



Quantification of hydrated cement products of blended cements in low and medium strength concrete using TG and DTA technique

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Abstract

Pozzolanic reaction of blended cements cause pore refinement of microstructure of concrete and reduces the permeability. Different factors can influence the extent of reaction in concrete, such as type of cement, water–cement ratio, cement content, hydration time and type and replacement level of mineral admixture. Among them, the hydration time is the most important factor on the stability and the transformation of hydrated phases. In the present study using thermogravimetric analysis (TG/DTA), the extent of pozzolanic reaction of two blended cements such as Portland pozzolana cement (PPC), Portland slag cement (PSC) has been studied in low (20 MPa) and medium strength concrete (30 and 40 MPa). Three hydration times namely 28, 90 and 365 days were studied. $\text{Ca}(\text{OH})_2$ and other calcium hydrates content were estimated. The study reveals that in addition to hydration time, cement content and water–cement ratio in proportioning the concrete mixes also play an important role in determining the pozzolanic reaction. Reduction in calcium hydroxide, $\text{Ca}(\text{OH})_2$, content in PPC and PSC concrete confirms the occurrence of pozzolanic reaction. In 20 MPa concrete which is having low cement content has maximum calcium hydrate content than 30 and 40 MPa concrete. This is because of its permeable pore structure which facilitates more pozzolanic reaction to occur whereas in the case of 30 and 40 MPa concrete, the higher cement content and more dense pore structure restrict further reaction to proceed and thus reduce the formation of calcium hydrates in the pore structure. The water permeability studies at three curing periods viz. 7, 28, and 90 days also reveals that, in PPC and PSC concrete, the co-efficient of water absorption is less than OPC concrete in all the concretes studied and thus confirms that the reduced permeability of PPC and PSC concretes is mainly because of densification of pore structure by forming additional calcium hydrates.

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1. Introduction

Well-designed concrete attains strength only after hydration of cement. Because of permeability of concrete, all hydrated cement products are subject to attack by sulphates, chlorides, acids and less by

water. During hydration of ordinary Portland cement (OPC) concrete, compounds present in the cement, such as C_3S and C_2S react with water and form calcium silicate hydrates (C–S–H) and calcium hydroxide, $\text{Ca}(\text{OH})_2$. The concomittant presence of sulphate and chloride ions in soils and marine environments causes deterioration of reinforced concrete structures due to reinforcement corrosion and sulphate attack

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[1,2]. Compared to Portland cement, the durability of blended cements to sulphate and acidic environments is due to the combined effects of better impermeability at a given w/c ratio and reduced calcium hydroxide in the hydrated cement products. When mineral admixtures, such as fly ash and slag, which are aluminosilicates are added with cement, these react with $\text{Ca}(\text{OH})_2$ to form additional calcium silicate hydrates in the hydrated cement matrix. These additional hydrates increase the density of the matrix and refine the pore structure. This is called 'Pozzolanic effect or pore size refinement' of blended cements [3,4]. This makes the concrete less susceptible to deterioration by reducing the permeability of the concrete. Some authors report that mineral admixtures are finer than cement particles and improve the particle packing of cement paste, in particular, in the transition zone between aggregate and cement paste and fill the pores, thus reducing permeability. This is known as 'filler effect or grain size refinement' of blended cements [5]. The rate of hydration of cement may be determined either directly by microscopic examination of the hydrated material or indirectly from determination of combined water or changes in density. Thermogravimetric analysis (TG/DTA) can be used to determine the amount of the pozzolanic reaction and hydration of blended cement pastes [6] by estimating $\text{Ca}(\text{OH})_2$ content and calcium hydrates content [7–10]. The DTA curve shows a sharp endotherm between 450 and 520 °C due to the decomposition of $\text{Ca}(\text{OH})_2$ formed during the hydration. Hussain et al., conducted TG/DTA analysis on fly ash blended cement pastes after hydration for 180 days and reported that $\text{Ca}(\text{OH})_2$ content was reduced by 53% when compared to ordinary Portland cement paste [11]. Feldman et al., conducted TG/DTA analysis on fly ash blended cement pastes and Portland cement pastes and investigated the effect of w/c ratio and hydration time on the variation of $\text{Ca}(\text{OH})_2$ content [12]. The studies revealed that $\text{Ca}(\text{OH})_2$ decreased with w/c ratio and hydration time in blended cement paste whereas in the case of Portland cement it increased. Hubbert et al., estimated the C–S–H phase indirectly with hydration time using the molybdate method by estimating unreactive SiO_2 in the hydrated cement powder [13]. The studies revealed that in blended cement pastes the unreactive SiO_2 was in the range of 6–9% whereas in Portland cement it was 15%. Less unreactive SiO_2 indicates

more C–S–H gel formation in the blended cement matrix.

In the above studies, TG/DTA analysis were carried out only on cement pastes. But from the standpoint of impermeability and durability, the effects of the pozzolanic reaction are more important in concrete than in hydrated cement paste [14]. Because of microcracks in the transition zone the permeability of concrete is generally much higher than the permeability of cement paste. The process of pore size refinement and grain size refinement strengthen the transition zone, thus reducing the microcracking and increasing the impermeability of concrete. From the application point of view, studies in concrete are more realistic than in paste or mortar. The presence of sand particles will dilute the cement phase but this is the situation that happens in actual concrete structures.

