

DOI 10.1007/s11595-015-1113-x

# Utilization of Lithium Slag as An Admixture in Blended Cements: Physico-mechanical and Hydration Characteristics

TAN Hongbo<sup>1</sup>, LI Xiangguo<sup>1\*</sup>, HE Chao<sup>1</sup>, MA Baoguo<sup>1</sup>, BAI Yun<sup>2</sup>, LUO Zhongtao<sup>3</sup>

(1. State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China; 2. Department of Civil, Environmental & Geomatic Engineering, University College London, London WC1E 6BT, the United Kingdom; 3. School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450052, China)

**Abstract:** Physical and mechanical properties variations of lithium slag were systematically investigated by three different ways such as physical, chemical activation, physical-chemical combined activation. Mechanisms of the cementitious properties and hydration process of lithium slag composite cement were studied by XRD and SEM. The results showed that specific surface area increased from 254 to 700 m<sup>2</sup>/kg while median particle size decreased from 14.97 to 8.45 μm with the increase of grinding time. Physical, chemical activation and combined activation improved the strength and hydration degree of lithium slag composite cement. Compared with original lithium slag, the flexural strength and compressive strength of mortars were improved significantly with the increase of grinding time. A higher strength of the cement with the lithium slag was attained; The sample with 10% lithium slag got the highest strength when the grinding time was 10 min; the compressive strength was higher than OPC at 28 days, which increased by 12.3%. When the Na<sub>2</sub>SO<sub>4</sub> content was 0.6%, the compressive strength increased by 1.4%; when the Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•18H<sub>2</sub>O content was 0.4%, the compressive strength increased by 5.8% at 28 days. Compared with the late strength, the improving degree of early strength was larger with the incorporation of activator. The results of XRD and SEM were consistent with the results of mechanical properties; it is also evident that lithium slag composite cement hydration products were mainly AFt, Ca(OH)<sub>2</sub>, CaSO<sub>4</sub>•2H<sub>2</sub>O, and C-S-H gel.

**Key words:** lithium slag; potential activity; grinding; sulfate activation; hydration

## 1 Introduction

Lithium slag is the by-product during the production of lithium carbonate based on sulfuric acid method after the spodumene ore has been calcined at the high temperature of 1 200 °C and the industrial waste discharged after leaching, filtration and washing of lithium carbonate. With the rapid development of lithium salt industry, the emission of lithium slags increases drastically. They take up a lot of land, causing huge environmental problems, but also a waste of resource. How to treat and reuse lithium slags safely

has become society and environment problem that needs to be urgently resolved.

Lithium slags are mainly composed of amorphous silica (usually more than 50%), alumina, and calcium oxide, which are quite similar to those of complementary cementitious materials such as granulated blast-furnace slag (GGBFS), pulverized coal fly ash (PFA)<sup>[1,2]</sup>. So they can be used as admixture instead of cement<sup>[3,4]</sup>, or used in the concrete industry<sup>[5-8]</sup>, which is indirectly beneficial for the environment because of the reduction of CO<sub>2</sub> emissions associated with the manufacture of Portland cement clinker. Various studies have investigated different ways to make use of this kind of slag. Li Chunhong<sup>[9]</sup> uses lithium slag in cement clinker, mixed materials, concrete, and got a good effect in his investigation. Zhang Lanfang<sup>[10]</sup> shows that lithium slag can replace a part of cement in concrete and improve the strength of concrete; applying lithium slag along replacing cement can make high-strength pumping delivered concrete whose compressive strength of 28 days is more than 100 MPa; it is very excellent in antifreezing

©Wuhan University of Technology and SpringerVerlag Berlin Heidelberg 2015

(Received: Oct. 19, 2013; Accepted: Sept. 12, 2014)

TAN Hongbo(谭洪波): E-mail: thbwhut@163.com

\*Corresponding author: LI Xiang-guo(李相国): Prof.; Ph D; E-mail: lxggroup@163.com

Funded partly by the National Natural Science Foundation of China (Nos. 51378408, 51408448) and State Key Laboratory of Silicate Materials for Architectures (Wuhan University of Technology) (No. SYSJJ2013-07)

**Table 1** Chemical compositions of OPC and lithium slag /wt/%

Item	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	So <sub>3</sub>	LOI <sup>a</sup>
OPC	24.08	4.72	2.46	58.24	0.27	1.02	1.95	2.31	3.82
Lithium slag	52.27	16.95	1.64	10.12	0.38	0.54	0.47	7.27	9.16

<sup>a</sup>LOI.: loss on ignition at 950-1 000 °C

performance if the concrete is mixed with lithium slag. Chen jianxiong<sup>[11]</sup> indicates that adding 15% lithium slag can obviously improve the fluidity and the compressive strength of concrete. However, the disadvantages of lithium slag such as coarse particles and low activity of the early age hinder the further use of lithium slag.

