



A study on the setting characteristics of sodium silicate-activated slag pastes

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Abstract

In this paper, we investigate which factor for a sodium silicate-based activator influences the setting time of alkali-activated slag (AAS) paste. Several factors, such as the pH value of the activator, the alkali modulus (AM) and the alkali activator dosage, were evaluated when the liquid/slag ratio was kept constant. It was found that the pH value and the AM have a strong relationship, however, they have no distinct relationship with the setting time. The activator dosage, which is defined as the sum of the SiO_2 and Na_2O concentrations, shows a significant trend with the setting time. It was also found that the influence of SiO_2 on the setting time is more apparent than that of Na_2O . Increasing amounts of SiO_2 decrease the pH value of the activator and increasing amounts of Na_2O increase the pH value of the activator. Phosphoric acid, used as a retarder, was found to have a strong retarding effect.

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Keywords: Alkali-activated slag paste; Activator; Alkali modulus; Setting time; Retarder

1. Introduction

Alkali-activated slag (AAS) is a new type of binder used in concrete manufacturing. This binder, based on 100% slag plus activator, has been used in Eastern Europe, Scandinavia and China and was discussed in two extensive reviews [1,2]. Its production utilizes industrial by-products, requires less energy than ordinary portland cement (OPC) and is associated with low CO_2 emissions. The AAS concrete (AASC) has recently received much attention from the academic field and many valuable research results have been reported. Several recent efforts on AASC are described as follows to the author's best knowledge. AASC has been found to have some superior properties as compared to OPC concrete, namely, low hydration heat, high early strength and excellent durability in an aggressive environment [3–6]. Hydration products of AAS cement are different from that of the OPC as reported by Wang et al. [7]. Regardless of the activator used, the main hydration product is a calcium silicate hydrate with low C/S ratio and varying degrees of crystallinity. Furthermore, a crystalline phase of hydrotalcite type is formed in slag activated with either NaOH or water glass. A crystalline phase

of AFm type is also formed in slag activated with NaOH [7]. Collins and Sanjayan [8] reported that the lack of moist curing of AASC increased the level of microcracking. Collins and Sanjayan [9] also reported on the effects of curing, aggregate type and incorporation of shrinkage-reducing chemical admixture on the cracking tendency of AASC. Bakharev et al. [10] has reported the effects of elevated temperature curing on properties of AASC. Fernández-Jiménez and Puertas [11] have reported that the reaction mechanism determined for AAS pastes was a diffusion mechanism and their activation energy was 57.6 kJ/mol. Shi [12] examined the effects of different activators on the strength, pore structure and permeability of AAS mortar. Collins and Sanjayan [13] reported that adding ultrafine fly ash in the AAS system significantly improved the workability. Bakharev et al. [10] recently reported that the AASC had lower resistance to alkali-aggregate attack than that of the OPC concrete of similar grade [14]. Kim and Hong [15] reported that the ion concentration change of liquid phase during hydration was different depending on the activator and the hydration time. However, this new binder has some problems, such as rapid set [16] and high drying shrinkage [17], which must be resolved before utilizing it in commercial practice.

It has been reported that the strength development of AASC depends on the activator type and concentration [12,18]. Sodium silicate-based activator (sodium silicate

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and sodium hydroxide) was found to have the best performance on strength development. However, the sodium silicate-based activator results in a most serious rapid set. Phosphate [16] and malic acid [19] were used as retarders in previous studies. In engineering practice, a binder should have a reasonable setting time. This means that concrete or mortar made using a binder should have a setting time long enough to permit transport time for the concrete or mortar. However, it becomes uneconomic if the setting time is too long. The setting times (initial and final) [16] have been used to study the retarding effect of phosphate.

