Pergamon

Cement and Concrete Research 30 (2000) 865–879

CEMENT AND CONCRETE RESEARCH

Durability of concrete with high cement replacement

W.W.J. Chan*, C.M.L. Wu

Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Hong Kong SAR, People's Republic of China

Received 3 March 1999; accepted 1 March 2000

Abstract

The durability of concrete made from various non-reactive waste materials, i.e. carbon black, silts and clays, and with various water contents were investigated. The compressive strength, workability, sorptivity, and water permeability of the concrete were studied to assess the durability. Further, the resulting change in the microstructure and cement hydration in these concrete were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy. It was found that the critical problem of maintaining or increasing the designed workability could be solved by using high specific surface area material and with the superplasticizer admixture. The present study also indicated that an alternative durable concrete could also be made with 25 vol.% of cement replaced with silts and clay using a water/cement (w/c) ratio of 0.5. That is, the cement and water contents were less than those in OPC. Also, the cost of concrete will be lowered. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cement replacement; Strength; Superplasticizer; Carbon black; Silts and clay; Cement hydration

1. Introduction

Since the early 1980s, there has been an enormous demand for the mineral admixtures by the cement and concrete industries. For various reasons, the future demand for these materials is expected to increase even more. It was estimated in early 1990s that the People's Republic of China (PRC), which produces about 200 million tons of cement annually, would consume approximately 15 million tons of zeolite, 25 million tons of blast-furnace slag, and over 10 million tons of fly ash as supplementary materials [1]. The latest demand can be conceived to be more than that originally estimated, in view of the fast development in the PRC.

The advent of superplasticizers and superpozzolans such as silica fume, rice husk ash, metakalin, pulverized fuel ash and granulated ground blast furnace slag has made it possible to utilize large proportions of these superplasticizers and superpozzolans in binary and ternary-component blended cements [1].

In studying the stone dust content in sand, Bonavetti and Irassar [2] stated that the gain of concrete strength was attributable to the acceleration of the cement hydration at early ages due to the effect of the stone dust. At the later ages, no detrimental effects were observed. The mortar porosity was lower than that of the corresponding mortar without dust at the same water/cement (w/c) ratio.

Many studies had identified that a minimum of 19% of original weight of cement could never hydrate. As a result, high strength concrete contains a high proportion of unhydrated cement [3]. Also, some modern cement has higher early strength than traditional ones, and induces more calcium hydroxide formation. This may have an adverse effect to the durability and cost of concrete.

In this respect, one of the incentives for the present study is to use non-reactive waste materials with OPC to study whether the hydration characteristic can be improved. Another incentive is from the aspects of quality and economy, so as to use the non-reactive waste materials to replace a portion of the cement to achieve the same strength and durability by using a w/c ratio of 0.5 for the concrete mix. Mechanical and physical tests, as well as microstructural examination were carried out to assess the properties of the various cementitious replacement concrete trial mixes.

* Corresponding author. Tan Shing Court, Flat 3, 10/F, Yan Hei House, Fanling, N.T. Hongkong, People's Republic of China. Tel.: +852-9101-9440; fax: +852-2489-8789.

E-mail address: andy123456@ctimail.com (W.W.J. Chan).

PII: S0008-8846(00)00253-2

2. Experimental details

The methodology of this project is given in Fig. 1.

For the fresh concrete, the slump of each mix was measured. Compressive strengths were tested at 3, 7, 28, and 56 days after casting. Slices cut from cylindrical specimens were used for sorption and water permeability tests.

After the 28-day compressive strength tests, the interfacial transition zone (ITZ) of the cement paste were examined using a scanning electron microscope (SEM) and analysed with an energy dispersive X-ray (EDX) spectrometer.

Further, some of the powder of the bulk cement paste and cement replacement materials, such as Types II and III, were studied for their compositions by X-ray diffraction (XRD).

2.1. Materials

Carbon black is always used in rubber product as filler to improve the strength, stiffness, hardness, and wear- and heat-resistance. Much of the sulfur in carbon black is not free, that is, it is not potentially reactive [4,5]. Although, some technologists [6] say that carbon has a retarding effect on the setting and hardening processes in concrete, it is believed that carbon black is a non-polar product and carbon has no absorption with the mixing water; both of them will create a repulsing force between each other. This is a great advantage in concrete workability, because this can reduce the w/c ratio and function as a superplasticizer.

In general, most researchers [6] expressed that the silts and clays could cause components to deteriorate. It is understood that when mixing concrete containing silts and clays, more water is added to achieve the same workability as in OPC. That is, the w/c ratio is increased. The addition of silts and clays increases the total surface area in contact with water. Therefore, in order to reach a similar workability as in OPC, more water is needed. The authors believe that it is the additional water that causes the strength to decrease.

For some high quality concrete, certain mineral admixtures such as silica fume, etc., are used. Also, a superplasticizer is added, while using the same w/c ratio as in OPC. The demand for water content for these mineral admixtures should be similar to that for silts and clays. It is therefore reasonable to predict that the use of superplasticizer and the same w/c ratio as in OPC for concrete containing silts and clays may also provide good quality concrete.

In this study, trial mixes of concrete with three different grades of waste materials were prepared to replace the cement content in the normal mix by three different percentages. Type I particles were bought from the commercial printing machine supplier. The specific gravity of these carbon black particles was less than 1 and the fineness was over 98 wt.% passing 45 μm. Type II particles were under 150 μm in size, obtained from crushed granite stone, silts and clays. Type III particles were sieved from crushed granite fines, so that the particles were between 75 and 150 μm. The major composition of these two materials is quartz (SiO_2). Figs. 2 and 3 show the analysis of the quartz material, where the SiO_2 peak was dominant.

GRACE Super 20 superplasticizer based on naphthalene sulphonates was used. The admixture was also prepared in bulk and test samples were made from the same admixture tank.

2.2. Concrete mixes

The proportions of constituents of the concrete mixes TM1–TM8 are shown in Table 1. It can be seen in the table that various amount of OPC and water were used. A fixed total volume was used for all types of concrete mixes. So by

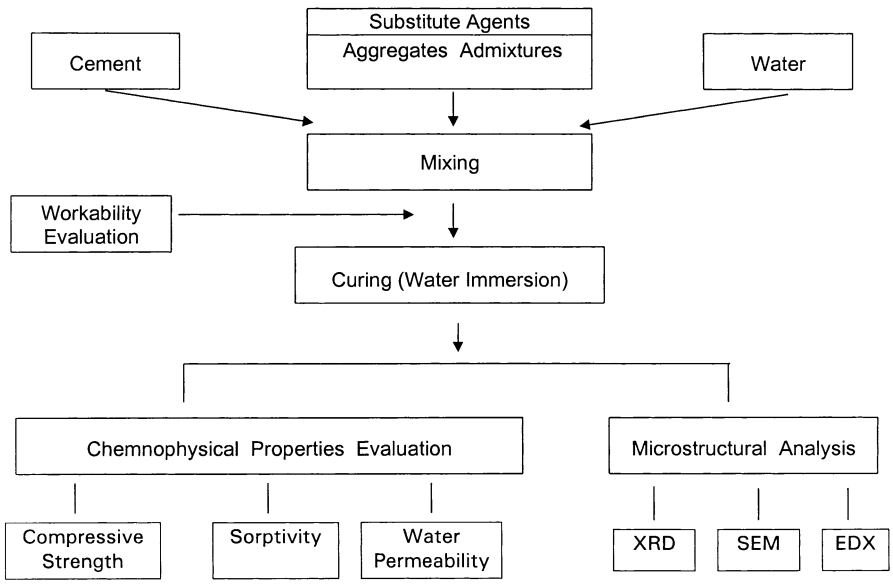


Fig. 1. Experimental procedure.

