

# EFFECTS OF EGGSHELLS ASH (ESA) ON THE SETTING TIME OF CEMENT

By

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## ABSTRACT

*Admixture properties of eggshells ash (ESA), with a focus on the setting time, were investigated. ESA was obtained by incinerating fowls' eggshells to ash. The ash was sieved through 75 $\mu$ m sieve. The ash passing the 75  $\mu$ m sieve was used in the investigation. Consistency test was carried out to establish the quantity of water required to constitute a standard cement paste of normal consistency in accordance to BS 12: 1991 [1]. Cement-eggshells ash (CESA) paste was constituted using 0%, 0.1%, 0.5%, 1%, 1.5%, 2.0% and 2.5% of ESA by weight of cement. Setting time test was conducted on the CESA paste in accordance to BS 12:1991 n[1]. Results show that the addition of ESA to the ordinary Portland cement (OPC) decreases the setting time of the cement. Conclusions drawn are that ESA is an accelerator; the higher the ESA content, the faster the rate of setting; all contents of the of the ESA employed in this investigation satisfy the setting time requirements of BS 12:1991 [1] for both the initial and final setting times. Thus, it is recommended that ESA can be used as an accelerator in concrete.*

**Keywords:** Admixture, OPC, ESA, Economy, Properties, Safe disposal, Setting time, Solid waste.

## 1.0 INTRODUCTION

Daily generation and dumping of solid waste on authorized dumpsites, such as landfills, and on unauthorised placed such as roadsides, side drains, and undeveloped plots of land in residential areas lead to the accumulation of solid waste in the environment. The resultant effects fo 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. Disposal and treatment 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. Attempts have been made by various researchers to convert solid waste to beneficial applications, with a high level of success, as a way of reducing solid waste accumulation. Among such researchers are Tiamiyu [1], Zain et al. [3], Osinubi and Ijimdiya [4], Jimoh [5], and Gbemisola [6]. The effects of solid waste on the hydration of OPC and performance of mortars have also been investigated with interesting results. Examples exist in Hwang and Sheen [7], de Rojas and Frias [8], Hsiu-Liag et al. [9], and Wang et al. [10].

Agricultural waste constitutes a sizeable proportion of the accumulated solid waste in many cities of the world. Eggshells are part of agricultural wastes that litter the environment. In the ever increasing endeavours to convert waste to wealth, the efficacy of converting eggshells to beneficial use becomes an idea worth investigating. The composition of the eggshells lends the effects of its ash on the cement to be articulated. It is scientifically known that the eggshell is mainly composed of compounds of calcium. Winton [11] presented eggshell as being composed of 93.70% calcium carbonate, 4.20% organic matter, 1.30% magnesium carbonate, and 0.8% calcium phosphate.

As previously mentioned, calcium trioxocarbonate (IV), [i.e., calcium carbonate, ( $\text{CaCO}_3$ )], is the major composition of the eggshell, accounting for 93.70% of the total composition of the eggshell. Odesina [12], also presented calcium trioxocarbonate (IV), as an important constituent of eggshells and seashells. Similarly, calcium trioxocarbonate (IV), [calcium carbonate, ( $\text{CaCO}_3$ )], is the primary raw material in the production of cement [12 – 14]. The produced OPC is composed of four main calcium compounds in the forms of dicalcium silicates, ( $\text{C}_2\text{S}$ ), tricalcium silicate, ( $\text{C}_3\text{S}$ ), tricalcium aluminate, ( $\text{C}_3\text{A}$ ), and tetra-calcium aluminoferrite, ( $\text{C}_4\text{AF}$ ), [14 – 16]. It is, therefore, indicated that cement and eggshells have the same primary composition in calcium compounds. The calcium trioxocarbonate (IV) which has been established to be common to eggshell and cement is a naturally abundantly available mineral. According to Osei [13], calcium

trioxocarbonate (IV) occurs abundantly in earth's crust as lime stone, marble, and chalk, and as well as in natural ores like calcite, dolomite, and Iceland spar. It is found in the caves in many parts of the world as stalactites and stalagmites. It is also an important constituent of bones and the external skeleton of organisms. Literature search did not show any previous research on ESA. This investigation, therefore is unveiling another area of interest in the continuous quest for safe and economically viable ways of getting rid of solid waste in the environment; and finding local substitutes for construction materials.

