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Experimental investigation of hydration of ternary blended cement paste

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Abstract

In this paper, ternary and binary blended cement pastes as well as pure Portland cement paste were prepared by Portland cement, ground granulated blast-furnace slag (GGBFS), limestone powder and water, which were then hydrated from 1 to 91 days at 20 °C in a sealed environment. At each curing age, the hydration kinetics of cement and slag was determined by XRD/Rietveld and selective dissolution method (EDTA), respectively. The content of $CaCO_3$ (limestone) was quantified by Thermogravimetric analysis (TGA) technique.

The degree of hydration of cement clinker was distinctly accelerated by the single addition of slag or limestone within 91 days of hydration. The coexistence of slag and limestone in ternary blended cement accelerated the hydration of cement clinker within the first 14 days of hydration, but lowered the degree of hydration of cement clinker after 91 days of hydration compared with other pastes. The degree of reaction of slag in blended cement pastes was about 8% and 35% after 1 and 91 days of hydration, respectively, which was almost not influenced by the addition of limestone powder. A small amount of limestone, i.e. around 2% of the total solid raw materials, was reacted in pastes, and mainly occurred at the early age.

Based on the experimental investigation, the results show that the hydration of calcium silicate phases of cement in pastes was enhanced by the presence of limestone, but hampered by slag. The hydration of calcium alumina phases of cement was greatly accelerated by the addition of slag, and also enhanced by the presence of limestone powder in binary blended limestone cement paste at early age. However, the coexistence of limestone with slag in ternary blended cement paste restrained the hydration of calcium alumina phases of cement.

Originality

The hydration process of blended cement paste is of significant importance, like it is for pure Portland cement. Limited work has been performed on ternary blended cement pastes due to complexity of ternary blended systems as well as the lack of advanced experimental techniques. Based on a series of experimental procedures, this paper experimentally investigated the hydration kinetics of ternary blended cement pastes as well as the corresponding reference pastes. The paper presents the results and shows the influence of each material on the others in the ternary blended cement paste and systematically compared with the relevant references. The results help understand the hydration behavior of ternary blended cement paste, which benefits the research on modeling of ternary blended cement paste.

Keywords: *Ternary blended cement, Slag, Kinetics, Limestone, Portland cement*

1. Introduction

In terms of the tendencies in the modern cement industry, the most important are those connected with economical and ecological factors. Over the last decades, Supplementary Cementitious Materials (SCMs) such as fly ash, silica fume and blast-furnace slag have been widely used in construction industry all over the world, because the use of SCMs brings several advantages over Portland cement. Firstly, the cost of SCMs is cheaper than Portland cement as they are usually by-products of industry. Secondly, the production of SCMs consumes less energy and reduces CO_2 emission compared to that

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of Portland cement. Thirdly, concrete made by SCMs can have better performance such as workability and durability.

SCMs blended cement is a promising route towards the sustainability of cement industry. For example, cement used in the famous Three Gorges Dam project was replaced by 30-40% fly ash (Wenwei Li et al., 2000) in order to obtain low heat evolution during casting and better durability for the whole service life. In another project in China, the 632 m's high skyscraper Shanghai Tower, over 7,000 tons of slag was used to cast the single huge foundation which consumed 61,000 m^3 concrete and was continuously cast within 60 hours (Baosteel Group, 2010). This would be almost impossible if only pure Portland cement had been used because the heat evolution during the early-age hydration would lead to thermal cracking (D. P. Bentz, 2008) especially in this kind of massive volume.

However, the quantity and availability of SCMs are still limited at least at some parts of the world. Efforts have been paid to the utilization of raw material limestone as replacement of relatively expensive cement. As it is well known that CO_2 emission occurs in the process of burning limestone to produce cement clinker, if limestone is directly used in cement, its footprint of CO_2 is nearly zero. A good example is the European Standard EN 197-1 (EN 197-1, 2000), which identifies two types of Portland-limestone cement containing 6-20% limestone (type II/A-L) and 21-35% limestone (type II/B-L), respectively.

