Analysis of the infrared spectrum and microstructure of hardened cement paste

X.F. Gao [a], Y. Lo [a,*], C.M. Tam [a], C.Y. Chung [b]

[a]*Department of Building and Construction, City University of Hong Kong, 83 Taf chee Avenue, Hong Kong, People's Republic of China*
[b]*Department of Physics and Materials Science, City University of Hong Kong, 83 Taf chee Avenue, Hong Kong, People's Republic of China*

Abstract

Phase transformation was found in hardened cement paste exposed to dynamic loading caused by typhoon and the normal static-dynamic loading. The concrete samples were obtained from a 20-year-old residential building. The bonding characteristics and microstructure of the hardened cement paste with different loading history have been carefully studied using scanning electron microscopy analysis and infrared spectrum technique. The scanning electron microscopy micrographs indicate that there is a morphological difference in the concrete microstructure. The infrared spectrum analysis has provided information for understanding the phase transformation characteristics of the primary bonds and secondary bonds. This has led to the establishment of a microscopic model describing the correlation between the behavior of the hydrate lime and the properties of the hardened cement paste. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Infrared spectrum; Microstructure; Bonding; Phase transformation; Typhoon; Dynamic loading

Our knowledge and understanding of the microstructure of hardened cement paste (HCP) have increased gradually. The widely accepted structure of the HCP is presented schematically in Fig. 1 [1,2]. With the help of advanced testing equipment and more sophisticated software for analysis, more accurate models on the microstructure of HCP were developed [3–7]. However, most of these experimental results were obtained from laboratory scale testing. Not many reports have been made on the microstructure and phase transformation of HCP in the real-size building under long-term influence of dynamic loading due to typhoon [8].

With the support from the University Grant Council of Hong Kong, the Structural Dynamics Research Centre of the City University of Hong Kong had started this investigation several years ago. The investigation aims at understanding the microstructural evolution and phase transformation of the HCP under the influence of typhoon. The primary bonds and secondary bonds in the HCP were studied by infrared (IR) spectrum analysis. This is worth studying because the alteration of the bonding characteristics might contribute to the change in HCP's mechanical properties and subsequently affect the remaining life of the concrete structure.

This paper presents findings of scanning electron microscopy (SEM) and IR analyses that were performed in order to study the microstructure and phase transformation of HCP in concrete of buildings suffering from long-term dynamic loading due to typhoon. In addition, a model based on the results from IR and SEM analysis describing the HCP microstructure is suggested.

1. Experimental procedure

The HCP samples were collected from a 26-storey double tower reinforced concrete residential building 20 years old. Two square ring-type towers with partitions were connected by a shared lift lobby. Both square towers have sky openings at the centre. Besides the normal dead and live loading, the structure also experienced severe dynamic loading during the summer typhoon seasons. The structure of the building was of shear-wall type. In the typhoon season, the amount of rainfall was usually high in that area.

Concrete samples were collected from the locations marked A, B, and C as shown in Fig. 2. They are chosen to reflect the differences in stresses under dynamic load of typhoon. It was estimated that the greatest stress magnitude was at position A followed by C and lastly B. Blocks of cylindrical concrete cores of diameter 150 mm were drilled from structural walls of the third floor and the twenty-fifth floor. The coring process was slow to prevent
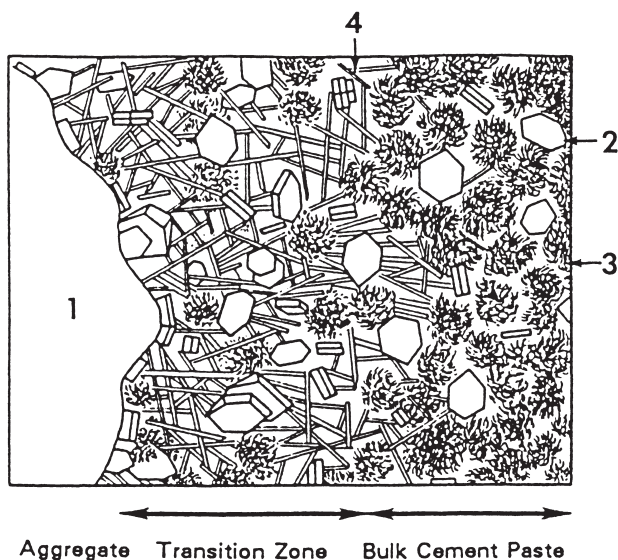
Fig. 1. Schematic representation of the transition zone in concrete. 1, aggregate; 2, Ca(OH)$_2$; 3, C-S-H; 4, Ettringite [1,13].