On the basis of the common compositional characteristics of cement and eggshells, it was reasoned in this study that the incineration of the eggshells could produce elements and/or compounds in the resulting ESA that could induce changes in the properties of cement. Consequently, the admixture properties of ESA, with a focus on the setting time of OPC, were investigated. If ESA is found suitable as an admixture, a means of safely and economically disposing the eggshells would have been found. The incorporation of ESA in concrete will not only solve the eggshells 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 eggshells to produce the ash. Further more, admixtures are items of imports to many countries; this constitutes a drain on the foreign reserves of the importing countries. Eggshells are available in most countries as waste, and the ash can cheaply be produced by simple incineration; thus achieving economy in the acquisition of ESA. The use of 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 concrete material and helping to conserve 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.

## 2.0 Experimental Procedure

The materials employed in this investigation include OPC, ESA, and water. Collected eggshells were air-dried and incinerated to ash. The ash was sieved through 75  $\mu\text{m}$  sieve. The ash passing the 75 sieve  $\mu\text{m}$  was used in the investigation. The water used in the investigation was clean tap water. Consistency test, in

accordance to BS 12: 1991 [1], was conducted to obtain the quantity of water required to prepare a standard cement paste of normal consistency.

ESA in the percentage of 0%, 0.1%, 0.5%, 1%, 1.5%, 2.0%, and 2.5% by weight of cement were added to the cement and mixed thoroughly. The quantity of water determined from the consistency test was added to the mixture of cement and ESA, and mixed thoroughly until a homogenous paste of CESA was produced. The CESA paste thus prepared was tested for setting time in accordance to BS 12: 1991 [1].

## 3.0 RESULTS: PRESENTATION AND DISCUSSION

### 3.1 Presentation of Results

The consistency tests results are presented in Table 1:

Table 1: Results of consistency tests

Test No.	Weight of cement (g)	Water content (%)	Equivalent volume of water (ml)	Penetration of plunger from bottom (mm)	Remark
1	400	30	120	17	Inconsistent
2	400	40	160	0	Inconsistent
3	400	35	140	10	Inconsistent
4	400	38	152	3	Inconsistent
5	400	37.5	150	3	Inconsistent
6	400	37.0	148	6	Consistent
7	400	39.0	156	1	Inconsistent

In Table 2, the setting time results are presented. Figure 1 shows graphical illustrations of the results. The percentage decreases in the initial, and final setting times are plotted against the ESA contents as shown in Figure.

Table 2: Setting time tests results

Test No.	Ash content (%)	Water content (%)	Volume of water (ml)	Initial setting time (mins)	Decrease in final setting time (%)	Final setting time (mins)	Decrease in final setting time (%)
1	0	37	148	143	-	247	-
2	0.1	37	148	141	1.40	240	2.83
3	0.5	37	148	129	9.79	221	10.53
4	1	37	148	118	17.48	203	17.82
5	1.5	37	148	109	23.78	182	26.32
6	2	37	148	105	26.57	175	29.15
7	2.5	37	148	97	32.17	163	34.01