For weaknesses of the utilization of lithium slag, we used some activation methods such as physical grinding, chemical activation, physical-chemical combined activation to improve the potential activity and utilization efficiency of lithium slag. In addition, the hydration characteristics of the blended cements with a combination of lithium slag were also investigated by means of SEM and XRD. The results can provide the basis for the safe and recycling utilization of lithium slag.

## 2 Experimental

### 2.1 Materials

Lithium slag was obtained from Xinjiang Lithium Salt Plant, China; The cement used in this research was ordinary Portland cement (OPC), with grade of 42.5, supplied by the Huaxin Cement Co. Ltd. The chemical compositions of lithium slag and cement are shown in Table 1.

### 2.2 Preparation of specimens

The lithium slag composite cement samples were prepared according to the methods as indicated in Table 3.

### 2.3 Test methods

The strength test was performed according to Chinese standard GB/T17671-2001 (equivalent to ISO 679:1989) by using 40 mm × 40 mm × 160 mm prism molds. After the specimens were cured in the chamber at 20 ± 1 °C with relative humidity (R.H.) >90% for 20-24 h, they were demolded and cured again in 20±1 °C water for 3, 7 and 28 days, respectively.

Isothermal calorimetric measurements were carried out on a TA Instruments TAM Air Calorimeter at 20 °C.

The chemical compositions of each sample were analyzed on an AXIOS advanced wavelength

dispersive X-Ray fluorescence spectrometer (WDXRF) by the fused disk method. Mineralogical compositions and microstructure were detected by X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The pastes were well mixed, and then cured in the >90% R.H. chamber at 20±1 °C until designated ages. Part of the hardened pastes were taken, then cracked and ground in an agate mortar with anhydrous alcohol till the entire pastes passed through a 0.08 mm sieve. After that the pastes were dried at 50 °C for 24 h and then tested by XRD and SEM.

## 3 Results and discussion

### 3.1 Physical properties of lithium slag

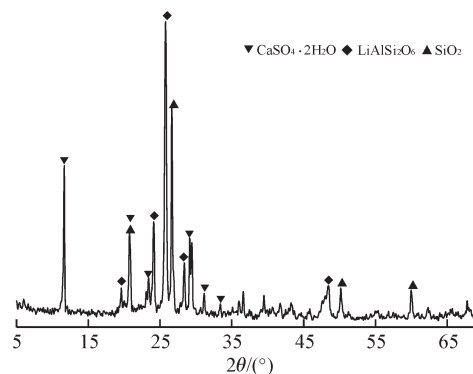


Fig.1 XRD patterns of lithium slag

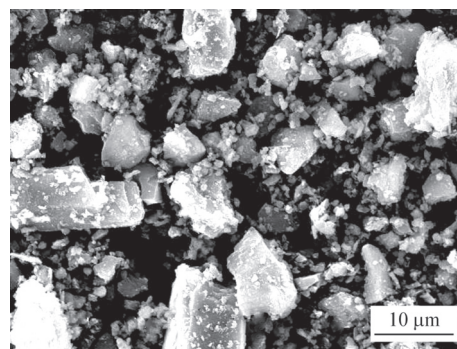


Fig.2 SEM image of lithium slag (2 000×)

Fig.1 and Fig.2 are the minerals and microstructure analysis results of lithium slag. It can be found from Fig.1 that lithium slag contains much SiO<sub>2</sub> and gypsum, and there are some residual unreacted spodumenes for the reason of the formation of lithium slag. As shown in Fig.2, the dominant particles of lithium slag comprise

**Table 2 Physical properties of ground lithium slag**

Sample	Grinding time/min	Median particle size/ $\mu\text{m}$	Retained on a sieve of 45 $\mu\text{m}/\%$	Blaine fineness/ $(\text{m}^2/\text{kg})$
FM0	0	14.97	15.09	254
FM1	5	11.92	12.75	466
FM2	10	10.85	12.63	554
FM3	15	9.37	11.23	630
FM4	20	8.45	9.02	700