Table 1
Composition of the concrete samples

Sample	Na$_2$O	SiO$_2$	CaO	Fe$_2$O$_3$	Al$_2$O$_3$	TiO$_2$	MgO	SO$_3$	Others
A	1.40	19.05	60.31	2.84	6.17	1.0	1.80	1.84	3.88
B	1.38	21.72	59.79	2.42	6.07	0.0	2.16	2.19	4.1
C	1.1	19.88	61.64	2.76	5.84	0.0	2.28	1.74	3.92

plates were broken by bending and the fracture surface was gold coated for SEM examination. An energy dispersive analyser (EDAX) was attached to the JEOL JSM-820 SEM for composition analysis. Composition of the concrete samples is given in Table 1. The morphology of the concrete samples was examined in the secondary electron mode with acceleration voltage and working distance of 15 keV and 5–9 mm, respectively.

The IR spectra were recorded using a FT-IR 20 SX Infrared Spectrophotometer (Perkin Elmer) with 4 cm^{-1} resolution. The results from the IR spectrum analyses were used for interpreting the microstructure observed in the SEM. The IR and SEM analyses formed the foundation for the construction of the microstructural model.

2. Results and discussion

2.1. SEM analysis

Figs. 3(a), 3(b), and 3(c) show the SEM micrographs of the HCP from concrete at the third floor, while Fig. 3(d) was obtained from the twenty-fifth floor. The imposed static and dynamic stresses of the concrete on the twenty-fifth floor should be lower. By comparing Figs. 3(a–c) and Fig. 3(d), significant morphological differences can be observed. The needle-shape crystals have almost completely disappeared in Figs. 3(a–c), which was attributed to the much higher stress concentrated at the third floor concrete. A gradual change in morphology of Figs. 3(a–c) is also noted, possibly due to the differences in imposed stresses. The concrete will have fewer needle-shape crystals when the imposed stress level is higher. From the EDAX analysis, it is found that the needles are mainly composed of various classes of silicate compounds. This leads us to believe that the needle crystals are HCP. The present investigation also indicates that the volume fraction of this needle-crystal clusters decreases with respect to loading time. It can be treated as an indication of the degree of phase transformation in the HCP, a metastable phase of cementitious material in the concrete transformed to a more stable phase under suitable conditions.

overheating the concrete samples and altering the water content. In the sample collection process, carbonation of concrete was noted. The influence of the concrete carbonation was eliminated by careful sample preparation. Thin plates were cut from the interior of the concrete core at a distance of more than 70 mm from the surface. The thin
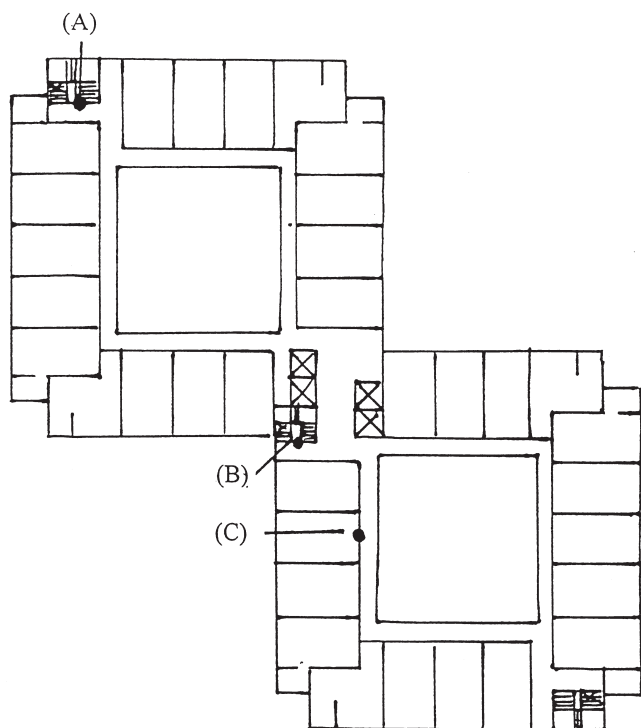

