The Tenth International Conference on Waste Management and Technology (ICWMT)

Hydration mechanism of Portland cement prepared from stonecoal vanadium slag

Pengyu Zhang[a,b], Leming Ou[a,b], Kun Liu[a,b,*]

aSchool of Minerals Processing & Bioengineering, Central South University, Changsha 410083, China
bKey Laboratory for Mineral Materials and Application of Hunan Province, Central South University, Changsha 410083, China

Abstract

This paper presents an objective study on the utilization of stone coal vanadium slag in preparing cement clinker. The hydrates and hydration mechanism of this cement were analyzed and studied by means of the hydration heat analysis, X-ray diffraction (XRD) and the differential thermal gravity (DTG) analysis. The results of experiments show that the hydration mechanism is similar to ordinary Portland cement. The hydration process can be divided into five stages: (I) initial period; (II) induction period; (III) acceleration period; (IV) deceleration period; (V) final period. And the hydrates are basically the same as Portland cement, mainly containing the calcium silicate hydrates (C-S-H), ettringite (AFt), portlandite (CH). It is proved that stone coal vanadium slag can be used as siliceous materials to prepare cement clinker. Furthermore, the addition of fine materials such as the waste and fly ash can accelerate cement hydration, which is the result of giving rise to water-to-cementitious ratio. On the other hand, the fine materials may provide the crystal nucleus for hydrates such as portlandite. Using the waste and fly ash to replace part of clinker can prepare series of cement, whose compositions and physical properties are fully complied with the requirements of national standard, and bring huge ecological and economic benefits.

Keywords: solid waste; stone coal vanadium slag; hydration mechanism; cement clinker

* Corresponding author. Tel.: +86-731-88877204; fax: +86-731-88877204.
  E-mail address: kliu@csu.edu.cn

1. Introduction

With the development of China's mining industry, more and more mineral waste residue is discharged year by year. These solid wastes cause varieties of resources and environmental problem on people's living area. While at the same time, the demands of cement are increasing with the remarkable development of the construction industry. Thus, in recent years, utilization of proper solid waste to prepare cement has become an efficient way to deal with the solid mineral wastes problems[1-7].

Stone coal is a type of inferior anthracite, in which the grade of vanadium is less than 1%. In China, it commonly extracts vanadium resources from stone coal by hydrometallurgical extraction process. In the process, a great deal of solid waste (named "vanadium slag") is inevitably produced. The vanadium slag mainly composites of quartz and silicate minerals. Due to this characteristic, it can be used as siliceous and correction materials to prepare cement clinker. Relevant researches about how to use vanadium slag to prepare cement clinker had been carried out and the qualified cement clinker production had been produced. However, to date, there has been relatively little research conducted on the mechanisms of the production. Especially, the hydration mechanism and property of the cement clinker production are unknown. These mechanisms are very important for the industrial design and practical production. Thus, the purpose of the current research is to characterize the hydration mechanisms of different classes cement prepared from vanadium slag.

2. Experiment

2.1. Raw materials

The cement clinker used in the current research is prepared by self in laboratory. It consists of following steps: (1) stone coal vanadium slag (3-16 wt%) blended with nitric phosphate slag (76-79 wt%) and other various aluminum and iron materials (7-20 wt%); (2) heated at 1350-1450 ℃ and then cooled to room temperature; (3) ground to granularity less than 0.074 mm. The waste used is from mining tailings and fly ash comes from thermal power plants. The mineralogical composition of cement clinker is listed in Table 1, and the chemical composition of materials is listed in Table 2.

Series preliminary experiments about material proportion have been conducted before the research. Among these experiment results, the material ratios of samples complied with the requirements (national standard of China) are picked out. The samples of B, C and D are up to the standard of 52.5#, 42.5# and 32.5# cement. The proportions and physical properties of samples are listed in Table 3.