**Table 3 Types and strength of blended cements**

Sample	Grinding time/min	Content /%	W1/%	W2/%	Flexural strength/MPa			Compressive strength/MPa		
					3 d	3 d	28 d	3 d	7 d	28 d
OPC					6.9	7.9	8.4	30.4	38.4	44.3
FM0	0	50	-	-	2.2	3.0	7.3	8.6	14.5	30.6
FM1	5	50	-	-	2.5	3.9	7.9	10.1	17.8	36.1
FM2	10	50	-	-	2.7	5.0	9.2	11.2	19.9	36.4
FM3	15	50	-	-	2.9	4.8	7.5	12.0	20.3	39.0
FM4	20	50	-	-	2.9	5.8	8.9	11.5	19.3	42.7
L10	10	10	-	-	7.4	9.3	9.4	32.4	43.0	50.1
L20	10	20	-	-	6.8	8.5	9.7	26.3	36.6	48.6
L30	10	30	-	-	5.5	7.6	10.0	22.9	30.9	42.1
L40	10	40	-	-	4.3	5.2	9.6	16.2	24.7	40.7
NS04	10	20	0.4	-	7.3	9.0	9.8	27.2	38.5	49.3
NS06	10	20	0.6	-	7.3	8.7	8.9	29.2	40.0	50.7
NS08	10	20	0.8	-	7.5	9.2	10.0	27.2	38.3	49.9
AS04	10	20	-	0.4	7.9	9.3	10.3	29.9	41.2	51.4
AS06	10	20	-	0.6	6.5	8.6	9.5	29.0	40.8	51.6
AS08	10	20	-	0.8	7.5	8.7	9.5	30.5	41.7	49.9

mainly coarse, angular, flaky, and drossy particles.

Table 2 shows the physical properties of ground lithium slag. It is indicated that with increase grinding time, the average particle size of the lithium slag decreases from 14.97 to 8.45  $\mu\text{m}$ ; when grinding time increases from 15 to 20 min, the average particle size of the samples decreases a little, but particles retained on a sieve of 45  $\mu\text{m}$  also become smaller; when the grinding time is 20 min, particles retained on a sieve of 45  $\mu\text{m}$  are 9.02%; it indicates that the particles of lithium slag are very fine. Meanwhile the specific surface area of lithium slag increases from 254 to 700  $\text{m}^2/\text{kg}$  with increasing grinding time; it indicates that grinding can improve the lithium slag fineness and specific surface area effectively.

### 3.2 Strength characteristics analysis of blended cements

The grinding time and mixing amount of lithium slag, the type and content of activators and strength are shown in Table 3.

The strength of cement with traditional granulated blast-furnace slag (GGBFS) or pulverized coal fly ash (PFA) (low in  $f\text{-CaO}$  and  $\text{SO}_3$ ) usually decreases with the increase of ash content in the cement-ash mixture due to the lower pozzolanic activity of the ash<sup>[12-14]</sup>, which is usually considered to be inert in cement paste in the early age of curing. For example, compared

with OPC, the compressive strength of FM0 at 3 days decreased by 71.7%, but the strength at 28 days only decreased by 30.9%, which may be due to the participation of amorphous silica, alumina, and calcium oxide in the hydration reaction. Improvement of the fineness and better dispersion performance make the mortar structure more compact; fine particles are more favourable to the second hydration reaction; in this way, the strength improved significantly.

Compared with the samples (L10 to L50 (FM4)), the strength decreases significantly with the increase of the content of lithium slag, which is due to the reduction of the cement content in the mixture. It is found that when the content is no more than 20%, the compressive strength at 28 days is higher than that of OPC; the strength decreases when the content is over 20%, but the strengths of mortars at 28 days are comparable to that of OPC. The reasons are that: when a small amount of lithium slag (10%, 20%) is mixed with cement paste, firstly, it is considered to be inert in the early age, and does not participate in the hydration reaction basically, which makes the larger water-cement ratio and promotes the formation of gel to increase the strength; secondly, lithium slag contains gypsum, which promotes the active silica and active alumina to produce much more C-S-H (hydrated calcium silicate, the main carrier of strength in hardened cement) and

hydrated calcium aluminate<sup>[15,16]</sup>.