Fig. 2. The plan of double-tower residential building studied.

2.2. IR spectrum analysis

2.2.1. Analysis of water in the concrete

Fig. 4 shows the corresponding IR spectra of the concrete samples after 20 years of service. In Figs. 4(a), 4(b), and 4(c), the characteristic peaks for the stretching vibration
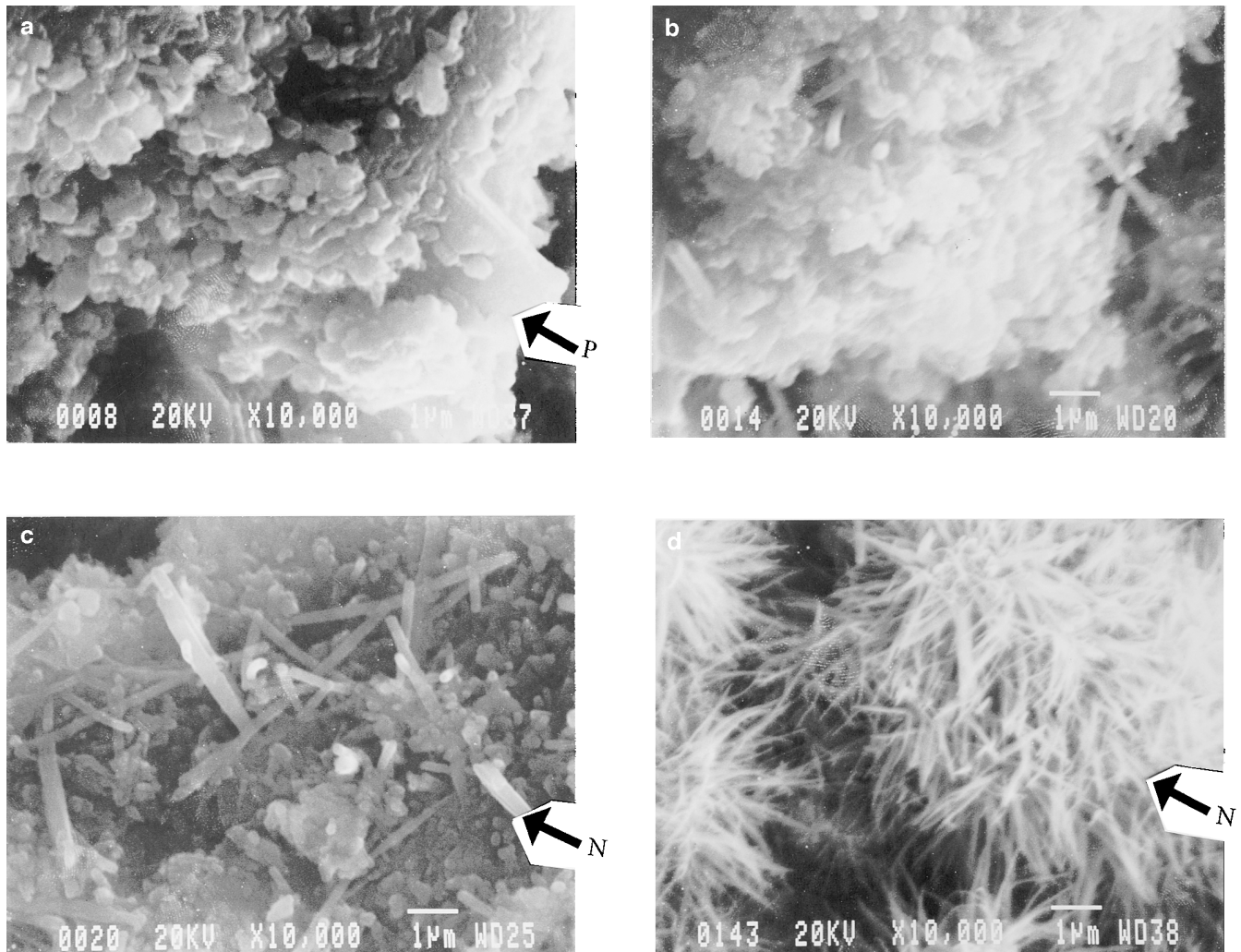
Fig. 3. SEM micrographs of the HCP samples taken from the third floor under *(a)* highest dynamic stress, *(b)* medium dynamic stress, and *(c)* lowest dynamic stress; *(d)* is the sample from the twenty-fifth floor, which experienced very little dynamic stress. (N, needle-sharp crystals; P, platelike crystals).

