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A study on the hydration properties of high performance slag concrete analyzed by SRA

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Abstract

The synchrotron radiation accelerator (SRA) was used to analyze the hydration properties of high performance slag concrete in this study. The results show that, as the water to binder ratio increases, the speed of hydration of alite and C_3A increase, as do the formation rates of CH and ettringite (AFt). Also, if the content of slag produces pozzolanic reaction, then the formation rate of CH will decrease, especially when the age increases. In short, the structures of CH, AFt and AFm can be analyzed both qualitatively and quantitatively by SRA.

Keywords: Synchrotron radiation; High performance concrete; Pozzolanic reaction; Water to binder ratio

1. Introduction

In 1947, it was observed for the first time that, with an electron synchrotron, the electron, running on the circular track with a speed approximate to the velocity of light, radiates an electromagnetic wave along the tangent line of the track, as a result of the centripetal force. It is the so-called "synchrotron radiation accelerator" (SRA) [1,2]. In 1980s, the nuclear magnetic resonance (NMR) system was employed to explore cement mortar and concrete. It was such a terribly troublesome matter because the hydration stopped when forming the specimens, and these specimens required vacuum-drying and then grinding in the bowl into tiny particles until they could pass through the sieve #325 [3]. The usage of SRA on the properties of the cement mortar and concrete was not applied until 1990s. Because of the high stability and the high intensity of the illuminant that SRA can provide, as well as the electrons in the storage ring that can retain their properties over the long-term, it is the most appropriate method for research on the crystallization and the amorphous [4]. In Taiwan, through the investigation of "A Study on The Hydration Behavior of Fly Ash Cement Paste" studied by C.L. Hwang and P.K. Chang in 1995, the application of SRA was first initiated in the field of cement research [5]. Taiwan, a country located on an island, is extremely short of natural resources. The over-exploitation of the stone and sand has caused awful damage to the entire ecology, and the problems of environmental protection seriously come into being. Slag, a by-product generated when China Steel (CS) refining steel, is abundant and, therefore, the reuse of these resources demands immediate attention. In 1990s, the research and development of high performance concrete (HPC) were aimed at improving the flaws of traditional concrete. By lowering the W/B ratio, improving the densified mixture proportion, applying SP and adding the pozzolanic material, it is certain to gain the superior properties of high strength, workability, durability, waterproofing, wear resistance, low shrinkage and creeping [6–11]. As for Taiwan, it is undoubtedly essential to apply the HPC, since the total amount of concrete used can be decreased, due to the high intensity and endurance of HPC, following the decrease of exploiting sandstone and gravel to reserve the completeness of the ecology. Furthermore, by way of adding the by-product slag to produce pozzolanic reaction, it not only improves the properties of the concrete, but also reduces CS pressure on disposing of the slag by fully reusing the resources. The most extraordinary characteristic of SRA is that it removes such inconvenient

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procedures like valuating, drying and grinding of the specimens. It is also unnecessary to end the hydration. This way, the growth and the transformation of the crystals can be clearly handled and the process of hydration is wholly monitored [11]. Under observation by SRA, the formation of CH is further evident and the formation of C–S–H gel can be also proved after the addition of the slag produces the pozzolanic reaction. Moreover, with the survey of SRA, the interaction between AFm and AFt will be thoroughly studied, along with their causes and amounts produced. Consequently, applying SRA to the analyses of the hydration properties of the concrete will be put in use much more widely [12].

2. Test program

The test materials employed in this study are as follows:

(1) Type I cement, produced by Taiwan Cement.
(2) Slag, produced by CS.
(3) Superplasticizer, Type G.