Table 1 Mineralogical composition of cement clinker

C_3S (%)	C_2S (%)	C_3A (%)	C_4AF (%)
56.62	19.08	7.98	10.23

Table 2 Chemical composition of materials

	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	LOSS (%)	Σ (%)
Clinker	21.56	5.16	3.37	65.01	2.12	0.40	0.27	97.89
Waste	62.31	10.33	6.71	6.83	1.29	0	8.67	96.14
Fly ash	53.17	27.68	6.08	2.88	1.14	0.31	7.52	98.78

2.2. Methods

Cement paste samples were prepared at the w/c (water/cement) of 0.4. The cement paste was placed in a cubic paste mould (20×20×20 mm) and cured for 24h in a certain atmosphere (temperature of 20±2 ℃ and relative humidity of above 90 %). Then, the formed cement cubes were sequentially maintained in water with temperature of 20±1 ℃ for a certain time. After the curing, the cement samples were crushed into small pieces and immersed into

ethanol for more than 20h to discontinue the hydration (the volume ratio of ethanol to cracked pieces was about 10:1). Cement paste samples were there taken out of ethanol and oven dried at 60 ℃ for at least 6h. The samples were pulverized using an agate pestle and mortar. The particle size of the final samples should less than 80 µm.

Hydration heat was measured by a SETARAM BT2.15I Calvet-type microcalorimeter with temperature of 20 ℃ and water cement ratio (by mass) of 2:1. The XRD analysis was performed on a fully automatic X-ray diffraction apparatus of Rigaku D/max 2550 VB$^+$ with Cu Kα radiation, an acceleration voltage of 40 kV and an emission current of 100 mA at a scanning rate of 2° per minute. The DTG analysis was carried out on a NETZSCH STA449C thermal analyzer with temperature from 50 to 1100 ℃, heating rate of 10 ℃/min and air atmosphere.

Table 3 Proportions and physical properties of samples

Code	Clinker (%)	Waste (%)	Gypsum (%)	Fly ash (%)	Strength of 3d (MPa)		Strength of 28d (MPa)	
					Flexural	Compressive	Flexural	Compressive
A	100.0	0	0	0	6.9	33.8	9.9	60.9
B	95.0	0	5.0	0	6.5	32.1	9.5	58.4
C	78.5	8.5	5.0	8.0	5.1	23.5	8.9	47.1
D	60.5	25.0	4.5	10.0	4.4	18.6	7.0	36.2

Code	Water demand for normal consistency (%)	Average particle size (µm)	Specific surface area (m^2/g)	LOSS (%)	Soundness	Setting time (min)	
						Initial	Final
A	23.40	2.2	359	0.27	Qualified	116	160
B	27.90	2.4	347	1.41	Qualified	239	292
C	27.80	3.6	345	4.62	Qualified	207	263
D	26.00	5.8	399	11.90	Qualified	217	275

3. Results and discussion

3.1. Hydration heat

Fig. 1 shows the hydration heat release rate curves of the samples at 20 ℃. The hydration process can be divided into five stages[8]: (I) initial period; (II) induction period; (III) acceleration period; (IV) deceleration period; (V) final period. Moreover, there are commonly two exothermic peaks in the cement hydration process. The first exothermic peak is in initial period. It is mainly caused by ion dissolution and reaction between C_3A and calcium sulfate, usually resulting in formation of ettringite. The second exothermic peak is in acceleration period. It mainly caused by hydration of C_3S, forming calcium silicate hydrates (C-S-H) and calcium hydroxide.

It can be seen in the Fig. 1 that the first peak of sample B is higher than that of sample C and sample D. It is because a relatively lower content of admixture and higher content of C_3A in sample B. Sample A is all clinker, which has little ettringite and hydration heat. The SO_4^{2-} in gypsum can significantly reduce the solubility of aluminate, which lead to prolonged hydration and delay the presents of induction period of sample B, sample C and sample D[9,10].

