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Carbonation around near aggregate regions of old hardened concrete cement paste

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Abstract

Analogous with most modern cities, waste disposal is a pressing issue due to limited landfill and public filling (land reclamation) areas in Hong Kong in which construction and demolition (C&D) waste forms the major source. Concrete, apportioning the largest portion of C&D waste, has the greatest potential for recycling. However, the knowledge on micro-structural behavior of concrete waste is immature to give adequate details on the macro-behavior of concrete waste. This paper attempts to examine the problems of recycling old concrete by investigating the microstructure and phase transformation of the concrete samples collected from buildings with 46 and 37 years of services. From the results of Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) examination, it is found that there are a lot of pores at the near layers of aggregate where carbonation of the hardened cement paste (HCP) is high. The pores may be generated as a result of poor workmanship such as insufficient concrete mixing time, trapping of air voids beneath coarse aggregate, inappropriate water to cement ratio, and the microclimate conditions such as humidity that affects the demand on water from the aggregate during mixing.

Keywords: Carbonation; Interfacial transition zone; SEM; Cement paste

1. Introduction

Akin to most developed countries, Hong Kong is facing the problem of exhausted landfill and land reclamation areas for handling the massive generation of construction and demolition (C&D) waste. Because of the running out of both reclamation sites and landfill spaces, the landfills will be filled up in 10–15 years, and approved reclamation projects will only provide outlets for the public fill until 2004 [1]. For sustainable development, Hong Kong can no longer rely solely on reclamation to accept most of the C&D material. The government is examining ways to reduce and also to promote the reuse and recycling of C&D material. As such, waste minimization techniques such as reuse, recycle and reduction have been advocated. There is a growing social pressure upon the government to minimize the waste generated from the construction sector, leading to the various measures such as the proposed bill on charging HK$125 per ton of waste dumped into the public landfill areas and the advocate of recycling and reuse of construction waste.

Construction wastes apportion a considerable share among all types of solid wastes in most developed countries as shown in Table 1. More than 50% of waste deposited in a typical landfill comes from construction [2] while 70 million tons of wastes are arisen from C&D in the United Kingdom [3]. About 14 million tons of wastes have been put into landfill each year, and 44% of the waste is attributed to the construction industry in Australia [4,5]. Around 29% of solid waste is from

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Table 1
Comparison of proportions of construction solid waste [1,17–19]

Country	Proportion of construction waste to total waste (%)	C&D waste recycled (%)
Denmark	25–50	80
Netherlands	26	75
Japan	36	65
Germany	19	40–60
Australia	44	51
United Kingdom	over 50	40
Finland	14	40
France	25	20–30
United States of America	29	25
Spain	70	17
Italy	30	10
Brazil	15	8
Norway	30	7
Hong Kong	38	no information

construction in USA [6] while about 38% of solid waste comes from construction in Hong Kong [1]. As most building structures in Hong Kong are in the form of reinforced concrete, concrete forms the major C&D inert waste, recycling of which provides opportunity for saving the environment. Furthermore, recycling and reduction of concrete waste can preserve quarries for aggregate in Hong Kong. Recycling of concrete waste includes the use of fine recycled aggregate (RA) for paving blocks, coarse RA for backfilling materials, concrete haunch for drainage pipes, roadwork sub-base, etc. However, the use of RA for structural concrete works is still limited by the lack of detailed knowledge on the microstructure behaviors of demolished concrete. In Hong Kong, the use of RA for new concrete is smaller than 1%, which demonstrates the high potential of future development and opportunity.

This paper presents findings from using Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) to study the near aggregate regions of concrete waste collected from buildings of 46 and 37 years of services. The study aims to identify the properties of old concrete in terms of microstructure behavior and phase transformation of hardened cement paste (HCP) in concrete from buildings suffering from long-term environmental exposure.

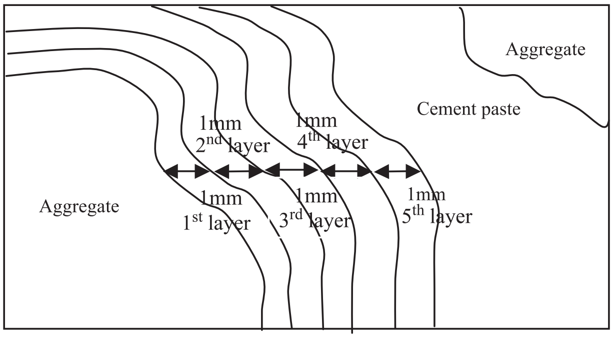

Fig. 2. Five layers of cement paste around aggregate for FT-IR examination.