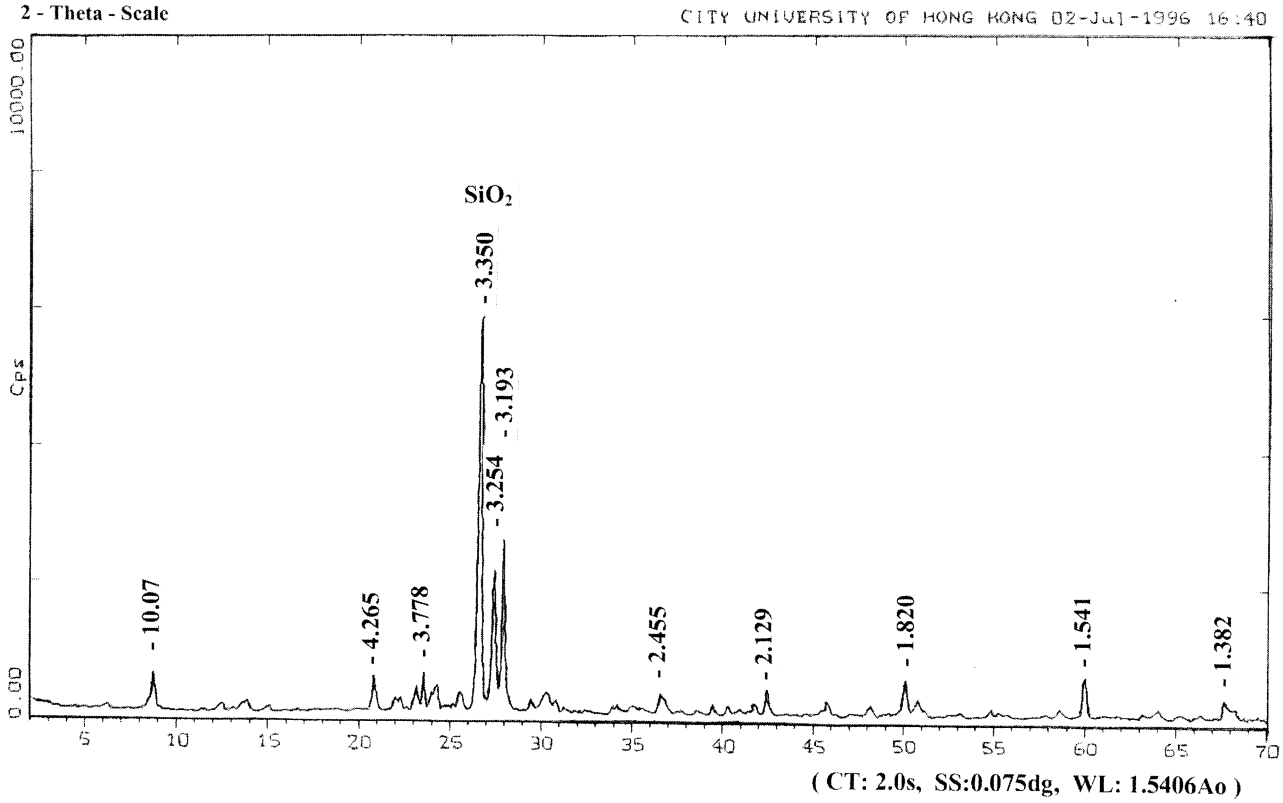


Fig. 2. Type II (crushed granite fines—passing 150 μm).

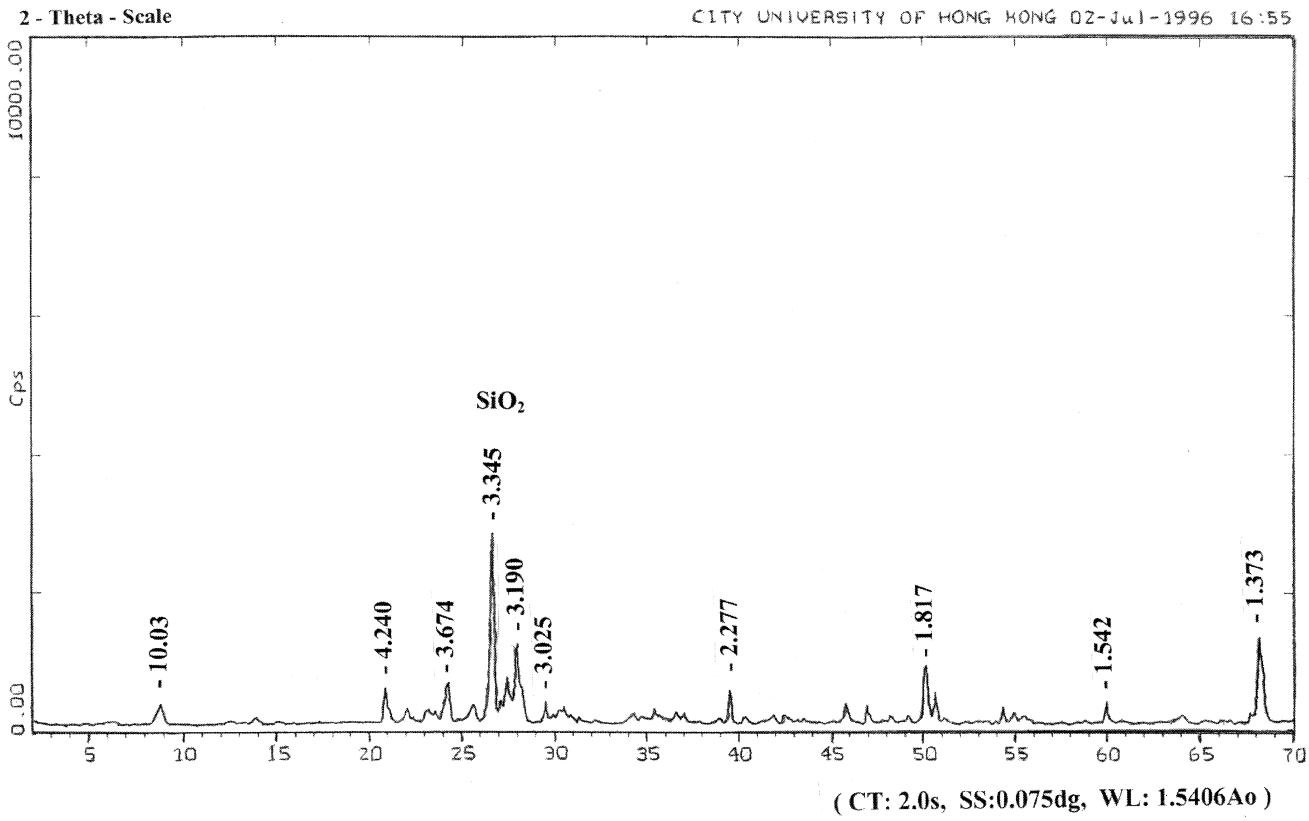


Fig. 3. Type III (crushed granite fines—between 75 and 150 μm).

defining the quantity of OPC in each mix, the amount of Type I, II or III particles used was then calculated given the required total volume.

2.3. Sampling

For each mix, eight 100-mm cubes were used for compressive strength test and a 95-mm diameter ×250-mm long cylinder was used for sorption and water permeability tests. The cubes and cylinders were then covered with wet hessian for 24 h.

After de-molding, the specimens were cured in water at 27 ± 2°C. One of cubes was strength-tested after 3 days of curing. Two cubes were tested after each of the 7, 28, and 56 days curing period.

2.4. Sorption test and porosity

A slice of 25-mm thick was trimmed from the cylindrical specimen. After the sample was vacuum-dried to a constant weight or was dried at a temperature of 105°C for 72 h, the sample was cooled in a desiccator for 24 h.

The 'sorptivity' was calculated from the volume of water absorbed per unit cross-section, A, and the square root of time, t. Values of sorptivity were given in mm^3/mm^2 per $min^{1/2}$.

Further, the water absorption from the start of the test to the end of the first phase might be taken as filling the "effective empty porosity," Z, of the concrete, such that

$$Z = 10^5 \frac{M_{sat} - M_0}{AL}$$

where Z = effective empty porosity (%), M_{sat} = mass of specimen at end of first phase of absorption (g), M_0 = mass of specimen at start of test (g), A = specimen cross-sectional area (mm^2), and L = specimen thickness (mm).

Although this was not an accurate method of determining porosity, it was a practical indication of relative porosity.

