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Journal of Chemical and Pharmaceutical Research, 2014, 6(4):1180-1184

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Hydration process study on the alkali-activated slag cementing materials

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ABSTRACT

The hydration process of alkali-activator slag(AAS) cementing material was studied by ultrasonic, and AAS's hydration heat was test too by changing the environment temperature, activator modules. The results show that the hydration process of AAS can be divided into three stages: the initial phase hydrolysis, hydration acceleration period and stable phase. The hydration rate and hydration heat of the AAS materials will remarkably accelerate as the temperature raise. The appearing time of the peak value of the hydration exothermic curve of the alkali activated cementitious material delays as the activator module increases, and the peak value also gradually decreases.

Key words: Hydration process, alkali-activator slag, Modules, Environment temperature,

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INTRODUCTION

The hydration of AAS cementing materials means the chemical reaction after the combination of the levigated superfine slag powder and the alkali activated liquor. The earliest "alkali-activated" theory was put forward by Purdon, etc[1]. In his research on the cement hydration process, he finds that NaOH can make aluminosilicate easily dissolves into Na2SiO4 and NaAlO2, those products then react with CH (calcium hydroxide) and creates hydration calcium metasilicate and calcium chlorate, after the hardening of cement, it will again generates NaOH, in the whole process, NaOH acts as a catalysis to the hardening process of cement. The hydration process of AAS cement is known to differ significantly from that of the Portland cement by the rapid reaction during the early hours, causing the quick strength development as well. Ettringite is the dominant hydration product after three hours that gives the early strength[2].Amorphous $Al(OH)_3$ may also be formed, but could not be identified in the X-ray diffraction (XRD) pattern[3]. The hydration factors that affect slag cement which excited by alkali are varied and complicated[4-5]. The features of superfine slag powder itself, the variety and dosage of activator[6-8], the dosage of admixture[9], and the environmental temperature[10] all have huge influence on the hydration and heat release of alkali - inspire slag cementing materials.

In this study, the ultrasonic is used to test the hydration process of the AAS cementing materials, and the hydration process is analysised from chemical point of view. In addition effects of the environment temperature, activator modules to AAS hydration react heat is investigated.

EXPERIMENTAL SECTION

Materials

The oxide compositions of materials obtained by using the X-ray fluorescence (XRF) technique are listed in Table 1. The slag is a water quenched slag with density of 3.051 g/cm^3. SEM images of the slag are shown in Fig.1 and its particle size distribution is plotted in Fig.3. The fig. 2 is the SEM image of the fly-ash. Three different solutions are prepared in the experiment, i.e. the water glass liquid, NaOH solution and de-ionized water. The coarse aggregates are crashed limestone gravel sizing between 5-35 mm.

Table 1. Oxide composition of materials (mass%)

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	L.O.I.
GGBS	30.39	11.64	0.42	42.27	8.46	0.59	0.42	1.47	2.05	1.26
Water glass	71.71	1.19	0.13	2.07	0.21	0.1	23.62	-	0.85	-
NaOH	0.1	0.064	-	-	-	-	99.8	-	-	-

The activator solution consists of water glass liquid, NaOH and water (extra water added to the solution). NaOH was added to change the n modulus (SiO_2 to Na_2O molar ratio) of the activator solution. $2NaOH \Rightarrow Na_2O + H_2O$. The chemical composition of solid sodium metasilicate is 71.71% Na_2O and 23.62% SiO_2. The molecular formula of commercially available industrial sodium silicate is $Na_2O \cdot nSiO_4$, sodium silicate modulus (Ms) is the ratio of fraction mole of silicon dioxide and the fraction mole of sodium oxide. According to modulus definition, the sodium silicate modulus can be adjusted through the introduction of sodium oxide. The following form is the calculated mode:

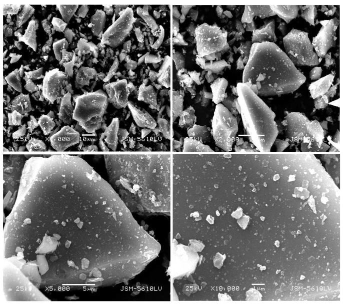

Fig. 1 SEM image of the slag

Alkaline activator modulus

Referring GB / T 4209-2008 "industrial sodium silicate" norms of China to test the sodium silicate modulus, and get the Na2O Mass Fraction is 24.12%, the SiO2 Mass Fraction is 73.08%, so the the sodium silicate modulus is 3.03（73.08%/ 24.12%). Solid content of the water glass liquid is 37.5%. The table 2 is the composition of the activator solution. The activator solution modulus is 1.5. Table 2 is the reconciliation sheet of alkali activator in different modules.

Table 2 Alkaline activator modulus adjusting table

Modules		1．0	1.3	1.5	1.7	1.9	2.5
Matching Wt%	Sodium silicate	100	100	100	100	100	100
	NaOH	24.1	15.9	12.3	9.5	7.3	2.9

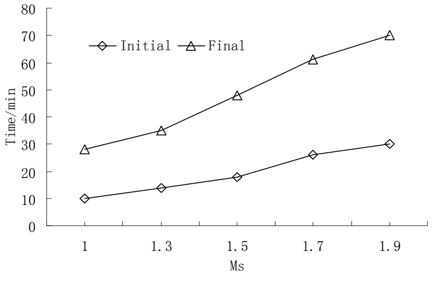

Fig. 2 The relationship between the alkalis activated modulus and setting time

A large amount of tests found that when the activator modulus is between 1.0 and 2.0, AAS cementing materials can be easily molded, mixing is easily conducted during the molding process, and the process has high mobility, and has higher strength in 1d. Figure 2 shows that when the modulus of the activator ranges from 1.0 to 2.0, as the module Ms increases, the sample's initial setting time and final setting time gradually increases. The sample whose module is 1.9 has the longest setting time. But its initial setting time and final setting time are very short. The initial setting time is 30 minutes, its final setting time is only 70 minutes.

Hydration heat

As to the above alkali activated cementing materials, in the mix proportion of static slurry, the activator modules are 1.0, 1.5, and 2.0, when doing the test of the process of the hydration exothermic changing test as the time changes, the test instrument of PTS-12S digital cement hydration heat measurement system, the test method refers to GB/T 12959-2008 The Determination Method of Cement Hydration Heat. Figure 3 shows the alkali activated cementitious material hydration exothermic curve under different modulus and same dosage of sodium silicate.

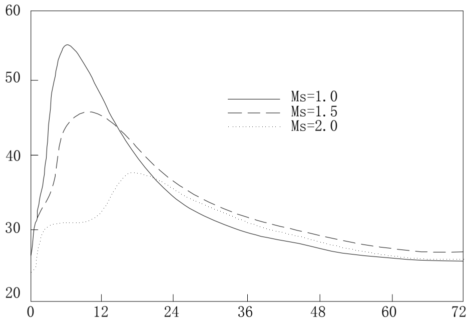

Fig.3 The alkali activated cementitious material hydration exothermic curve under different modulus

Fig. 3 shows that under the same conditions, the appearing time of the peak value of the hydration exothermic curve of the alkali activated cementitious material delays as the activator module increases, and the peak value also gradually decreases. It is mainly because as the activator module decreases, the initial basicity of the solution will increases, the content of NaOH also increases, according to the alkali-activated theory, the increase of NaOH in the solution will accelerate the early hydration of the alkali activated cementitious material, so under the condition of low module activator, the early hydration reaction is more fierce, the related peak value of hydration temperature will also be in advance.