The physical and chemical properties are shown in Table 1, and the mixture proportion of cements in Table 2, having the water to binder (W/B) ratios of 0.28, 0.32 and 0.40, and the ages of 7, 28 and 56 days. Taking 200 g of high performance slag concrete pastes, with different W/B ratios, the observation of SRA proceeds in order. The pastes are carefully moved into the transparent test sheet plastic, and then the opening is sealed with 3M's invisible tape. After all the procedures are arranged, the specimens are placed under the SRA light source to be observed. The synchrotron radiation is projected from the electric storage ring, through the guidance of various optical elements and finally into the experimental station. Using the wavelength λ and the spacing *d*-spacing, The Bragg Angle, also called the diffraction angle, can be determined. Then, the spectrogram is obtained as the *x*-axis is based on the fixed crystals angle θ of the hydration products or the parallel space *d*-spacing and the *y*-axis based on the radiation strength. The integration of the area under the curve of different time leads to the values of the radiation strength. These values represent the sizes of the hydration products under different parameters such as the ages and the W/B ratios. This data is gathered and calculated by computers and the specimens are detected under natural conditions. Thus, the results are quite reliable and their precision is relatively enhanced. According to these analyses, the degree of hydration of the cement pastes can be determined. By way of the wavelength provided by the SRA, a light source can be tuned with a broad range, distinct substances; with their specific physical and chemical properties, they will get different reactions to various wavelengths. Therefore, this unique light source applied to the basic scientific research and the material science will absolutely benefit the quality of human life very much.

Table 1
Properties of cement and slag

Test program			Cement (Type I)		Slag
			CNS61	TC	CS
Chemical properties (%)	SiO_2 (S)		–	22.01	34.86
	Al_2O_3		–	5.57	13.52
	Fe_2O_3 (F)		–	3.44	0.25
	S + A + F		–	31.02	48.63
	CaO		–	62.8	41.77
	MgO		Max: 6.0	2.59	7.18
	SO_3		Max: 3.0	2.08	1.74
	f-CaO		–	1.05	–
	TiO_2		–	0.52	–
	Na_2O		–	0.40	–
	K_2O		–	0.78	–
	V_2O_5		–	0.05	–
	Ignition loss		Max: 3.0	0.51	0.31
	Insoluble residue		Max: 0.75	0.08	–
	Potential clinker	C_3S	–	40.10	–
		C_2S	–	32.08	–
		C_3A	–	8.90	–
		C4AF	–	10.50	–
Physical properties	Fineness		Min: 2800	2970	4350
	Specific gravity		–	3.15	2.88
	Initial setting (min:s)		45	04:37 (w/c = 0.47)	–
	Final setting (min:s)		06:15	08:22	–

Table 2
The mixture proportion of HPC

Mixture proportion	1	2	3	4	5	6
W/B	0.28	0.32	0.40	0.28	0.32	0.40
Slag	0	0	0	15%	15%	15%

3. Test results and discussion

This study is about the hydration behavior of the high performance slag concrete pastes. Such crystals, as CH, Alite, C_3A, AFt and AFm, have different strengths of absorbing synchronic radiation and different lattice spacing, d*hkl*. According to the specific lattice spacing belonging to

Table 3
The radiation strength of alite of various HPC pastes, which vary in W/B ratio, the growing age and the contents of slag (counts/s)

Age (days)	W/B					
	0.28	0.32	0.4	0.28	0.32	0.4
	Slag (%)					
	0	0	0	15	15	15
7	449	341	305	398	317	250
28	387	321	252	354	290	195
56	336	295	180	321	265	139

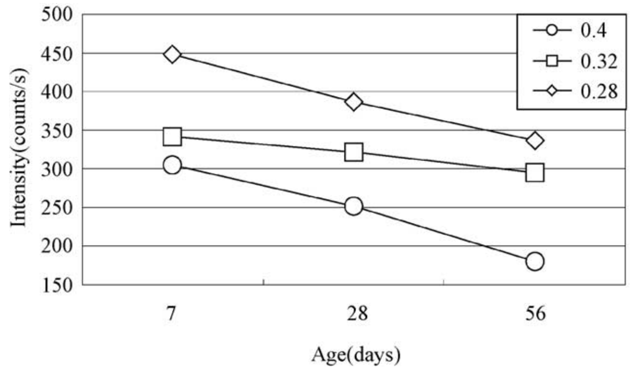

Fig. 1. The relationship between the radiation strength and the age of alite of the pastes, with different W/B ratios, containing no slag.

the individual hydration product, showing the relevant position and property on the synchrotron radiation spectrogram, the integration is calculated from the peak with the age moving on. Then, judging from the relationship between the age and the strength, the value of hydration products can be determined. But the value of the background interference should be eliminated first, in case the