2.5. Water permeability

Water permeability of concrete specimens was measured by using the 5 bars water pressure test similar to the recommendation from the Concrete Society.

The flow rate was calculated by Darcy's Equation, such that:

$$\frac{Q}{t} = \frac{KPA}{d} \times 10^4$$

where Q/t = the average flow rate (cm^3/s), K = water permeability (m/s), P = pressure in m of water head, A = cross-sectional area of sample (cm^3), and d = thickness of the sample (cm).

2.6. X-ray diffraction

After the 28-day compressive strength measurement, the fractured bulk cementitious paste of the mixes was analysed using a Siemens-D500 XRD (35 kV/30 mA; CuK_α). The particles were ground into very fine powder. They were then sieved to obtain particles of less than 150 μm. Powder XRD was used to determine the bulk mineraology and the hydration reaction products of this bulk cementitious paste powder. Data were collected automatically using a Diffract Databox. Scan parameters for qualitative scans were typically with 0.075° step size for 2 s count time over a typical 2θ range of 2–70°.

2.7. Scanning electron microscopy

Fracture of strength-tested specimens usually occurs at the interface between aggregate and cementitious paste. The fracture surface was observed using the SEM (JEOL JSM-5200 and 820). An operating voltage of 15–25 kV was selected for all operation modes.

In order to properly characterize the cementitious materials, all specimens were cleaned with methyl alcohol. They were then bonded onto aluminum discs by Dotite Paint (Type XC-12 Carbon). All samples were also carbon-coated prior to SEM analysis.

2.8. Energy dispersive X-ray

All samples studied in the JEOL JSM 820 SEM were also examined using EDX (LINK EDS AN 10/85 S) to

Table 1
Mix proportion

Mix no.	OPC (kg)	Type I (kg)	Type II (kg)	Type III (kg)	Water (l)	CRF (kg)	10 mm (kg)	20 mm (kg)	Water reducing admix (cm^3)	Superplasticizer (cm^3)	Actual slump (mm)	w/c ratio	Observation
TM1	400	–	–	–	200	720	285	685	2670.0	–	120	0.5	Normal
TM2	300	32	–	–	150	720	285	685	2002.5	1800	105	0.5	Good
TM3	300	–	90	–	150	720	285	685	2002.5	2400	100	0.5	Cohesive
TM4	300	–	–	89	150	720	285	685	2002.5	3000	130	0.5	Good
TM5	260	45	–	–	130	720	285	685	1735.5	3600	150	0.5	High performance
TM6	260	–	125	–	130	720	285	685	1735.5	4500	115	0.5	Slight shear
TM7	200	–	180	–	100	720	285	685	1335.0	5000	–	0.5	Not workable
TM8	200	64	–	–	100	720	285	685	1335.0	5000	–	0.5	Not workable

Table 2
Summary of test results of sorptivity, permeability, and strength

Mix no.	OPC (kg)	Sorptivity index ($mm/min^{1/2}$) (28 days, vacuum-dried)	(56 days, vacuum-dried)	(56 days, oven-dried)	Effective empty porosity (%)	Water permeability ($\times 10^{-12}$)	Compressive strength (MPa) 3 days	7 days	28 days	56 days
TM1	400	0.023	0.017	0.157	9.739	2.31	31.0	41.0	50.5	52.0
TM2	300	0.023	0.018	0.109	8.488	–	30.0	39.0	46.5	48.5
TM3	300	0.024	0.017	0.116	9.147	0.94	32.0	42.5	51.0	53.0
TM4	300	0.023	0.023	0.121	7.850	1.65	32.0	42.0	52.0	53.5
TM5	260	0.022	0.019	0.082	7.807	5.52	30.0	39.0	47.0	48.0
TM6	260	0.022	0.017	0.097	7.731	–	32.0	43.5	53.0	54.5
TM7	200	–	–	–	–	–	28.5	36.0	43.0	47.0
TM8	200	–	–	–	–	–	26.5	27.0	42.0	45.0

analyze their chemical compositions, at an acceleration voltage of 15 keV.

3. Results and discussion

The test results of all eight mixes, TM1 to TM8, were summarized and tabulated in Tables 1 and 2. It was found that for mixes TM7 and TM8 in which the cement was replaced by 50 wt.%, they failed to be workable.

3.1. Workability test

Table 1 provides the information on the amounts of water reducing admixture and superplasticizer used in mixing the concrete, as well as slump test results. The main reason to conduct the slump test was to ensure that the concrete was indeed workable, before proceeding to study other aspects such as strength. The water-reducing admixture to OPC volume ratio was set at a constant value normally used for the industry for all types of concrete. In general, as more replacement particles are added, leading to the decrease in cement and water contents, the concrete becomes less workable. This is easily understood, as we have fixed the w/c ratio in this paper, reduction in cement content will lead to reduction in water content for the total volume of OPC and replacement particles and will make the concrete less workable. If necessary, a superplasticizer is added to increase the slump value, i.e. to make the concrete workable. From TM2 to TM8, the amount of superplasticizer needed was experimented first to achieve a slump value larger than 100 mm, so as to provide workable concrete.

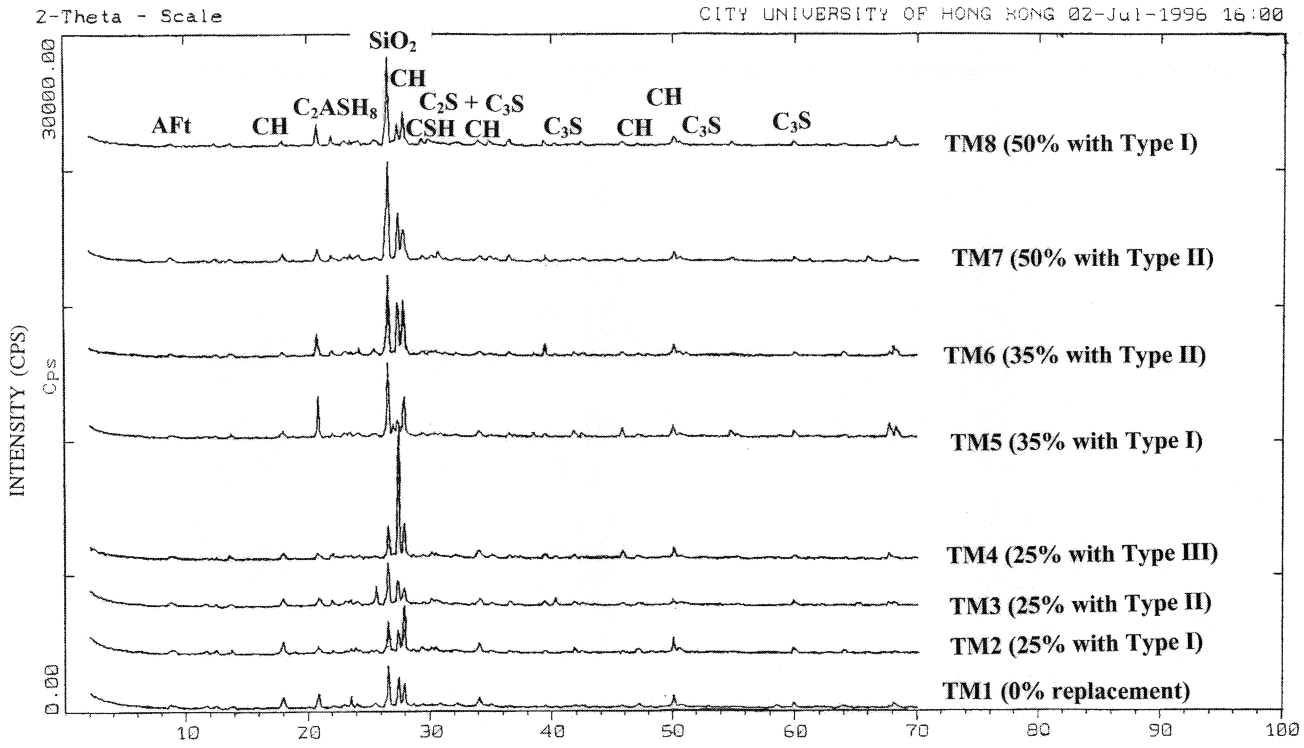


Fig. 4. X-ray diffractograms of hydrated blended cements after curing for 28 days.

