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Characteristics of Portland blast-furnace slag cement containing cement kiln dust and active silica

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Abstract This investigation dealt with the effect of active silica, silica fume (SF) or rice husk ash (RHA), on the mechanical and physico-chemical characteristics of the hardened blended cement pastes made of Portland blast-furnace slag cement (PSC) containing cement kiln dust (CKD) cured under normal conditions. Two blends made of PSC and CKD, improved by SF and two blends made of PSC and CKD improved by RHA were investigated. Hardened blended cement pastes were prepared from each cement blend by using water/cement ratio (W/C) of 0.30 by weight and hydrated for various curing ages of 1, 3, 7, 28 and 90 days at the normal curing conditions under tap water at room temperature. Each cement paste was tested for its physico-chemical and mechanical characteristics; these characteristics include: compressive strength and kinetics of hydration. The phase composition of the formed hydration products was identified using X-ray diffraction (XRD) and differential thermal analysis (DTA). It was found that the partial substitution of PSC by 10% and 15% of CKD is associated with an increase in the rate of hydration and a subsequent improvement of compressive strength of hardened PSC–CKD pastes. In addition, the replacement of PSC, in PSC–CKD blends, by 5% active silica was accompanied by further improvement of the physico-mechanical characteristics of the hardened PSC–CKD pastes.

1. Introduction

Portland blast-furnace slag cement is a mixture of ordinary Portland cement and not more than 65 wt.% of granulated slag. It is generally recognized that the rate of hardening of slag cement is somewhat slower than that of ordinary Portland cement during the first 28 days but thereafter increases so that at 12 months the strengths become close to or even exceed those of Portland cement. The slag cement is more sulfate resistant than Portland cement. Granulated blast-furnace slag by itself is hydraulically very weak. Due to its glassy structure, a highly alkaline medium is required in order to disintegrate the silicate–aluminates network of the slag glass; the liberated free lime during the hydration of Portland cement clinker is normally used to provide this alkalinity (Wanga et al., 2010).

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The idea of adding slags and pozzolana such as fly ash, rice husk ash or silica fume to Portland cement concrete is widely practised because it helps to reduce cost and conserve energy resources and environment. Burning of rice husk ash at low temperature (450–600 °C) yields a silica ash consisting of 85–94% amorphous silica with high surface area (Ganesan et al., 2008; Chindaprasirt and Rukzon, 2008). Silica fume consists of 85–96% amorphous active silica with a specific surface area of 20–25 m^2/g.

Nataraja and Nalanda (2008) investigated a variety of slag, fly ash, and cement dust in the performance of industrial by-products in controlled low-strength materials. The object of study was to determine the effect on cement quality when low levels of by-product additives are incorporated into Portland cement. Blended/multi-blended cements based on industrial pozzolanic materials like fly ash, calcined clay, micro silica, granulated slag, etc., are the best examples of cementitious materials. This class of cements shows improved long-term strength and durability (Nochaiya et al., 2010). Mechanisms and kinetics of slag hydration in hydrated slag cements were discussed by Daimon (Daimon et al., 1980) and others (Lee et al., 2009). Slag grains develop membranes that control diffusion and densify the paste matrix that exhibits low permeability; $Ca(OH)_2$ is gradually consumed by slag grains and Mg content forms hydrotalcite.

The effect of CKD substitution instead of ordinary Portland cement OPC, blast furnace slag cement BFSC, and sulfate resistance cement SRC on the mechanical properties of some concrete mixes containing them, and also, the determination the optimum quantity of CKD which could be recycled in the manufacture of these types of cements were studied (Shoaib et al., 2000).

The utilization of CKD and some other industrial solid wastes in the field of cement industry and other building products was also reported (Abo-El-Enein, 1997, 2005).

Yajun and Cahydi (2003) studied the effects of 0–20% silica fume on microstructure and compressive strength of blended cement pastes; the strength of Portland cement paste was improved in the presence of silica fume (SF) as a result of interaction with lime and water to produce additional amounts of calcium silicate hydrates. In addition, the physico-mechanical characteristics of autoclaved blended cement pastes were improved by addition of silica fume as reported in an earlier publication (EL-Shimy et al., 2004). The hydraulic reactivity of rice husk ash was affected by thermal treatment leading to a type of active silica available for different application (EL-Hosiny et al., 1996).

The object of this work is to study the effect of partial substitution of PSC by CKD and active silica SF or RHA on the physico-chemical and mechanical characteristics of the hardened slag cement pastes.