In this study, two stages were conducted sequentially. In the first stage, how the dosage of sodium silicate and sodium hydroxide influences the paste setting time was studied. Keeping the liquid/slag ratio constant, some possible mixing factors such as the pH value [20], alkali modulus (AM) [21] and total activator dosage were taken into account. The initial and final setting times were both measured. Experimental results revealed that the total activator dosage has a definite relationship with the setting time, both initial and final. In the second stage, phosphoric acid was added as a retarder. The influence of the phosphoric acid concentration on the paste setting time was studied by controlling $\text{SiO}_2 = 123 \text{ g/l}$ and $\text{Na}_2\text{O} = 122 \text{ g/l}$. It was found that appropriate usage of phosphoric acid could retard the setting time.

2. Experimental

2.1. Materials

The chemical composition and physical properties of the slag used are tabulated in Table 1. Blast furnace slag is a granulated product ground to a fineness of about $383 \text{ m}^2/\text{kg}$, with a particle size range of $5\text{--}75 \mu\text{m}$. This material is neutral with a basicity coefficient $K_b = (\text{CaO} + \text{MgO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ equal to 0.93. The hydration modulus (HM) is defined as

$$\text{HM} = \frac{\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3}{\text{SiO}_2}. \quad (1)$$

It is suggested that the HM of slag should exceed 1.4 to ensure sound hydration property. From Table 1, the HM of

Table 1
The chemical and physical properties of slag

The main chemical composition of slag (wt.%)	SiO_2	33.87
	Al_2O_3	14.42
	Fe_2O_3	0.69
	CaO	39.54
	MgO	5.35
	SO_3	2.47
	Basicity coefficient	0.93
Physical properties	$K_b = (\text{CaO} + \text{MgO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$	
	Specific gravity	2.90
	Ignition loss (%)	0.28
	Fineness (m^2/kg)	383.00

Table 2
Sodium silicate-based alkali activator mixes

Mix no.	Alkali modulus	Na_2O (g/l)	SiO_2 (g/l)	w/s
1	2.05	81	166	0.41
2	2.05	76	154	0.42
3	2.05	65	133	0.43
4	2.05	64	132	0.43
5	2.05	60	123	0.44
6	2.05	52	106	0.45
7	1.63	81	132	0.42
8	1.63	76	123	0.43
9	1.63	65	106	0.45
10	1.23	100	123	0.41
11	1.22	123	150	0.38
12	1.01	131	132	0.39
13	1.01	122	123	0.40
14	1.01	105	106	0.42
15	1.01	81	82	0.45
16	1.01	76	77	0.45
17	1.01	65	66	0.46
18	0.99	123	122	0.40
19	0.82	150	123	0.38
20	0.81	123	100	0.41
21	0.62	123	76	0.42
22	0.49	123	60	0.43

slag is 1.75. Sodium silicate has a chemical composition of $\%\text{SiO}_2 = 37.0$ and $\%\text{Na}_2\text{O} = 17.7$ and the mole ratio is 2.09.

2.2. Design of variables

2.2.1. Stage 1: activator

The alkali activator studied is a sodium silicate-based activator. This means that the activator contains sodium silicate and sodium hydroxide. Different mixes of sodium silicate-based activators were examined and are tabulated in Table 2. In a previous study [22], the AM, which is defined as $\text{AM} = [(\text{SiO}_2)/(\text{Na}_2\text{O})]$, was used for activator preparation. One direction for preparing the activator is to have different activators at different mix amounts for SiO_2 and Na_2O but with the same AM. In Table 2, Mixes 1–6 all have an AM equal to 2.05, Mixes 7–9 have an AM equal to 1.63 and so on. Another direction is to prepare activators by fixing the concentration of one part, for example, SiO_2 , and then changing the concentration of the other part (Na_2O correspondingly). The fix concentration for SiO_2 or Na_2O is 123 g/l. The liquid/slag ratio was kept at a value of 0.54 for all mixes. Since the liquid/slag ratio is constant, the water/slag (w/s) ratio varies as shown in Table 2.

