite (HA) is also known as osseous or phosphocalcic hydroxoapatite, is a complex compound of hydrated calcium tetraoxophosphate (V), chemically composed of 10 calcium atoms, 6 phosphorus atoms, 26 oxygen atoms, and 2 hydrogen atoms (Chai and Ben-Nissan, 1994; Garbuz *et al*., 1998; Azom, 2001; Dunn Jr., 2009; Teknimed, 2009; Wikipedia). The chemical formula of HA, according to Chai and Ben-Nissan (1994), Weng *et al*. (1994), Garbuz *et al*. (1998), Liao *et al*. (1999), Azom (2001), Dunn Jr. (2009), Teknimed (2009) is as given below.

$$Ca_{10}(PO_4)_6(OH)_2$$

The formula can also be written as $3Ca_3(PO_4)_2.Ca(OH)_2$

The formula indicates that 65 to 70% of bone is a mineral compound, HA, that is composed of nothing more than calcium, phosphorous, oxygen and hydrogen. However, Blincoe (1973) contends that in addition to calcium, other alkali earth elements are found in bone in small amounts. Pongkao *et al*. (1999) observed that HA is very close to our life as the main compound of bone and tooth minerals.

When cows are slaughtered for meat, the bones that remain after removing the flesh are usually stock-piled in heaps as waste in the vicinity of abattoirs. Some of the bones also find their ways into the environs of the abattoirs. Cow bones are agricultural waste and constitute a sizeable proportion of the accumulated solid waste in many cities. The heaps of cow bones constitute aesthetic problem to the environment and exude unpleasant odour that pollutes the environment. Therefore, cow bones need to be safely disposed to have a cleaner and healthier environment. In the ever increasing endeavours to convert waste to wealth, investigation into the potentials of converting cow bones to useful applications in concrete becomes apt. Cow bone is mainly composed of compounds of calcium; the presence of calcium compounds in bone as well as in cement warrants effects of bone ash on cement to be envisaged.

As noted earlier, hydrated calcium tetraoxophosphate (V), $Ca_{10}(PO_4)_6(OH)_2$, (i.e, HA), is the major composition of bone, accounting for 65-70% of the total composition of the bone. Similarly, calcium trioxocarbonate (IV), ($CaCO_3$), (i.e, calcium carbonate), is the primary raw material in the production of cement (Neville, 2003; Housecroft and Constable, 2006; Osei, 2007; Odesina, 2008). The produced cement is, therefore, basically composed of calcium compounds. The OPC consists of four main calcium compounds in the forms of dicalcium silicates (C_2S), tricalcium silicate (C_3S), tricalcium aluminate (C_3A), and tetra-calcium aluminoferite (C_4AF), (Cement and Concrete Association, CCA, 1979; Shirley 1980; Neville, 2003). It is, therefore, indicated that cement and bone have similar primary composition in calcium compounds. Literature search did not show any previous research on the use of BA as an admixture in concrete. This investigation, therefore is unveiling another area of interest in the continuous quest for safe and economically viable ways of getting rid of the solid waste in the environment, and finding local substitutes for ingredients in concrete.

On the basis of the similar compositional characteristics of cement and bone, it was reasoned in this study that the incineration of the cow bones to ash could produce elements and/or compounds in the resulting BA that could induce changes in the properties of cement. Consequently, the admixture potentials of BA, with a focus on the setting time of OPC, was investigated. If BA is found suitable as an admixture, another means of safely and economically disposing the cow bones would have been found. The incorporation of BA in concrete will not only assist in solving the cow bones disposal problem, but will also, as an admixture, help in improving on some of the properties of concrete. In addition, admixtures presently in use require a high level of technology to produce when compared to the simple incineration of the cow bones to produce the BA. Further more, admixtures are items of imports to many countries; this constitutes a drain on the foreign reserves of the importing countries. Cow bones are available in most countries as waste; the ash can cheaply be produced by simple incineration; thus achieving economy in the acquisition of the BA. Suitability of BA as an admixture in concrete will not only contribute to environmental protection, it will also go a long way in reducing the consumption of energy in the production of admixtures, and will also help to conserve the foreign reserve of many countries by providing a local substitute for imported admixtures. Essentially, the conversion of solid waste to construction material, economy in the production of admixtures, and the protection of the environment are the main objectives of this study.