2. Experimental

Portland blast-furnace slag cement (PSC) was obtained by mixing of 65% ordinary Portland cement (OPC) with 35% granulated blast-furnace slag (GBFS). Very fine powder of cement kiln dust (CKD) was supplied from Turah Cement Company, Egypt, and condensed silica fume (SF) was provided by Ferro-silicon alloys Company, Kom-Ombo, Aswan, Egypt. Rice husk ash (RHA) was obtained from burning of rice husk in an electric furnace at 600 °C for 2 h. The chemical oxide composition of these starting materials is given in Table 1.

The ingredients of the different mixes were mixed for one hour using a ball mill using three balls to attain complete homogeneity. The samples were kept in airtight containers until the time of paste preparation. The mix composition of the different mixes is given in Table 2.

The different blended cement pastes were prepared from each cement blend by using the initial water/cement (W/C) ratio of 0.30, and then molded into cubic steel molds having the internal dimensions $2 \times 2 \times 2$ cm. Immediately after molding, the molds containing specimens were cured in a humidity chamber at 100% relative humidity at a constant temperature 23 ± 2 °C for the first 24 h. The cubic specimens were demolded and then cured under tap water until the desired time of testing, such as 3, 7, 28 and 90 days were reached.

At each hydration time, all pastes were tested for their compressive strength, bulk density, total porosity, phase composition of the formed hydration products and hydration kinetics in order to study the effect of partial substitution of slag cement by CKD and/or SF or RHA on the physico-mechanical characteristics of Portland blast-furnace slag cement pastes.

3. Results and discussion

3.1. Compressive strength

The results of compressive strength kg/cm^2 of the various blended cement pastes are given in Table 3 at all ages of hydration.

Table 2 Mix composition of the various blended cements.

	Mix No.						
	M *control*	M-a	M-b	M-c	M-d	M-e	M-f
PCS%	100	90	85	85	80	85	80
CKD%	0	10	15	10	15	10	15
SF%	0	0	0	5	5	0	0
RHA%	0	0	0	0	0	5	5

Table 1 Chemical oxide composition of starting materials.

Materials	Oxide (%)									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	L.O.I*	Cl^-	Free CaO
PSC	21.81	6.18	3.25	60.24	2.14	2.43	0.53	0.11	2.39	0.007	2.70
CKD	8.17	1.90	1.12	44.32	1.61	4.02	2.43	11.13	15.63	6.71	15.9
SF	96.10	0.52	0.70	0.21	0.48	0.10	0.31	0.49	1.14	0.00	0.43
RHA	95.6	0.3	0.3	0.4	0.3	–	0.2	1.3	1.6	1.0	–

* L.O.I = Loss of Ignition.

Table 3 Compressive strength, kg/cm^2 of the hardened cement pastes made of PSC, PSC–CKD and PSC–CKD–SF or RHA blends after curing up to 90 days.

Days	Mix No.						
	M *control*	M-a	M-b	M-c	M-d	M-e	M-f
1	221.85	291.25	227.30	316.20	300.70	318.75	305.90
3	349.25	379.30	377.90	426.15	387.5	402.90	371.65
7	453.10	484.40	465.75	555.90	489.00	524.30	479.75
28	613.00	690.15	652.85	731.85	637.5	703.00	676.50
90	717.50	799.35	757.00	823.65	777.15	797.35	755.75

The results of Table 3 indicated that the compressive strength increases with the increase of curing age for the hardened PSC–CKD blended cement pastes. Therefore, larger amounts of cement hydrates and more cementing (strength-producing) materials are formed with increasing age of hydration; these hydrates act as binding centers between the unhydrated parts of cement grains. At the same time, the initial formation of hydration products and their deposition within the pore system (originally water – filled spaces) of the hardened paste lead to a continuous decrease in the total porosity of the hardened paste with increasing age of hydration. In addition, the increased values of compressive strength with the presence of CKD is mainly due to the enhanced activation of the granulated slag fraction of slag cement with the alkalis present in CKD leading to the formation of excessive amounts of hydration products; these hydrates act as binding centers between the unhydrated parts of cement grains leading to relatively higher strength values. This positive effect is actually valid for the hardened PSC–CKD pastes having CKD contents up to 10% Mix (M-a). However, for the PSC–CKD blends containing higher contents of CKD a negative effect on the mechanical properties and durability is obtained at later hydration ages; this is due to the higher contents of alkalis, sulfates and chlorides of the blends having relatively higher CKD contents. Therefore, the optimum partial substitution of PSC by CKD is mainly restricted to 10%.