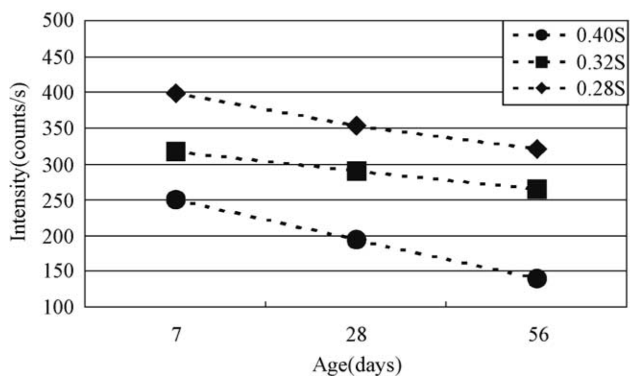

Fig. 2. The relationship between the radiation strength and the ages of alite of the pastes, with different W/B ratios, containing 15% slag.

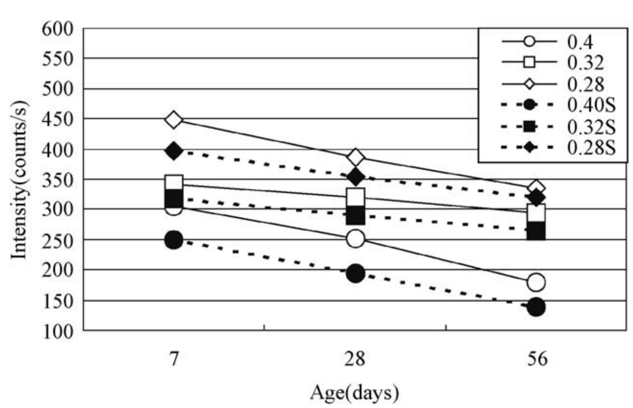

Fig. 3. The relationship between the radiation strength and the age of alite of the pastes, with different W/B ratios and different contents of slag.

Table 4
The radiation strength of CH various HPC pastes, which vary in the W/B ratio, the growing and the contents of slag (counts/s)

Age (days)	W/B					
	0.28	0.32	0.4	0.28	0.32	0.4
	Slag (%)					
	0	0	0	15	15	15
7	8150	8540	8900	7850	8300	8700
28	8420	8810	9325	7590	8050	8400
56	8705	9220	9600	7195	7700	7900

spectrogram is disturbed by the noise, causing the actual yield of the hydration products to become unpredictable. Thus, the ideal statistics can be gathered to help analyzing. The test results are as follows.

(1) When alite (C_3S containing mineral Impurities) meets the water, immediately there is violent hydration produced. The greater the water and the calcium content of the alite are, the faster the reaction proceeds. The alite contents of the cements vary with the degree of hydration. The degree of hydration will increase if the initial moisture contents and the age increase as well. Shown as Table 3 and Figs. 1–3, the radiation strength of alite is decreasing inversely with the age. This results from the C_3A with impurities hydrating, forming the C–S–H and the $Ca(OH)_2$, cursing the curve of the alite content to decline. When the age increases, the content of alite commons correctly decreases, indicating that alite participates in the hydration reaction. And if the W/B ratio increases, that is, more water is consumed, the reacting value of alite will increase. By this property, the data of reasonable qualitative and quantitative strength, from pastes mixed up and produced at different time and with different mixture proportions, can be obtained. (2) CH, with a striped structure of no pores and well-formed crystal structure, is produced from the calcium silicate in the cement. If bleeding occurs in the concrete, the aggregate often piles up on the interface, and when loads are added to the concrete, the shear failure takes place easily along the interface of the crystals. When water permeates into the concrete, hydrolysis

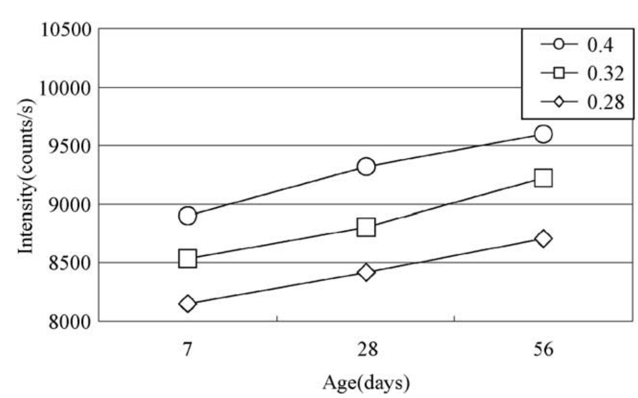

Fig. 4. The relationship between the radiation strength and the ages of CH of the pastes, with different W/B ratios, containing 0% slag.