INVESTIGATION PROCEDURE

The materials used in this study include OPC, BA, and clean tap water. Cow bones were sourced from an abattoir. The bones were air-dried and incinerated to ash. The obtained ash was sieved through 75µm sieve. The ash passing the 75µm sieve was used in this study. Cement-bone ash (CBA) mixture was prepared by adding 0%, 0.10%, 0.15%, 0.20%, 0.25%, 0.5%, 1.0%, 1.5%, 2.0%, and 2.5% of BA by weight of cement to the OPC. The mixture was thoroughly mixed to achieve uniform distribution of OPC and BA in CBA. Consistency test was carried out in accordance with BS EN 196-3: 2005+A1: 2008 to determine the quantity of water required to produce a cement paste of normal consistency. The quantity of water determined from the consistency test was added to the CBA, and mixed thoroughly until a homogeneous mixture of CBA paste was obtained. Setting time test was carried out on the CBA paste in accordance with BS EN 196-3: 2005+A1: 2008

DISCUSSION OF RESULTS

The results of the consistency test, Table 1, revealed that 30% (equivalent to 120 ml) of water by weight of cement is the quantity of water required to produce a standard cement paste of normal consistency of the OPC used. This represents 0.30 water/cement ratio.

As can be observed in Table 2 and Figure 1, the addition of BA to OPC decreases the setting time of OPC. As the content of BA in CBA increases, the decrease in the setting time of OPC increases. It can also be observed that the reduction in the setting time of OPC as the BA content increases is generally gradual for both initial and final setting times. That BA deceases the setting time of OPC indicates that BA is an accelerating admixture. The setting time for all the percentage contents of BA used in this research satisfy the required conditions for the setting time of OPC in accordance with BS EN 196-3: 2005+A1: 2008. It should be recalled that BS EN 196-3: 2005+A1: 2008 requires that the initial and final setting times of OPC should not be less than 45 minutes, and not greater than 10 hours, respectively. Since all the percentage contents of BA used in this research satisfy the required conditions for the setting time of OPC, it follows that any of the percentage contents used in this study can be deployed to accelerate the setting of OPC. The main condition that may guide the choice of a given percentage will be how rapid will be the required setting.

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Presentation of Results

At standard weight of 400 g, the consistency of cement was obtained at water content of 30% by weight of cement as presented in Table 1.

Table 1: Results of the Consistency Test

Sample No.	Weight of water (g)	Water content (%)	Equivalent volume of water (ml)	Penetration of plunger from the bottom (mm)	Remark
1	400	20.0	80	4.0	Inconsistent
2	400	25.0	100	2.5	Inconsistent
3	400	30.0	120	6.0	Consistent
4	400	30.5	122	4.0	Inconsistent
5	400	30.25	121	4.0	Inconsistent

From the consistency test results, the water-cement ratio was calculated.

Weight of cement = 400 g
Water content = 30%
Water volume = 120 ml
Therefore, the water-cement ratio = 0.30

The results of the setting time test on the CBA paste are presented in Table 2.

Table 2: Results of Setting Time Test

BA content (%)	0	0.1	0.15	0.2	0.25	0.50	1.0	1.5	2.0	2.5
Initial setting time (mins)	71	69	67	63	60	57	55	50	48	46
Final setting time (mins)	151	149	149	147	138	120	115	105	101	92