The results of compressive strength of blended cement pastes made of PSC–CKD–SF blends of Mixes (M-c and M-d) are given in Table 3. The results indicated that the compressive strength increases with the increase of curing age. Evidently, the substitution of 5% PSC by SF in Portland slag cement containing 10% and 15% CKD, Mixes (M-c and M-d), however, leads to an improvement in strength values as compared with those of PSC at all ages of hydration. The role of silica fume in the improvement of the strength results is mainly due to the interaction of the reactive silica fume with the free lime and alkalis released from OPC clinker and CKD hydration. This leads to the formation of additional amounts of calcium silicate hydrates which results in an increase in the total content of binding centers in the specimens leading to an increase in the strength values of the hardened PSC–CKD–SF pastes. Again, the hardened paste made of PSC–CKD blend containing 10% CKD and 5% SF, Mix (M-c), possesses the highest strength values. This indicates that the optimum composition of PSC–CKD–SF blend is represented by Mix (M-c).

The results of compressive strength of the PSC–CKD–RHA blended cement pastes, made of Mixes (M-e and M-f), indicate that the compressive strength increases with the increase of curing age. Obviously, substitution of 5% PSC by SF, as an active silica, in PSC–CKD blends (M-a and M-b) leads to an improvement in the strength values at the early ages of hydration as compared with those of PSC–CKD blends.

3.2. Kinetics of hydration

3.2.1. Chemically combined water content (Wn, %)

The results of chemically combined water content (Wn, %) of the various blended cement pastes investigated are given in Table 4 at all curing ages.

The results of Table 4 show that the chemically combined water content increases with increasing age of hydration for all of the blended cement pastes investigated. When Portland blast-furnace slag cement (PSC) is mixed with water, the Portland cement fraction is the first to hydrate to give the initial hydration products, mainly as calcium silicate hydrates and free calcium hydroxide. Then, the free calcium hydroxide liberated as a result of hydration of Portland cement clinker acts as an activator for granulated slag leading to the formation of hydration products similar to those of Portland cement; therefore, $Ca(OH)_2$ causes a sort of breaking of the silica framework of granulated slag leading to a continuous hydration of slag grains. From the results of Table 4 the chemically combined water content (Wn, %) increased with the presence of CKD at all ages of hydration with optimum 10% CKD content; these results confirm the variation of compressive strength values.

Evidently, the blended cement paste made of Mix (M-c) gives the highest Wn-values as compared with the pastes made of Mixes (M *control*) and (M-d). Therefore, silica fume, due to its very high surface area and very small grain size, interacts rapidly with the free calcium hydroxide, liberated from clinker hydration, leading to the formation of excessive amounts of calcium silicate hydrates (CSH). Also the results show that the variations of Wn – values with increasing age of hydration are almost parallel to the changes in the compressive strength values shown in Table 3.

Table 4 Chemically combined water content of the hardened cement pastes at different ages of hydration.

Days	Chemically combined water content (Wn, %)						
	Mix No.						
	M *control*	M-a	M-b	M-c	M-d	M-e	M-f
1	9.89	10.13	10.06	10.12	10.03	9.98	10.00
3	12.51	13.84	13.75	14.13	13.95	13.79	13.81
7	14.16	15.61	15.25	15.90	15.75	15.66	15.40
28	16.31	17.20	16.90	16.77	16.53	16.53	16.42
90	17.85	18.98	18.70	18.60	17.96	18.29	17.88

Table 5 Free lime content of the hardened blended cement pastes at different ages of hydration.

Days	Free lime content (CaO, %)						
	Mix. No.						
	M *control*	M-a	M-b	M-c	M-d	M-e	M-f
1	6.17	6.60	6.23	6.65	6.55	6.61	6.45
3	7.70	7.80	7.72	7.95	7.85	7.85	7.77
7	8.05	8.11	8.02	8.62	8.54	8.50	8.33
28	7.54	7.91	7.60	8.12	8.08	8.02	7.90
90	7.37	7.88	7.51	7.98	7.65	7.88	7.50

Table 6 Bulk density and total porosity of blended cement pastes made of Mixes (M *control*, M-a and M-b) at different hydration ages.