When comparing TM2 with TM3 or TM4, it can be seen that the workability of TM2 can be formulated at about 100 mm with less quantity of superplasticizer added than in TM3 or TM4. This is because TM2 contained non-polar particles, i.e. high specific surface area carbon black material, which greatly improved the workability.

3.2. Compression test

The compression test results were given in Table 2. It can be seen that except for TM7 and TM8, which were concrete with excessive cement replacement, the compressive strength after 3 days did not vary too much. The same pattern applies for test

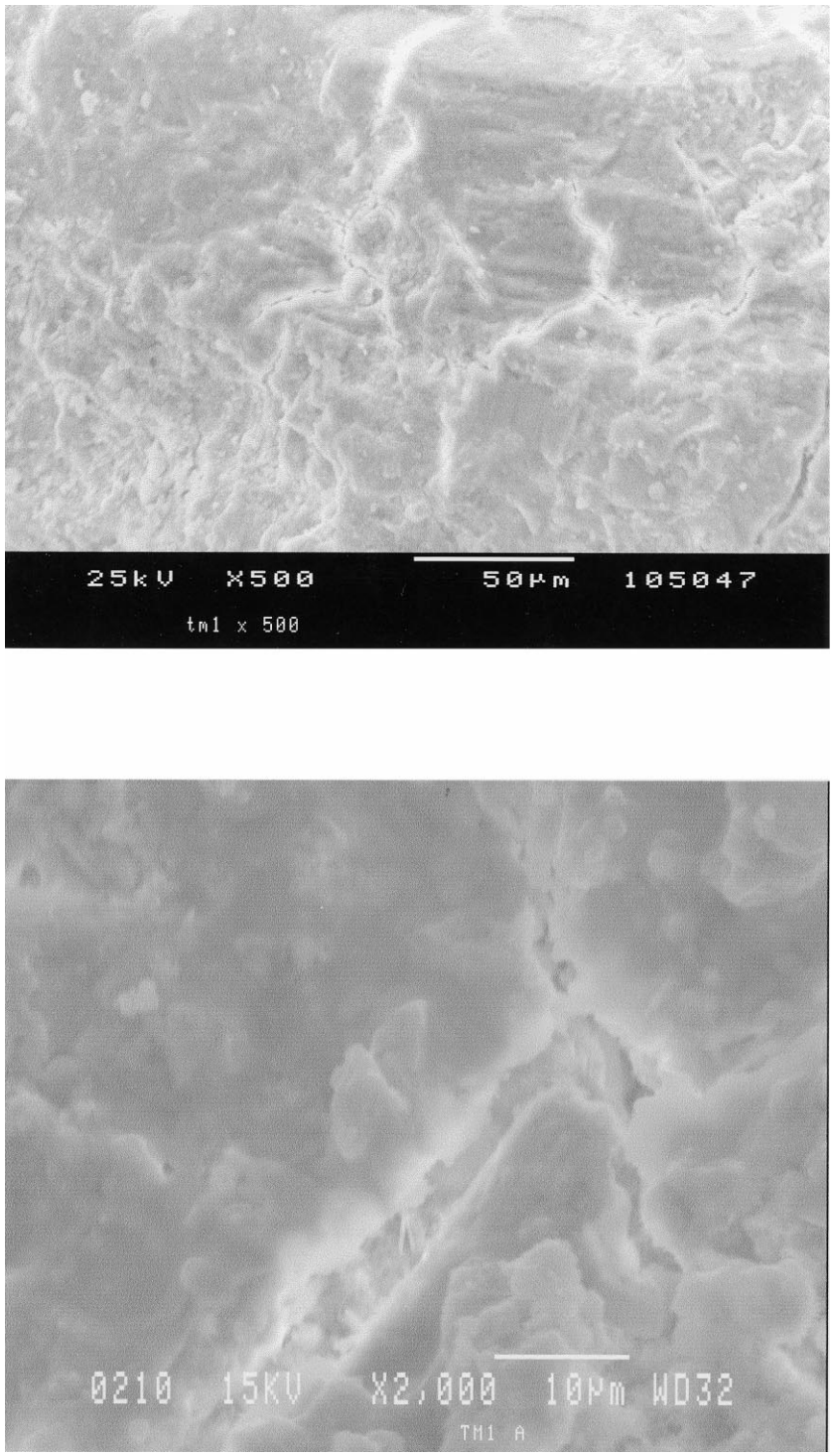


Fig. 5. (A) TM1 (×500). (B) TM2 (×2000).

after 3, 7, 28, and 56 days. These results showed that for the present constant w/c ratio, reduction in cement content within permissible limits did not significantly reduce the strength.

Although the variation between strength of various concrete mixes was not large, the strength of concrete containing Type I particles, i.e. TM2, TM5 and TM8 were slightly lower than that of the remaining mixes.

3.3. Sorption test and porosity

The results of sorption tests for 28- and 56-day samples were given in Table 2. The 28-day vacuum-dried record indicated that the sorptivity index of TM1 to TM6 ranged from 0.022 to 0.024 mm/min$^{1/2}$. In the 56-day vacuum-dried sorption test, the sorptivity index range of TM1 to

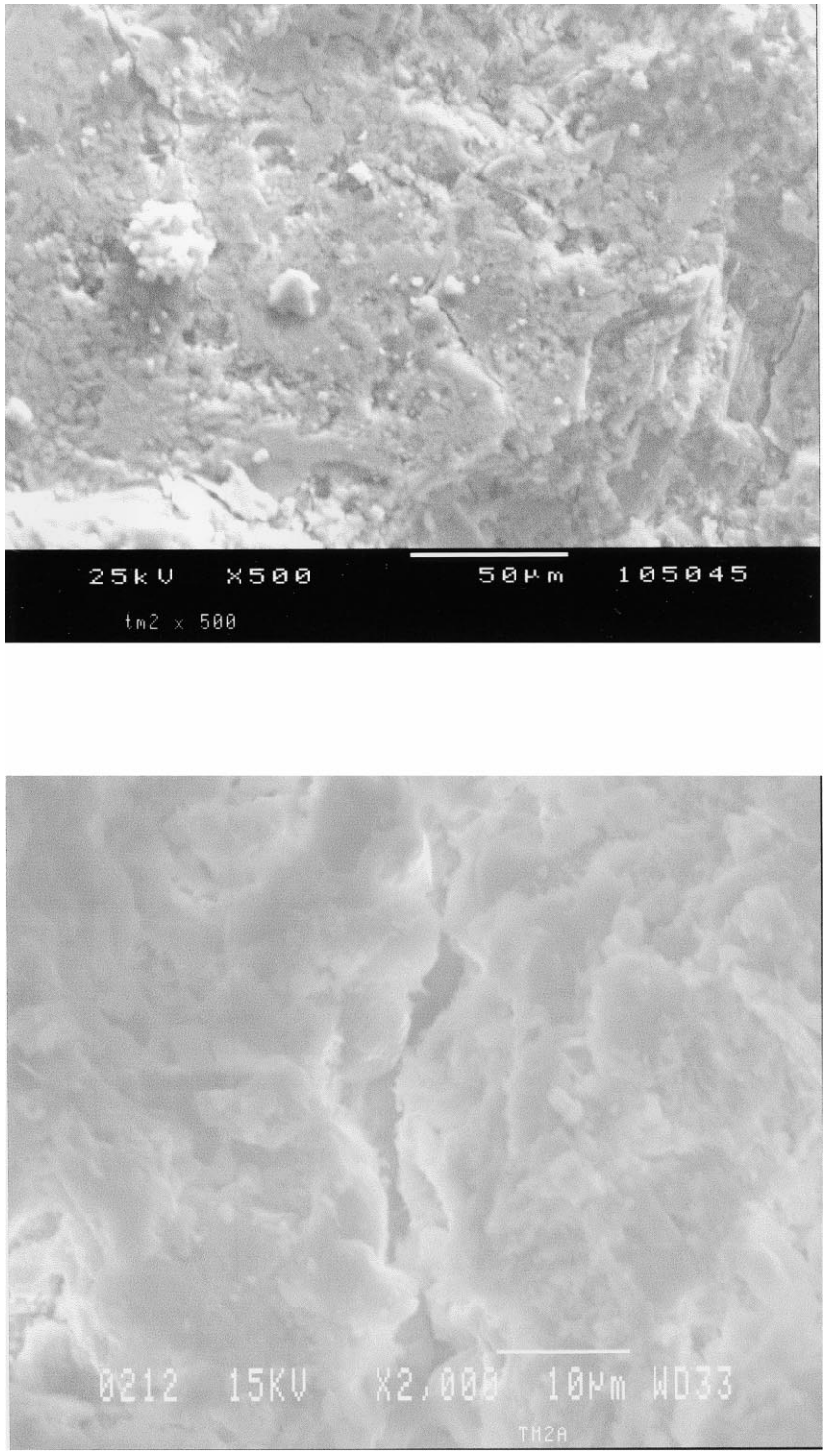


Fig. 6. (A) TM2 (×500). (B) TM2 (×2000).