The present studies were carried out to identify the extent of pozzolanic reaction in blended cements in low and medium strength concretes using TG/DTA. Water permeability characteristics were measured by an oven-drying method. Two types of blended cement, Portland pozzolana cement (PPC), and Portland slag cement (PSC) were used. Three concretes having 28 days compressive strength of 20, 30, and 40 MPa and having different pore structures were studied. The results are compared with concretes made with ordinary Portland cement (OPC).

2. Experimental

The mix proportions used for casting the concrete using three types of cements are given in Table 1. Number 43 grade ordinary Portland cement (equivalent to Type I of ASTM standard) conforming to I.S. 8119, Portland pozzolana cement conforming to I.S. 2340, and Portland slag cement conforming to I.S. 450 were used. In pozzolana and slag cements, Portland cement was replaced with 25% fly ash and 50% slag, respectively. The chemical composition of the cements is given in Table 2. Well-graded river sand and good quality crushed blue granite were used as fine and coarse aggregates respectively. The different size fractions of coarse aggregate (20 mm down graded and 12.5 mm down graded) were taken and recombined to a specified grading as shown in Table 3. In mix proportion, cement content and w/c ratio were kept constant

Table 1
Details of mix proportions

Strength (MPa)	Type of cement	W/C ratio	Cement (kg/m ³)	Water (kg/m ³)	Fine aggregate (kg/m ³)	Coarse aggregate (kg/m ³)	28 Day compressive strength (MPa)	Slump (mm)
20	OPC	0.67	284	190	770	1026	27	50
	PPC	0.67	284	190	770	1026	23	60
	PSC	0.67	284	190	770	1026	28	10
30	OPC	0.54	352	190	739	1026	37	30
	PPC	0.54	352	190	739	1026	28	30
	PSC	0.54	352	190	739	1026	39	20
40	OPC	0.42	452	190	655	1026	54	40
	PPC	0.42	452	190	655	1026	39	0
	PSC	0.42	452	190	655	1026	48	10

Table 2
Chemical composition of three types of cement

Compound	Ordinary Portland cement (%)	Portland pozzolana cement (%)	Portland slag cement (%)
Silicon dioxide (SiO ₂)	20–21	28–32	26–30
Aluminium oxide (Al ₂ O ₃)	5.2–5.6	7.0–10.0	9.0–11.0
Ferric oxide (Fe ₂ O ₃)	4.4–4.8	4.9–6.0	2.5–3.0
Calcium oxide (CaO)	62–63	41–43	44–46
Magnesium oxide (MgO)	0.5–0.7	1.0–2.0	3.5–4.0
Sulphur trioxide (SO ₃)	2.4–2.8	2.4–2.8	2.4–2.0
Loss on ignition	1.5–2.5	3.0–3.5	1.5–2.5

for both blended cement concrete and Portland cement concrete. Potable water was used for casting the concrete. Concrete specimens of 100 mm × 100 mm × 100 mm size were cast. After curing for 28, 90, and 365 days the specimens were broken and concrete samples were collected from the interior portion of the specimen. Samples were powdered in a silica mortar

and sieved through 75 m sieve. About 1 g of sample was collected in a closed plastic container from each mix proportion at the end of each hydration period. TG/DTA was done with Polymer laboratories (UK), Thermal Science Division STA 1500 thermal analyzer with a resolution of 0.01 mg. Type R thermocouple (Pt-13% Rh/Pt) is used for temperature measurements in this instrument. The sample was taken in a ceramic crucible and heated from room temperature to 900 °C at a heating rate of 20 °C/min using air as a medium under static condition. Alumina powder was used as the reference material. TG/DTA were done simultaneously. The upper temperature was mainly limited because of crystallization of hydrated compounds at higher temperature. The sharp endotherm in the DTA curve around 465 °C indicates the decomposition of Ca(OH)₂ formed during hydration [15]. The Ca(OH)₂ was estimated from the weight loss measured from the TG curve between the initial and final temperature of the corresponding TG peak by considering the

Table 3
Grading of coarse and fine aggregate

Coarse aggregate		Fine aggregate	
Sieve size (mm)	Cumulative % retained	Sieve size (mm)	Cumulative % retained
20	0	4.75	0
16	25	2.36	12
12.5	52	0.600	49
10	72	0.300	85
4.75	100	0.150	97
		<0.150	100

following decomposition reaction [16].



The total weight-loss including that due to loss of water from other hydrates [17] was measured from the difference in weight between 100 and 600 °C.