With sample L20 as the base pattern, 0.4%-0.8%  $\text{Na}_2\text{SO}_4$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  were added in the pastes. The results shows that when the  $\text{Na}_2\text{SO}_4$  content is 0.6% or the  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  content is 0.4%, they get the best compressive strength. When they meet water, sulfate activators dissolve rapidly and produce many  $\text{SO}_4^{2-}$  to promote the dissolution of active silica or alumina in the lithium slag; in this way, the strength has been improved<sup>[17-20]</sup>. When the mix amount of  $\text{Na}_2\text{SO}_4$  is 0.6%, NS06 gets a 1.4% higher compressive strength than that of L20, and when the mix amount of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  is 0.6%, AS04 gets a 5.8% higher compressive strength than that of L20. Comparing the ages (3, 7, 28 d), we find that the active effect of sulfate activator on lithium slag mainly reflects on the early ages (3, 7 d) strength<sup>[21]</sup>.

### 3.3 Hydration heat of cement pastes

From the strength characteristics analysis of blended cements, we can see that grinding, sodium sulfate and aluminum sulfate can strengthen the hydration activity and improve the early age degree of hydration. This is the same conclusion as the analysis of hydration heat.

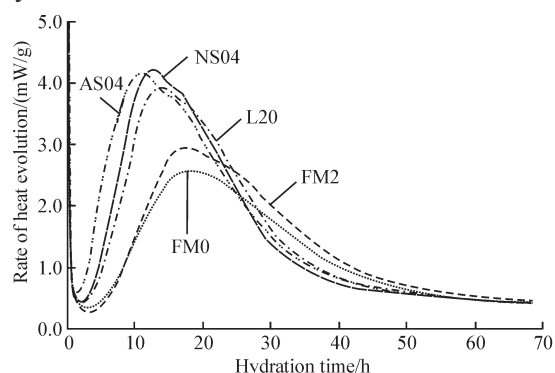


Fig.3 Rate of heat evolution of cement pastes with  $W/C$  of 0.32

Fig.3 shows the rate of heat evolution of cement pastes with  $W/C$  of 0.32. From the figure, we can see that the rate of heat evolution of FM2 was significantly higher than that of FM0 which was ground for 10 min. It is to say that grinding can significantly improve the hydration activity of blended cements. The hydration rate of NS04 and AS04 was significantly higher than that of L20, which reveals that sodium sulfate and aluminum sulfate can stimulate the early hydration activity of blended cement minerals. Comparing the L20, NS04 and AS04, the rate of heat evolution of FM0 and FM2 is reduced and the exothermic peak is delayed, which reveals that lithium slag can delay hydration of blended cements and cut down the hydration heat. So blended cements with lithium slag can be used in mass

concrete to prevent temperature cracks<sup>[22,23]</sup>.

## 3.4 Hardened products microscopic analysis

### 3.4.1 XRD analysis

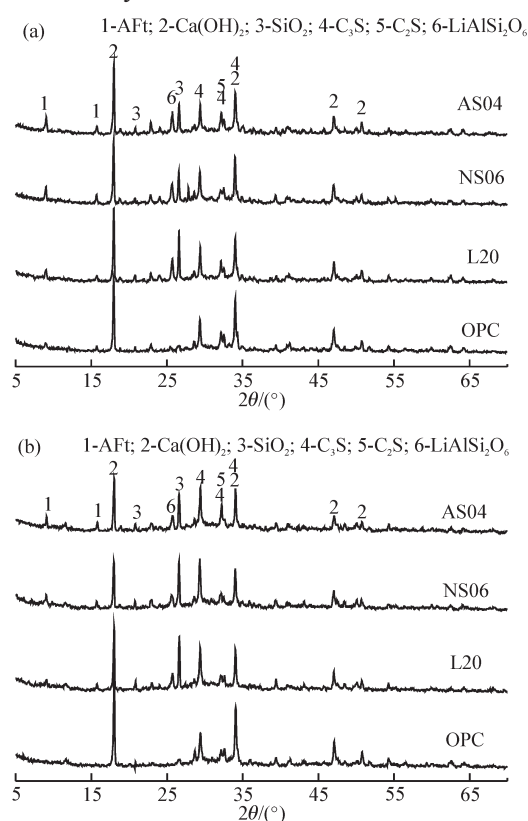


Fig.4 The XRD analyses of hydration of pastes: (a) 3 days; (b) 28 days

Figs.4 (a) and (b) show the X-ray diffraction patterns of blended cements of some pastes after 3 and 28 days, respectively.