Binary blended cements such as cement blended with slag or limestone powder have long been used for casting concrete, e.g. the domestic market share of CEM II (binary blended cement) in Cembureau countries was as high as 56.1% in the year of 2005 (G Menéndez el al., 2003) and stayed stable over the past ten years. However, research shows that well designed ternary blended cements, e.g. Portland cement blended with slag and limestone powder, have complementary performance (L. Bagel, 1998, M. F. Carrasco, 2005, E. F. Irassar et al.). The use of limestone filler in the ternary blends increases the early hydration of Portland clinker; while slag contributes to the later hydration. This complementary behavior of limestone filler and slag addition permits to obtain concrete with similar strength development as normal Portland cement but with much less clinker. As for durability, it is reported (E F Irassar et al.) that ternary cement containing a limited proportion of limestone filler (no more than 12%) and 20 to 30% of slag provided a good resistance to chloride ingress and good performance in sulphate environment.

Compared with the intensive research work on Portland cement and even binary blended cement, the research work on the hydration of ternary blended cement is extremely limited. On the one hand less attention has been paid to this field, and on the other hand less reliable experimental techniques are available to investigate the hydration of ternary blended cement due to the complexity of blended cements. However, understanding the hydration process definitely benefits the usage of ternary blended cement. In this paper, ternary and binary blended cement pastes as well as pure Portland cement paste were prepared by Portland cement, GGBFS, limestone powder and water, which were then hydrated from 1 to 91 days at 20 °C in a sealed environment. At each curing age, the hydration kinetics of cement and slag was determined by XRD/Rietveld and EDTA selective dissolution method, respectively. The content of $CaCO_3$, i.e. calcite from limestone, was quantified by Thermogravimetric analysis (TGA) technique. The aim of this study is trying to understand the hydration kinetics of ternary blended cements.

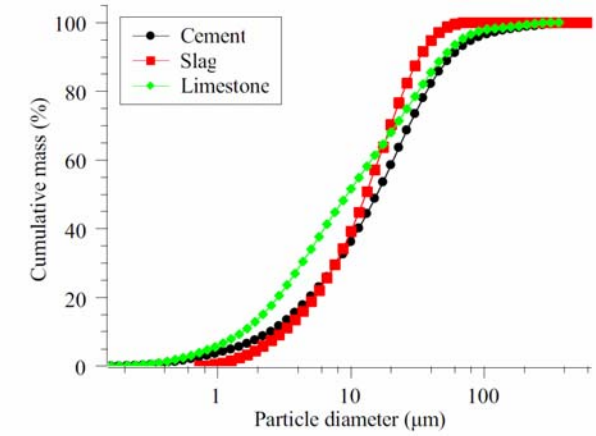

Figure 1 Particle size distribution of raw materials.

2. Experiments

2.1. Raw materials

Three materials, i.e. Portland cement (P in short), grand granulated Blast-furnace slag (B) and Limestone power (L), were chosen as the raw materials in this research. Ordinary Portland cement (OPC) was CEM I 52.5 complying with the European standard EN 197-1 (2000) (EN 197-1, 2000). Slag was offered by ORCEM company, with a hydraulic modulus (C+A+M/S) 1.66, which is higher than the minimum 1.0 according to German specification (H. F. W. Taylor, 1997). Limestone powder was produced from carboniferous limestone with a high purity of 98.3% $CaCO_3$ (by mass) quantified by TGA technique.

The chemical compositions of cement, limestone powder and slag are listed in Table 1. Fig. 1 shows the cumulative particle size distribution (PSD) curves of the three materials measured by laser diffraction method.

2.2. Mix design of pastes

In order to have references of neat Portland cement and binary blended cements, four groups of pastes were designed as follows:

1. PC: 100 wt% Portland cement.
2. PL: 10 wt% limestone powder blends with 90 wt% Portland cement.
3. PB: 30 wt% Portland cement blends with 70 wt% slag.
4. PBL: 10 wt% limestone and 60 wt% slag blended with 30 wty% Portland cement.