2.2.2. Stage 2: retarder

In this stage, the retarder concentration added in the activator is a major concern. For this reason, we fixed the activator with $\text{Na}_2\text{O} = 122 \text{ g/l}$ and $\text{SiO}_2 = 123 \text{ g/l}$. The liquid/slag ratio was kept at a value of 0.54. The retarder was added into the activator as a part of the activator. Phosphoric acid was chosen as the retarder. In a previous study [16], sodium phosphate was used as the retarder. The reason we adopted phosphoric acid instead of sodium phosphate is described as

follows. Once sodium phosphate is used, it will affect the Na_2O concentration. In order to keep Na_2O concentration in the activator–liquid constant, we used phosphoric acid as a retarder. Various concentrations of phosphoric acid (0, 0.78, 0.81, 0.84 and 0.87 M) were examined.

2.3. Experiments

2.3.1. Stage 1

The activator was prepared according to Table 2. After activator preparation, the pH value for the activator was then measured when the temperature of the activator lowered to 25 °C. The precision range of pH value using the electrode type pH meter was ± 0.1 . When the activator and slag were mixed together using a mixer, the initial and final setting times were both measured using the Vicat test according to ASTM C191. For each group, experiments were performed eight times and an average value was taken.

2.3.2. Stage 2

The activator is composed of $\text{Na}_2\text{O} = 122$ g/l and $\text{SiO}_2 = 123$ g/l. Phosphoric acid of designated concentrations was then added into the activator. The liquid/slag ratio was kept at a value of 0.54. Initial and final setting times were measured using the Vicat test according to ASTM C191.

3. Results and discussions

Fig. 1 shows that the AM has a significant relationship with the pH value of the activator. From this figure, it can be concluded that increasing the AM means a decrease in activator pH value. If the AM is the same or very close, the activators show a similar pH value. In our experiments, two groups had pH values higher than 14. The maximum pH value is 14.07. It is well known that the pH value cannot exceed 14 theoretically. Considering the precision of the

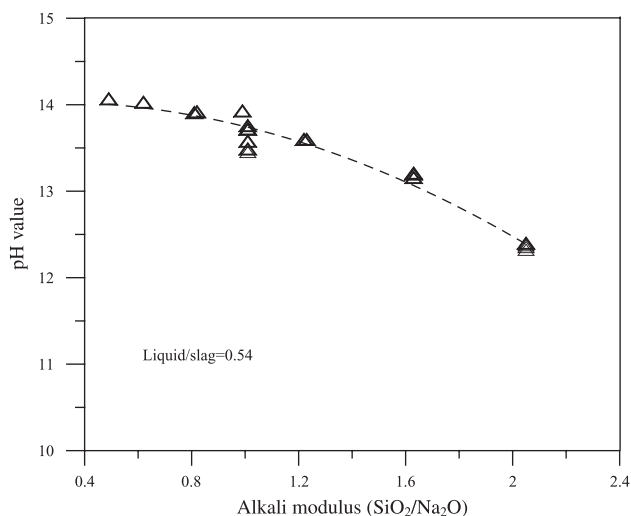


Fig. 1. Relationship between the AM and pH value.

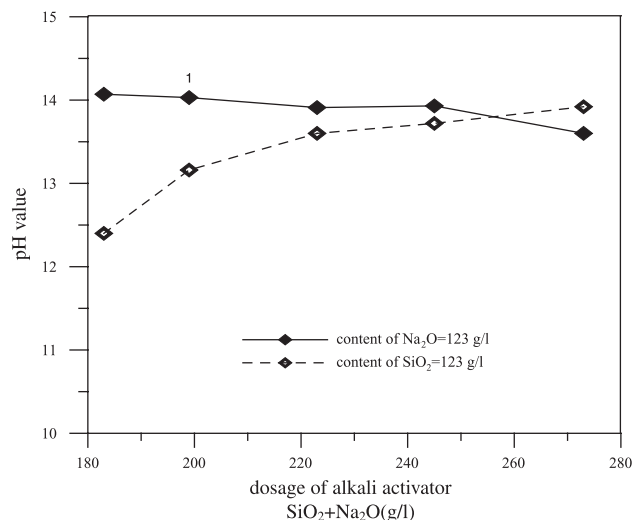


Fig. 2. Influence of Na_2O and SiO_2 concentrations on the pH value of the activator.

apparatus we used, the measured pH value could possibly exceed the theoretical limit.