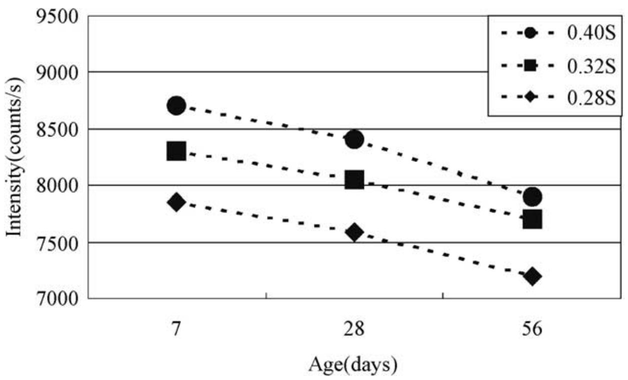

Fig. 5. The relationship between the radiation strength and the ages of CH of the pastes, with different W/B ratios, containing 15% slag.

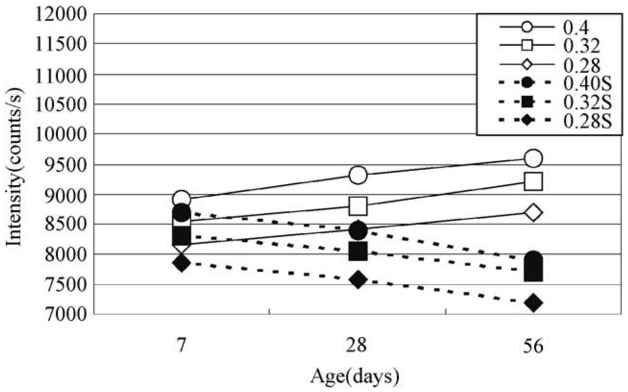

Fig. 6. The relationship between the radiation strength and the ages of CH of the pastes, with different W/B ratios and different contents of slag.

occurs easily and the efflorescence is then produced, thus harming on the durability. Table 4 and Fig. 4 indicate that, with the W/B ratio, the moisture content and the age increasing, there is more CH produced, and the trend shows that the radiation strength of CH weakens as the W/B ratio declines. Adding slag to the concrete, the main function aims at improving the quality of the concrete by reducing the CH content, resulting from pozzolanic reaction forming C–S–H and C–A–H with the hydration product CH of concrete. If the W/B ratio is the same, the one with slag added has lower radiation strength compared with that

Table 5
The radiation strength of C_3A of various HPC pastes, which vary in the W/B ratio, the growing age and contents of slag (counts/s)

Age (days)	W/B					
	0.28	0.32	0.4	0.28	0.32	0.4
	Slag (%)					
	0	0	0	15	15	15
7	66	57	45	53	48	39
28	59	49	38	42	37	30
56	50	40	33	35	32	26

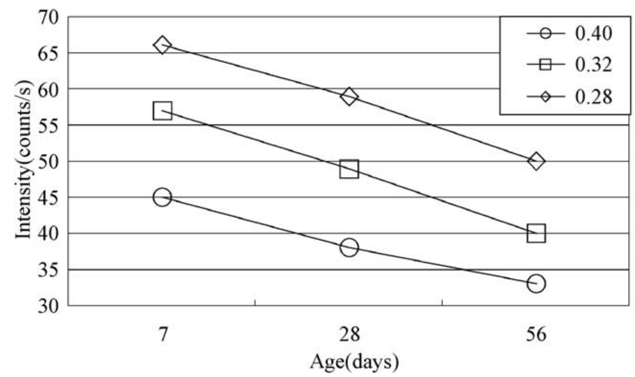

Fig. 7. The relationship between the radiation strength and the ages of C_3A of the pastes, with different W/B ratios, containing no slag.

without slag. That is, while aging the one with slag added gets fewer CH because of the pozzolanic reaction forming the C–S–H gel and the C–A–H. Table 4, Figs. 5 and 6 show that, as the age increases, the value of CH decreases and the pozzolanic reaction proceeds. This tendency is obvious. (3) Table 5 and Figs. 7–9 illustrate the transforma-