The water to powder ratio (w/p) of the four groups of mixes was constantly fixed at 0.40, i.e. 1.00 g solid material(s) was mixed with 0.40 g water.

The mixing procedure was taken from European standard EN 196-1:2005 with the consideration of the addition of slag and limestone. First, slag and/or limestone powder were/was added and mixed at low speed for two minutes to well disperse the slag and/or limestone powder in cement. Later, the mixing procedure was strictly carried out as described in EN 196-1:2005. For each sample, the well mixed paste was cast in a sealed plastic cylinder bottle with a volume of 90 cm^3. The sealed paste was rotated at a speed of 2.5 revolutions per minute in a room with temperature 20°C for 24 hours to avoid bleeding. Later the sample was cured at the same temperature till each due curing age. The curing age was scheduled as 1, 3, 7, 14 and 91 days counted exactly from the start point of casting.

Table 1 Chemical compositions of raw materials (wt%).

	Cement (P)	Limestone (L)	Slag (B)
CaO	63.95	55.05	38.14
SiO_2	20.29	0.8	35.82
Al_2O_3	4.52	0.17	12.05
Fe_2O_3	2.53	0.1	0.41
MgO	2.22	0.5	9.37
K_2O	0.94	/	0.48
Na_2O	0.2	/	0.16
SO_3	3.35	/	1.76
C_3S	59	/	/
C_2S	12.6	/	/
C_3A	8.01	/	/
C_4AF	9.4	/	/

2.3. Sample preparation **and** ***test methods***

When each due curing age was reached, the hydrating sample in the sealed plastic bottle was cracked into small pieces (around 1 cm^3) and immediately immersed in liquid nitrogen (-195 °C) for 5 minutes to stop the ongoing hydration (Guang Ye, 2003). Later, the frozen sample was placed in a freeze-dryer in which the temperature and vacuum were kept at -20°C and as low as 10^{-1} Pa, respectively, therefore, passing directly from solid to gaseous state, the free water was sublimed in the process of lyophilization (B Kolani et al., 2012). The water loss during the drying process of each sample was weighed approximately every 24 hours until a stable mass loss of 0.01%/day was reached.

The procedure of grinding sample for X-ray diffraction measurement was taken from the work of (Lieven Machiels, 2010). A representative amount of each dried sample (50-100 g) was crushed by hand in a porcelain mortar, and then passed through a sieve with aperture sized at 500 μm. The crushed sample was ground further by wet milling in a McCrone Micronizing mill, avoiding the amorphization of hydration products during the grinding process.

The mineralogy of samples was determined by quantitative X-ray powder diffraction analysis (QXRPD, Philips PW1830). Diffraction patterns were measured in 2θ range of 10-70° using CuKα radiation of 45 kV and 30 mA, with a 0.02° step size and step time of 2 s.

Quantitative results were obtained adopting the Rietveld method (H.M. Rietveld, 1966, 1969), using the “Topas Academic” software (A. A. Coelho, 2004). A fundamental parameter approach was used, meaning that instrumental contributions to the peak shapes were calculated directly (R. W. Cheary et al., 1992) and the standard parameters such as cell parameters, crystallite size, lattice strain, diffraction optical effects and background were refined.

The EDTA (Ethylenediaminetetraacetic Acid) selective dissolution method applied in this research was taken from (Guang Ye, 2006) based on (J.S. Lumley et al., 1996, Karen Luck et al., 1987), aiming to quantify the unreacted slag in blended cement pastes. Three possible error sources were considered. (1) Raw materials of cement and limestone powders were dissolved by EDTA solution using the same procedure as for real samples, aiming to find out the exact proportion of undissolved cement and limestone in EDTA solution. (2) Raw material of slag was dissolved by EDTA solution, quantifying the undissolved proportion of slag. (3) The hydrotalcite in the residue, the amount was quantified by XRD/Rietveld experiment when analyzing the hydration products of each paste.

As soon as the original unreacted mass of slag in a sample is obtained by EDTA experiment, the degree of hydration of slag is readily calculated as the unreacted amount of slag relative to the original.