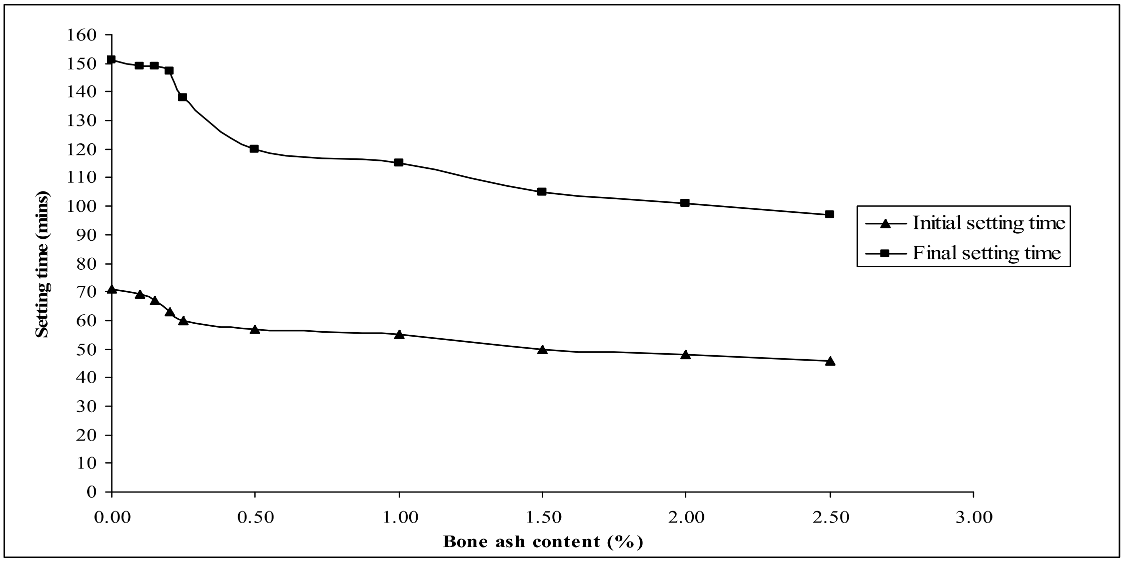

Figure 1: Setting Time Versus BA Content

Reaction Mechanisms

This study has identified BA as an accelerator**;** BA can, therefore, be used as admixture in concrete. To this extent, the main objectives of this study have been achieved. However, additional contribution is being made to articulate and develop reaction mechanisms to provide explanation for the accelerating effect of BA on the hydration of OPC.

Clearly, results have shown that BA has accelerating effect on the setting of OPC. However, the exact role BA plays in causing rapid hydration of OPC is not well understood. It is apt to mention at this juncture that the hydration of OPC itself is still not properly and completely understood. This statement is strongly backed by Bogue and Lerch (1934), and Neville (2003) who observed that the hydration of cement is not satisfactorily understood. In addition, Diamond (2004) states that the internal structures of hydrated cement pastes and concretes are poorly understood by most concrete engineers and technologists, and even by many researchers. Furthermore, Escalante-Garcia and Sharp (2004) remarked that the understanding of the chemistry of hydration of Portland cements remains an area of opportunity for many researchers. Probably because of these limitations, most literatures on accelerators and retarders stopped at the identification of a substance as an accelerator or as a retarder without providing adequate information on the intricacies of the reactions between the substance and the cement that resulted in the accelerating or retarding effect. In a sharp deviation from this trend, this study did not stop at only identifying that BA is an accelerator but has gone a step further to develop reaction mechanisms, from the much that is known about the setting of cement, to explain the likely reactions that would result in the increase in the hydration of the OPC with the addition of BA.

To start with, OPC is polymineralic. The polymineralic nature of OPC would influence the effect of BA on the rate of hydration of OPC. Different matrices of hydrated cement paste would result under different conditions and compositional characteristics. The reasons for the kind of matrix of hydrated cement paste under a given set of conditions and compositional characteristics are not sufficiently understood. This reflects Bougue and Lerch (1934) that posits that the products of hydration reaction may influence one another, or may themselves interact with other components in the system. The polymineralic nature of cement and the heterogeneous phase distribution of cement, coupled with compositional characteristics of cement and hydration conditions make the hydration process of cement difficult to be properly and completely understood. Since the hydration of cement is still far from being satisfactorily understood, and since complex reactions are involved among the cement compounds, and between the cement compounds and admixture during hydration, it will be difficult to realistically present stoichiometrically, the mechanisms being developed in this study to explain these complex reactions between the cement compounds and BA constituents that will lead to the accelerating effect of BA on the cement. Notwithstanding the foregoing limitations, attempt has been made in this paper to provide explanations of the plausible reasons for the increase in the rate of hydration of the cement due to the addition of BA.