Because we can have the same AM by adjusting the amount of SiO_2 and Na_2O , we wondered how the SiO_2 or Na_2O concentration influences the pH value. In Fig. 2, we demonstrate two lines. The solid line with a solid prismatic symbol represents activators with an Na_2O concentration equal to 123 g/l and varying SiO_2 concentrations. The dotted line with a hollow prismatic symbol represents activators with an SiO_2 concentration equal to 123 g/l and varying Na_2O concentrations. The total alkali activator dosage, defined as the sum of the SiO_2 and Na_2O concentrations, is used as the horizontal axis in this figure. For example, let us take a look at the point with the label '1' in this figure. The concentration of Na_2O is kept at a value of 123 g/l on this solid line. The dosage of alkali activator in this mix is 199 g/l, the SiO_2 concentration can be calculated as 76 g/l. When the Na_2O (or SiO_2) concentration is a constant, higher value of alkali activator dosage means a higher value of SiO_2 (or Na_2O) concentration. From the definition of the AM, it can be said that when the Na_2O concentration is a constant, a higher alkali activator dosage means a higher AM. Conversely, when the SiO_2 concentration is a constant, a higher alkali activator dosage means a lower AM.

Two things can be learned from this figure. When the Na_2O concentration is a constant, increasing the SiO_2 concentration decreases the activator pH value. In addition, when the SiO_2 concentration is a constant, increasing the Na_2O concentration increases the activator pH value. This makes sense since more SiO_2 means more SiO_3^{2-} that helps the resolution of H^+ ions in solution. Conversely, more Na_2O means more Na^+ that helps the resolution of OH^- ions in solution. The second thing we can learn from this figure is that when the total dosage of the alkali activator is the same we will have different pH values. It

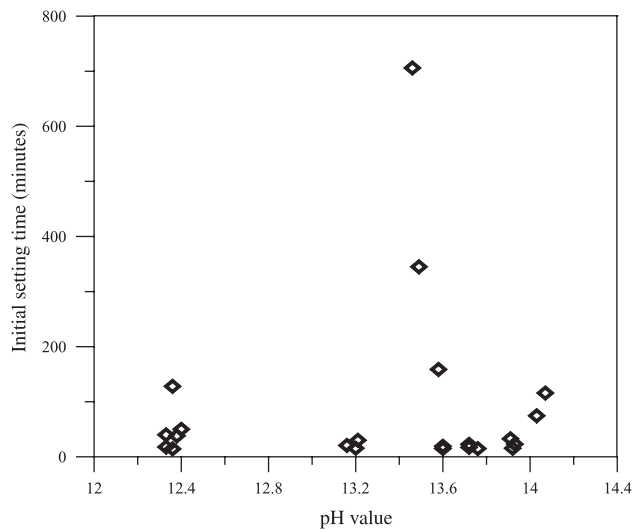


Fig. 3. No definite relationship between pH values and initial setting times.

means that the dosage of the alkali activator has no relation with the pH value (as well as the AM).

It has been reported [20] that when the pH value is higher, the activator shows better slag hydration capacity activation. From Figs. 3 and 4, we can see that there is no definite relationship between the pH value and the initial setting time (or final setting time). From Fig. 1, we have already mentioned that the pH value and the AM had a definite relationship. It can then be concluded from these evidences that there should not exist any definite relationship between the AM and setting times (initial and final) consequently.