The amount of $CaCO_3$ in the hydrating pastes was quantified by TGA/DTA method. The freeze died samples were first ground to small particles and passed through a sieve with aperture sized at 90 µm. Later, about 40 mg of the ground powder was exposed under an inert atmosphere (nitrogen) to increasing temperatures, ranging from 20 till 1100 °C at a rate of 10 °C/min (TA Instruments 2950). However, only the data points lower than 900 °C were analyzed in this research due to crystallization of hydrated compounds occurred at higher temperatures (R Vedalakshmi et al., 2003).

For the interpretation of the TGA experimental results, it is assumed that in this research the evaporable water is driven off at temperatures lower than 145 °C, as researchers confirmed that adsorbed water can be lost between temperature 105 °C and 145 °C and chemically bound water of hydration products may be lost even at temperature lower than 105 °C (De Weerdt, 2011). Mass loss between 400 °C and 550 °C is mainly caused by the decomposition of hydration product $Ca(OH)_2$, while that during the temperature range of 600-850 °C (Carlos Rodriguez-Navarro et al., 2009) represents the decomposition of $CaCO_3$ resulting in escaping CO_2.

The exact temperature ranges of decomposition of $Ca(OH)_2$ and $CaCO_3$ were determined by their corresponding DTG curves. In addition, the water loss during the decomposition temperature range of $Ca(OH)_2$ and $CaCO_3$ was removed by a so-called MARSH function embedded in the NETZSCH Proteus Thermal Analysis software. Since $Ca(OH)_2$ was only formed by the hydration of cement clinker, its amount was normalized by the mass of original cement in order to make comparison among the four groups of samples. As already mentioned in the determination of original mass of slag using EDTA test, the original mass of cement in each sample was quantified by TGA test, by subtracting the total bound water in each sample and then calculating the mass of cement according to the mix proportion.

3. Results and discussion

In order to better interpret the XRD/Rietveld results of cement clinker, amounts of C_3S and C_2S were summed together as calcium silicate phases and expressed by % of the original mass. In the same way, the amounts of C_3A and C_4AF were summed as calcium alumina phases.

3.1. Kinetics of calcium silicate phases

Fig. 2 shows the content of calcium silicate phases of samples at different ages quantified by XRD/Rietveld method. The hydration of calcium silicate phases in all pastes proceeded very fast in the first 7 days, e.g. the original content of calcium silicate phases in the raw material cement was 74.49% (by mass) tested by XRD/Rietveld analysis, it decreased to 38.76% at 7 days and 32.71% after 91 days of hydration in PBL paste. As for PC, PL and PB, the corresponding values decreased from the original 74.49% to 20.91%, 18.42% and 30.33% at 91 days, respectively.

For cement pastes containing slag, i.e. PB and PBL, the amount of unreacted calcium silicate phases was constantly higher than that of PC and PL pastes over the whole age, showing the relatively slow hydration of calcium silicate phases in PB and PBL pastes, indicating that the hydration of calcium silicate phases was suppressed by the presence of slag. This is completely different from the observation of Seiichi Hoshino et al. (Hiroshi Hirao, et al., 2006), which claims that the hydration of C_3S in binary (slag:cement:water = 0.4:0.6:0.3, by mass) and ternary (slag:cement:limestone:water = 0.4:0.6:0.04:0.3, by mass) slag blended cement pastes was accelerated by slag up to 28 days of hydration. However, the experimental investigation of Kocaba (Vanessa Kocaba, 2009) shows that the substitution of cement by slag seems to result in a delay in the hydration of belite in the first days.

Comparing the content of calcium silicate phases in PL paste to that of PC paste, it is clear that the presence of limestone accelerated the hydration of calcium silicate phases at early age. However, the acceleration effect of limestone on hydration of calcium silicate phases did not occur in PB and PBL pastes, since the content of calcium silicate phases in PB and PBL did not show much difference over the whole curing age except for the value at 1 day.

