Asian Journal of Chemistry; Vol. 25, No. 10 (2013), 5689-5692

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.OH64

Experimental Study on Hydration Mechanism of Lime-Gypsum Fly Ash Cement Paste†

ZIFANG XU*, ZHENG YANG and YONGKANG TANG

School of Materials Science and Engineering, Anhui University of Science and Technology, Huainan, Anhui Province, P.R. China

*Corresponding author: Fax: +86 554 6668643; Tel: +86 554 6668649; E-mail: zhfxu@aust.edu.cn

AJC-13307

This work is based on the study of the fly ash lime gypsum cement paste setting time, the hydration heat and the compressive strength, by using differential scanning calorimeter-thermal gravimetry, scanning electron microscope and X-ray diffraction to separately analysis effects of different blending proportion fly ash on the hydration properties of cement paste. The results show that the hydrating capacity of early age is weak, but long term is-lasting, an increase of fly ash replacement causes a longer setting time of cement-based materials, a decrease of hydration heat; when fly ash replacement is 40 %, compressive strength decrease evident. The main hydration products of early age of fly ash lime gypsum is a large quantity of calcium silicate hydrate gel (C-S-H), without hydrate calcium silicate, smack ettringite and calcium hydroxide. The main hydration products fill with the pore space and mutual cross linking, efficiency improve the fly ash cement paste strengths.

Key Words: Lime gypsum, Fly ash cement, Hydration property, Activate.

INTRODUCTION

Using a variety of industrial residues to produce building materials to improve the performance of cement based materials, such as compressive strength, durability, *etc*. The key is how to improve the activity of residue, but for long time on the fly ash and how to effectively improve the fly ash activity, has been a hot topic in this filed. Fly ash for calcium handing can greatly improve the activity of fly ash, on the basis of ensuring the quality of cement based materials, to increase the fly ash in cement content, reduce costs, improve economic efficiency and reduce environmental pollution[1,2]. In order to make better use of fly ash, proven hydration properties of calcium fly ash cement paste firstly is necessary[3-5]. Although many studies had been made both at home and abroad, such as report of the studies on interface structure, pore structure of cement paste when blended with fly ash or other residue, but the research contents of hydration mechanism of high fly ash blending proportion raw materials by the stimulate of lime-gypsum has not seen the detail reports both in domestic and foreign literatures[6,7]. This article reports on the hydration mechanism of fly ash cement paste by the stimulate of lime-gypsum, using traditional study methods combined with phase analysis, scanning electron microscope, differential thermal analysis and the heat of formation measurement of hydration products. In order to find a better way that the industrial residues can play a better effect in the fields of building materials[8,9].

EXPERIMENTAL

The cement used in the experiment is 42.5 ordinary Portland cement produced by Huainan Mining Bureau cement plant, fly ash is original gray from Huainan Luohe power plant. The main chemical composition showed in Table-1.The small amount of activator lime-gypsum is local purchase, the granularity grinded can through 75 um square hole sieve (200 mesh sieve), the residue on sieve less than 10 %.

TABLE-1
CHEMICAL COMPOSITIONS OF CEMENT AND FLY ASH

Composition	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	SO_3	TiO_2
Cement	21.40	4.58	2.69	2.02	63.65	0.67	2.63	0.20
Fly ash	58.75	31.48	4.52	1.34	1.74	0.60	0.15	0.15

Replacement of cement by fly ash and comparison coal gangue is 0, 10, 20, 30, 40 and 45 %. Mixing amount of lime is 10 %, plaster for 5 % of the total. According to the method of GB/T 1346-2001 standard consistency water, setting time, stability test to determine the consistency water consumption and the setting time of lime-gypsum fly ash cement system. According to GB/T 12959-1991 determine the hydration heat of 28 d lime gypsum cement paste mixing with fly ash. The producing of the block according with standard mortar strength test block, standard curing for 24 h before demoulding, then determine the compressive strength after 20 ºC water conserva-

†Presented to the 6th China-Korea International Conference on Multi-functional Materials and Application, 22-24 November 2012, Daejeon, Korea

tion to the specified age. Take the center of the optimal sample, for DSC-TG (differential scanning calorimeter-thermal gravity) hydration heat formation mechanism analysis; SEM (scanning electron microscopy) scanning and analysis of phase composition using D/MAX type X-ray diffractometer.