Some authors report that the approximate chemical composition of calcium hydrates is the same whether formed from the reaction of cement and water or pozzolan and calcium hydroxide [18]. It is also reported that quantification of the amount of non-evaporable water chemically combined in hydrated silicates and aluminates is the good indication of hydration degree [19]. In the present investigation, the calcium hydrates content which is a total of calcium silicate hydrate, calcium aluminate hydrate and calcium sulfoaluminate hydrate formed during hydration was calculated by deducting calcium hydroxide content from total weight-loss [20]. Hence, it is an indirect measurement of calcium hydrate content as total water content. The addition of mineral admixture does not accelerate the hydration degree in the cement paste up to 7 days. During early ages two competing reactions occur simultaneously. One is the hydration reaction in which the cement produces hydrates and calcium hydroxide, another is the pozzolanic reaction in which calcium hydroxide is consumed by silicates and aluminates present in the fly ash and slag. After 7 days these reactions proceed with different intensity at the different states of hydration [21]. Hence in this study, after allowing longer curing time, i.e. at the end of 28, 90 and 365 days, the Ca(OH)_2 and calcium hydrates were estimated.

2.1. Water permeability studies

The permeability of concrete is a measure of the rate at which a liquid will pass through it. Permeability depends upon the pore network which arises from excess water used during mixing and the initial hardening process. The permeability can be measured by conducting a water permeability test as per se, by a water absorption test, or an initial surface absorption test [22,23]. In the present study, the overall porosity is determined by water absorption which measures the pore space indirectly by the procedure given in ASTM C 642-90 by oven-drying [24]. For this test, 100 mm × 100 mm × 100 mm size concrete cubes were

cast in duplicate. After demoulding, the specimens were kept immersed in water. The experiment was conducted at the end of three curing periods viz. 7, 28 and 90 days to evaluate the effect of curing on overall porosity. At the end of each curing period, the specimens were taken from the curing tank and air-dried to remove surface moisture. After this, the specimens were dried in an oven at a temperature of 100 ± 10 °C for 48 h allowed to cool to room temperature, and the weight of the specimens measured to an accuracy of 1 g using a digital balance. Then the specimens were kept immersed in water for 1 h and increase in weight was measured. From this the co-efficient of water absorption was calculated using the following formulae [4]

$$K_a = \frac{[Q/A]^2}{t} \quad (\text{ii})$$

where K_a is the co-efficient of water absorption, and Q the quantity of water absorbed by the oven-dry specimen in time, t , and A the total surface area of concrete specimen through which water penetrates, $t = 60$ min. The coefficient of water absorption was calculated for each curing period.

3. Results and discussion

Typical plots of TG/DTA curves for the samples collected at the end of 28 days in 20, 30, and 40 MPa concrete are given in Figs. 1–6. From the DTA curves it can be seen that each curve consists of three zones. Zone one between 100 and 300 °C which is attributed to the dehydration of C–S–H and ettringite [25]. The temperature at which these compounds lose water depends upon the available $\text{CaO}:\text{SiO}_2$ ratio in the hydrated cement matrix. The peak observed around 350 °C denotes the formation of Fe_2O_3 solution [7]. Zone two includes from 290 to 350 °C characterizing the decomposition of calcium aluminate silicate hydrate, calcium aluminate hydrate and calcium chloroaluminate [26]. The third zone ranging from 450 to 510 °C is attributed to the dehydration of calcium hydroxide. An endotherm around 700 °C indicates the decarbonation of calcium carbonate in the hydrated compound. Similar curves are observed at the end of 90 and 365 days, but the intensity of the peak varies with hydration time, type of blended

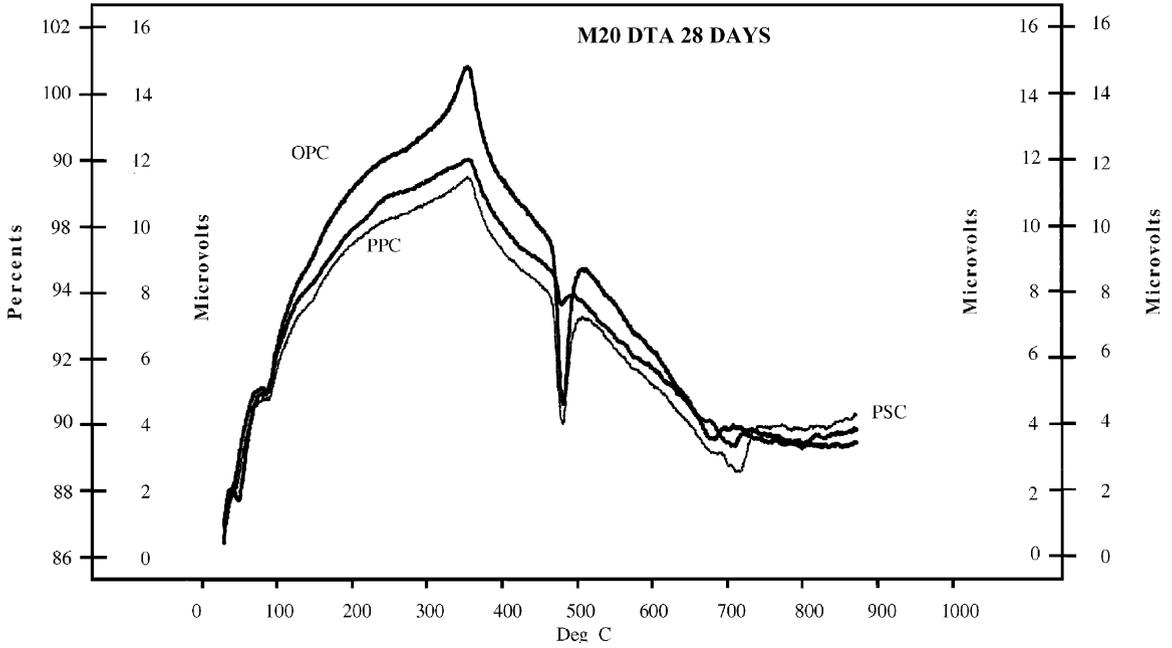


Fig. 1. DTA curves of three cements in 20MPa concrete hydrated for 28 days.