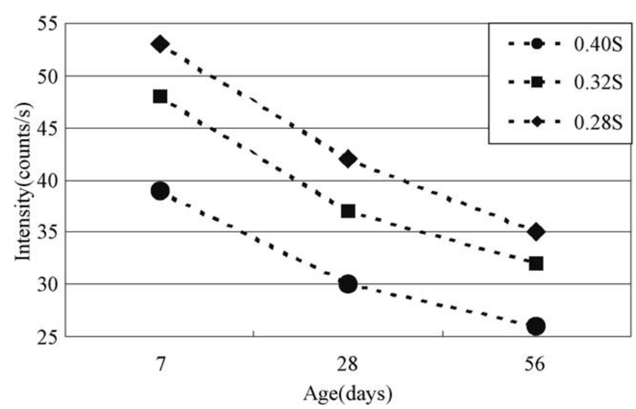

Fig. 8. The relationship between the radiation strength and the ages of C_3A of the pastes, with different W/B ratios, containing 15% slag.

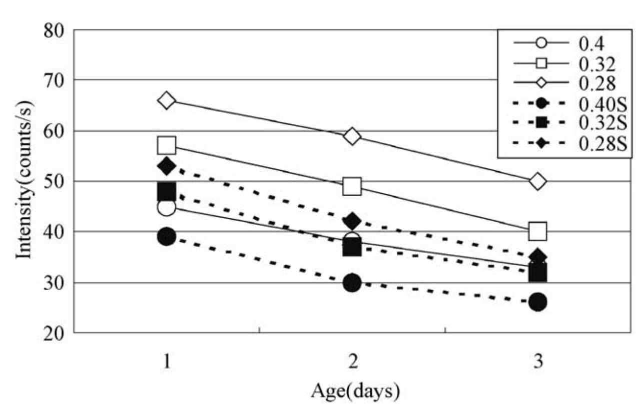

Fig. 9. The relationship between the radiation strength and the ages of C_3A of the pastes, with different W/B ratios and different contents of slag.

Table 6
The radiation strength of AFt of various HPC pastes, which vary in the W/B ratio, the growing age and the contents of slag (counts/s)

Age (days)	W/B					
	0.28	0.32	0.4	0.28	0.32	0.4
	Slag (%)					
	0	0	0	15	15	15
7	395	403	420	329	332	350
28	380	430	451	318	350	377
56	363	360	370	295	300	309

tion radiation strength of C_3A within the HPC pastes from the 7th to 56th days. The hydration rate of the aluminate is much greater than that of the silicate, and the hydration behavior of the aluminate is similar to the violent exothermic reaction right after throwing ordinary exothermic substances into water. Owing to the large storage of exothermic energy after C_3A is put into water, it will immediately hydrate and collapse, and then pieces of fragmental hydration products appear. Sometimes, it needs to add proper volume of gypsum CSH_2 to reduce the hydration rate. The hydration heat of C_3A equals 1350 J/g, two times higher than that of the C_3S. Its first heat peak appears with in 1 h in the reaction, and the second heat peak varies with the contents of gypsum, but basically speaking, the completion is made within 7 days. The diagrams above demonstrate that the hydration rate of C_3A increases commensurately with the moisture content, and that the radiation strength of C_3A declines considerably as the ages increase. These facts mean that during the early phase of the whole age the main hydration of C_3A is mostly complete, and so the early hydration behavior of C_3A is much more important that the latter one. In this aspect, the models of the hydration behavior are expected to be further studied. (4) The hydration products of AFt are produced mainly from the calcium aluminate of the cement. As the W/B ratio increases, with more moisture

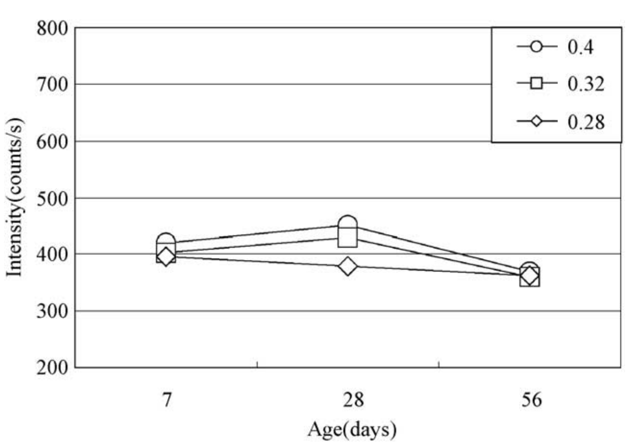

Fig. 10. The relationship between the radiation strength and the ages of AFt of the pastes, with different W/B ratios, containing 0% slag.