TM6 was within 0.017 to 0.019 mm/min$^{1/2}$, with the exception of sample TM4 with a high sorptivity index of 0.023 mm/min$^{1/2}$. This might have been caused by local defects or poor compaction.

However, the sorptivity index of oven-dried samples was significantly lowered while the water content was reduced, particularly in comparison with vacuum-dried samples. For example, the sorptivity of TM1 is 0.157 mm/min$^{1/2}$, whereas the indices of TM5 and TM6 were 0.082 and 0.097 mm/min$^{1/2}$, respectively.

It was indicated that lower free water content and cement replacement by inert finer materials could take advantage of the high temperature condition.

The data for the 28-day effective empty porosity (Z) were illustrated into the Table 2. The range of porosity index was 9.739% to 7.731% in TM1 to TM6, respectively. It was also

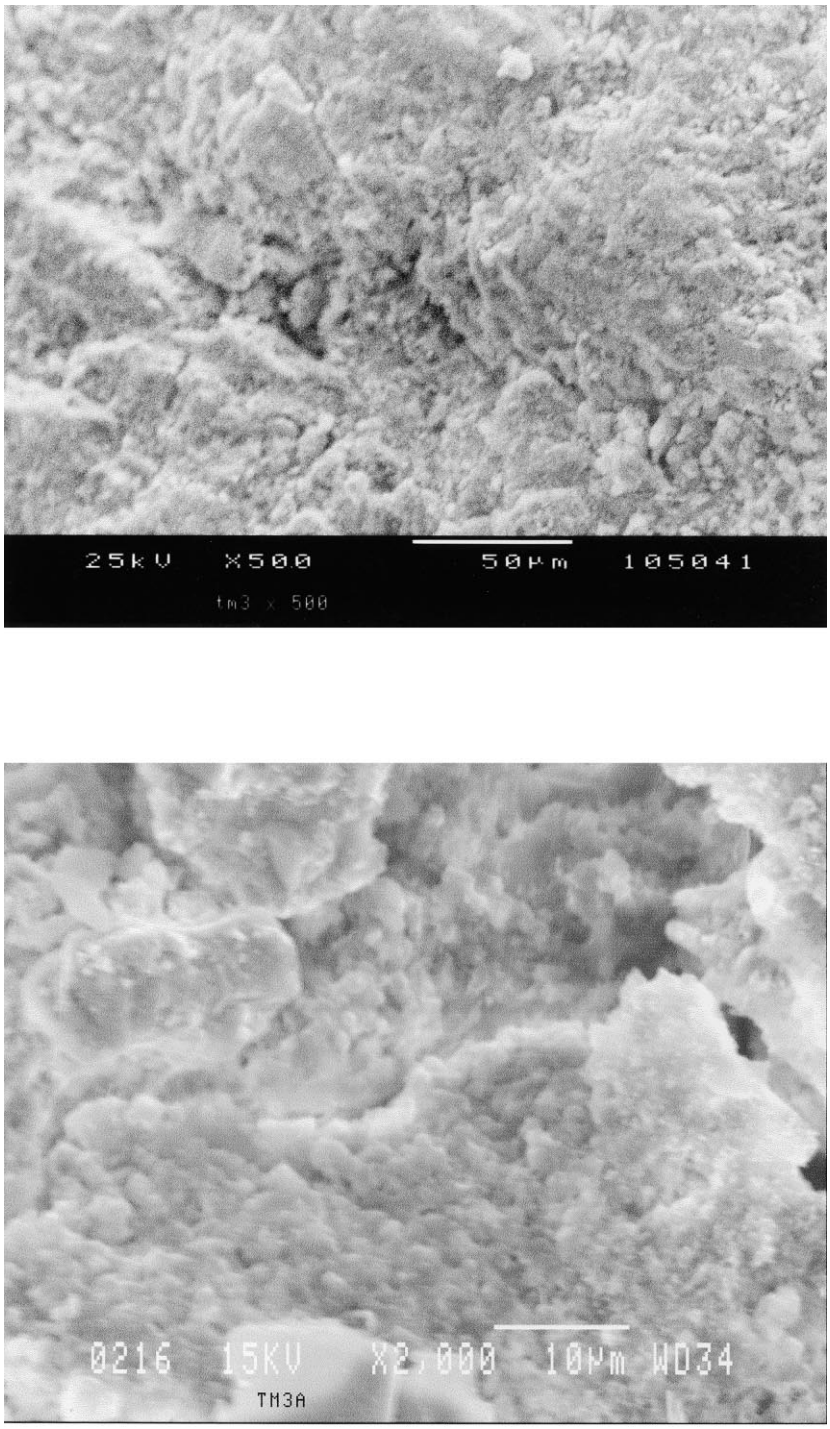


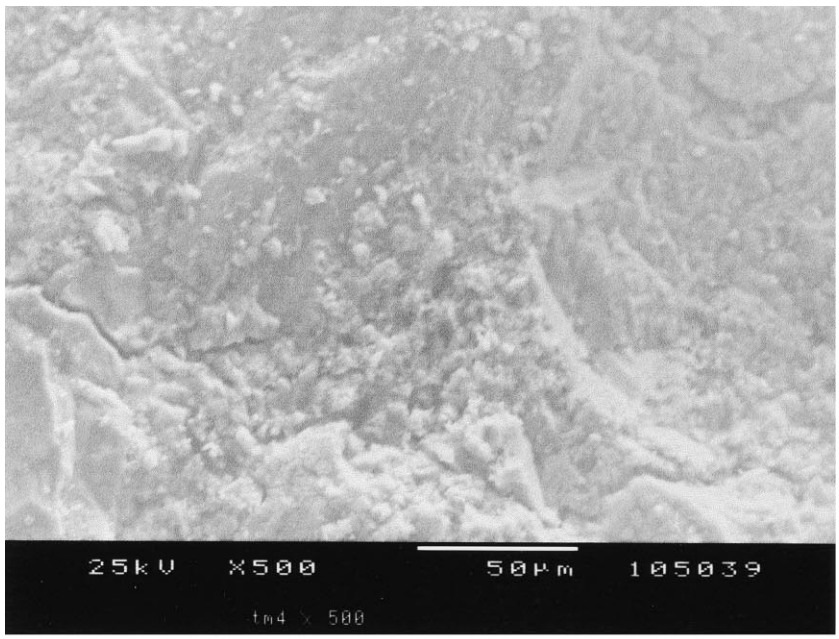
Fig. 7. (A) TM3 (×500). (B) TM3 (×2000).

shown that lower free water volume could create lower porosity content.

3.4. Water permeability

The results of the 28-day water permeability tests were given in Table 2. The specimens of TM2 and TM6 mixes showed leakage of water within the test period, indicating the presence of weak spots or crack within the specimen. Hence, their results were disregarded.