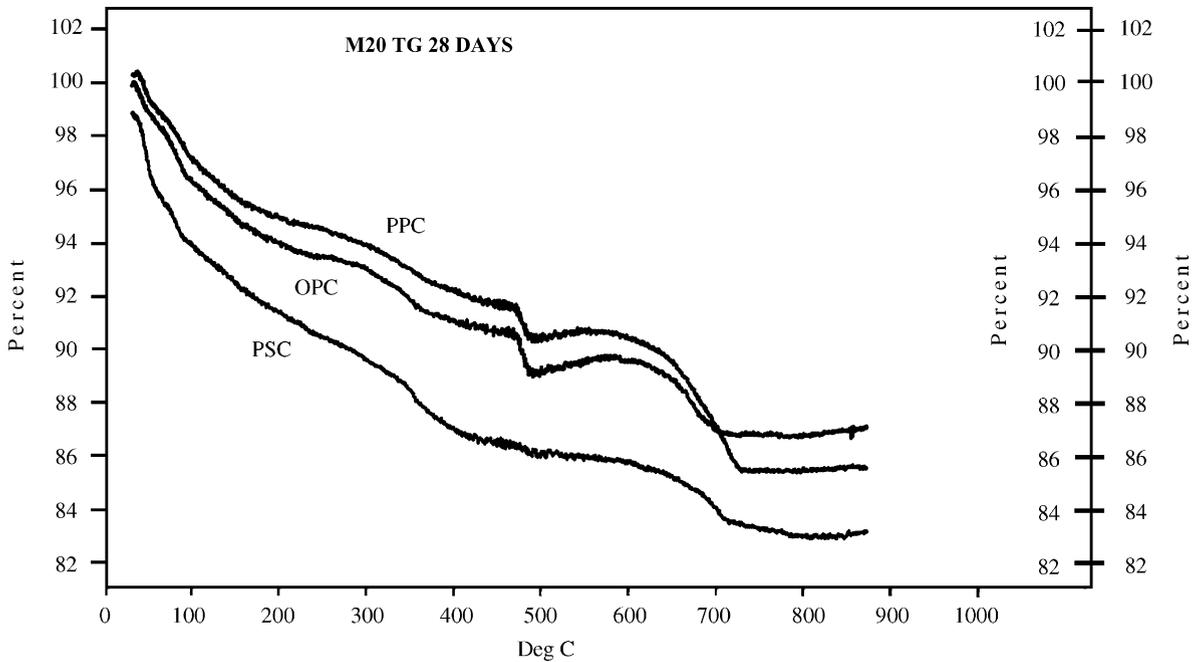


Fig. 2. TG curves of three cements in 20MPa concrete hydrated for 28 days.

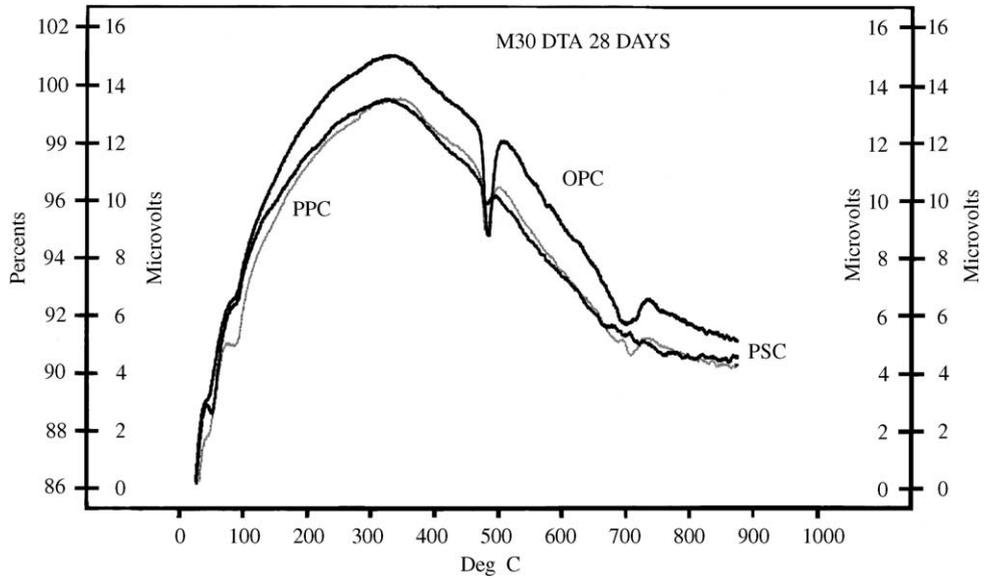


Fig. 3. DTA curves of three cements in 30 MPa concrete hydrated for 28 days.