It can be seen that the main hydration products in all the samples are Ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3 \cdot 32\text{H}_2\text{O}$ , AFt), gypsum and portlandite as well as unhydrated  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  (Figs.4(a), 4(b)). At 3 days, because lithium slag contains gypsum and the added sulfate activator, which promote the hydration reaction between  $\text{Ca}(\text{OH})_2$  and active silica and alumina to produce much C-S-H and AFt, L20, NS06, AS04 have higher AFt peak value and lower  $\text{SiO}_2$  and  $\text{Ca}(\text{OH})_2$  peak value than that of OPC. Compared with NS06, AS04 has a higher AFt peak and lower  $\text{SiO}_2$  peak, which indicates that  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  is more applicable to the activity of lithium slag, which is also demonstrated in the strength results. Compared with the XRD pattern of 3 days, the type of cement paste hydration products at 28 days have not changed much, but  $\text{Ca}(\text{OH})_2$  and  $\text{SiO}_2$  are significantly reduced. This is due to the growth with age, which promotes the hydration reaction between  $\text{Ca}(\text{OH})_2$  and active silica and alumina to produce more products such as C-S-H and AFt.



### 3.4.2 SEM analysis

The SEM images of some pastes are presented in Fig.5.

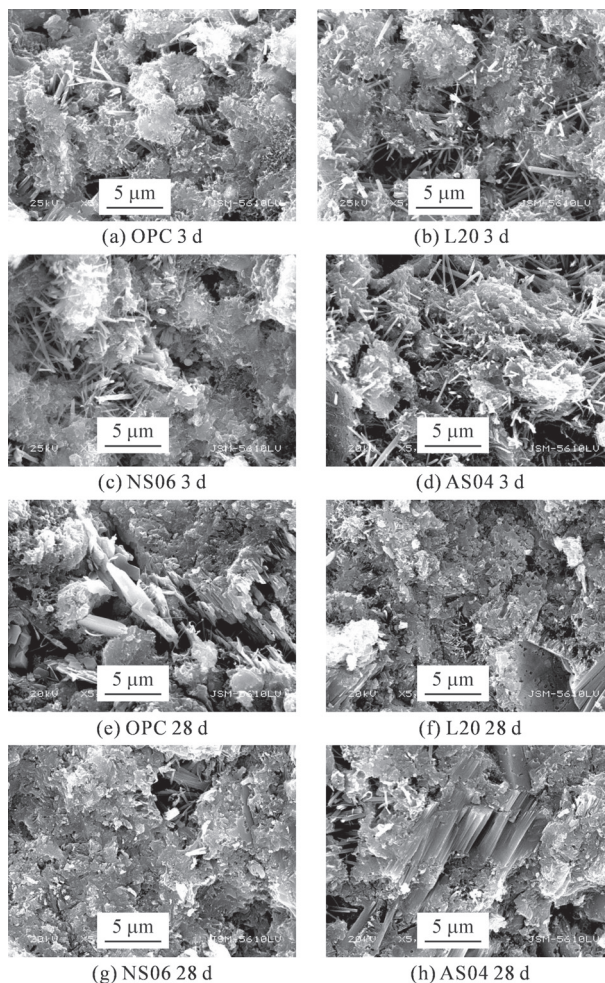


Fig.5 SEM images of hardened pastes (5 000×)

Fig.5 shows that more rod-like AFt crystals are detected in the pastes with composite lithium slag and sulfate activator at 3 days. Compared with the hydration pastes of OPC at 28 days, we almost do not see hexagon-shaped crystals  $\text{Ca}(\text{OH})_2$  in L20, NS06, AS04 pastes obviously. Some rod-like AFt crystals interlude among the different particles and enhance the contacts of the solid phases, which contributes a lot to the material's strength formation and illustrates that amorphous silica, alumina, and calcium oxide join the hydration reaction sufficiently.

## 4 Conclusions

Grinding can easily increase the specific surface area of lithium slag and compressive strength of blended cements. The compressive strength of blended cements with 50 wt% of lithium slag ground for 20 min

is comparable to OPC at 28 days.

The strength decreases significantly with the increase of the content of lithium slag, while it is found that when the content is no more than 20%, the compressive strength at 28 days is higher than that of OPC, and the strength decreases when it is over 20%, but the strengths of mortars at 28 days are comparable to that of OPC.

The addition of sulfate accelerates the early hydration of blended cements, which improves the lithium slag cement strength effectively, especially the early strength, significantly higher than that without adding activator.