The range of water permeability coefficient was between 0.94 and 5.52 $\times 10^{-12}$ cm^3/s. Most test values were in the same order. However, the sample with Type II particles, i.e. TM3 showed the best result than others. The sample with carbon black, i.e. TM5, provided the worse record in this test. It might be caused by the non-



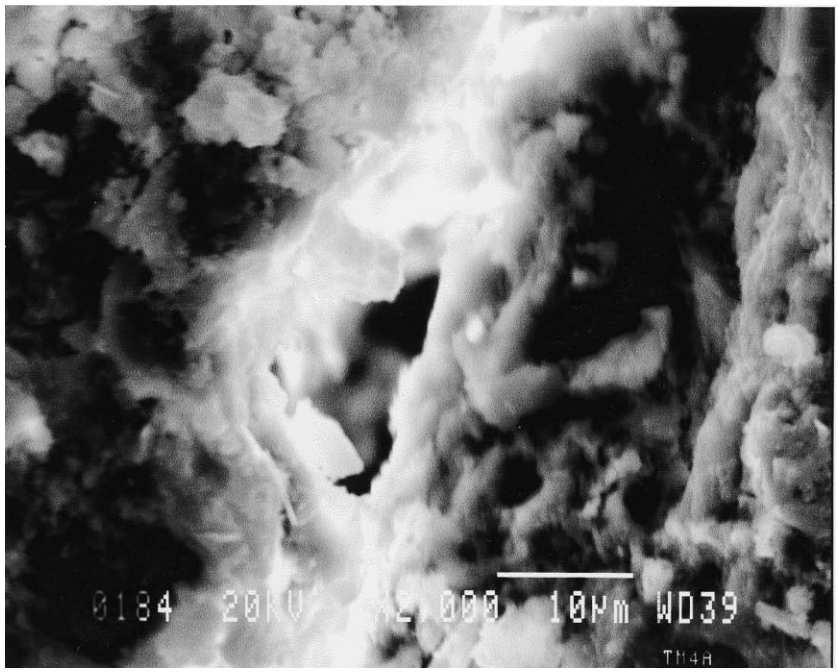


Fig. 8. (A) TM4 (×500). (B) TM4 (×2000).

polar property of carbon black inducing poor bond ability with other particles in the concrete.

3.5. X-ray diffraction

Fig. 4 shows the XRD patterns of bulk paste for TM1 to TM8, which were cured in 28-day water immersion. All of them contained Portlandite (CH) as a major phase.

From the diffractograms patterns in Fig. 4, it was observed that the intensity of CH is higher and the C-S-H was lower in higher cement content mix.

It might be indicated that the degree of hydration in concrete with high cement replacement was better than normal mix under the same w/c ratio. The reason might be that the inert materials could provide more micro-filler effect and nucleation sites for cement hydration [7–9].

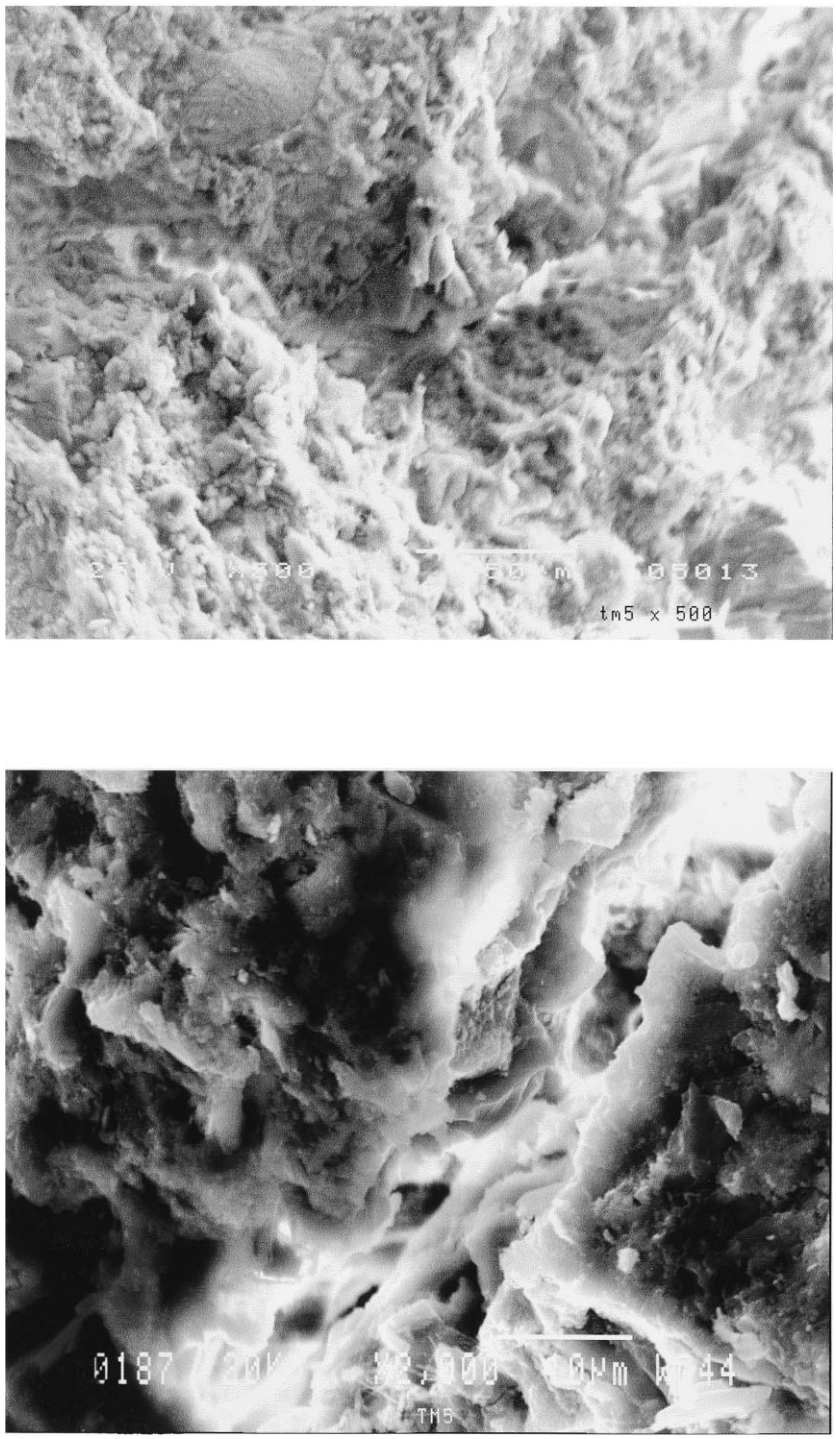


Fig. 9. (A) TM5 (×500). (B) TM5 (×2000).

Further, higher dosage in superplasticizer also provided better particle dispersion in cement paste [1].

3.6. Scanning electron microscopy

The micrographs of TM1 to TM8 illustrated the ITZ of concrete with typical hydration products. They were shown in Figs. 5–12 at magnifications of 500 and 2000 times.

Fig. 5(a) and (b) showed a few microcracks or water paths on the ITZ of TM1. Most cracks appeared in light color. Further, the cement paste had cracked through, but the composition was seen to be more homogeneous than other samples.