2. Near aggregate regions

Previous research works have identified the microstructure of HCP, which is presented schematically in Fig. 1. Concrete is of a three-phase system, comprising coarse aggregate, mortar matrix with fine aggregate, and interfacial zones between the coarse aggregate and the mortar matrix [7–9]. In concrete, the interfacial zone between cement paste and aggregate plays a critical role in determining mechanical performance. At the meso-level, concrete is a composite material consisting of discrete aggregates dispersed in a continuous cement-paste matrix [10]. As with other composites, the bond between these two major components of concrete is a critical component determining the mechanical performance. Therefore, the bonding region or transition zone in concrete between matrix and aggregate has been a subject of research in recent years.

3. Sampling and experimental procedures

In order to understand the microstructure and phase transformation of HCP in old concrete, this study has

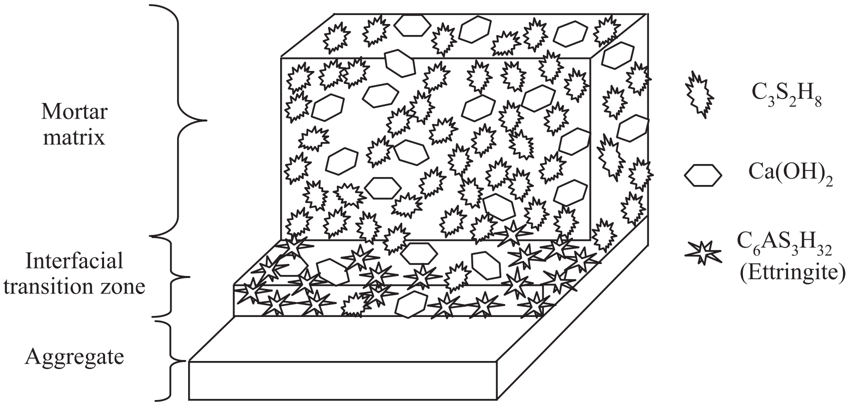

Fig. 1. Schematic representation of the transition zone in concrete.

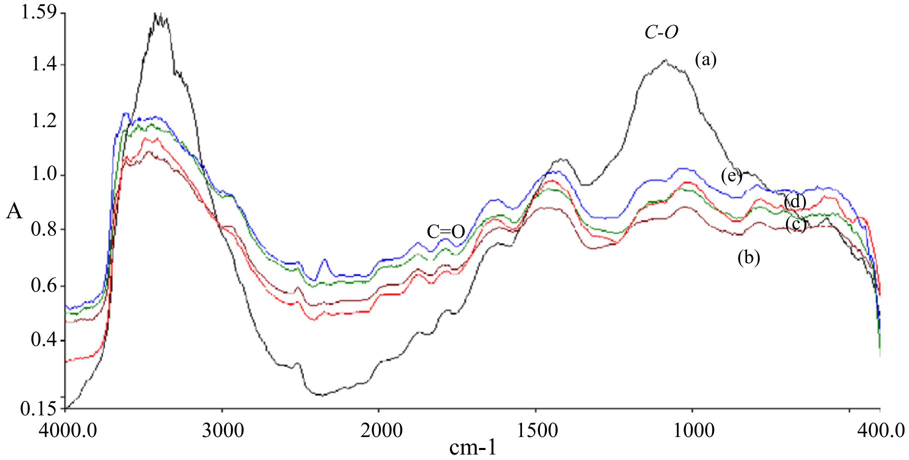

Fig. 3. Comparison of FT-IR absorbance spectra of Sample 1. (a) 1st layer of cement paste; (b) 2nd layer of cement paste; (c) 3rd layer of cement paste; (d) 4th layer of cement paste; and (e) 5th layer of cement paste.

analyzed four HCP samples collected from two construction demolition sites. Samples 1 and 2 are collected from a site located next to Victoria Harbour on the Hong Kong Island; the buildings are 46 years old constructed in 1957 and demolished in 2003 with seven single towers in a form of 11-storey high reinforced concrete residential building structures. The samples were collected from the external wall facing Victoria Harbour, within 5 cm deep from the surface of the structure.

Samples 3 and 4 were collected from a public housing estate composing of five tower blocks adjoined by another public estate and an industrial building in the New Territories, of 37 years old constructed in 1966 and demolished in 2003 in a form of 8- to 11-storey high reinforced concrete residential building structure. Again, the samples were collected from the external wall within 5 cm deep from the surface of the structure.