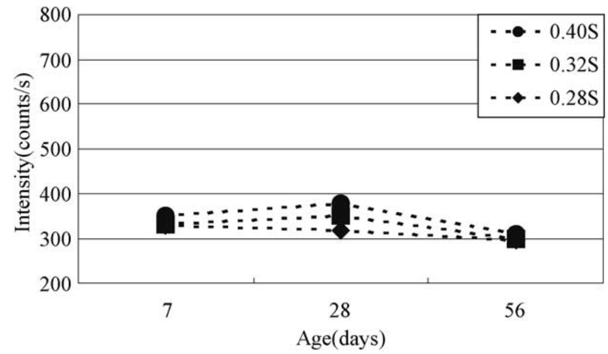

Fig. 11. The relationship between the radiation strength and the ages of AFt of the pastes, with different W/B ratios, containing 15% slag.

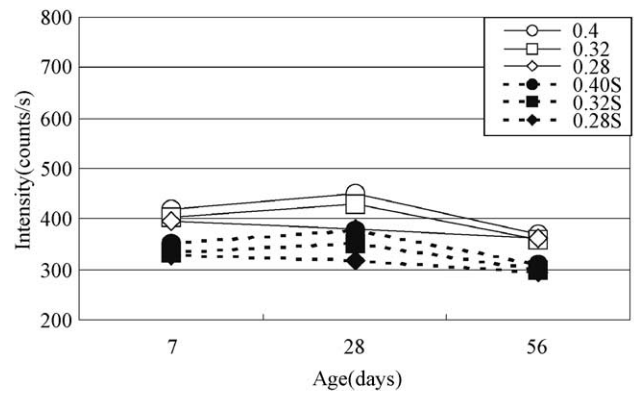

Fig. 12. The relationship between the radiation strength and the ages of AFt of the pastes, with different W/B ratios and different contents of slag.

content, the reaction rate of aluminate and the content of AFt will increase also. Table 6 and Figs. 10–12 indicate this tendency obviously. The hydration product AFt is mostly completed before the age of the 7th day and, hence, during the 7th to 60th days, there is no evidence of the addition of the radiation strength of AFt. The diagrams above can prove this inference. The AFt often causes the concrete to expand in volume, resulting in the producing of pores, and then the strength of the concrete is influenced. (5) In the reaction that C_3A absorbs and then the ettringite is formed, if the gypsum in the cement is deleted, the ettringite will come into the

Table 7
The radiation strength of AFm of various HPC pastes, which vary in the W/B ratio, the growing age and the contents of slag (counts/s)

Age (days)	W/B					
	0.28	0.32	0.4	0.28	0.32	0.4
	Slag (%)					
	0	0	0	15	15	15
7	15	23	32	10	20	28
28	22	27	37	18	25	36
56	29	35	49	25	33	45

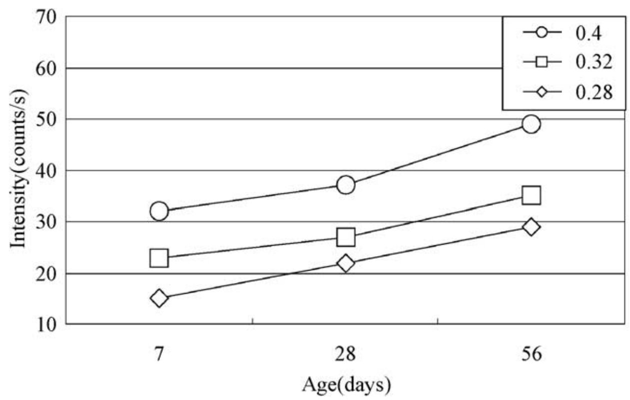

Fig. 13. The relationship between the radiation strength and the ages of AFm of the pastes, with different W/B ratios, containing slag.