Moreover, from Fig. 1, the hydration heat rate of sample D and sample C is significantly higher than that of sample A. Besides, the acceleration time is relatively shorter. Obviously, the partial replacement of the cement by fine materials (mainly fly ash and high-silicon waste stone) accelerates the cement hydration reaction. These fine minerals are served as crystal nucleus to ensure the growth of hydrates (such as portlandite)[11,12]. The additional of admixture result in a faster separation out of portlandite and decreasing the concentration of Ca^{2+}. Thus, in this case, the cement hydration is accelerated and the hydration of the second exothermic peak is increased.

Comparing to sample C, sample D adds with more mineral admixture, which makes a faster crystallization velocity and higher second exothermic peak. Moreover, in the acceleration period, the hydration heat release rate of sample C is lower than sample B. It attributes to the slow pozzolanic reaction of fly ash. By using the same amount of fly ash to replace clinker, it can significantly reduce the temperature peak[13-15].
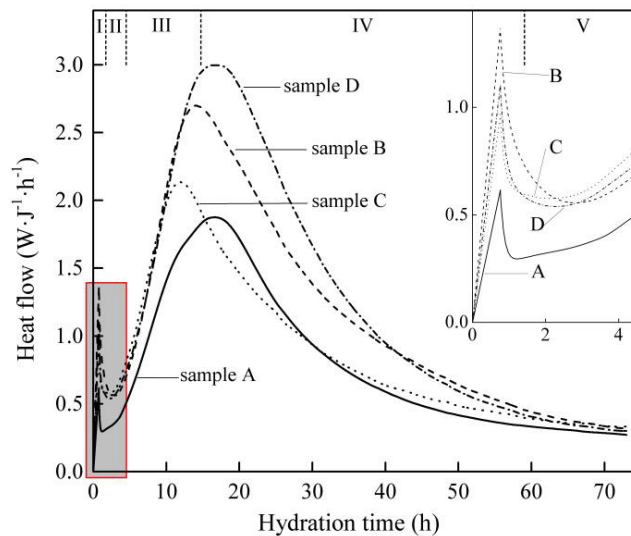
Fig. 1. Heat evolution rate curves of samples at 20 ℃
I—initial period; II— induction period; III—acceleration period; IV—deceleration period; V—final period

The hydration of the fly ash requires the alkaline excitation of the cement hydration product[16,17]. So, a certain period of time is necessary for destroy the vitreous surface and the integument formed by the cement hydration product. In the later stage, the activity of fly ash increases and the pozzolanic effect takes action, which makes a higher hydration release rate. The completely hydrated cement clinker (mainly C_2S) in sample B begins to release hydration heat slowly. Moreover, because of the largest amount of admixture dosage (25 %, mass fraction), the cement clinker content in sample reduces. It results in lower exothermic rate of sample D than sample B after 42 hours later.

3.2. XRD

Samples hydrated for 3d and 28d are analyzed by X-ray diffraction analyzer, as presented in Fig. 2. The main hydration products are basically the same. They are the ettringite (AFt), portlandite (CH), traces of $CaCO_3$ (from carbonation of portlandite), unhydrated clinker and unreacted admixtures. Compared to sample A and sample B, sample C added with more admixtures (16.5 wt%), resulting in a more diffuse peaks as illustrated in Fig. 2. With the further increasing amount of admixtures, it makes the diffuse peaks of sample D further increased. Contrast with Fig. 2(a) and Fig. 2(b), it can be seen that the clinker in samples is reducing along with the increasing of hydration time. At the same time, the hydration products present an increasing trend under this condition.