Figure4 and figure 5 are the hydration heat release curves after the combination of 500mg slag and alkali-activator solution under the conditions of 20℃ and 40℃. From figure 4 and 5 , the hydration heat release curves of AAS cementing material and portland cement[9] are very similar. According to the piecewise form of hydration heat release curve of portland cement, the hydration heat release process of the AAS cementing materials can also be divided into 5 stages: (I) Quick reaction period OA (the early period of induction); (II) Induction period AB; (III) Acceleration period BC (late induction period); (IV) Deceleration period; (V) Stabilization period DE (diffusion control period). In the quick reaction period, when the environmental temperature is 20℃, the peak value of hydration heat release curve of cementing materials is 2.406mw, it appears at 0.663h, while the temperature is 40℃，the peak value of hydration heat release curve of cementing materials is 10.755mw，it appears at 0.173h. This shows that when the environmental temperature rises from 20℃ to 40℃, the peak value of hydration heat release curve of cementing materials dramatically increases. In the third period of acceleration, when the environmental temperature is 20℃, the peak value of hydration heat release curve of cementing materials is 0.686mw, it appears at 16.800h. While the temperature is 40℃, the peak value of hydration heat release curve of cementing materials is 4.304mw, appears at 3.402h. At 20℃, the average value of the total amount of hydration heat release of the alkali activated cementing materials is 161.287 J/g. Under the same condition, at 40℃, the average value of the total amount of hydration heat release of the alkali activated cementing materials is 301.915 J/g. Under the same condition, the heat release of inorganic cementing materials at 40℃ is 1.872 times of that at 20℃. By the above analysis data, under the same condition, as the temperature rises, the rate of hydration heat release of the alkali activated cementing materials accelerates, the total amount of hydration heat release increases.

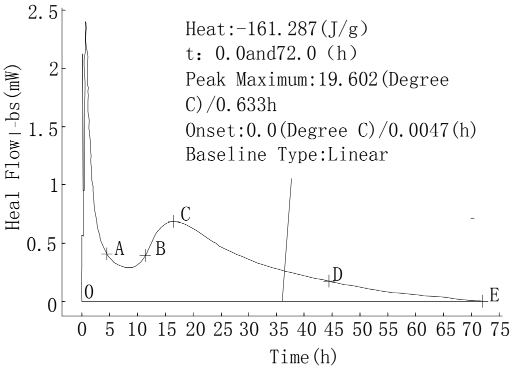

Fig. 4 20 ℃ hydration exothermic curve

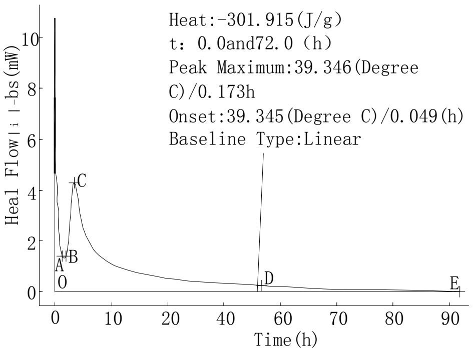

Fig.5 40 ℃ hydration exothermic curve

Hydration process

The hydration process test used Pundit lab Ultrasonic tester produced by PROCEQ Testing Instruments company in Switzerland. To undertake ultrasonic test. The testing apparatus are showed in fig. 6. Via testing the wave velocity change of alkali activated cementitious material and the test on ultrasonic, its hydration process can be reflected. During the testing process, in order to get the early hydration wave velocity of the slurry, the sample's molding process should be seriously controlled. After the mixing of the slurry, it should be quickly put into the ultrasonic testing mold and be vibrated tensely, then the two test probes of ultrasonic should be instantly aimed at both sides of the mold center, butter was used as the coupling agent between the probe and the mold, then fix the probe, open the instrument, and set the parameter. The data of the whole test was collected by computer, the interval settings of the data was collected once per minute. As regard to the laboratory conditions, the temperature should be controlled at 20±3□, the humidity should be controlled at 70±10%.