of the -OH bonds are located at 3440 cm^{-1}. These characteristic peaks are diffused and overlapped with each other; this represents a strong deformation vibration of the -OH bonds in the concrete. The samples for Figs. 4*(a–c)* were collected from concrete at different locations of the third floor. The imposed stress was the highest for *(a)* and the lowest for *(c)*.

There is a graded variation in the IR absorbance for the -OH characteristic peaks in Figs. 4*(a)*, 4*(b)*, and 4*(c)*. The lower the imposed dynamic stress, the higher the IR absorbance was recorded. The difference can be attributed to the variation of water content and location of the -OH bonds of water in the concrete materials. The water in the concrete (including the water of crystallization, the chemically bonded water, and the surface-absorbed water) will transform and react differently with other constituting elements under different stressing conditions.

In summary, water in the concrete has undergone crystallographic changes and phase transformation with different transformation rates under different imposed stresses. The transformation involved is affected by the changes in the primary and the secondary bonding. Severe static and dynamic loading should be one of the conditions for activating such transformation.

2.2.2. Analysis of the hydrogen bonds (H-bond)

Hydrogen bond may form between a hydrogen atom in a molecule with other atoms of higher electronegativity either inter- or intramolecularly. The structure of a hydrogen atom is quite unique because there is only one electron orbiting around the nucleus. When the hydrogen atom forms a compound with other elements having higher electronegativity, the electron from the hydrogen atom will be occupied by that atom. The nucleus of the hydrogen atom becomes exposed (or uncovered) and forms strong H-bonds with elements possessing higher electronegativity. The bond length of H-bond is relatively long. It is a weak bond with strength of 20–40 kJ mol^{-1} when compared with strengths of 150–

(a)

(b)