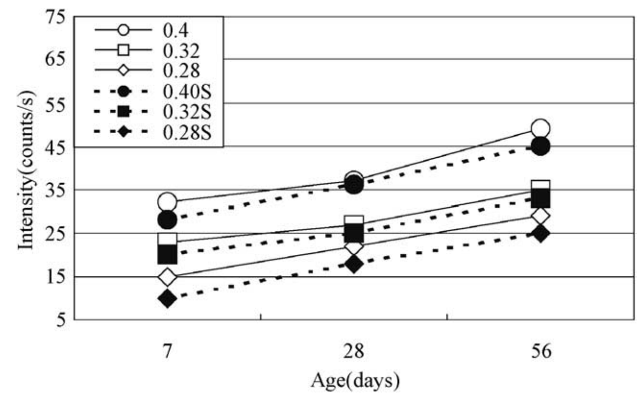

Fig. 15. The relationship between the radiation strength and the ages of AFm of the pastes, with different W/B ratios and different contents of slag.

second reaction with C_3A, forming the monosulfoaluminate (AFm). The reaction mentioned above is transformed continuously. Similarly, the C_4AF reacts in a familiar way. Observing Table 7 and Figs. 13–15, there is a low strength peak of AFm in the diagram. One can see from this that, while the ettringite with the C_3A has a reaction rate that is extremely high, the amount of C_3A remaining is low. And in the second-time reaction, it must compete for the free water with the other reactions. If there is a shortage of the quantities of C_3A and free water, the formation of AFm definitely will be influenced. With W/B = 0.32 and 0.28, that is, with more moisture content, the value of strength peak decreases with the age moving on. And if the W/B ratio increases and along with the supply of free water, the radiation strength of AFm will increase. When the concrete is placed in an environment containing sulfate, under the circumstance of moisture and water supplied, the action $Ca_2{}^{+}$ and the anion OH^{-}, freed from the calcium hydroxide through permeation, react with $SO_4{}^{2-}$ to form the gypsum. Such reaction is called the reaction of gypsum expansibility. The formation of the gypsum gives opportunities for the AFm in the concrete, with the agent water, to produce the expanded ettringite AFt, which possibly reduces the safety of the structure. From the ACI specifications, ACI 318-99 "the structural concrete," the prevention of this situation is made possible by adding pozzolanic materials and lowering the W/B ratios.

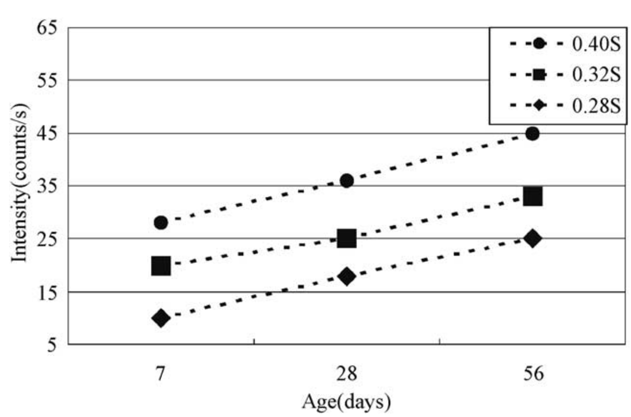

Fig. 14. The relationship between the radiation strength and the ages of AFm of the pastes, with different W/B, containing 15% slag.

4. Conclusion and suggestion

4.1. Conclusion

(1) Alite decreases with the increase of the W/B ratio and the age. The hydration rate of C_3A is extremely high. As the age advances, the radiation strength of C_3A declines.

(2) The amount of CH increases proportionally to the W/B ratio and the age. Adding the slag to consume CH, the pozzolanic reaction proceeds obviously. AFt is mostly formed by the hydration before the age of the 7th day, and there is no obvious increase of the radiation strength from the 7th to 60th days.

(3) With the W/B ratio lowering, AFm appears a peak value of the low strength. This probably occurs for the following reason: while in the second- time reaction, it must compete against other reactions for the free water, and if the amount of the free water is low, the formation of AFm would necessarily be influenced.

4.2. Suggestion

(1) If other analytic techniques can be combined with SRA when studying the hydration property of the slag pastes, it might get even better effects.

(2) The influences on the hydration property, when adding pozzolanic materials with different proportion and type, are expected to be studied further in greater detail.

Acknowledgements

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