The content of clinker minerals (C_3S and C_2S) and hydration products of portlandite under different hydration time were semi-quantitative analyzed from the X-ray diffraction data. The results are shown in Fig. 3 and Fig. 4. It can be seen in Fig. 3 that the content of C_3S and C_2S sharply declines during 24h. When the hydration time exceeded 24h, this change becomes not evident. The main reason is amount of hydration products quickly generated at the beginning[18,19]. These generated hydration products would cover on the unhydrated particle surface and decelerate the hydration rate. The sequence unhydrated C_3S and C_2S content is: A, B, C, D. The sequence of clinker minerals reducing rate is: D, C, B, A. The reason for that lies in two aspects. On one hand, the addition of admixtures lowers the total content of clinker minerals, which results in a less content of C_3S and C_2S in the samples. On the other hand, the admixtures accelerate the hydration rate due to its nucleation, which leads to a more obvious clinker reduction rate of sample C and sample D. After 28d hydration, unhydrated clinker was still existed. The main reason is the slow hydration rate of C_2S.
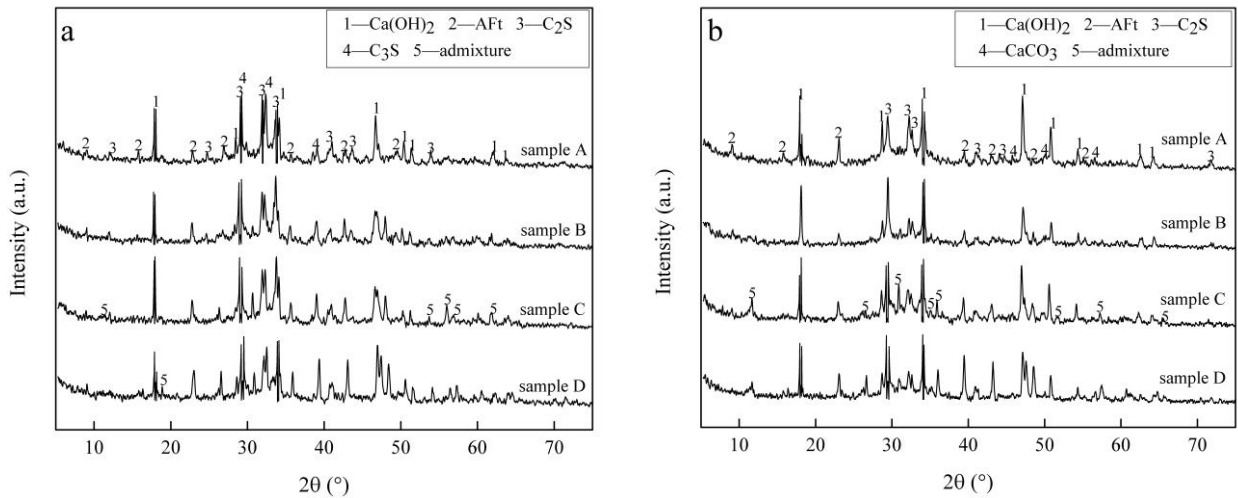
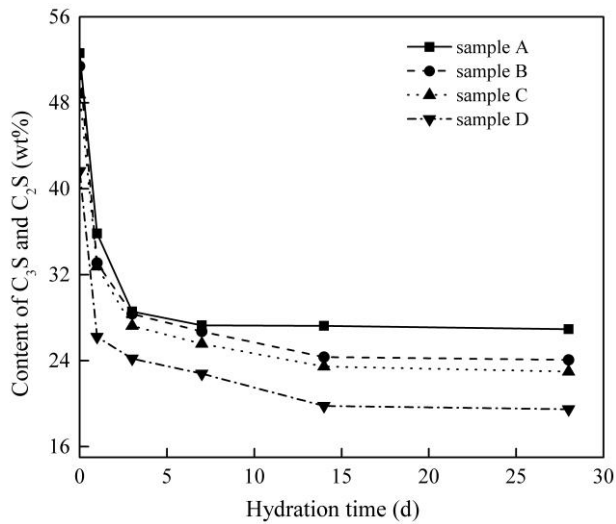Fig. 2. X-ray diffraction (XRD) patterns of samples hydrated for 3 d (a) and 28 d (b)