(c)
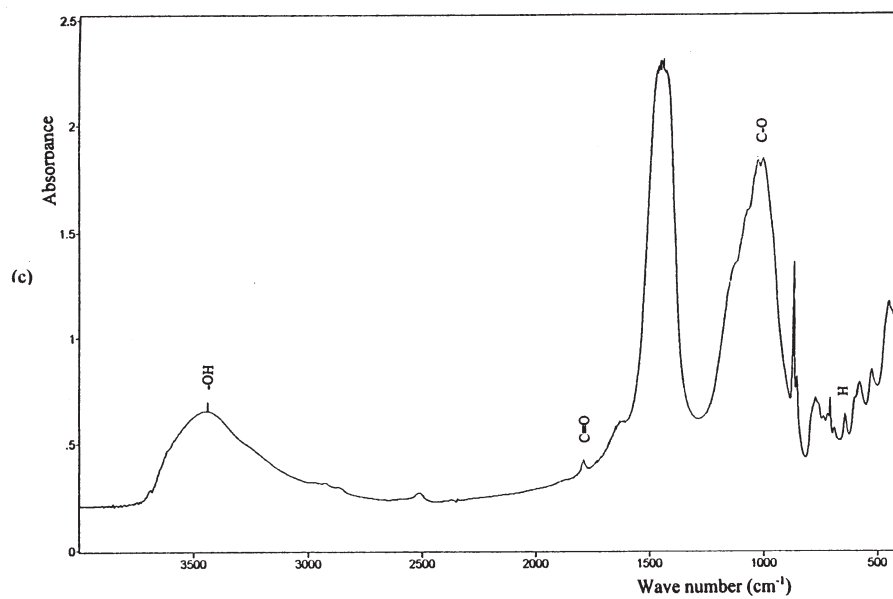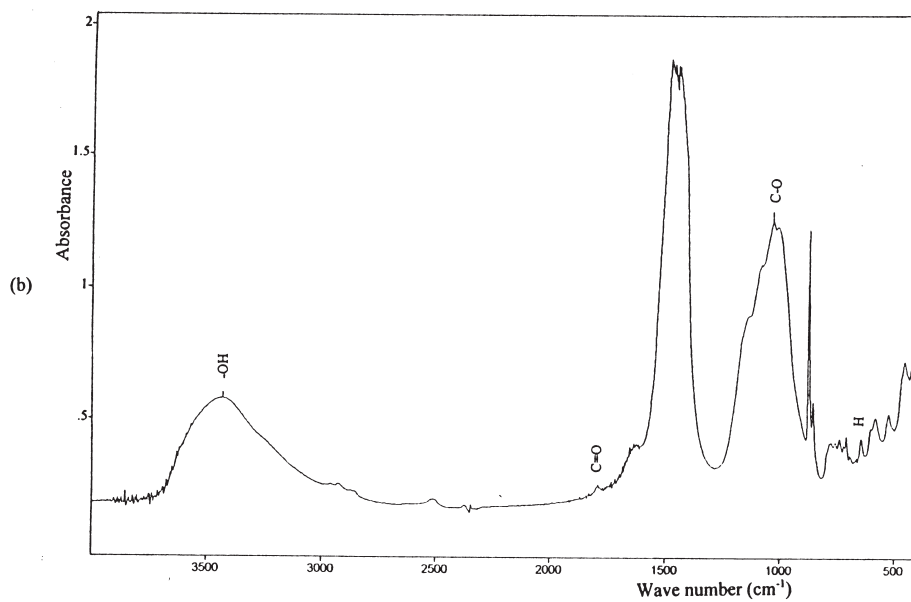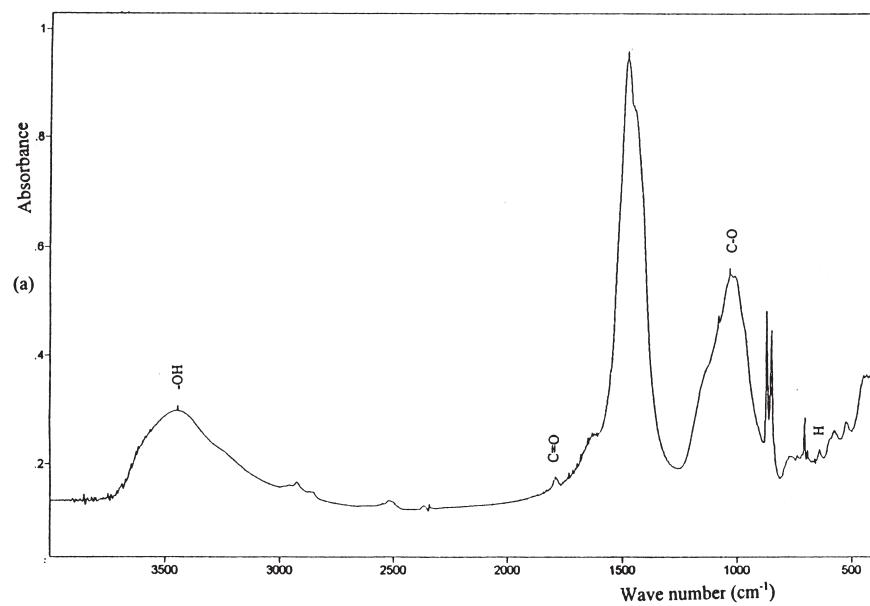
500 kJ mol^{-1} for normal covalent bonds. However, this is much stronger than the Van Der Waals' attraction between molecules.