RESULTS AND DISCUSSION

Influence of lime-gypsum to fly ash cement paste: Table-2 shows that the cement standard consistency water is reduced with the increase of fly ash, but when the content of fly ash increased to 40 %, the standard consistency water is no longer reduce or even a slight increase. This is because fly ash particles itself is beads with smooth surface. These smooth spherical particles in the cement paste have the function of lubricating and rolling, improve the liquidity of fly ash system and to reduce the water consumption. At the same time fly ash particles surface appear electric double layer structure because of adsorption, to strengthen the lubrication, playing a effect of water decreasing. On the other hand, fly ash particles are much smaller than the cement particles, when filled to the cement particles, not only reduce the porosity of the cement paste but also a corresponding reduction in the fill water. But fly ash particles are much smaller than the cement particles, moisture for wrapping fly ash particles will naturally be increased, when the fly ash content increased further, water required for fly ash particles is much higher than those released from the fly ash particles, expressed as increase in the standard consistency water. Setting time of cement is extending with the increase blend of fly ash. This is because equal amount of fly ash to replace the cement when product the paste so that the quantity of cement reducing, also relatively lower concentration of cement paste. It just effective water-cement ratio increasing is unfavorable to the cement hydration rate. The rate of generated gel moderated when hydration rate slows down, the rate of spatial network structure forming by cement-based system also slow down, expressed as the initial and final setting time of the cement extended. The concentration reduced rate of cement paste is greater when fly ash replacement is higher, hydration rate slows down, initial and final setting time also extended more.

TABLE-2
EFFECTS OF LIME GYPSUM FLY ASH CEMENT PASTES ON WATER DEMAND AND SETTING TIME

Sample number	Mixture ratio (%)		Water requirement for normal consistency (%)	Setting time (h)	
	Cement	Fly ash		Initial set	Final set
A0	100	0	25.3	2.7	3.2
A1	90	10	25.0	2.8	4.0
A2	80	20	25.1	3.0	3.9
A3	70	30	26.4	3.1	4.0
A4	60	40	26.8	3.8	5.0
A5	55	45	26.2	4.1	5.3

Determination of fly ash-lime-gypsum silicate product hydration heat: Fig. 1 showed that the hydration heat of fly ash samples is lower than the same age pure cement paste. On the one hand, the hydration rate of paste decreases when mixed with fly ash, the formation of hydration products will be affected and thus directly affect the compressive strength. But on the other hand it can improve the safety of the cement-based materials because of the low heat release and thermal expansion of fly ash when used in mass concrete. Comparative experiment found proportion of hydration heat reduction of fly ash less than that of gangue. The macroscopic properties of the intensity with fly ash is less than the gangue. It also been verified in the experimental mechanical properties. The decrease range of value of the heat hydration with residue content from 0 to 10 % is very large, Other sample changes in magnitude is not large, because changes in relative raw material composition of other samples is not so high, the decrease of heat hydration is of the active substances in fly ash need energy when to be aroused, which cause the secondary reaction, So that the heat hydration is less than pure cement slurry.

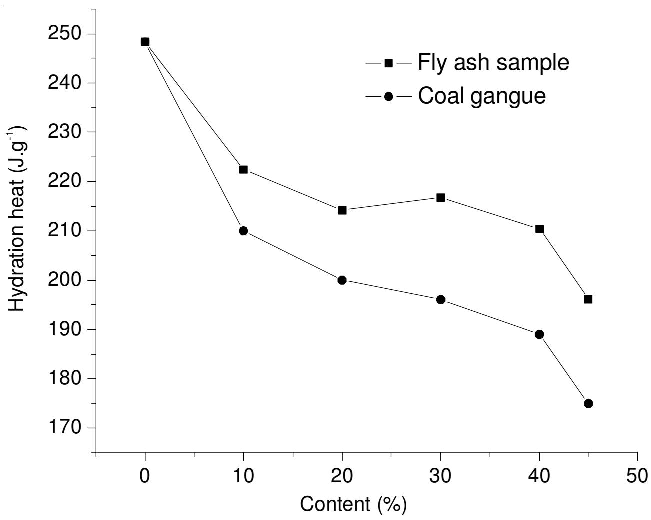


Fig. 1. Effects of fly ash admix rate at 28 days hydration heat of cement

Effects on mechanical properties of fly ash-lime-gypsum silicate products: The effects of fly ash to paste compressive strength of each age is shown in Fig. 2.The figure showed that with the stimulate of lime-gypsum the paste strength of early and late age all decreased when blended with fly ash, and also when have a low blending by 10 %, the 3 d and 7 d early compressive strength have a faster decreasing rate. Because when blended with fly ash, the proportion of effective cement mineral in early system decreased, the activity of lime gypsum did not play a role and fly ash early hydration activity is very low, play the only role of physical filling, so have small number of hydration products. The link between hydration product particles is not close enough, performance of low intensity. 28 d compressive strength decreasing rate significantly slowed down, because at this time the activity of fly ash is stimulated by lime-gypsum, so paste structure tends to be dense and adverse effects on the strength weakened. However when content of fly ash more than 40 %, the late strength dropped, therefore even there is activator, but fly ash contenting still can not be too high.