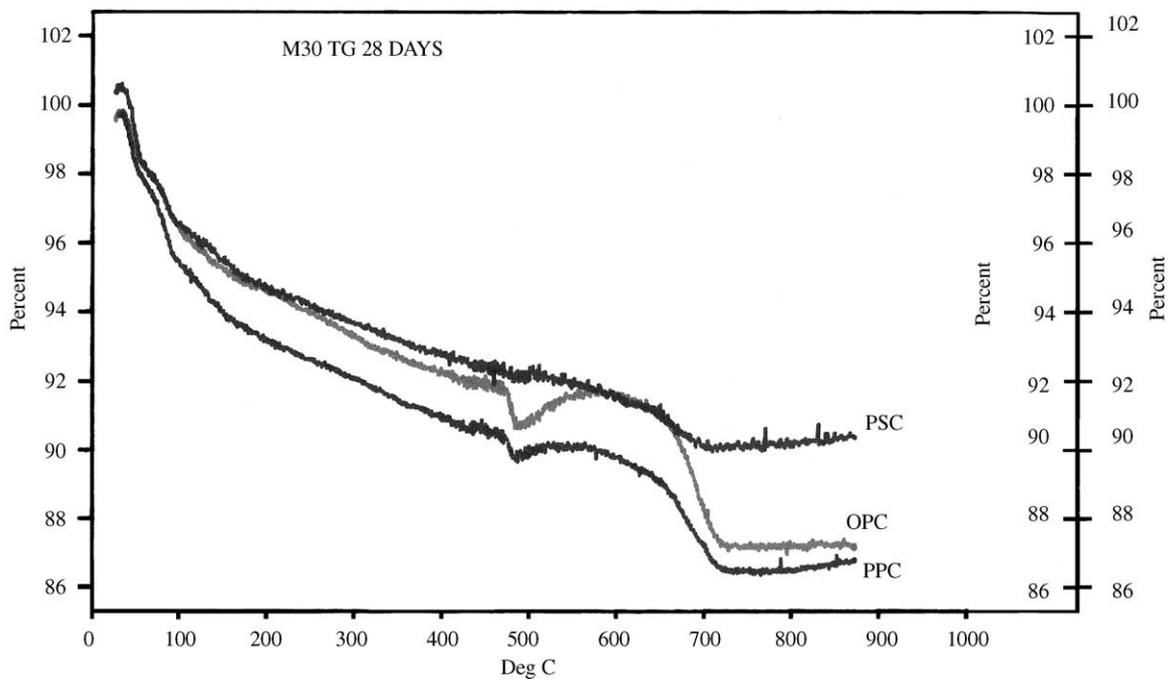


Fig. 4. TG curves of three cements in 30 MPa concrete hydrated for 28 days.

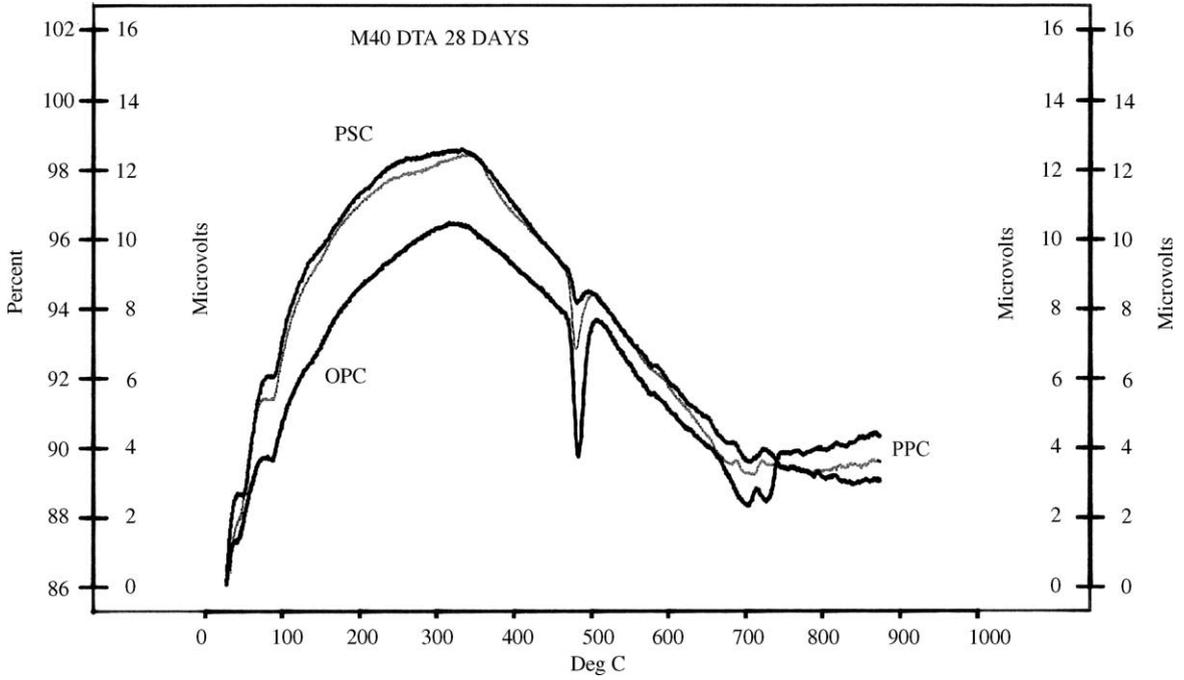


Fig. 5. DTA curves of three cements in 40MPa concrete hydrated for 28 days.