Fig. 7 is the cementing materials ultrasonic wave velocity changes with time diagram with 0.35 water solid ratio, 1.5 alkali excitation agent module. It can be seen that 30 minutes before testing, the ultrasonic wave velocity slowly increases, soon afterwards, the wave velocity mushroomed. As the hydration continues, around 100 minutes, the ultrasonic wave velocity obviously slowed down, then flattened out, and the hydration rate dramatically declined. The figure shows that the inflection point of Point A and Point B has roughly the same condensation time with alkali activated cementitious material. Via ultrasonic wave velocity changes with time diagram of fig. 7, the hydration process of alkali activated cementitious material system can be roughly divided into three stages: the initial phase hydrolysis, hydration acceleration period and stable phase. The first stage: the reactions happened in the initial phase hydrolysis are mainly that after the fuse of alkali activated cementitious material system (solid phase) and alkali-activator solution (liquid phase), sodium silicate gradually hydrolyzed, a large number of OH- was formed in the solid phase solution, at the same time, a large amount of Si(OH)4 was formed. As the reaction continued, $Si(OH)_4$ was resolved into active SiO_2. The whole process is a heat releasing reaction, it produced mass hydration heat, but during the whole process, the solid phase almost did not take part in the hydration reaction, this is the main reason why early ultrasonic wave velocity is not high. Second stage: hydration acceleration period. Hydration heat produced in the first stage make the Si-O, Al-O and Ca-O in the surface of the solid phase easier to crack with the polarization of OH-, the solid and stable net structure in the surface of the solid phase was destroyed. OH- was carried into the inner part of the phase. Amount of Ca^{2+} formed in the pore of the solid phase, these positive ion reacted with active SiO_2 dissolved and produced in the first stage and produce a large amount of C-S-H gelatin, this gelatin connects the solid phase particles which are hydrated and not hydrated. As a result, the whole system is well connected. When the connection reached a certain degree, the system transformed from plastomer to elastomer. The whole process happened around 30 minute to 100 minute during the hydration. The third stage: the C-S-H gelatin product was formed in the second stage, as the reaction continued, the gelatin gradually incased the solid phase surface, and it became thicker and thicker. As the exist of the incased layer, the liquor phase and the solid phase were isolated. The solid phase particle could not continue to get OH-, so a polarization reaction would not occur. As a result, the solid phase connectivity could not continue to increase. Thus, at this moment, the ultrasonic wave velocity became slower because it could not increase any more.

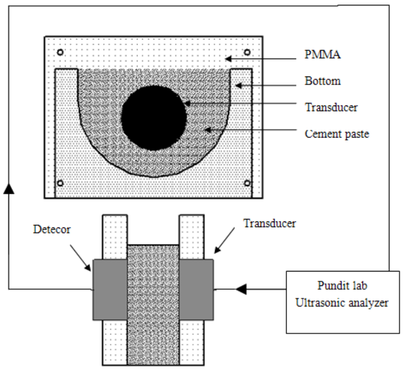

Fig. 12 Ultrasonic automatic acquisition instrument

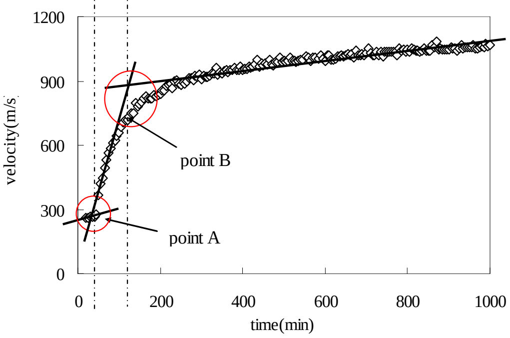

Fig. 13 ultrasonic wave velocity changes with time diagram

RESULTS AND DISCUSSION

AAS cementing materials can be easily molded and mixing is easily conducted when the activator modulus is between 1.0 and 2.0. The AAS cementing materials' initial setting time and final setting time gradually increases with the the modulus of the activator increased from 1.0 to 2.0. The temperature can remarkably effect the hydration heat and the production of the AAS cementing hydration is the main reason why the Velocity change during test.

CONCLUSION

The AAS cementing materials’ initial setting time increased by improving the activator modulus. Increasing the external temperature can remarkably increased the hydration of AAS cementing materials. The hydration process of AAS can bee divided into three stages: the initial phase hydrolysis, hydration acceleration period and stable phase.

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