Fig. 3. Variations of C_3S and C_2S in different samples vs hydration time
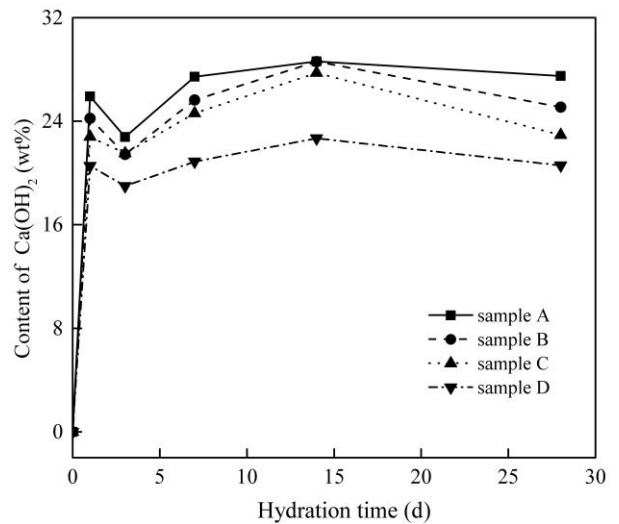
Fig. 4. Variations of $Ca(OH)_2$ in different samples vs hydration time

From Fig. 4, it can be seen that the content sequence of portlandite is: A, B, C, D. It is because the addition of admixtures lowers the clinker content, resulting in a less formation of hydration products. The SiO_2 in admixtures gradually react with portlandite and overbasic calcium silicate hydrates to generate low-alkaline calcium silicate hydrates[20]. Moreover, $Ca(OH)_2$ would also react with Al_2O_3 in the admixtures and generate calcium aluminate hydrates, which increasing the consumption of $Ca(OH)_2$ (as presented in Fig. 4). The $Ca(OH)_2$ content decreased after the samples hydrated 3d, as the result that the hydration of clinker (C_3A, C_4AF, C_3S) has reached the final period within 72h. And at the same time, because of the slow hydration rate of C_2S, the generation of $Ca(OH)_2$ would relatively reduce.

3.3. DTG

The thermal decomposition characters of the sample were examined by the differential thermal gravity (DTG) analysis. The results are shown in Fig. 5. From the diagram, it can be calculated that the hydration products are

basically the same as Portland cement, which is agree well with XRD analysis results, These hydration products are mainly composited of calcium silicate hydrates (CSH), ettringite (AFt), portlandite (CH) and $CaCO_3$.
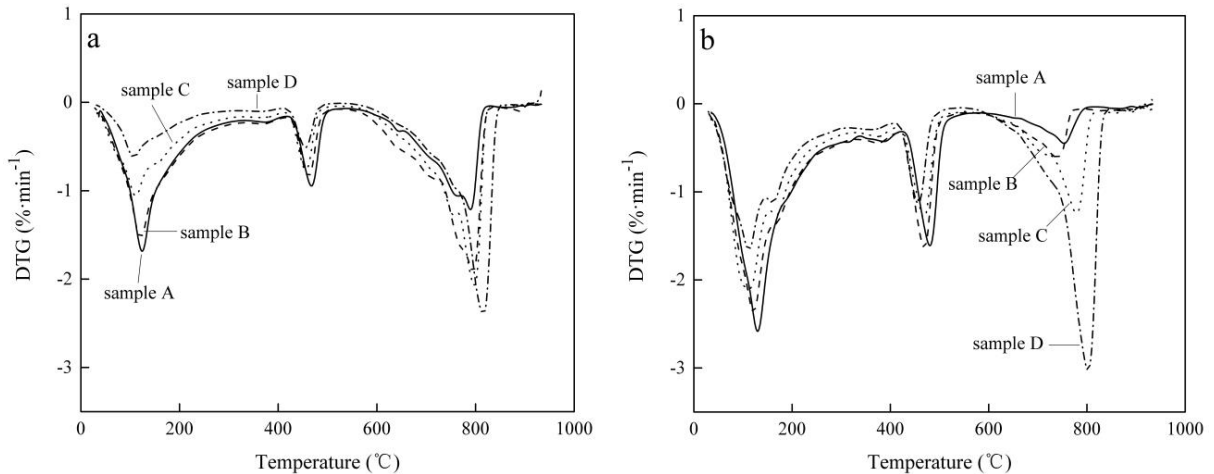