We used a parameter, alkali activator dosage, which is the sum of the SiO_2 and Na_2O concentrations, to see whether it has a definite relationship with the setting times. From Figs. 5 and 6, there exists a trend between the alkali activator

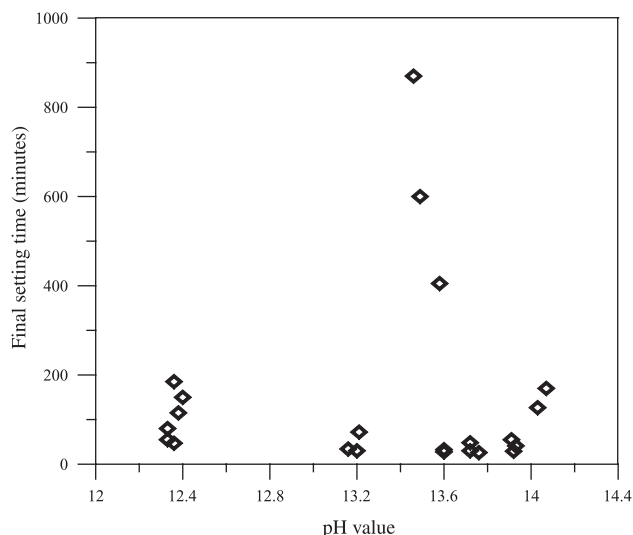


Fig. 4. No definite relationship between pH values and final setting times.

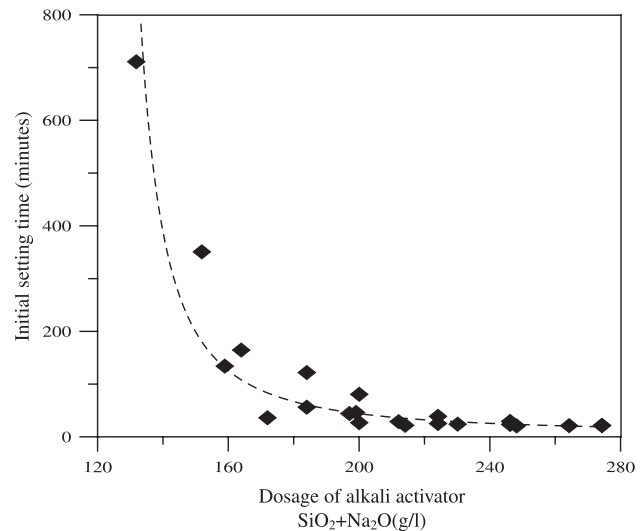


Fig. 5. A trend exists between the initial setting time and sodium silicate-based alkali activator dosage.

dosage and setting times (initial and final). When the alkali activator dosage is higher, the setting time becomes faster.

In a previous study [20], it was shown that during the hydration of AAS using a sodium silicate-based activator, five stages similar to that of OPC including initial, induction, acceleration, deceleration and decay could be found in the hydration process but the mechanisms were different. Shi and Day [23–25] have also found that due to the variation of activator, the hydration of alkali–slag cements can be described by three models, namely: Type I—one initial peak occurs during the first few minutes and no more peaks appear thereafter; Type II—one initial peak appears before the induction period and one accelerated hydration peak appears after the induction period; Type III—two peaks (one initial and one addition initial) appear before