Days	Mix. No.					
	Bulk density, g/cm^3			Total porosity, %		
	M *control*	M-a	M-b	M *control*	M-a	M-b
1	2.165	2.173	2.170	27.64	26.95	25.73
3	2.169	2.182	2.177	25.87	24.45	23.28
7	2.185	2.195	2.186	22.91	21.36	20.14
28	2.190	2.202	2.186	21.61	20.47	19.80
90	2.200	2.210	2.223	19.62	19.45	19.25

The results in Table 4 indicate that blended cement pastes made of slag cement admixed with both of CKD (10% and 15%) and RHA (5%) give higher Wn-values as compared with those made of slag cement containing CKD alone. The additional formation of (C–S–H) during the interaction between RHA, as an active silica, with free lime released accounts for higher strength values of the hardened PSC–CKD–RHA paste.

3.2.2. Free lime content (CaO, %)

The results of free lime contents (CaO, %) of the hardened blended cement pastes made of all mixes are given in Table 5 as a function of curing age.

From the results of the Table 5 the free lime content increases with increasing age of hydration during the early ages and up to 7 days for all of the hardened PSC–CKD blended cement pastes; this was followed by a gradual decrease in the free lime content up to 90 days of hydration. In fact, the free lime content is released as a result of hydration of Portland cement clinker fraction of slag cement; while the activated hydration of granulated slag leads to a consumption of free lime. Therefore, the values of free lime contents reported in Table 5 represent a net effect between the amounts of free lime liberated by clinker hydration and the free lime consumed as a result of activation of slag hydration.

The results of free lime contents given in Table 5 indicate that the free lime content also increases with increasing age of hydration during the early ages up to 7 days for the hardened PSC–CKD–SF and PSC–CKD–RHA blended cement pastes; this was followed by a gradual decrease in the free lime content up to 90 days of hydration. Again, this indicates that a net increase in the free lime content of these pastes is obtained at the early hydration ages (up to 7 days) which was followed by a net decrease in the free lime content at the later ages of hydration for the hardened PSC–CKD–SF and PSC–CKD–RHA pastes.

3.2.3. Bulk density and total porosity

The results of bulk density and total porosity for hardened PSC–CKD pastes are given in Table 6.

The bulk density increases and total porosity decreases with curing time up to 90 days for all blended cement pastes. Evidently, the addition of CKD to PSC gives high bulk density and low total porosity at all ages of hydration. As the hydration proceeds the hydration products fill parts of the total pore volumes; therefore, the bulk density increases and the total porosity decreases.

3.2.4. Phase composition of the formed hydrates

The phase composition of the formed hydration products was studied by means of X-ray diffraction (XRD) and differential thermal analysis (DTA).

X-ray diffractograms of the hardened blended cement pastes shown in Fig. 1 for (PSC *control*), and Fig. 2 for Mix (M-a) contain of PSC + 10% CKD indicated that the main phases identified are calcium silicate hydrates (CSH), calcium hydroxide (CH) and gehlenite-like calcium aluminosilicate hydrate (C_2ASH_8) as well as calcium carbonate (CC^-).

The diffractograms of (Fig. 2) obtained for the PSC–CKD paste made of Mix (M-a) indicated the formation of the same hydration products shown in Fig. 1 for the hardened PSC paste (M *control*) with only one main basic difference, namely, the increased intensity of the peaks characterizing calcium hydroxide in the hardened PSC–CKD paste of Mix (M-a). This indicates the larger amounts of free calcium hydroxide liberated from CKD in addition to the Portland cement fraction of slag cement (PSC).

Figs. 3 and 4 show the X-ray diffractograms of the formed hydration products obtained for PSC–CKD–SF and PSC–CKD–RHA pastes of Mixes (M-c) and (M-e), respectively. The main phases identified are calcium silicate hydrates (CSH), calcium hydroxide (CH), calcium carbonate (CC^-) and gehlenite-like calcium aluminosilicate hydrate (C_2ASH_8). The results of Figs. 3 and 4 are similar to those of the paste made of Mix (M-a), shown in Fig. 2, with an exception of