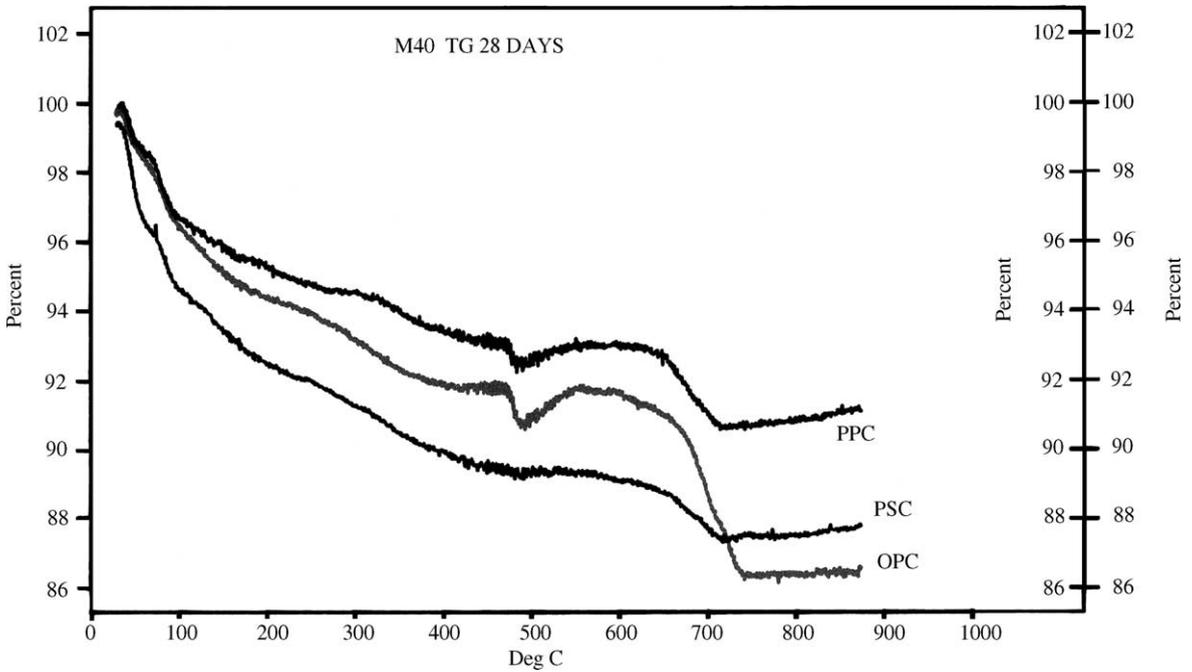


Fig. 6. TG curves of three cements in 40MPa concrete hydrated for 28 days.

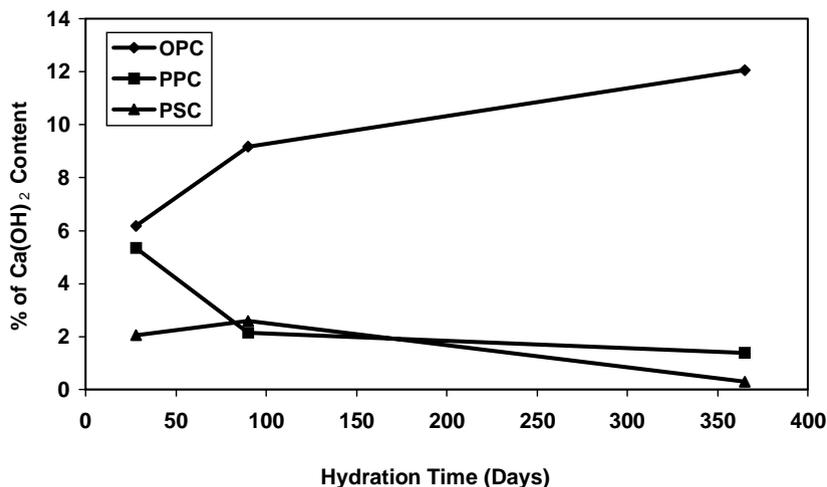


Fig. 7. Variation of $\text{Ca}(\text{OH})_2$ content with hydration time in 20 MPa concrete.

cement and strength of concrete. In all the concretes the $\text{Ca}(\text{OH})_2$ peak is at $465\text{--}469^\circ\text{C}$ which indicates no change with age and confirms that there is no major change in phase chemistry.