As for the combination of limestone and slag in the ternary blended cement paste, i.e. PBL, the hydration of calcium silicate phases was slightly hindered by the presence of limestone at early age (less than 3 days) compared with PB paste, since there was 53.99% and 60.57% unreacted calcium silicate phases in PB and PBL pastes at 1 day, respectively. Considering the accuracy of XRD/Rietveld analysis, we did not observe distinct difference of kinetics of calcium silicate phases between PB and PBL pastes in later ages, i.e. after 3 days of curing.

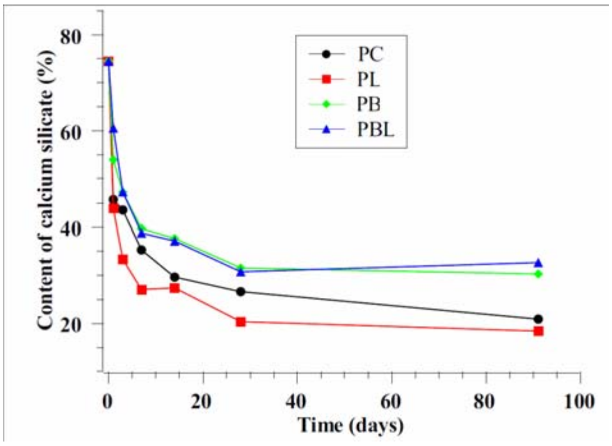

Fig. 2 The evolution of calcium silicate phases of all pastes measured by XRD/Rietveld method.

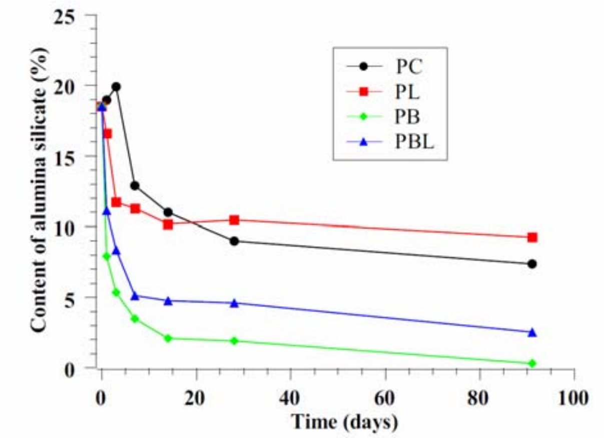

Fig. 3 The evolution of calcium silicate phases of all pastes measured by XRD/Rietveld method.

3.2. Kinetics of calcium alumina phases

Fig. 3 demonstrates the amount of calcium alumina phases of all samples from start of mixing to 91 days of hydration quantified by XRD/Rietveld analysis. Similar to the case of calcium silicate phases, the hydration of calcium alumina phases proceeded fast in the first 14 days. Calcium alumina phases of all blended pastes, i.e. PL, PB and PBL pastes, showed faster hydration kinetics compared with that of PC paste over the whole tested age, with the exception of PL paste after 14 days, for the ratio of unreacted calcium alumina phases in PL paste was constantly higher than PC paste after 14 days of hydration.

The presence of slag significantly enhanced the hydration of calcium alumina phases at both early and late ages. Although the addition of limestone in PL accelerated the hydration of calcium alumina phases up to 14 days compared to that of PC paste, the combination of limestone and slag in PBL paste showed distinct negative influence on the hydration kinetics of calcium alumina phases, as the content of calcium alumina phases in PBL paste was constantly higher than that in PB paste at all testing ages.

3.3. Degree of hydration of cement clinker in all pastes

The term degree of hydration of cement is traditionally defined as the ratio between the amount of cement that has hydrated at time *t* relative to the its original amount (Klaas van Breugel, 2006). In this research, the original content of clinker (C_3S + C_2S + C_3A + C_4AF) of cement quantified by XRD/Rietveld analysis was 92.98% (by mass). As the amount of other components of cement was small (7.12%) and difficult to be quantified by XRD/Rietveld, we focused on the hydration of clinker instead of the whole cement. For this reason, we defined a term degree of hydration of clinker. It is mathematically defined as the ratio of *hydrated amount of clinker* at time *t* to *the original amount*, which approximately represents the degree of hydration of cement if not exactly.