Infrared spectra were recorded using a FT-IR spectrometer spectrum 1000 (Perkin Elmer). Five layers of cement pastes, 1 mm apart counting from the surface of aggregate as shown in Fig. 2, were analyzed using FT-IR to investigate their phase transformation.

The microstructure of the samples was investigated using SEM. The samples were cut into 2 mm think plates; the fracture surface was gold-plated for SEM examination by a JEOL JSM-820 scanning microscope.

4. Results and discussion

The corresponding FT-IR absorbance spectra of the four HCP samples (46 and 37 years of service) on the 1st, 2nd, 3rd, 4th and 5th layers of cement paste are shown in Figs. 3–6. Carbon–oxygen single bonds (C–O) and carbon–oxygen double bonds (C=O) from the FT-IR spectra recorded can be used to explain the carbonation conditions of the concrete samples in qualitative terms. The total absorbance of C–O bonds and C=O bonds measured from the FT-IR spectra can be used to assess the degree of carbonation quantitatively; the phase transformation can be

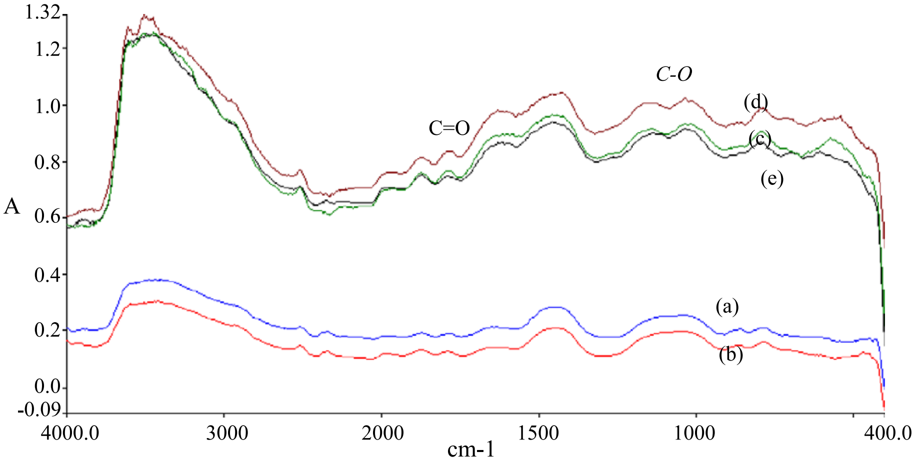

Fig. 4. Comparison of FT-IR absorbance spectra of Sample 2. (a) 1st layer of cement paste; (b) 2nd layer of cement paste; (c) 3rd layer of cement paste; (d) 4th layer of cement paste; and (e) 5th layer of cement paste.

Table 2
Absorbance peak and total absorbance on C–O and C=O for Samples 1 to 4

Sample	Layer	C–O		C=O	
		Absorbance peak (cm^{-1})	Total absorbance (A cm^{-1})	Absorbance peak (cm^{-1})	Total absorbance (A cm^{-1})
1	1st	1086.75	100.9276	1778.06	1.7689
	2nd	1042.67	15.0480	1794.99	1.1168
	3rd	1034.21	18.8345	1786.25	1.1275
	4th	1024.58	21.0851	1784.69	1.2648
	5th	1039.74	22.3666	1791.03	1.4928
2	1st	1038.57	21.5963	1794.86	0.1955
	2nd	1035.53	22.7698	1790.83	0.6362
	3rd	1017.74	21.0780	1792.37	0.6365
	4th	1038.35	16.6799	1794.54	0.5411
	5th	1038.28	15.4050	1795.50	0.4223
3	1st	1032.13	40.7833	1779.97	1.0646
	2nd	998.37	23.8413	1784.66	0.8615
	3rd	997.54	44.4014	1781.56	1.3522
	4th	1000.59	47.4144	1785.68	0.9637
	5th	991.82	52.7842	1783.23	0.9715
4	1st	1020.36	21.9485	1776.62	0.2255
	2nd	1020.15	41.7710	1782.34	0.5424
	3rd	991.50	19.5300	1783.07	0.2119
	4th	1032.61	45.4978	1782.44	0.5121
	5th	1025.05	52.7264	1782.47	1.0443

inferred. The absorbance peaks and the total absorbance of the C–O and C=O bonds at the 1st, 2nd, 3rd, 4th and 5th layers of cement paste for Samples 1 to 4 are summarized as in Table 2.