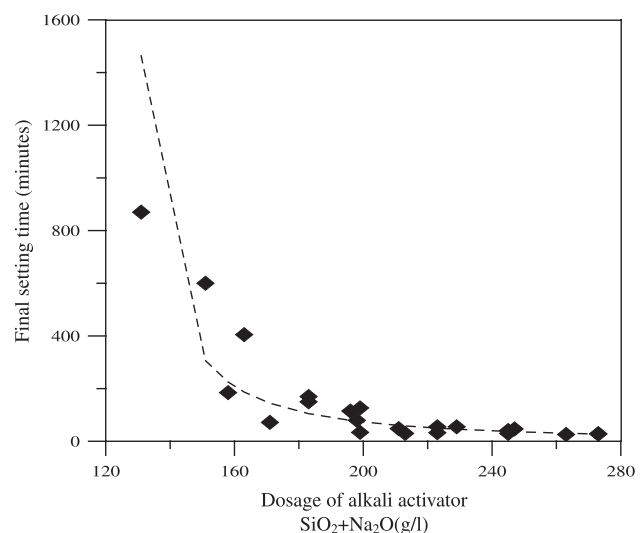


Fig. 6. A trend exists between the final setting time and sodium silicate-based alkali activator dosage.

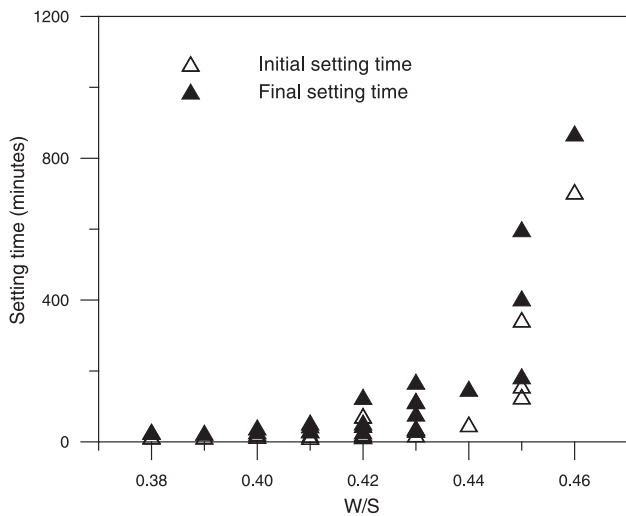
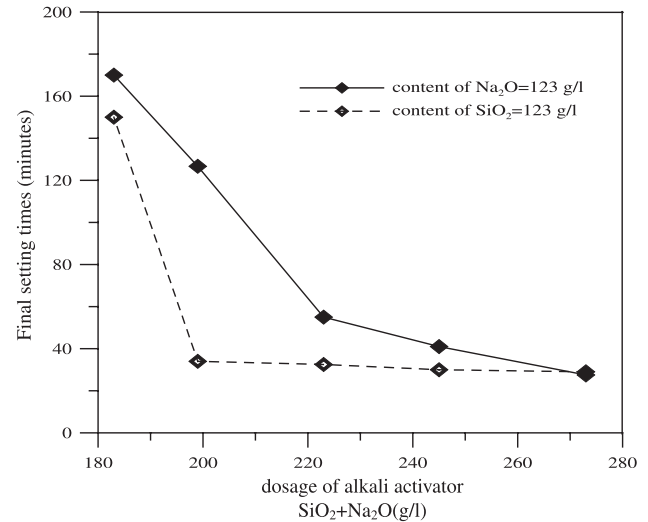