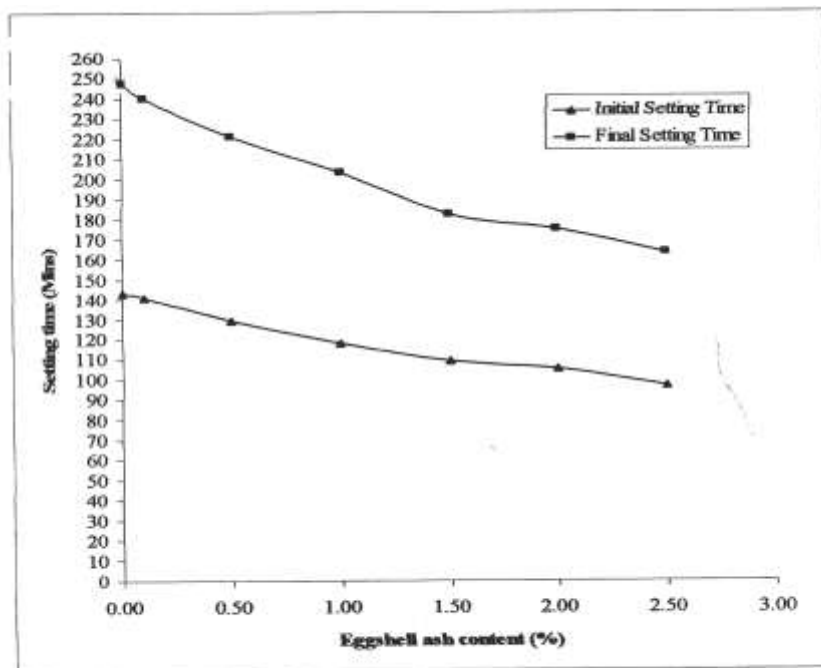
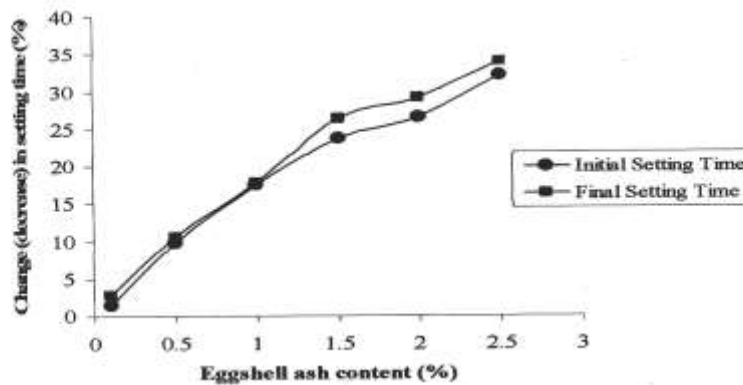


Figure 1: Setting time versus ESA content.



## 3.2 DISCUSSION

### 3.2.1 Discussion of Results

As shown in Table 1, the amount of water required to make a standard cement past of normal consistency is equal to 148ml. This is equivalent to 37% by weight of OPC used. This translated to 0.37 water/cement ratio, which was employed in constituting the CESA paste on which was conducted the setting time test.

From the results of the setting time test in Table 2, and graphically illustrated in Figure 1, the CESA paste sets faster than the cement-paste alone. This indicated that the addition of ESA to the cement decreases the setting time of cement. From the percentage decreases in the initial and final setting times presented in Table 2 and plotted in Figure 2, it can be seen that the higher the contents of ESA in the cement paste, the faster the setting of the cement. For all the percentage contents of ESA used, both the initial and final setting times satisfy the requirements of BS 12: 1991 [1]. It should be recalled that BS 12:1991 [1] requires that the initial and final setting times of OPC should not be less than 45 minutes, and not greater than 10 hours, respectively. It can also be observed that ESA has a similar decreasing effect on the initial and final setting times of cement. This similar effect being that the decrease in the setting time of OPC between successive percentage additions of ESA is generally gradual for the initial setting time as well as for the final setting time. The decrease in the setting time of the OPC due to the addition of ESA portrays ESA as an accelerator. Therefore, ESA can be used to advantage as an admixture in concrete.

### 3.2.2 Reaction Mechanisms

To the extent of identifying that ESA is an accelerator and can be used as an admixture in concrete, the main objectives of this study have been achieved. Further, additional contribution is being made to explain the mechanisms of the reactions leading to the accelerating effect of ESA on the hydration of cement.