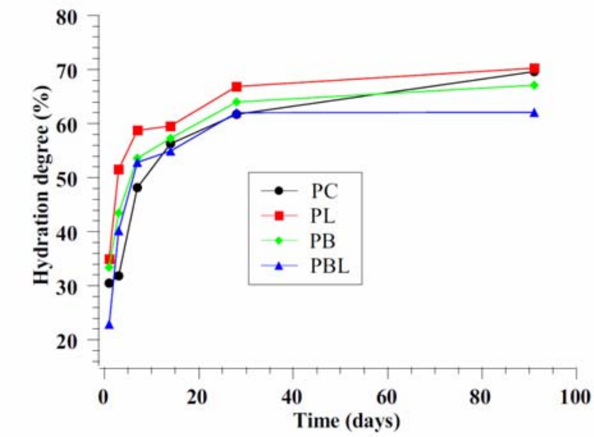

Fig. 4 Degree of hydration of clinker in four pastes at different curing ages.

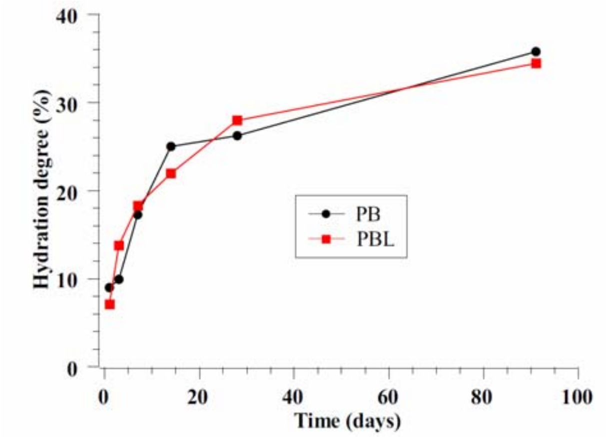

Fig. 5 Degree of reaction of slag in PB and PBL pastes at different ages.

Fig. 4 plots the degree of hydration of cement clinker in all samples from 1 day to 91 days of hydration. Most of the hydration of cement occurred at early age, e.g. at least 22% of clinker of PBL paste reacted after 1 day of hydration and as high as 59% of clinker of PL reacted within 14 days. Hydration of cement clinker at early ages, i.e. less than 14 days, were accelerated by the presence of slag and/or limestone except for the value of PBL at 1 day. Hydration of cement clinker in all blended pastes (PL, PB and PBL) after 14 days proceeded noticeably slow compared with that within the first 14 days. The hydration of clinker in PC paste was relatively faster than the three blended cement pastes at late age, i.e. after 28 days.

It is clear that the single addition of limestone accelerated the hydration of cement clinker over the whole curing age. The acceleration effect was typically strong in the first 14 days, which is confirmed by the fact that the degree of hydration of clinker of PL paste was much higher than the corresponding PC up to 14 days of curing age. However, the degree of hydration of cement clinker in PC paste finally reached almost the same level of PL paste after 91 days of hydration.

Compared with PC paste, the single addition of slag in the PB paste, i.e.70% of cement replaced by slag, exhibited positive influence on the hydration kinetics of the cement clinker. The degree of hydration of cement clinker in PB paste was higher than that of PC paste at all tested ages except for 91 days, showing the acceleration effect on hydration of cement clinker caused by slag. However, the acceleration effect brought by slag in PB was not as strong as that by limestone in PL, as the degree of hydration of cement clinker in PL is always higher than that in PB at all tested ages.

In terms of the hydration kinetics of cement clinker, the degree of hydration of cement clinker in PBL paste is more complex compared with any other paste in this study. Degree of hydration of cement clinker in PBL paste was the lowest at 1 day among the four pastes, i.e. only 22.88% of clinker in PBL was hydrated at 1 day, which was significantly lower compared with other pastes. Compared with the acceleration effect on hydration of cement clinker brought by single addition of limestone or slag, i.e. PB or PL paste, the combination of limestone and slag in PBL slightly but clearly hindered the hydration of clinker at 1 day.