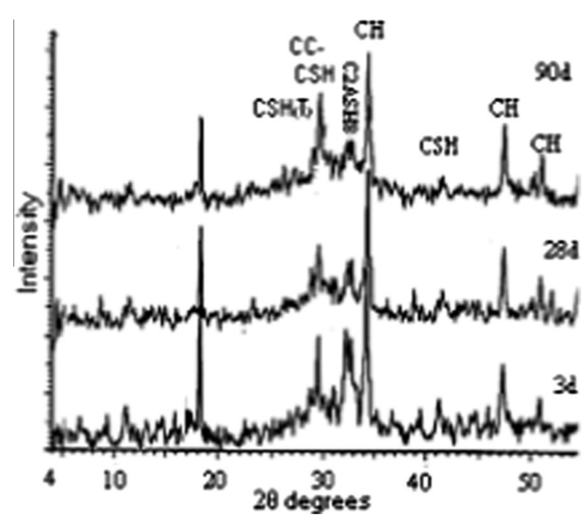

Figure 1 XRD pattern of hardened cement pastes of Mix (M *control*) curing after 3, 28 and 90 days.

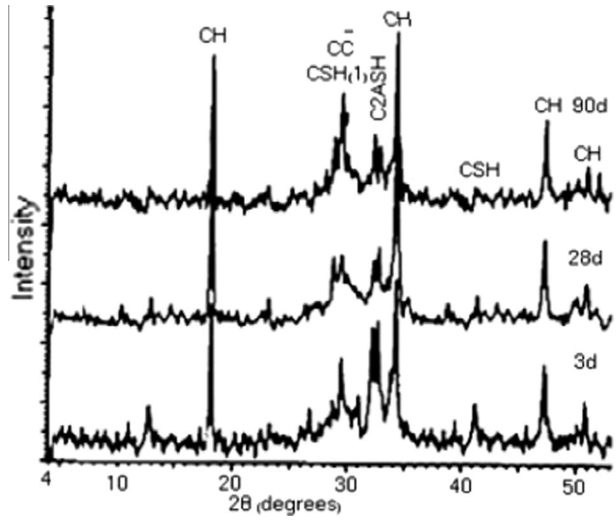

Figure 2 XRD pattern of the hardened cement pastes of Mix (M-a) curing after 3, 28 and 90 days of hydration.

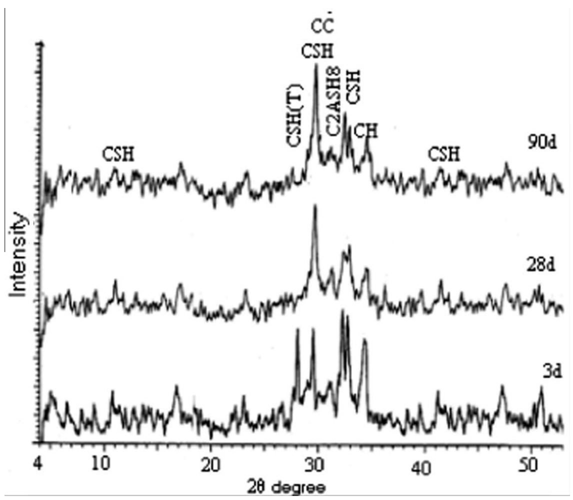

Figure 3 XRD patterns of the hardened cement pastes for Mix (M-c) curing after 3, 28 and 90 days of hydration.

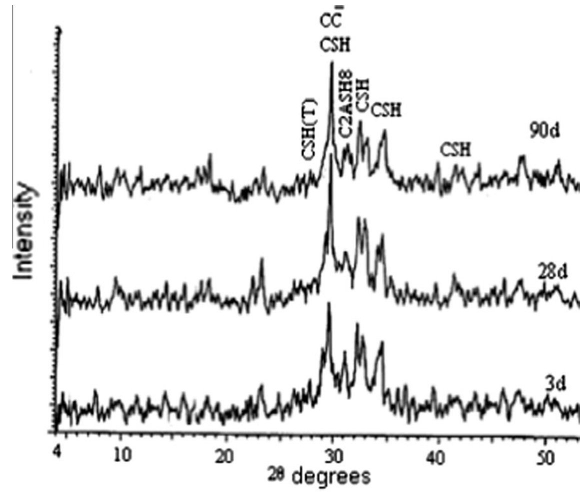

Figure 4 XRD patterns of hardened cement pastes of Mix (M-e) curing after 3, 28 and 90 days of hydration.