3.1. $\text{Ca}(\text{OH})_2$ content

Variation of $\text{Ca}(\text{OH})_2$ content with hydration time in 20, 30, and 40 MPa concretes is presented in Figs. 7–9. As shown in Fig. 7 in 20 MPa OPC concrete the $\text{Ca}(\text{OH})_2$ content increases with time whereas in

PPC and PSC concretes it decreases with time. The reduction in $\text{Ca}(\text{OH})_2$ in blended cement concretes indicates its consumption in pozzolanic reaction. This shows in PPC and PSC concretes during hydration, lime is consumed, whereas in OPC concrete, lime is produced. This is the main advantage of using blended cements to decrease the permeability of the concrete to 30 MPa and concrete show a similar reduction of $\text{Ca}(\text{OH})_2$ content in blended cements. The reduction of $\text{Ca}(\text{OH})_2$ content is greater in PSC concrete than in PPC concrete indicating more pozzolanic reaction

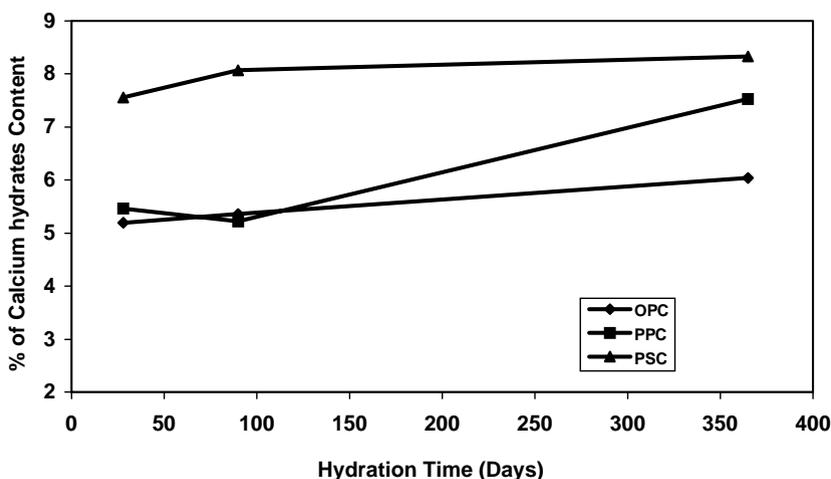


Fig. 8. Variation of calcium hydrates content with hydration time in 20 MPa concrete.

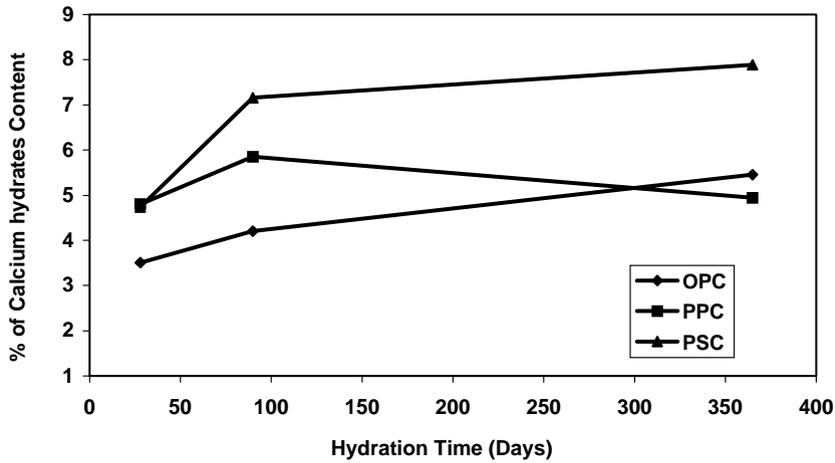


Fig. 9. Variation of calcium hydrates content with hydration time in 30 MPa concrete.

of slag concrete. Slag cement contains 50% slag whereas in pozzolana cement the fly ash content is limited to 25%. The reduction of $\text{Ca}(\text{OH})_2$ content with hydration time in pozzolan and slag cements was reported earlier by conducting TG/DTA analysis on cement pastes [27]. From the earlier discussion it can be inferred that, in the case of pozzolana and slag cements the reduction of calcium hydroxide is due to both the dilution effect and pozzolanic reaction.

3.2. Calcium hydrates content

The main hydrated phases produced during the pozzolanic reaction at ambient temperature are CSH, C_2ASH and C_4AH . Different factors can influence the reaction kinetics and the amounts of the phases produced, but the hydration time is the most important factor. Variation of calcium hydrates content with hydration time in 20, 30, and 40 MPa concrete are given in Figs. 8–10.

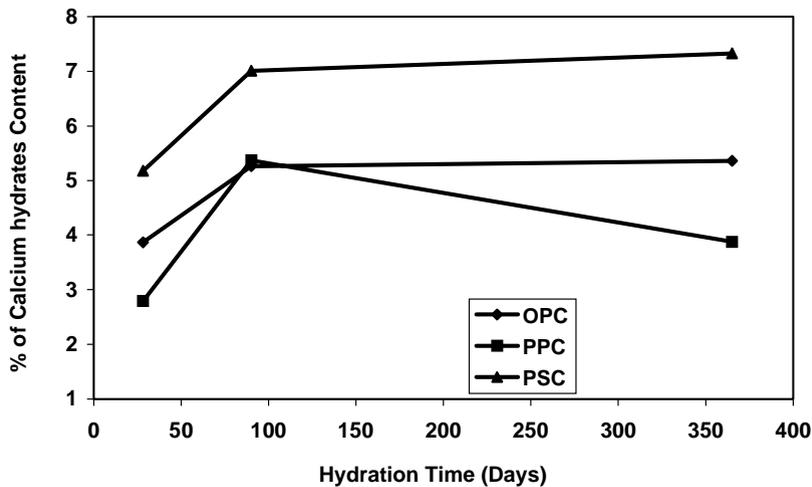
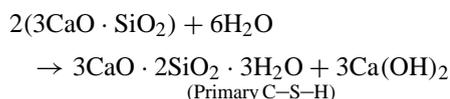