Analysis of hydration process heat mechanism of fly ash-lime-gypsum silicate products: Fig. 3 is the thermal formation mechanism curve of the forming process of hydration

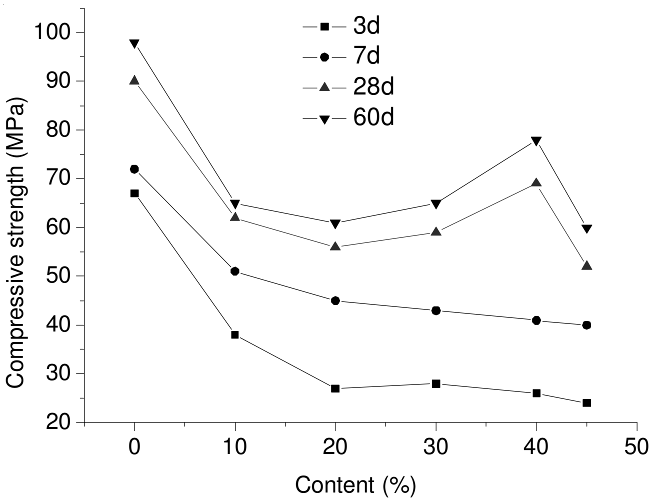


Fig. 2. Effects of fly ash replacement on compressive strengths of cement pastes

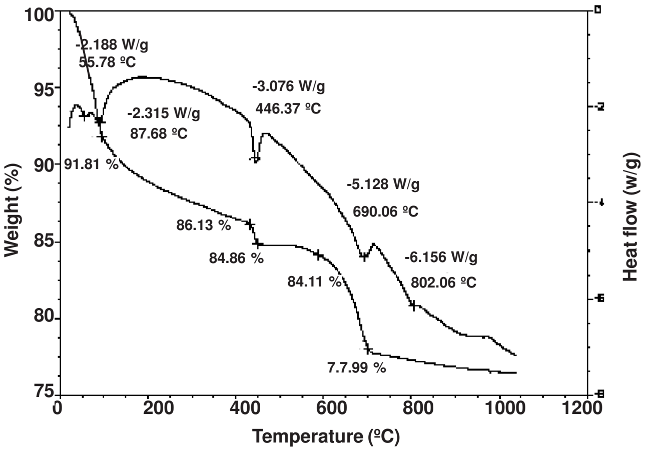


Fig. 3. DSC-TGA curves of 40 % fly ash sample at 7 days

products with 40 % fly ash age of 7d. Fig. 3 showed that the first endothermic peak is at 56 ºC and the rate of weight loss is 3.7 % mainly due to losing the free water and adsorbed water. The second endothermic peak is at 87 ºC, accompanied by weight loss and the rate of weight loss is 5 % mainly due to losing the free water, adsorbed water, as well as weak crystal water of some hydration products. Ettringite (AFt for short), whose range of dehydration temperature is relatively wide, loses crystal water when the temperature is from 50 to 150 ºC and has a fierce reaction of dehydration at 74 ºC. When the temperature reaches 113-144 ºC, AFt becomes the ettringite with eight waters quickly. The third endothermic peak which is deep and wide at about 446 ºC corresponding to the temperature range of 425-475 ºC, has a rate of weight loss about 1.25 %. There are a strong endothermic peak and weight loss at about 446 ºC, which is mainly due to the $Ca(OH)_2$ crystals that is hydration products losing the strong crystal water (hydroxyl ion). The fourth endothermic peak at about 690 ºC corresponding to the temperature range of 670-725 ºC, is wide and accompanied by weight loss with the rate of weight loss about 3.2 %. Strong endothermic reaction occurs at this stage, which is due to the lose of strong crystalline water, the occurrence of decomposition reactions and the crystal transformation. The main reactions are: (a). $CaCO_3$ decomposes to the lime of CaO and CO_2, which absorbs a lot of heat. $Ca(OH)_2$ in the sample carbonizes to $CaCO_3$ in the air; (b). Crystalline and semi-crystalline hydration products lose the strong crystal water, which also absorbs a lot of heat and occurs weight loss; (c). At about 700 ºC β-C_2S will be transformed to α-C_2S and strong endothermic reaction occurred; (d). The fifth endothermic peak appear near 802 ºC, section of the corresponding temperature is about 730-810 ºC, have a high heat absorption and accompanied by weight loss, weight loss rate is about 6.1 %, because lime, fly ash, and cement raw materials are likely to contain a small amount of non-decomposed $CaCO_3$. Therefore it absorb a lot of heat in this stage $CaCO_3$ decompose into quicklime CaO and release CO_2.