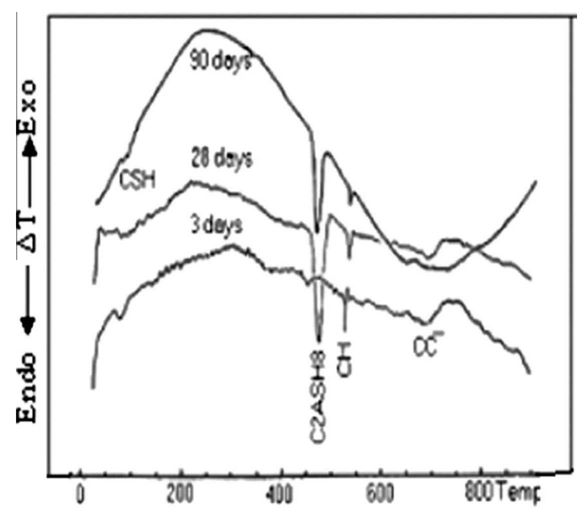

Figure 5 The DTA thermogram of the hardened cement paste Mix (M *control*) cured up to 90 days.

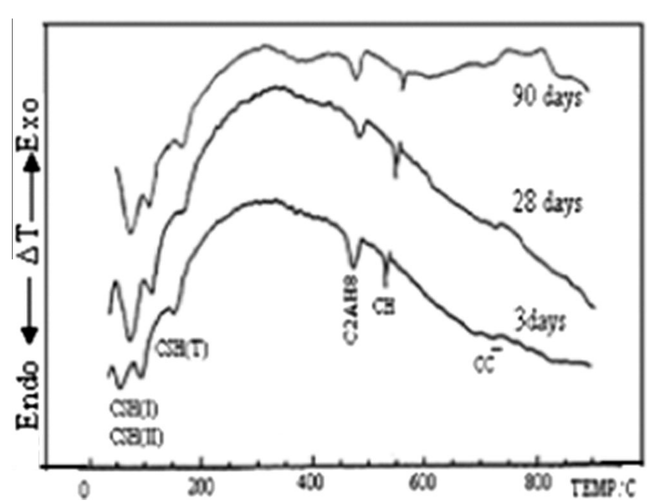

Figure 6 The DTA thermogram of the hardened cement pastes of Mix (M-e) cured up to 90 days.

the amount of free calcium hydroxide which is almost consumed as a result of its interaction with the active SF or RHA leading to the formation of excessive amounts of calcium silicate hydrates.

The results of DTA thermograms obtained for the hardened PSC paste of Mix (M *control*) are shown in Fig. 5. There appeared four endothermic peaks in the thermograms; these are located at 120, 450, 525 and 680 °C. The endotherms located at 120 and 450 °C are mainly due to the decomposition of calcium silicate hydrates (CSH) and gehlenite hydrate (C_2ASH_8), respectively; whereas the endotherms appeared at 525 and 680 °C are attributed to the decomposition of calcium hydroxide (CH) and the small amounts of calcium carbonate (CC^-), respectively. Evidently, the peaks characterizing the (CSH and C_2ASH_8) phases become more distinguishable after 28 and 90 days of hydration.

The results of DTA thermograms obtained for the hardened PSC–CKD–RHA paste of Mix (M-e) are shown in Fig. 6. This shows the presence of the six endotherms. These endotherms are located at 100, 150, 180, 470, 530 and 670 °C. The first three endotherms located at 100, 150 and 180 °C are mainly due to the removal of adsorbed water and the decomposition of the three types of calcium silicate hydrates, namely: high-lime calcium silicate hydrate (CSH-II), low-lime calcium silicate hydrate (CSH-I) and tobermorite-like calcium silicate hydrate (CSH-T), respectively. The two endotherms located at 470 and 530 °C are mainly attributed to the decomposition of gehlenite-like calcium silicate hydrate (C_2ASH_8) and calcium hydroxide (CH), respectively. The weak endotherm located at 670 °C is mainly attributed to the decomposition of calcium carbonate ($C\bar{C}$).

4. Conclusions

The main conclusion derived from this study is summarized as follows:

1. Addition of cement kiln dust (CKD) to Portland blast-furnace slag cement (PSC) leads to an improvement of the physico-chemical and mechanical properties of the hardened (PSC–CKD) pastes with an optimum constitution of PSC (90%)–CKD (10%) blend.
2. The partial replacements of (PSC) by active silica (SF or RHA) lead to an improvement of the physico-mechanical characteristics of the hardened PSC–CKD pastes made with the optimum constitution (PSC, 90% and CKD, 10%).
3. The results of hydration kinetics and phase composition of the formed hydrates could be related to the results of compressive strength of the various hardened cement pastes.

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