Comparing the C–O and C=O peaks, it can be concluded that the spectra represent materials with similar molecular characteristics with respect to the fingerprint spectrum.

5. Discussion

From the above results, it can be observed that there is a gradual increase in the total absorbance of C–O and C=O bonds in Sample 1 and of C–O bonds in Sample 3 from the 2nd to 5th layers of cement paste and of C–O and C=O bonds in Sample 4 from the 3rd to 5th layers of cement paste and of C–O bonds in Sample 2 and of C=O bonds in Sample 3 from the 4th to 5th layers of cement paste. The change in gradient can be observed in Figs. 3–6 for Samples 1, 2, 3 and 4, respectively, representing the sign of carbonation.

From the SEM examination on Samples 1 to 4, it is observed that there are a lot of pores in the samples. Those pores are mostly distributed and occurred in the layers of cement pastes close to the aggregate surface. Fig. 7 show the SEM micrographs in the 1st layer of cement paste in Sample 1; Fig. 8 shows the SEM micrograph in the 1st layer cement paste in Sample 3. All show the existence of pores in the closer layers around aggregate in the HCP samples. After the examinations of the pore distribution, it can be concluded that the occurrence of pores has a direct relation with carbonation of the old concrete.

Theoretically, cement paste far from the inner aggregate should be exposed to a higher degree of carbonation from the external wall. Therefore, the total absorbance of C–O and C=O bonds should be gradually decreasing from the 5th layer to the 1st layer of cement paste. However, the results from the four selected samples show that the scenario is just reverse. The total absorbance of C–O and C=O bonds in the layers near to the aggregate surface, such as the 1st or 2nd layers of cement paste, is higher. For example, the total of 100.9276 A cm^{-1} absorbance of C–O bonds was measured at the 1st layer of cement paste, which is six times that (15.0480 A cm^{-1}) of the total absorbance of C–O bonds at the 2nd layer of cement paste in Sample 1. As regards C=O bonds, a total absorbance of 1.7689 A cm^{-1} was recorded at the 1st layer of cement paste, 50% more than that of the 2nd layer of cement paste. Similar scenarios happen in Samples 2, 3 and 4 but to a lesser extent when compared to Sample 1.

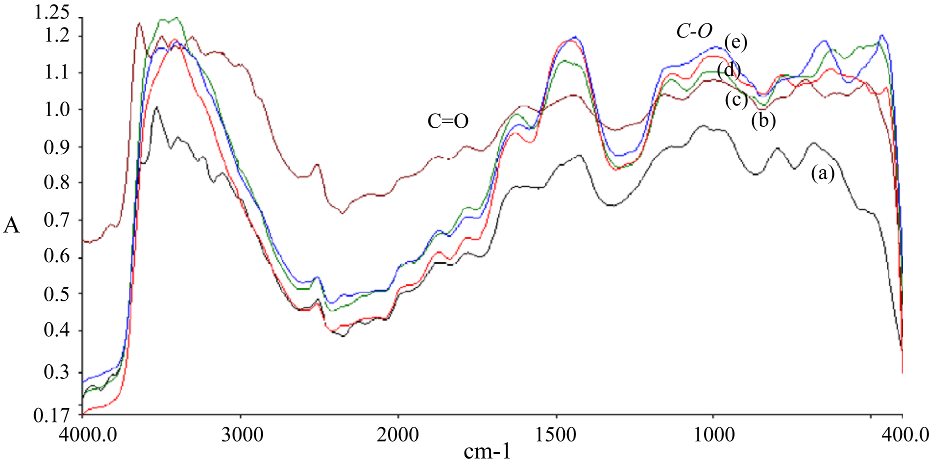

Fig. 5. Comparison of FT-IR absorbance spectra of Sample 3. (a) 1st layer of cement paste; (b) 2nd layer of cement paste; (c) 3rd layer of cement paste; (d) 4th layer of cement paste; and (e) 5th layer of cement paste.