From the results, ESA has clearly been indicated to have an accelerating effect on the setting of OPC. However, the exact role ESA plays in inducing rapid hydration in OPC is not clearly understood. It should be emphasized at this juncture that the hydration of OPC itself is still not properly and completely understood. This statement is strongly supported by Bogue and Lerch [17], and Neville [14] who observed that the hydration of cement is not satisfactorily understood. In addition, Diamond [18] submits 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 [19] remarked that the understanding of the chemistry of hydration of Portland cement is still an area of opportunity for many researchers. Most literatures on accelerators and retarders stopped at the identification of a substance as an accelerator or as a retarder without providing information on the intricacies of the reactions between the substance and the cement that resulted in the accelerating or retarding effect. Nevertheless, from the much that is known about the setting of cement, some reaction mechanisms have been developed in this study to explain the likely reactions that would result in the

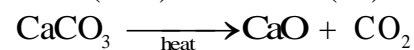
increase in the hydration of the OPC in the presence of ESA.

The OPC is polymineralic. The polymineralic nature of the OPC influences ESA effects on the rate of hydration of the OPC. Different matrices of hydrated cement paste would result under different conditions and compositional characteristics; the reasons for the kind of matrix assumed by hydrated cement past under a given set of conditions and compositional characteristics are not well understood. The polymineralic nature of cement and hydration conditions make the hydration process of the cement difficult to be properly and completely understood. Since the hydration of cement is still not satisfactorily understood, and since complex reactions are involved among the cement compounds, and between the cement compounds and admixtures during hydration, it will be difficult to realistically present stichometrically, these complex reactions between the cement compounds and ESA constituents that will lead to the accelerating effect of ESA on the cement, However, attempt has been made to provide explanations of the reasons for the increase in the rate of hydration of the cement in the presence of ESA.

It has already been pointed out in this paper that the main compounds in the cement are dicalcium silicate ( $C_2S$ ), tricalcium silicate ( $C_3S$ ), tricalcium aluminate ( $C_3A$ ), and tetracalcium aluminoferrite ( $C_4AF$ ). It should be noted, however, that in addition to the main compounds, minor oxides such as sodium oxide, ( $Na_2O$ ), potassium oxide ( $K_2O$ ), manganese (III) oxide ( $Mn_2O_3$ ), tin oxide ( $TiO_2$ ), and magnesium oxide ( $MgO$ ) are also present in the cement. While the main

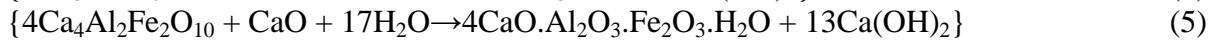
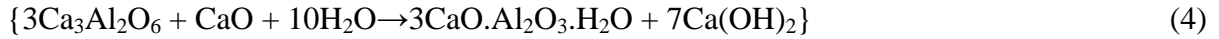
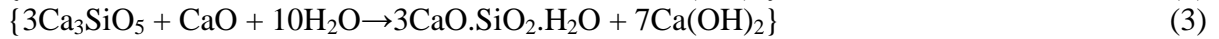
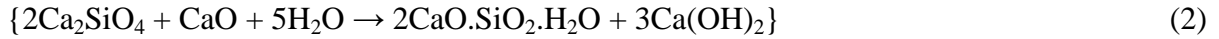
OPC compounds play the prominent role in the hydration of the OPC, the minor oxides are also relevant in the hydration of OPC. Neville [14] explains that  $K_2O$  and  $Na_2O$  are referred as mirror oxides because of the quantities present, but they play vital role in the hydration of cement. The setting of cement is effected 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.

In the eggshell, the dominating compound is the calcium trioxocarbonate (IV), ( $CaCO_3$ ). During the incineration to ash, the  $CaCO_3$  will decompose to calcium oxide ( $CaO$ ) and carbon (IV) oxide, ( $CO_2$ )



The  $CO_2$  will escape as gas, while  $CaO$  remains in the ash. As has already been shown in the results, the ash accelerates the hydration of OPC. Since  $CaO$  is the main chemical composition of the ash, it is strongly believed in this paper that the  $CaO$  is responsible for the decrease in the setting time of the OPC.