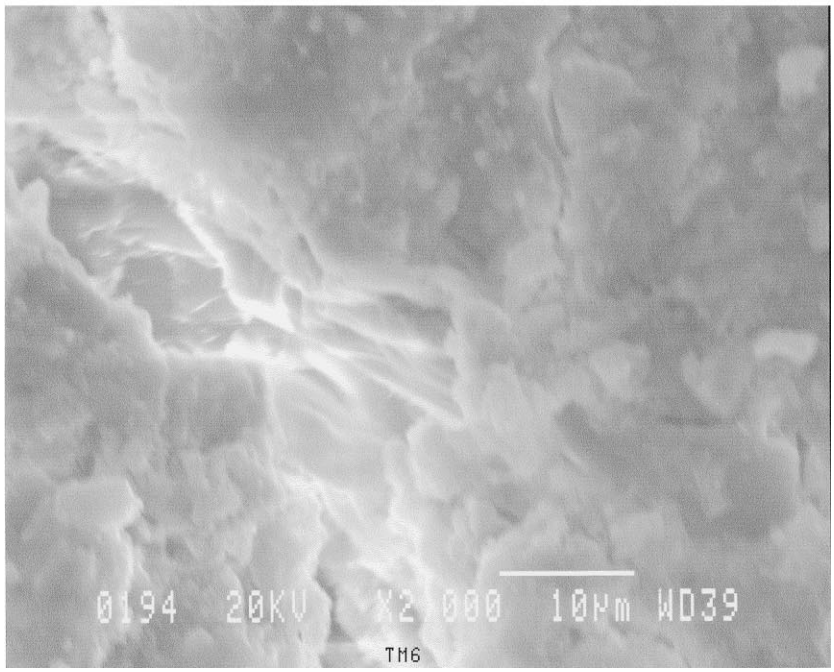
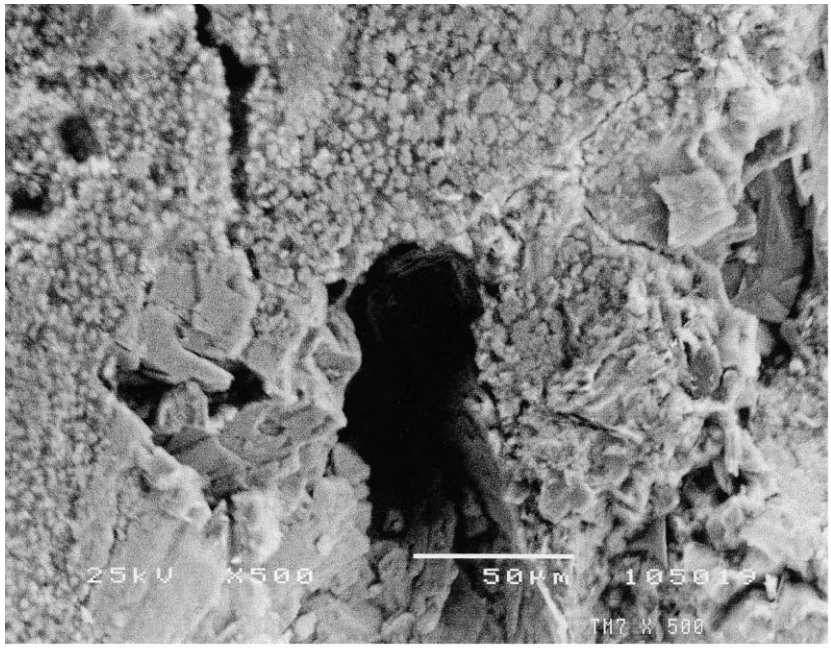


Fig. 10. (A) TM6 (×500). (B) TM6 (×2000).

The micrographs of carbon black substitutes were illustrated in Fig. 6(a) and (b) for 25% (TM2), Fig. 9(a) and (b) for 35% (TM5) and Fig. 12(a) and (b) for 50% (TM8). These mixes contained Type I substitutes according to the classifications in this paper, as given earlier in Table 1. It could be seen that the number of microcracks was less than that of the TM1. The cracks were underneath the carbon black particles, and passed through the paste. Further, the carbon black particles did not appear to bond with other cementitious products.

With a higher percentage of cementitious replacement, a large number of non-typical hydration products were observed, and was similar to the Ettringite product (sulfate ions react with calcium aluminates).



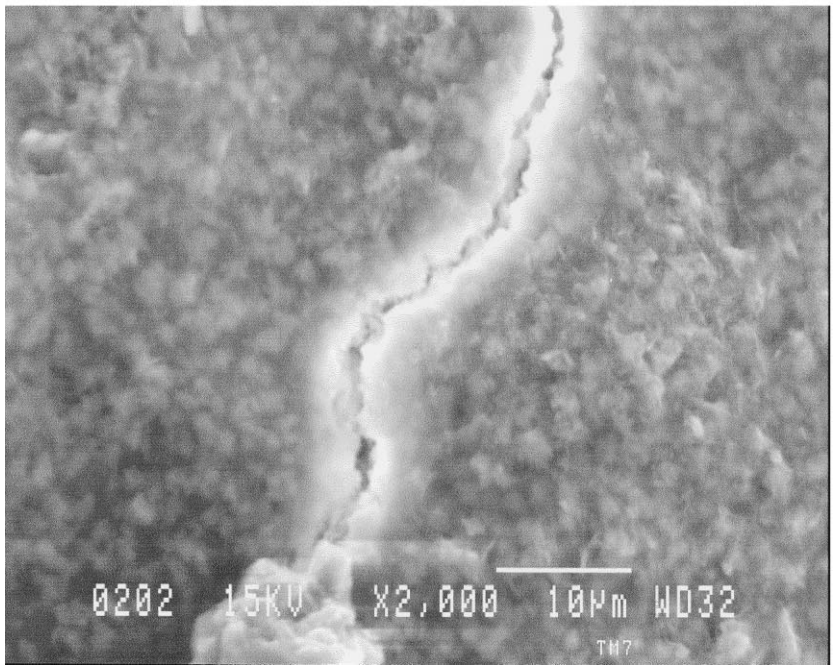


Fig. 11. (A) TM7 (×500). (B) TM7 (×2000).

(Figs. 7, 10 and 11) were the micrographs of TM3, TM6, and TM7 mixes, respectively. These mixes were formed with Type II substitutes of crushed granite passing 150 μm. It was also interesting to compare the cement paste pattern of TM1 in Fig. 5 with the cement paste and crushed granite compound in TM3, TM6 and TM7. The latter mixes had less microcracks than those in TM1. This was an indication of better crack resistance of TM3, TM6 and TM7 than that of TM1. It was also apparent that the crack resistance increased with the percentage of OPC replacement. This might be due to the precipitation effect, in which small and hard particles