Composition analysis of phase in fly ash lime gypsum silicate hydration process: Fig. 4 is the 7d hydration product formation mechanism graph with the fly ash added 40 %. It shows that there are a variety of hydration products, such as ettringite Aft, calcium hydroxide CH, calcium silicate hydrate C-S-H, single sulfur hydration sulphoaluminate AFm, the hydration garnet C_3ASH_4 and tobermorite $Ca(Si_5O_{18}H_2)_4H_2O$; most are aluminates. As the hydration of C_3A is fastest, it is difficult to see C_3A in the graph, which proves its full hydration. However, the diffraction peak of aluminates (except for the AFt) are not strong, along with the main peak forms the secondary peak, AFt is likely to shift to a single sulfur sulphoaluminate AFm. With the increase of hydration age, the gypsum has been consumed continuously, and when lack of gypsum, the AFt will change to single sulfur hydration sulphoaluminate AFm. There are a large number of $Ca(OH)_2$, and SiO_2 peaks in the map which proves that the reaction of fly ash is less, and its activity is rarely stimulated. But there is a small amount of tobermorite $Ca(Si_5O_{18}H_2)_4H_2O$ form, which shows that the active mullite and vitreous of the fly ash partly react.

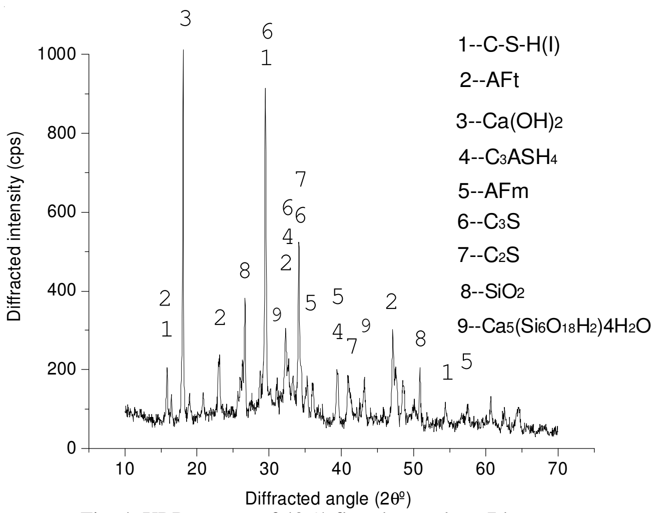
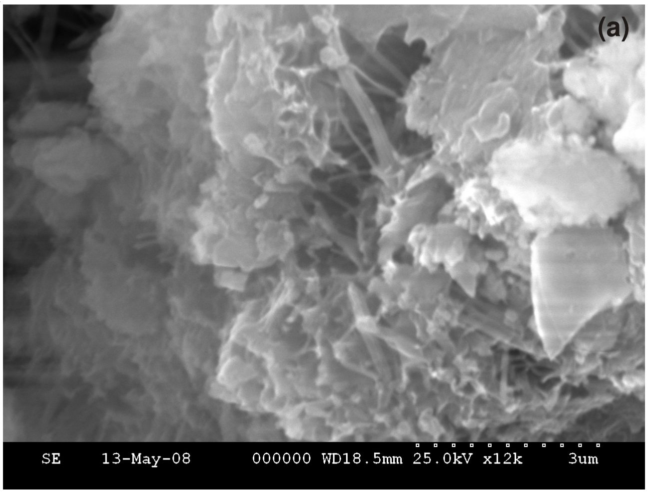