As earlier stated, the polymineralic nature of the OPC influences ESA effects on the hydration of the OPC. This paper posits that when ESA is mixed with cement in the presence of water, the  $CaO$  in the ESA reacts with the compounds of the cement resulting in reaction products that favours the acceleration of the hydration of the OPC. The proposed reaction equation in this paper of the  $CaO$  of ESA with the main compounds of cement in the presence of water are as presented in equations (2) to (5)



Equations (2) through (5) are the proposed reaction equations for the hydration process.

Equations (2) to (5) show the typical products of the hydration of OPC which are composed of the respective hydrates of dicalcium silicates, (2), tricalcium silicates, (3), tricalcium aluminate, (4), and tetracalcium aluminoferrite, (5). A common product to the four equations is calcium hydroxide  $[\text{Ca}(\text{OH})_2]$ . The quantities and reactivity of the four main compounds of cement have been presented [20 – 23]. The typical products of hydration of cements which are calcium silicate hydrates (C-S-H) and calcium hydroxide (CH) have been described as the dominant products of hydration [14, 19, 23, 24].

At the early stage of hydration, the C-S-H and CH are produced mainly by the selective hydration of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ . Between the  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ , the  $\text{C}_3\text{S}$  reacts the first and dominates the reaction within the first few days of hydration [14, 24]. Kjellsen and Justnes [23] described  $\text{C}_3\text{S}$  as the most important phase of cement. The C-S-H gel resulting from these reaction is reported to be principally responsible for the mechanical properties of hydrated cement [19, 24]. Therefore, this paper considers that the formation of the C-S-H and CH, and their chemical behaviours during the process are very vital in the explanation of how the accelerating affect is produced in the OPC by the ESA.

According to Escalante-Garcia and Sharp [19], C-S-H gel is generated by the interaction of the added material (such as ESA used in this study) to the cement with

the CH liberated during the hydration of the  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  present in the cement. It should be noted that complete hydration of the cement grains is not instantaneous; it takes place over a long period time and is dependent on some factors. Information on the gradual process of hydration of cement are presented in Harrison et al. [21], Diamond et al. [25], Diamond [18], Escalante-Garcia and Sharp [19], Kjellsen and Justnes [23], Scrivener [24], and Stutzman [22]. As soon as the C-S-H and CH start forming, further hydration will be influenced by the micro-structural characteristics of the C-S-H and CH. On the effect of CH on the hydration of cement, Diamond [25] reported that the irregularity and geometrical complexity of many CH particles in Portland cement system reflects the tortuous character of the capillary pore space in the hydrated OPC. 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 [24]. Furthermore, Scrivener [24] reported that the additional solid as a result of hydration, bridges the space between the cement grains. It is relevant to point out here that “additional solid” resulting from hydration is composed mainly of the C-S-H and CH. It can be readily appreciated that when the “additional solid” bridges the space between the cement grains, the hydration process is affected. If and when higher quantities of C-S-H and CH are present in the cement paste, there will be faster consumption of the  $\text{C}_3\text{S}$  at the early stage of

hydration. This will result in a rapid hydration process; consequently, a decrease in setting time will be observed.

From the foregoing discussion, the implication of equations (2) to (5), in the opinion of this paper, 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 ESA, since CaO is inherent in cement, but with the presence of the CaO of ESA there will be higher quantity of CaO in the CESA paste than that of the cement paste alone. Therefore the high quantity of CaO in CESA paste provides additional C-S-H and CH for the rapid consumption of C<sub>3</sub>S in the OPC which resulted in the acceleration of hydration of the OPC. Hence the setting time of the OPC is decreased in the presence of ESA.

#### 4.0 CONCLUSIONS AND RECOMMENDATION

##### 4.1 Conclusion

From the results of the study, it is concluded that:

- i. Eggshells ash (ESA) is an accelerator.
- ii. The higher the content of the ESA, the greater the accelerating effect.
- iii. For all the ESA contents used in this study, the requirements of BS 12: 1991 are satisfied for both the initial and final setting times of the OPC.

##### 4.2 Recommendation

From the findings of the study, the use of ESA as an accelerator in concrete is recommended.

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