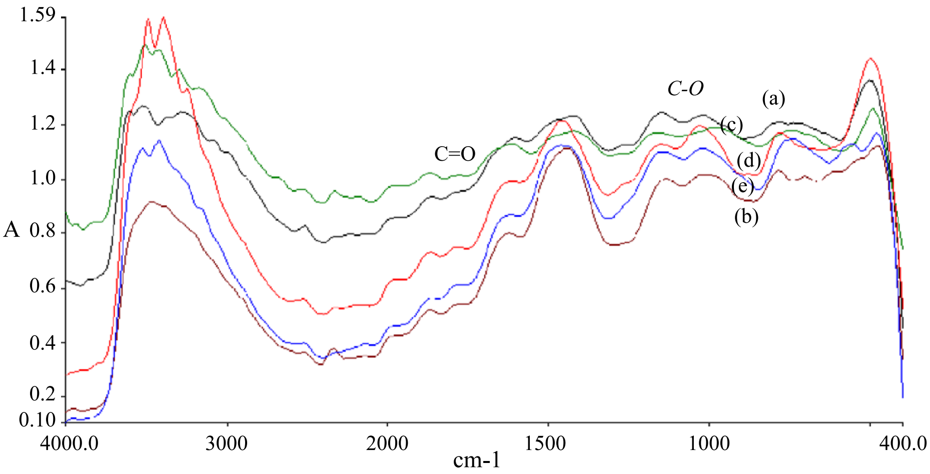

Fig. 6. Comparison of FT-IR absorbance spectra of Sample 4. (a) 1st layer of cement paste; (b) 2nd layer of cement paste; (c) 3rd layer of cement paste; (d) 4th layer of cement paste; and (e) 5th layer of cement paste.

CO_2 in the atmosphere reacts, in the presence of moisture, with hydrated cement minerals. The reaction of CO_2 takes place even at small concentrations such as in the rural air, where the CO_2 content is about 0.03% by volume. In an unventilated laboratory, the content may rise above 0.1% and in large cities, on average to 0.3%, and exceptionally to 1% [11]. The rate of carbonation increases with an increase in the concentration of CO_2, especially at high water to cement (w/c) ratios. Carbonation of hardened cement matrix most commonly takes place by the reaction of both calcium hydroxide and cement hydrates with atmospheric carbon dioxide [12]. An extensive literature review of the carbonation of reinforced concrete [13] and of damage classification [14] has been reported by Parrott. The reaction has also led to the breakdown of the original equilibrium in the material system, leading to the formation and accumulation of $CaCO_3$ as shown in Eqs. ((1)–(4)), and thus, C–O and C=O bonds within concrete are:

$$Ca(OH)_2+CO_2 \rightarrow CaCO_3+H_2O \tag{1}$$

$$\text{Calcium silicate hydrate}+CO_2 \rightarrow \text{Various intermediates} \rightarrow CaCO_3+SiO_2nH_2O+H_2O \tag{2}$$

$$\text{Aluminate hydrates}+CO_2 \rightarrow CaCO_3+\text{hydrated alumina} \tag{3}$$

$$\text{Ferrite hydrates}+CO_2 \rightarrow CaCO_3+\text{hydrated alumina and iron oxides} \tag{4}$$

Such a complete decomposition of calcium compounds in hydrated cement is chemically possible even at the low pressure of CO_2 in normal atmosphere but carbonation penetrates beyond the exposed surface of concrete only

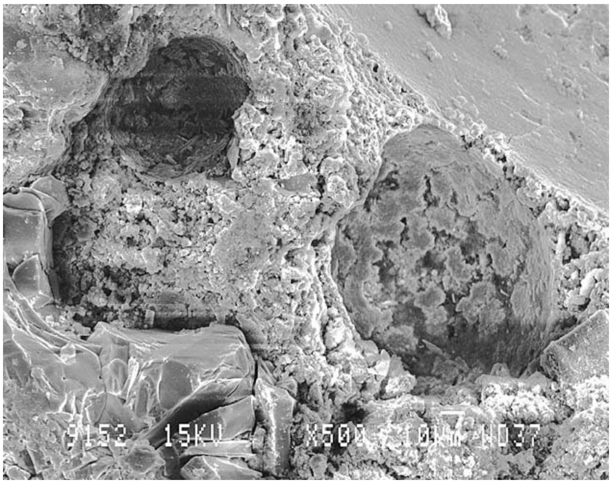

Fig. 7. SEM micrographs showing pores around aggregate in the 1st layer of cement paste in Sample 1.