Fig. 5. Differential thermal gravity (DTG) spectra of samples hydrated for 3 d (a) and 28 d (b)

Moreover, from Fig. 5, the first endothermic valley is at the point of 110 ℃ and the corresponding temperature range is 30 to 200 ℃. Under this temperature region, it is mostly the peak of aqueous phase dehydration, including inter-calcium silicate hydrates (CSH), ettringite (AFt) and single sulfur-type monosulfate (Afm)[21,22]. The dehydration temperature is different due to the combinative state of water in each product is different. Samples hydrated for 28 days have deeper valley than that of 3 days. It is mostly caused by the continuous generation of C-S-H and other products. Because part of clinker replaced by admixtures the hydration products is relatively reduces. It makes the valley of sample C and sample D are lower than A's. This phenomenon on sample D contained with 25 wt% waste material is most prominent. After hydrated for 28 days, the pozzolanic activity of admixtures appears. It makes the first valley depth of sample C and sample B nearly the same. The second endothermic valley is in the vicinity of 470 ℃ and the corresponding temperature region is 430 to 500 ℃. It is mainly because that the $Ca(OH)_2$ in cement decomposes and draws lots of heat at this point[23]. According to the Fig. 5, the depth of the second valley is increasing along with the time, which can be attributed to the constant generation of portlandite in cement[24].

In addition, from Fig. 5, sample C and sample D have shallower valley. There are two reasons for that. Firstly, part of clinker replaced by admixtures results in a relative reduction of hydration products. Secondly, due to the pozzolanic activity of fly ash, it consumes portlandite for a secondary hydration. The third endothermic valley is around 800 ℃ and the corresponding temperature range is 600 to 900 ℃. This endothermic process is mainly caused by the thermal decomposition of $CaCO_3$ and the dehydration of hydrated silicate structure water[25].

4. Conclusions

The hydration mechanism of the cement clinker (prepared from stone coal vanadium slag as siliceous materials) is similar to ordinary Portland cement. The hydration products, mainly containing the calcium silicate hydrates (C-S-H), ettringite (AFt) and portlandite (CH), are basically the same with Portland cement. During the hydration process, the fine materials (mainly the waste and fly ash) could provide crystal nucleus for hydrates such as portlandite, and accelerate cement hydration. The fly ash in cement paste has pozzolanic activity under the alkaline excitation. As well, the performance of cement prepared from stone coal vanadium slag conforms to national standards of China. As a result, the stone coal vanadium slag can be used as raw materials to produce qualified cement products, which brings ecological and economic benefits greatly.