However, the result shows an obvious acceleration effect on hydration of cement clinker in PBL paste during the curing age from 1 to 14 days, e.g. 40.18% and 52.81% of clinker in PBL paste was hydrated after 3 and 7 days of hydration, respectively, which were both higher than the corresponding values of PC paste even considering the accuracy of XRD/Rietveld analysis. The hydration of cement clinker in PBL paste had no progress over the curing age from 28 to 91 days, as the degree of hydration of clinker only changed from 61.99% to 62.08% at the two ages, while the corresponding values of PC at these two ages increased from 61.68% and 69.59%, respectively. The degree of hydration of cement clinker in PBL paste at 91 days is also the lowest compared with the other three types of pastes, i.e. PC, PL and PB.

Based on the comparison results with reference pastes, i.e. PC, PL and PB, the combination of limestone and slag in ternary blended cement paste PBL paste did not show synergistic effect on the hydration kinetics of cement clinker. Instead, the hydration kinetics of cement clinker in PBL was the lowest at both 1 and 91 days comparing with any other type of paste in this research.

As revealed in the analysis of hydration of calcium silicate phases and calcium alumina phases, the relatively low degree of hydration of clinker in PBL is the combination of negative influence brought by slag and limestone on hydration of calcium silicate phases and calcium alumina phases, respectively.

3.4. Degree of reaction of slag in all pastes

Fig. 5 presents the degree of reaction of slag in slag blended pastes (PB and PBL) measured by EDTA selective dissolution method. The degree of reaction of slag in both PB and PBL pastes was only about 8% and 35% of slag reacted after 1 and 91 days of hydration, respectively. Both values were generally much lower than that of cement clinker of all pastes at all ages. However, curves in Fig. 5 show an increasing trend of slag hydration at later curing age for both PB and PBL pastes comparing to the relatively flat curves of cement clinker (Fig. 4), which is readily interpreted as that slag is a latent cementitious material with most part of reaction undergone at later age.

The degree of reaction of slag tested by EDTA method in this research agrees well with the data from literature (K. Luke, et al., 1988), as summarized by Taylor (H. F. W. Taylor, 1997) that at water to solids ratios of 0.4-0.6 and 20 °C 30-55% of the slag reacts in 28 days and 45-75% in 1-2 years. G. Ye (Guang Ye, 2006) also reported similar results using SEM image analysis and EDTA method.

It is worthwhile to note that there was already a noticeable amount of slag reacted even just after 24 hours of hydration. Using SEM image analysis, Breugel et al. (K. van Breugel, et al., 2006) performed a series of experiments on slag blended cement pastes to quantify the degree of reaction of slag. In their results, two slag pastes with similar slag replacement level as used in this research (70% of cement replaced by slag) and two water to powder ratios (0.4 and 0.5) show degree of reaction 8.0% and 7.3% at 1 day, respectively, which agree very well with the results of this research, indicating the reliability of EDTA method and confirming the noticeable amount of slag reaction even within 24 hours. In addition, their results revealed that the degree of reaction of slag at 1 day increases as slag replacement level decreases.

As for the influence of limestone addition on reaction kinetics of slag in PBL, there was no fixed trend between the degrees of reaction of slag in PB and PBL pastes as shown in Fig. 5, since the degree of reaction of slag in PBL was only slightly higher than that of PB paste at the ages of 3 and 28 days. Limited results of Seiichi et al. (Hiroshi Hirao, et al., 2006) showed that 4% of limestone addition did not have significant influence on the reaction kinetics of slag in ternary blended cement paste, in which the paste was mixed at the ratio of cement:slag:limestone:water = 60:40:4:30 and cured at 20 °C.