The main active compounds of the cement are dicalcium silicate (C_2S), tricalcium silicate (C_3S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). The quantities and reactivity of the four main compounds of cement have been presented (Taylor, 1985; Harisson *et al.*, 1997; Stutzman, 2004; Kjellsen and Justnes, 2004). It should be made clear, however, that in addition to these main active compounds, minor oxides such as sodium oxide (Na_2O), potassium oxide (K_2O), manganese (III) oxide (Mn_2O_3), tin oxide (T_iO_2), and magnesium oxide (MgO) are also present in OPC. While the main OPC compounds play the dominant role in the hydration of OPC, the minor oxides are also important in the hydration of OPC. Neville (2003) explains that K_2O and Na_2O are referred to as minor oxides because of the quantities present, but they play vital role in the hydration of cement. The setting of cement proceeds by selective hydration of the cement compounds. During the selective hydration of the cement compounds, the C_3S and C_2S dominate the process of hydration at the early stage. Between the C_3S and C_2S, the C_3S is more dominant in the early period of cement hydration.

It is posited in this study that during incineration of the bones to ash, decomposition of the complex hydrated calcium tetraoxophosphate (V), $Ca_{10}(PO_4)_6(OH)_2$, (i.e, HA), which is the main compound in bones, will take place to produce anhydrous calcium tetraoxophosphate (V) (apatite), calcium oxide (CaO), and a loss of the bound water in the compound. The proposed process in this study is represented in equation (1).

$$Ca_{10}(PO_4)_6(OH)_2 \xrightarrow{heat} 3Ca_3(PO_4)_2 + CaO + H_2O \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

This study believes that the collagen which is an organic material mainly of fibrous protein will be burnt off during the ashing of bones. This belief is in line with Hortling *et al*. (1999) that observed that heated bones have no carbon. Therefore, the main constituents of BA are the complex compound of calcium tetraoxophosphate (V) and calcium oxide.

$$3Ca_3(PO_4)_2 + CaO$$

Studies that have been conducted on the decomposition of HA show that HA is thermally unstable (Chai and Ben-Nissan, 1994; Weng *et al*., 1994; Liao *et al*., 1999; Azom, 2001; Barralet *et al*., 2002). According to Azom, (2001) HA decomposes at temperature from 800-1200°C depending on its stoichiometry. It begins to dehydroxylate at about 800°C to form oxyhydroxyapatite. This process is gradual and takes place over a range of temperatures. When bone is thermally decomposed, the resulting ash consist mainly of complex products on which, so far, there is no consensus opinion. As presented in Chai and Ben-Nissan (1994), two mechanisms have been proposed for the decomposition of HA as follows equations 2 & 3:

$$Ca_{10}(PO_4)_6(OH)_2 \xrightarrow{heat} 2\beta\text{–}Ca_3\,(PO_4)_2 + Ca_4\,P_2O_9 + H_2O \quad \text{------------}(2)$$

$$Ca_{10}(PO_4)_6(OH)_2 \xrightarrow{heat} 3\beta\text{–}Ca_3\,(PO_4)_2 + CaO + H_2O \quad \text{-------------------}(3)$$

It can be seen that in (2), the products of thermal decomposition of HA are 2-β apatite, CaO, and water; while in (3), the products of thermal decomposition of HA are 3-β apatite, CaO, and water. In both equations, the water component is lost during thermal decomposition; this agrees with the position of this study. Of equations (2) and (3), equation (3) (except for the inclusion of 3β) is in consonance with the proposed decomposition mechanism presented in equation (1) in this study. Therefore, the proposed equation (1) in this study for the thermal decomposition of bones is accepted and adopted for the explanation of how BA accelerates the setting of OPC.

When water is added to the mixture of OPC and BA, a reaction process that causes a shift in the normal hydration of OPC is set up. Faster rate of hydration is induced in OPC by the BA. That the reaction of the OPC and BA in the presence of water results in the reduction of the setting time of OPC suggests, in the opinion of this study, that reaction products with decrease in C_2S content and an increase in the C_3S content which favours the fast setting of OPC are encountered. With the reduction in the C_2S and an increase in the C_3S, the hydration of CBA paste will proceed faster than that of OPC paste alone. Hence BA accelerates the setting time of OPC. In addition, this paper posits that during the hydration of the CBA paste, the apatite activity is negligible, while the CaO remains the main active compound in the BA. The CaO of BA reacts with the major components of the cement resulting in reaction products that favours the acceleration of the hydration of OPC. The proposed reaction equations in this paper of the CaO of BA with the main compounds of OPC in the presence of water are as presented in equations (4) to (7).