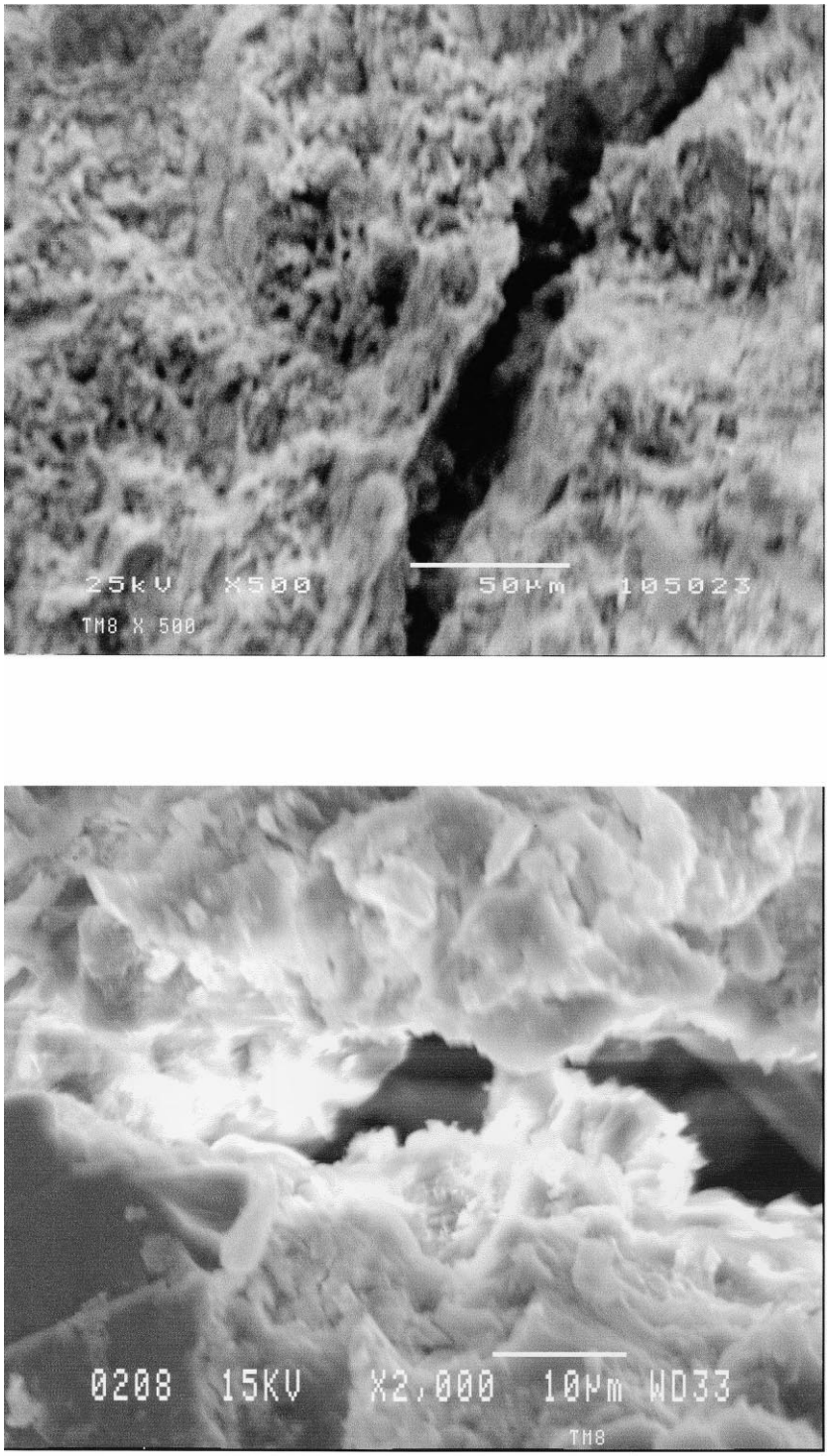


Fig. 12. (A) TM8 (×500). (B) TM8 (×2000).

Table 3
Chemical composition in EDX analysis

Element (%)	TM1 (100%) OPC	TM2 (25%) I	TM3 (25%) II	TM4 (25%) III	TM5 (35%) I	TM6 (35%) II	TM7 (50%) II	TM8 (50%) I
Ca	66.591	61.722	52.502	61.706	66.917	48.536	59.363	58.333
Si	18.715	21.751	30.089	23.763	17.598	29.131	24.361	21.762
Al	6.765	9.778	7.622	6.297	5.088	9.117	6.929	8.628
Fe	1.691	1.350	1.852	1.853	7.089	2.627	3.373	5.789
Mg	2.410	2.467	3.299	2.090	0.914	0.635	0.384	1.029
Na	0.955	0.721	1.503	1.433	0.416	0.853	0.484	1.324
K	0.717	0.286	1.201	0.705	0.757	7.905	3.170	1.510
S	2.155	1.924	1.930	2.151	1.222	1.196	1.935	1.623
Ca/Si	3.56	2.84	1.74	2.60	3.80	1.67	2.44	2.68

block the movement of dislocations and thus raise the yield strength [7–9]. A similar situation had been described in Ref. [10] for hardened cement paste (HCP), in which large unreacted particle remaining in the HCP promoted resistance to crack propagation. The other reason for the increase in crack resistance might be due to the creation of nucleation site for crystallization of hydration products in TM3, TM6 and TM7 [8,11]. A more homogeneous microstructure was formed for these three types of concrete.

Fig. 8 shows the micrograph of TM4 (Type III—crushed granite between 75 and 150 μm). It was observed that the C-S-H of the TM4 sample contained no reticulation. This was slightly different from that of samples with Type II material.

3.7. Energy dispersive X-ray

It is widely accepted that EDX results have percentage error of about 5% for a homogeneous material, and can be larger for the present concrete materials. The present EDX results were obtained to indicate the approximate chemical composition in the concrete. It is also noted that the current EDX did not include light elements such as carbon.

The EDX spectrums of the ITZ of samples TM1 to TM8 were obtained. The approximate chemical compositions of the concrete samples were summarized in Table 3. The Ca/Si element percentage ratio of the paste was also calculated.

It is remembered that TM2 and TM5 had cement contents replaced by carbon black. As carbon black is fairly pure in carbon and without the accurate detection of carbon in the present EDX, the results of TM2 and TM5 should be very similar to that of TM1. Indeed, within the accuracy of EDX, the chemical compositions in these three concrete mixes were fairly similar. In other words, their Ca/Si ratio should also be very similar. This was in reasonable agreement with Ca/Si ratios of TM1 and TM5. The Ca and Si contents in TM2 deviated from those in TM1 and TM5, resulting in a Ca/Si ratio different from those of TM1 and TM5.

It was clear that the Ca/Si ratio of replacement concrete not using carbon black, i.e. TM3, TM4, TM6, TM7 and TM8, was lower than that of OPC (TM1). This is mainly because of the extra silicate contents in the replacement particles, i.e. Types II and III. Also, it might be said that the decrease in weight percentage ratio of Ca/Si, despite an increase in the amount of C-S-H in the mixture, was caused by the silicate ions dissolved from glass and the filler effect of inert particles. This phenomenon matched the results in compressive strength. However, the lower Ca/Si ratio of TM7 and TM8 than that in TM1 did not give better strength. It was caused by the high void contents in cementitious paste of TM7 and TM8.

4. Conclusions

The current test data offer valuable information on the design of durable concrete. The primary requirements of durability of concrete are strength, workability and impermeability. The present results indicated that these could be satisfied even with 25% of the cement replaced by waste or recyclable material. The use of this type of new formulation will be environmentally friendly.

The sorptivity and permeability of a given concrete mix were found to be independent of the cement content to provide nearly the same compressive strength. However, water sorptivity and permeability decreased with increasing concrete strength. As a result, water content and densification of mix proportion would be the governing factors to sorptivity and permeability.

Further, XRD, SEM and EDX results indicated that the inert materials could also give more micro-filler effect and nucleation sites for cement hydration. It was observed that the silts and clays of granite aggregate could be used as reactive minerals.

Finally, the problem of maintaining or increasing the designed workability can be solved by using high specific surface area material with a superplasticizer admixture.

References

[1] P.K. Mehta, Mineral admixtures for concrete—An overview of recent developments, in: M.W. Grutzeck & S.L. Sarkar (Eds.), Advances in Cement and Concrete, Proceedings of an Engineering Foundation Conference, New York, (1994) 243–256.

[2] V.L. Bonavetti, E.F. Irassar, The effect of stone dust in sand, Cem Concr Res 24 (1994) 580–590.
[3] A.M. Neville, Properties of Concrete, 3rd edn. Longman, Essex, England, 1981.
[4] H.O. Pierson, Handbook of Carbon, Graphite, Diamond and Fullerences: Properties, Processing and Application, Noyes Publications, New Mexico, 1993.
[5] K. Kinoshita, Carbon—Electrochemical and Physicochemical Properties, Wiley-Interscience, New York, 1987.
[6] Advisory Note—Impurities in Aggregates for Concrete: Number 18, Cement and Concrete Association, London.
[7] J. Bijen, H. Pietersen, Mineral admixtures—Reactions, micro-structure and macro-properties, in: M.W. Grutzeck & S.L. Sarkar (Eds.), Advances in Cement and Concrete, Proceedings of an Engineering Foundation Conference, (1994) 293–328.
[8] J.A. Larbi, J.M. Bijen, Effects of water–cement ratio on the evolution of calcium hydroxide in set portland cement pastes and mortars, in: J.M. Bijen (Ed.), The Cement Paste–Aggregate Interfacial Zone in Concrete, Technical University of Delft, Netherlands, 1991, pp. 25–39.
[9] J.P. Ollivier, M. Massat, Microstructure of the paste–aggregate interface, including the influence of mineral additions, in: M.W. Grutzeck & S.L. Sarkar (Eds.), Advances in Cement and Concrete, Proceedings of an Engineering Foundation Conference, New York, 1994, pp. 175–185.
[10] T. Nishikawa, M. Takatsu, Fracture behavior of hardened cement paste incorporating mineral additions, Cem Concr Res 25 (1995) 1218–1224.
[11] D.E. Macphee, E.E. Lachowski, A.H. Taylor, T.J. Brown, Microstructural development in pore reduced cement, Mater Res Soc Symp Proc 245 (1992) 303–308.