3.5. Content of calcite measured by TGA

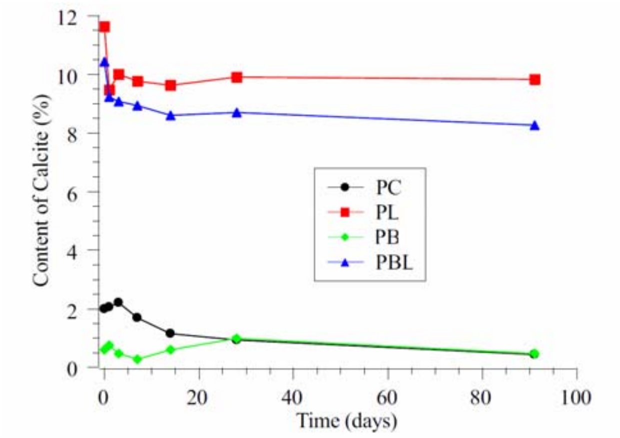

Fig. 6 Content of $CaCO_3$ measured by TGA.

Fig. 6 shows the content of $CaCO_3$ of all four pastes from 0 to 91 days of hydration quantified by TGA experiments. It has to be noted that the cement (CEM I 52.5) used in this research contained 2.0% $CaCO_3$ (by weight) tested by TGA. This amount of $CaCO_3$ in CEM I 52.5 is allowed according to the European standard (EN 197-1). TGA analysis also shows that 98.3% of limestone in this research was $CaCO_3$. Since the content of $CaCO_3$ in cement is at the same order of magnitude of that contained in limestone (10%), it should be considered in the content of $CaCO_3$ that was analyzed by TGA test during all testing ages. According to the content of $CaCO_3$ in raw materials, i.e. cement and limestone, the original mass of $CaCO_3$ in PL and PBL pastes was 90%*2.0% + 10%*98.3% = 11.63% and 30%*2.0% + 10%*98.3% = 10.43% of the total original solid raw materials, respectively.

Compared with the relatively stable content of $CaCO_3$ in PC paste over the whole age, the content of limestone in PL sharply decreased from the original 11.63% of all solid raw materials to 9.47% after 1 day of hydration, and fluctuated afterwards between 9.63-10%. Similar trend of limestone change also occurred in PBL paste. Over the whole curing age of 91 days, the content of $CaCO_3$ reacted was approximately 1.6-2.2% of the total solid raw materials except for PB paste that had almost no $CaCO_3$ in raw materials (0.6%), which generally agrees with the reported values (H. F. W. Taylor, 1997, V.S. Ramachandran, 1988) that the maximum quantity of $CaCO_3$ that can react appears to be 2-3% with most cements.

The only difference of the limited $CaCO_3$ reaction among PC, PL and PBL pastes is that the main part of $CaCO_3$ reaction occurred at the very early age (1 day) in the cases of PL and PBL pastes, which could be caused by the relatively large supply of limestone in PL and PBL pastes. However, the presence of $CaCO_3$ from raw cement in PC also resulted in a detectable amount of $CaCO_3$ reacted with clinker within the first 14 days of hydration.

4. Conclusions

In this study, the kinetics of four groups of cement pastes, i.e. PC, PL, PB and PBL pastes, were studied by a serials of systematic experiments. According to the analyzed results, the main conclusions are drawn as follows.

1. The hydration of calcium silicate phases of cement in pastes was enhanced by the presence of limestone, but hampered by the addition of slag.

2. The hydration of calcium alumina phases of cement was greatly accelerated by the addition of slag, it was also enhanced by the presence of limestone in binary blended limestone cement paste at early age. However, the coexistence of limestone with slag in ternary blended cement paste shows that limestone restrained the hydration of calcium alumina phases of cement.
3. The degree of hydration of cement clinker was distinctly accelerated by the single addition of slag or limestone within 91 days of hydration. The coexistence of slag and limestone in ternary blended cement accelerated the hydration of cement clinker between the curing ages from 1 to 14 days, but lowered the degree of hydration of clinker after 91 days of hydration compared with other pastes.
4. The degree of reaction of slag in blended cement pastes was about 8% and 35% after 1 and 91 days of hydration, respectively, and it was almost not influenced by the addition of limestone.
5. TGA tests show that a small amount of limestone, i.e. around 2% of the total solid raw materials, was reacted in pastes, mainly at early age.

Acknowledgements

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