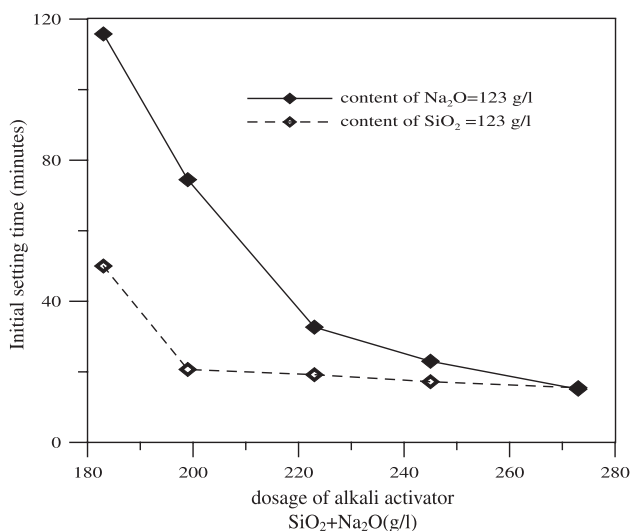
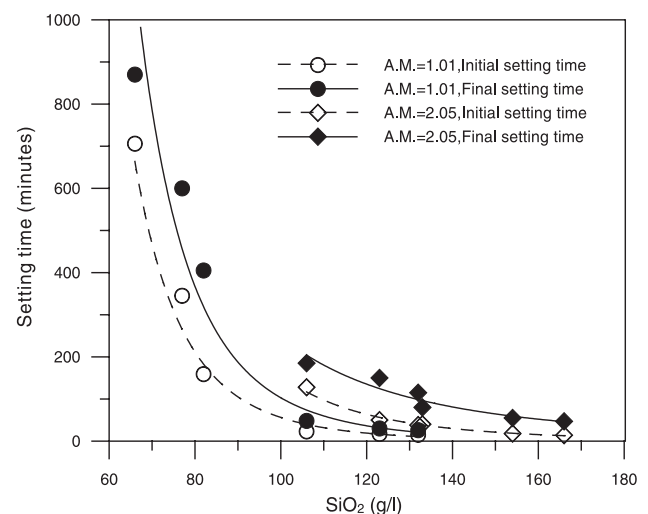
Fig. 7. Influence of w/s ratio on the setting times.

induction period and one accelerated hydration peak appears after the induction period. In Ref. [26], it was mentioned that the slag hydration process must be considered with regard to the oxygen forms present in slag, double-fixed in the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bond, single fixed in $\equiv\text{Si}-\text{O}-\text{Me}$ bonds and “free” in $-\text{Me}-\text{O}-\text{Me}-$ bond and the conditions of hydrate formation. The first destruction step under high concentration of OH^- can be described as the breaking of $\text{Me}-\text{O}$ ($\text{Me}=\text{Ca}$, or Mg), $\text{Si}-\text{O}-\text{Si}$, $\text{Al}-\text{O}-\text{Al}$ and $\text{Al}-\text{O}-\text{Si}$ of the slag grain. Since the $\text{Me}-\text{O}$ bonds are much weaker than $\text{Al}-\text{O}$ and $\text{Si}-\text{O}$ bonds, more Ca and Mg enter into water than Al and Si , and an Si/Al -enriched layer forms quickly on the surface of the slag [27,28]. The phase structure of the slag provides channels for OH^- ions to enter the bulk to complete the hydration process. Besides, the dispersed medium has a high concentration of $[\text{SiO}_4]^{4-}$ from water glass and the first step may correspond to the

Fig. 9. Influence of Na_2O and SiO_2 concentrations on the final setting time.

hydration and hardening of the water glass or the reaction between $[\text{SiO}_4]^{4-}$ and Ca^{2+} dissolved from the surface of slag grain. Usually, the first initial peak and the additional initial peak on the heat evolution diagram appear within 3–6 min immediately after addition of an activator [20,29] and the second peak following the induction period appears after 10 to 30 h depending on the activator and slag. It is well known that the first initial peak (and the additional initial peak) corresponds to the setting of AAS cement and the second peak corresponds to the strength development of AAS cement. Increasing the water glass dosage increases the released heat and shortens the peak time [29]. In Ref. [20], they reported that the silicate acid only affected the early hydration of AAS.

The alkaline dosage contains two parts: the content of SiO_2 (from water glass) and the content of Na_2O (from NaOH and water glass). Increasing the dosage may mean

Fig. 8. Influence of Na_2O and SiO_2 concentrations on the initial setting time.Fig. 10. The influence of SiO_2 concentration on the setting times of mixes with the same AM.