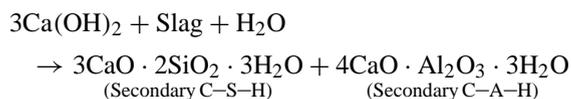
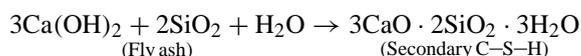
Fig. 10. Variation of calcium hydrates content with hydration time in 40 MPa concrete.

In 20 MPa concrete as presented in Fig. 8, calcium hydrates content is more in PPC and PSC concrete than OPC concrete. It increases with time up to 365 days. This clearly shows that in blended cement concretes in presence of water both fly ash and slag react with $\text{Ca}(\text{OH})_2$ to form secondary calcium hydrates (both aluminate hydrate and silicate hydrate). This secondary calcium hydrates fills the large capillary voids and this process of transformation is referred as “pore size refinement” [28]. The reactions are as follows:

Primary hydration reaction (for both OPC and blended cements):



Secondary hydration reaction (for blended cements only):



These secondary hydration products are not observed in OPC concrete as indicated by the lower value. When compared to PPC concrete, PSC concrete has more hydrates because of higher alumina and calcium oxide content of slag in slag cement. Similarly, using TG/DTA technique, Fias et al. reported CSH increase with hydration time up to 31 days and remains constant thereafter up to 125 days in metakaolin-lime mixture [29].

In 30 MPa concrete as shown in Fig. 9 calcium hydrates are more in PPC and PSC concrete than OPC concrete. But when comparing the hydrate content of 30 MPa concrete to 20 MPa concrete, at each hydration time, there is a reduction in hydrate content in all cements. This indicates that the higher cement content and low w/c ratio, which densifies the pore structure, might also be restricting the reaction, and hence reduce the formation of additional hydrates.

This behaviour is also observed in 40 MPa concrete. The result shows that the hydrate content is reduced further in 40 MPa concrete. This confirms that in concrete having higher cement content most of the cement particles are not able to hydrate because of the dense

Table 4
Comparison of coefficient of water absorption

Type of Cement	Period of curing	Coefficient of water absorption ($10^{-10} \text{ m}^2 \text{ s}^{-1}$)		
		M20 grade	M30 grade	M40 grade
OPC	7	16.6	9.17	6.76
PPC	7	9.86	5.64	4.46
PSC	7	8.27	4.88	5.71
OPC	28	15.1	7.81	8.43
PPC	28	7.71	5.0	4.46
PSC	28	5.80	5.32	5.06
OPC	90	7.64	6.68	1.72
PPC	90	4.94	5.13	2.24
PSC	90	3.32	4.40	1.93

pore structure where the cement acts as a filler irrespective of the type of cement. Hence the beneficial effect of blended cements in reducing the permeability in medium strength concretes having cement content in the range of 353–452 kg/m^3 is mainly attributed to the high cement content and low w/c ratio and not to the pozzolanic reaction.

From the earlier discussion it is inferred that $\text{Ca}(\text{OH})_2$ formation is more in 20 MPa concrete than in 30 and 40 MPa concrete. Higher porosity in 20 MPa concrete permits more pozzolanic reaction to occur before 28 days and this is continued till 365 days. The reduction in hydrates content is observed in 30 and 40 MPa irrespective of type of cement.

3.3. Water permeability studies

Table 4 compares the coefficient of water absorption in 20, 30 and 40 MPa concrete. In general, the PPC and PSC concretes have lower coefficients of water absorption than OPC concrete, and the coefficient also decreases with grade.

Thus, in all the curing period, the coefficient of water absorption in blended cement concrete is less than in OPC concrete. Hence the reduced permeability of PPC and PSC concrete is mainly because of densification of pore structure by forming additional calcium hydrates and this was proved by TG/DTA analysis.

4. Conclusions

1. TG/DTA technique can be used to identify the extent of pozzolanic reaction in blended

cement concrete in low and medium strength concretes.

2. More reduction in $\text{Ca}(\text{OH})_2$ content has been observed in PPC and PSC concretes than in OPC concretes in low and medium strength concretes and this confirms the pozzolanic reaction of blended cement concretes.
3. The $\text{Ca}(\text{OH})_2$ content decreased with hydration time and w/c ratio.
4. The calcium hydrates content is more in PPC and PSC in all concretes studied and increases with hydration time. It is more in PSC than PPC. In 30 and 40 MPa concrete the pozzolanic reaction is reduced in blended cement concretes because of the dense pore structure.
5. Co-efficient of water absorption is less in blended cement concretes than OPC concrete and is reduced further with increase of curing period and strength of concrete.
6. The reduced permeability of blended cement concrete is mainly attributed to pozzolanic reaction in low strength concrete, but rather by high cement content and low w/c ratio in medium strength concretes.

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