Fig. 4. XRD pattern of 40 % fly ash sample at 7days

Microscopic structure and morphology analysis of the fly ash lime gypsum silicate hydration products: Fig. 5 are respectively the hydration products SEM images of 3 days and 28 days sample of with 40 % fly ash. It show that the hydration products of C-S-H gel, $Ca(OH)_2$, AFt, AFm can be formed in the early hydration. But the porosity is high, crystal morphology is not yet fully developed. Such as the $Ca(OH)_2$ have not formed the six-party plate structure. The C-S-H gel are mainly the type II, the same size particles type II C-S-H is difficult to find. So the three days sample hydration is just shallow, the hydration products is poorly developed; sample of 40 % fly ash containing more ettringite AFt, because blank samples containing more cement relatively, more C-S-H gel is formed in the hydration. 40 % fly ash mixed sample can form ettringite AFt. 28 d hydration products are mainly the formation of fibrous particles and the particles of calcium silicate hydration C-S-H gel of the same size (type III),calcium ettringite AFt that is more than tens of micron in length, a large number of cubic, rectangular and hexagonal plate structure of $Ca(OH)_2$, flowers liking AFm. Hydration products is well developed relatively and intertwined, and also keep growing into the gap to form a compact overall structure, more ettringite are formed with the stimulation of gypsum and lime in the sample, later strength improved.



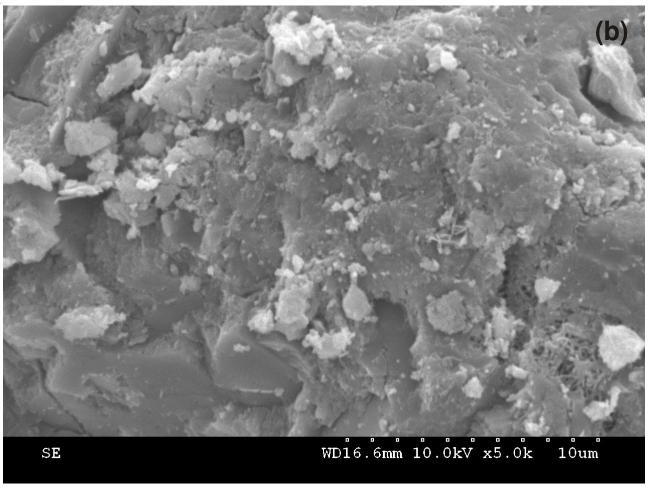


Fig. 5. SEM image of 3d (a) with 40 % fly ash sample and 28 d (b)

Conclusion

1) The setting time of cement-based sample delayed significantly with a increase content of fly ash when calcium increased.

2) Fly ash and coal gangue can not be highly contented in low-grade cement-based materials because of the weak performance of the early hydration even if activate the fly ash and gangue with a increasing amount of calcium.

3) Multiple endothermic peak are formed in the DSC-TG graph and endothermic obvious but also accompanied by weight loss, content of early free water and $CaCO_3$ are high, there are the formation of a high amount of $Ca(OH)_2$, C-H-S, the AFt and other hydration products in the late age, so that the fly ash cement have a weak performance of the early hydration but a higher performance of the late in the process of hydration when calcium increased.

4) XRD patterns and SEM shows that the early activity of gangue is better than that of fly ash, so we can take the advantage of the complementary nature of the gangue and fly ash activity to expand the field of waste utilization. The formation of C-S-H gel, $Ca(OH)_2$, AFt, AFm and other hydration product in the early hydration of fly ash cement-based materials, and with the interconnectivity and filling of six-party, cube shape, C-S-H of type I, C-S-H of type II, C-S-H of type III so that the strength of cement-based materials improved, the stimulation of lime and gypsum have a role in promoting in the formation of ettringite AFt in the early and the occurring of $Ca(OH)_2$ secondary reaction to form C-S-H gel, AFt, AFm and other hydration products in the late and the durability.

ACKNOWLEDGEMENTS

[Foundation supported]: Supported by "Educational Commission of Anhui Province of China "(KJ2012A078).

REFERENCES

1. F. Collins and J.G. Sanjayan, *Cem. Concr. Res.*, **30**, 1401 (2000).
2. A.A. MeloNeto, M.A. Cincotto and W. Repette, *Cem. Concr. Res.*, **38**, 565 (2008).
3. C.D. Atis, C. Bilim, O. Çelik and O. Karahan, *Constr. Build. Mater.*, **23**, 548 (2007).
4. D.J. Ming and W.P. Ming, *J. Build. Mater.*, **10**, 77 (2007).
5. H. Bao, X.Y. Jun and L.B. Ju, *Cement*, **12**, 4 (2003).
6. H.S. Guang and W. Xiao, *Cement*, **8**, 5 (2005).
7. G. Wei, L.D. Xu and C.J. Hua, *J. Chin. Ceram. Soc.*, **33**, 897 (2005).
8. K.J. Mun, W.K. Hyoung and C.W. Lee, *Const. Build. Mater.*, **21**, 1342 (2007).
9. H.W. Wan, Z.H. Shui and Z.S. Lin, *Cem. Concr. Res.*, **34**, 133 (2004).