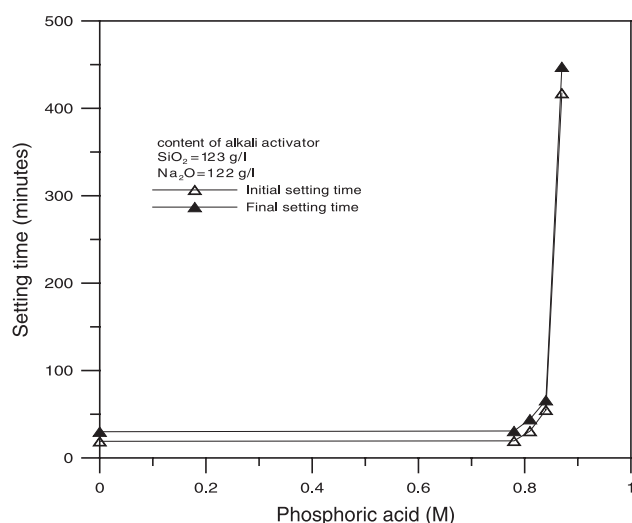


Fig. 11. Influences of the phosphoric acid concentration on retarding the setting times.

increasing either water glass or NaOH. From previous results [20,29], we can say that increasing water glass results in a higher concentration of $[\text{SiO}_4]^{4-}$ and consequently increasing the reaction rate (a higher concentration of reactants induces a higher reaction rate). On the other hand, a higher concentration of NaOH helps the resolution of Ca^{2+} from the slag grains and consequently increases the reaction rate as well based on the same reason mentioned previously.

In Fig. 7, it can be found that the setting times (both initial and final) decreased as the w/s ratio decreased. In our experiments, a fixed liquid/slag ratio is chosen and consequently the amount of water used should have a relationship with the alkaline activator dosage (sum of the concentration of SiO_2 and Na_2O). Remember that the alkaline activator contains NaOH, sodium silicate and water. It is not surprising that the setting times have a relationship with water when the liquid/slag ratio is a constant. The setting times for the mixes with a lower w/s ratio are closer as shown in this figure. It means the trend between setting times and total dosage (as well as the w/s ratio) is more apparent for high alkali dosage.

To study the respective effects of SiO_2 and Na_2O , we fixed the concentration of one and changed the concentration of the other to see how it affected the setting time as we did previously in Fig. 2. From Figs. 8 and 9, with the SiO_2 concentration fixed (123 g/l), increasing the Na_2O initially reduced the setting times (both initial and final). However, after the Na_2O concentration exceeded 76 g/l, the reduction effect became insignificant. With the Na_2O concentration fixed at 123 g/l, increasing the SiO_2 reduced the setting times. It once again confirmed that the concentration of water glass affected the early hydration of AAS [20]. Na_2O (correspondingly NaOH) only helps the resolution of Ca^{2+} from slag particles.

In Fig. 10, we further examine the setting times of mixes with the same AM. It can be found in this figure that under the same AM, increasing the SiO_2 concentration (more sodium silicate) decreases the setting times.

Fig. 11 illustrates the retarding effect of phosphoric acid. It can be found that increasing the phosphoric acid concentration retarded the setting time. After the phosphoric acid concentration exceeded 0.84 M, a dramatic increase in the setting time can be found. This implies that the setting time is very sensitive to the phosphoric acid concentration. For the group using 0.87 M phosphoric acid as a retarder, the initial setting time exceeded 6 h, which is too long in engineering practice. This result is consistent with those in Ref. [16].

4. Concluding remarks

In this study, the factors that influenced the setting times of the AAS binder using a sodium silicate-based activator were investigated. It was found that using a fixed value of liquid/slag ratio, neither the AM nor the pH value had a definite relationship with the initial and final setting times although a strong relationship existed between them. Increasing the Na_2O concentration increased the activator pH value, while increasing the SiO_2 concentration reduced the pH value. We found that, using a constant liquid/slag ratio, the alkali activator dosage influenced the setting times. Increasing the alkali activator dosage reduced the setting times, both initial and final. Phosphoric acid was found to significantly retard the setting time after reaching some critical concentration.

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