Acknowledgements

References

1. Shen W, Gan G, Dong R*, et al*. Utilization of solidified phosphogypsum as Portland cement retarder. *J Mater Cycles Waste* 2012;**14**:228-33.
2. Kai W, Shi H, Guo X. Utilization of municipal solid waste incineration fly ash for sulfoaluminate cement clinker production. *Waste Manage* 2011;**31**:2001-8.
3. Liu X, Zhang N. Utilization of red mud in cement production: a review. *Waste Manage Res* 2011;**29**:1053-63.
4. Celik O, Elbeyli IY, S P. Utilization of gold tailings as an additive in Portland cement. *Waste Manage Res* 2006;**24**:215-24.
5. Puertas F, García I. Ceramic wastes as alternative raw materials for Portland cement clinker production. *Cem Concr Compos* 2008;**30**:798-805.
6. Tsakiridis PE, Papadimitriou GD, Tsivilis S*, et al*. Utilization of steel slag for Portland cement clinker production. *J Hazard Mater* 2008;**152**:805-11.
7. Chen Y, Chang J, Shih P*, et al*. Reusing pretreated desulfurization slag to improve clinkerization and clinker grindability for energy conservation in cement manufacture. *J Environ Manage* 2010;**91**:1892-7.
8. Bullard JW, Jennings HM, Livingston RA*, et al*. Mechanisms of cement hydration. *Cem Concr Res* 2010;**41**:1208-23.
9. Pourchet S, Regnaud L, Perez JP*, et al*. Early C3A hydration in the presence of different kinds of calcium sulfate. *Cem Concr Res* 2009;**39**:989-96.
10. Fu X, Yang C, Liu Z*, et al*. Studies on effects of activators on properties and mechanism of hydration of sulphoaluminate cement. *Cem Concr Res* 2003;**33**:317-24.
11. Zhen H, Yang H, Hu S*, et al*. Hydration mechanism of silica fume-sulphoaluminate cement. *J Wuhan Univ T* 2013;**28**:1128-33.
12. Lawrence P, Cyr M, Ringot E. Mineral admixtures in mortars: Effect of inert materials on short-term hydration. *Cem Concr Res* 2003;**33**:1939-47.
13. Sakai E, Miyahara S, Ohsawa S*, et al*. Hydration of Fly Ash Cement. *Cem Concr Res* 2005;**35**:1135-40.
14. Wang A, Zhang C, Sun W. Fly ash effects: ii. The active effect of fly ash. *Cem Concr Res* 2004;**34**:2057-60.
15. Gao Y, Zhou S. Influence of ultra-fine fly ash on hydration shrinkage of cement paste. *J Cent South Univ T* 2005;**12**:596-600.
16. Lin K, Wang K, Tzeng B*, et al*. Hydraulic activity of cement mixed with slag from vitrified solid waste incinerator fly ash. *Waste Manage Res* 2003;**21**:567-74.
17. Stefanovic G, Cojbasic L, Sekulic Z*, et al*. Hydration study of mechanically activated mixtures of Portland cement and fly ash. *J Serb Chem Soc* 2007;**72**:591-604.
18. Ogawa K, Uchikawa H, Takemoto K*, et al*. The mechanism of the hydration in the system C3S-pozzolana. *Cem Concr Res* 1980;**10**:683-96.
19. He T, Shi C, Li G*, et al*. Effects of superplasticizers on the carbonation resistance of C3S and C3A hydration products. *Constr Build Mater* 2012;**36**:954-9.
20. Qing Y, Zhang Z, Chen R*, et al*. Interaction of nano-sio_2 with portlandite at interface between hardened cement paste and aggregate. *J Chin Ceram Soc* 2003;**31**:517-22.
21. Stepkowska ET, Blanes JM, Real C*, et al*. Hydration products in two aged cement pastes. *J Therm Anal Calorim* 2005;**82**:731-9.
22. Zhang X, Glasser FP, Scrivener KL. Reaction kinetics of dolomite and portlandite. *Cem Concr Res* 2014;**66**:11-8.
23. Dong J, Wang L, Zhang T. Study on the strength development, hydration process and carbonation process of NaOH-activated Pisha Sandstone. *Constr Build Mater* 2014;**66**:154-62.
24. Lilkov V, Petrov O, Tzvetanova Y*, et al*. Mössbauer, DTA and XRD study of Portland cement blended with fly ash and silica fume. *Constr Build Mater* 2012;**29**:33-41.
25. Malliou O, Katsioti M, Georgiadis A*, et al*. Properties of stabilized/solidified admixtures of cement and sewage sludge. *Cem Concr Compos* 2007;**29**:55-61.