$$2Ca_2SiO_4 + CaO + 5H_2O \rightarrow 2CaO.SiO_2.H_2O + 3Ca(OH)_2 \ldots\ldots\ldots(4)$$

$$3Ca_3SiO_5 + CaO + 10H_2O \rightarrow 3CaO.SiO_2.H_2O + 7Ca(OH)_2 \ldots\ldots(5)$$

$$3Ca_3Al_2O_6 + CaO + 10H_2O \rightarrow 3CaO.Al_2O_3.H_2O + 7Ca(OH)_2 \ldots\ldots\ ..(6)$$

$$4Ca_4Al_2Fe_2O_{10} + CaO + 17H_2O \rightarrow 4CaO.Al_2O_3.Fe_2O_3.H_2O + 13Ca(OH)_2 \ldots.(7)$$

Equations (4) to (7) show the typical products of the hydration of OPC which are composed of the respective hydrates of dicalcium silicates, (4); tricalcium silicates, (5); tricalcium aluminate, (6); tetracalcium aluminoferrite, (7). The product in common to the four equations is calcium hydroxide $Ca(OH)_2$. The typical products of hydration of cements which are calcium silicate hydrates (C-S-H) and calcium hydroxide (CH), as clearly presented in equations (4) to (7), have been described as the dominant products of hydration (Neville, 2003; Escalante-Garcia and Sharp, 2004; Kjellsen and Justnes, 2004; Scrivener, 2004).

At the early stage of hydration, the C-S-H and CH are produced mainly by the selective hydration of C_3S and

C_2S. Between the C_3S and C_2S, the C_3S reacts first and dominates the reaction within the first few days of hydration (Neville, 2003; Scrivener, 2004). Kjellsen and Justnes (2004) described C_3S as the most important phase of cement hydration. The C-S-H gel resulting from these reactions is reported to be principally responsible for the mechanical properties of hydrated cement (Escalante-Garcia and Sharp, 2004; Scrivener, 2004). Therefore, this paper considers that the formation of the C-S-H and CH, and their chemical behaviours during the hydration process are also very vital in the explanation of how the accelerating effect is produced in OPC by BA.

It should be noted that complete hydration of the cement grains is not instantaneous; it takes place over a long period of time and is dependent on some factors. Information on the gradual process of hydration of cement are presented in Harrison *et al.* (1997), Diamond (2001), Diamond (2004), Escalante-Garcia and Sharp (2004), Kjellsen and Justnes (2004), Scrivener (2004), and Stutzman (2004). As soon as the C-S-H and CH start forming, further hydration will be influenced by the micro-structural characteristics of the formed C-S-H and CH. The deposition of the C-S-H and CH phases in the microstructure of the hydrated cement is quite distinct; C-S-H is deposited mainly around the cement grains, while CH is precipitated in the water filled pores. The C-S-H and CH solids resulting from hydration will bridge the spaces between the cement grains. When the C-S-H and CH solids bridge the spaces between the cement grains, the hydration process is affected. When higher quantities of C-S-H and CH are present in the cement paste, there will be faster consumption of the C_3S at the early stage of hydration with the result that no substantial solids will be available to bridge the spaces between the cement grains. Therefore, the surfaces of the cement grains will constantly be exposed for hydration. This will result in a rapid hydration process; consequently, a decrease in setting time will be observed.

From the foregoing explanations, the implication of equations (4) to (7), developed in this paper for the reaction mechanisms, is that, although the typical hydration products of OPC (i.e., C-S-H and CH) can be formed with or without the CaO of BA since CaO is inherent in cement, but with the addition of the CaO from BA, there will be higher quantity of CaO in the CBA paste than that of OPC paste alone. Therefore the high quantity of CaO in CBA paste provides additional C-S-H and CH for the rapid consumption of C_3S in OPC which resulted in the acceleration of hydration of OPC. Hence the setting time of OPC is decreased when mixed with BA.

CONCLUSIONS

From the results of this study, the following conclusions are drawn.

(i) Bone ash is an accelerator.

(ii) The higher the content of BA, the greater the accelerating effect.

(iii) For all the percentages of BA contents used in this study, the requirements of BS EN 196-3: 2005+A1: 2008 are satisfied for both the initial and final setting times of OPC.

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