## References

- [1] Zhang T, Yu Q and Wei J. Efficient Utilization of Cementitious Materials to Produce Sustainable Blended Cement [J]. *Cement & Concrete Composites*, 2012, 34(5): 692-699
- [2] Lilkov V, Petrov O and Tzvetanova Y. Mossbauer, DTA and XRD Study of Portland Cement Blended with Fly Ash and Silica Fume [J]. *Construction and Building Materials*, 2012, 29: 33-41
- [3] Arizzi A and Cultrone G. Aerial Lime-Based Mortars Blended with a Pozzolanic Additive and Different Admixtures: a Mineralogical, Textural and Physical-Mechanical Study [J]. *Construction and Building Materials*, 2012, 31: 135-143
- [4] Beushausen H, Alexander M, Ballim Y. Early-age Properties, Strength Development and Heat of Hydration of Concrete Containing Various South African Slags at Different Replacement Ratios[J]. *Construction and Building Materials*, 2012, 29: 533-540
- [5] Li X, Lv Y and Ma B. Utilization of Municipal Solid Waste Incineration Bottom Ash in Blended Cement [J]. *Journal of Cleaner Production*, 2012, 32: 96-100
- [6] Tkaczewska E, Mróz R and Lój G. Coal-biomass Fly Ashes for Cement Production of CEM II/A-V 42.5R [J]. *Construction and Building Materials*, 2012, 28(1): 633-639
- [7] Wongkeo W, Thongsanitgarn P, Chaipanich A. Compressive Strength and Drying Shrinkage of Fly Ash-bottom Ash-silica Fume Multi-blended Cement Mortars [J]. *Materials and Design*, 2012, 36: 655-662
- [8] Frias M, Sanchez de Rojas M, Garcia R. Effect of Activated Coal-mining Wastes on the Properties of Blended Cement [J]. *Cement & Concrete Composites*, 2012, 34(5): 678-683
- [9] Li C and Fei W. Lithium Residue Utilization in Cement Industry [J]. *Cement Technology*, 2001, 5: 57-58
- [10] Zhang L. Experiment Study on High-performance Lithium-slag Concrete [J]. *Journal of Liaoning Technical University*, 2007, 6: 877-880
- [11] Chen J. Study on Lithium Slag and Lime Stone Self-compacting High Strength High Performance Concrete [J]. *Construction Technology*, 2007, 4: 52-54
- [12] Zhang Y, Sun W and Yan H. Hydration of High-volume Fly Ash Cement Pastes [J]. *Cement and Concrete Composites*, 2000, 22(6): 445-452
- [13] Goñi S, Frias M and Vegas I. Effect of Ternary Cements Containing Thermally Activated Paper Sludge and Fly Ash on the Texture of C-S-H Gel [J]. *Construction and Building Materials*, 2012, 30: 381-388
- [14] Zhang T, Yu Q and Wei J. Study on Optimization of Hydration Process of Blended Cement[J]. *Journal of Thermal Analysis and Calorimetry*, 2012, 107(2): 489-498
- [15] Li J, Wang Z, Wang Y. Study on Reaction Dynamics of the Activated Fly Ash-cement-water System [J]. *Natural Science Journal of Harbin Normal University*, 2000(1): 69-73
- [16] Zhou L, Wang Z and Li J. Study on Activity Agents of Fly Ash [J]. *Low Temperature Architecture Technology*, 2004(2): 8-10
- [17] Khmiri A, Samet B and Chaabouni M. A Cross Mixture Design to Optimize the Formulation of a Ground Waste Glass Blended Cement [J]. *Construction and Building Materials*, 2012, 28(1): 680-686
- [18] Fraay A.L.A. *Fly Ash a Pozzolan in Concrete* [D]. Delft: Delft University of Technology, 1990
- [19] Liu B, Liang H and Yang Y. Alkaline Activated Fly Ash in Aement-fly Ash System [J]. *Journal of railway Science and Engineering*, 2009(5): 51-56
- [20] Zhong S, Ni K and Li J. Properties of Mortars Made by Uncalcined FGD Gypsum-fly Ash-ground Granulated Blast Furnace Slag Composite Binder [J]. *Waste Management*, 2012, 32(7): 1 468-1 472
- [21] Ogawa S, Nozaki T and Yamada K. Improvement on Sulfate Resistance of Blended Cement with High Alumina Slag [J]. *Cement and Concrete Research*, 2012, 42(2): 244-251
- [22] Cheng A. Effect of Incinerator Bottom Ash Properties on Mechanical and Pore Size of Blended Cement Mortars [J]. *Materials and Design*, 2012, 36: 859-864
- [23] Sheng G, Li Q and Zhai J. Investigation on the Hydration of CFBC Fly Ash [J]. *Fuel*, 2012, 98: 61-66