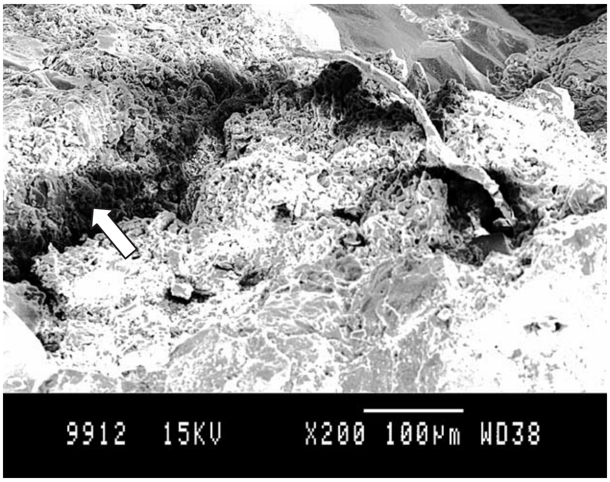

Fig. 8. SEM micrographs showing pores around aggregate in the 1st layer of cement paste in Sample 3.

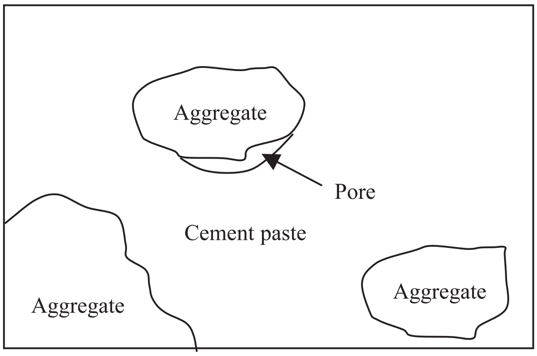

Fig. 9. Schematic diagram showing formation of pores under aggregate during concreting.

extremely slowly [11]. Carbonation may have a deleterious effect on the hardened cement paste as it appears to decrease strength and increase porosity [12,15]. Carbonation causes a marked increase in porosity and reduction in strength of super-sulfated cement probably due to the carbonation of the ettringite [16]. At this stage of carbonation, it is probable that the cement hydrates have been largely destroyed.

For the practical purpose of explaining the depth of carbonation observed, the major controlling factors are the w/c ratio, the porosity of the aggregates, curing and the environment to which the structure is exposed [11]. The depth of carbonation is roughly proportional to the square root of time, doubling between 1 and 4 years, then again doubling between 4 and 10 years; there is probably a further doubling up to 50 years [10]. When carbonation depths exceed 5 mm, the nature of the carbonation zone may change. Islands of uncarbonated cement paste are often present in the carbonation zone and isolated areas of carbonation may be seen beyond the carbonation zone in the paste and around some aggregates [11]. As regards the four selected samples, these isolated patches of carbonation indicate that a porous pathway is present out of the plane of the section. The margins of the carbonation zone are irregular and carbonation will penetrate deeply into cracks if these are present. This behaviour is an expression of the localized variability, which occurs in concrete especially in the porous surface areas of concrete. Therefore, the four selected samples may have a lot of pores around aggregates; the carbonation will also easily react with the calcium hydroxide and carbon dioxide to form $CaCO_3$.

The existence of pores at the near aggregate regions of the four selected samples may be explained by the following four major issues: (1) inadequate mixing time of concrete causing some large pores left; (2) coarse aggregate trapping some voids underneath as shown in Fig. 9; (3) inappropriate w/c ratio either too dry or too wet causing the formation of pores; and (4) microclimate conditions such as humidity in the environment affecting the demand on water from aggregate during mixing.

6. Conclusion

In Hong Kong, the landfill consumption is so high that the landfill areas will be running out in the next 10 years. Hence, it is necessary to reduce concrete waste by recycling. However, the hydrated cement paste sticking onto the surface of recycled aggregate (RA) changes the mechanical and chemical performance of RA in new concrete. This paper aims to investigate the microstructure and phase transformation of HCP in concrete waste with the aid of FT-IR. It is found that there is an increase in the C–O and C=O bonds at the near layers of aggregate, inferring the formation of pores that affects the concrete performance, which was confirmed by the SEM investigation. This study used FT-IR to identify the gradient of carbonation at the near aggregate regions of demolished concrete waste, which was further correlated with the gradients of pores discovered from SEM. The whole exercise shows the relationship between carbonation and the existence of pores at the near aggregate regions that concludes the poor quality of demolished concrete waste to be used as recycled aggregate. Inadequate mixing time, trapping of void underneath coarse aggregate, inappropriate w/c ratio and the microclimate conditions such as humidity of the environment are the likely reasons for the formation of pores. These pores increase the water absorption of RA and decrease the compressive strength of new concrete. Further studies on ways to reduce or even fill up these pores using innovative technology need to be explored in the future, enabling recycled aggregate competitive with the virgin aggregate.

Acknowledgments

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