The IR characteristic peak of the H-bond locates at 650 cm^{-1}. From Fig. 5, we found that the H-bonds in the concrete were affected after loading for 20 years. The amount of H-bond decreased when the dynamic loading was higher. This implies that many H-bonds had been broken due to the severe dynamic loading imposed on the HCP. The breakage of the H-bonds will lead to the increase of the diffusive activities of the free hydrogen protons. The increase in the concentration of hydrogen ion might increase the reactivity of Ca(OH)$_2$ and the transformation of water molecules in the concrete. Subsequently, phase transformation of microcrystal and gel-like structures toward the thermodynamic equilibrium would be allowed and enhanced.

According to the principle of conservation of energy, it is obvious that the chemical reaction and phase transformation are facilitated by the energy from the external work done that is absorbed by the structural materials through the damping phenomenon. If the temperature rise due to damping is not considered, then the damping energy may be consumed in activating the phase transformation and chemical reactions in the concrete. At present, the distribution of the energy used for facilitating the chemical reaction and the phase transformation is unknown. However, this will not weaken the conclusion that would be established.

2.2.3. Analysis of the carbon-oxygen single bonds and carbon-oxygen double bonds

Phase transformations characteristics of the carbon-oxygen primary bonds were investigated with the IR spectra recorded. The characteristic peaks for the stretching vibration of the carbon-oxygen double bonds (C=O) locate at 1760 cm^{-1}. The behaviour of the C=O bonds with respect to imposed stresses is similar to that of the -OH bonds. The IR absorbance of the C=O bonds is the lowest after the concrete has been exposed to the highest dynamic stresses. This implies that the C=O bonds in the concrete material will decrease with respect to increase in applied dynamic stress. It is proposed that the following chemical reaction shown in Eq. (1) has been induced and accelerated by increasing the imposed dynamic stresses:

$$CaCO_3 + H_2O \leftrightarrow CO_2 + Ca(OH)_2 \qquad (1)$$
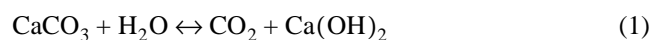
This is an endothermic and reversible reaction. The static and dynamic loading may provide the energy required for such a reaction. In other words, external work must be done on the concrete materials and subsequent absorption of the energy must occur to facilitate this endothermic reaction.

Obviously, the consumption of the energy during the dynamic loading (or vibration motion) of the concrete materials should also contribute to the damping ability of the concrete material. Part of the mechanical energy (kinetic energy and elastic strain energy) is transformed to chemical energy, which is then stored in the material as internal energy. The magnitudes of the loading and the local microscopic stress concentration on the material should have a close relationship with the possible occurrence of this reaction.

The characteristic peaks of the C-O bonds are 1036 and 1010 cm^{-1} for the stretched state and the erected state, respectively. By comparing the C-O related peaks in Fig. 5, it is concluded that the same systematic variation of the IR absorbance with respect to the imposed stress is similar to that of the C=O bonds.

Change in gradient between peaks is observed; the sign of carbonation is noted in Fig. 5. It is strange and contradictory to the sample condition because the top 70 mm of the concrete core is cut. The possibility of carbonation is eliminated in the first place. Also, the presence of carbonated product may not be due to difference in CO$_2$ concentration with elevation since samples are taken from the same floor level. A plausible explanation is lacking at present and worth for further investigation.

The reaction has also led to the breakdown of the original equilibrium in the material system. This would lead to the formation and accumulation of Ca(OH)$_2$ (i.e., CH) in the concrete and the concrete will become more alkaline. The gradual increase in CH may enhance the crystallinity and affect the stability of the HCP. The effect of this reaction on the rate of concrete carbonation is not known. Further investigation is required to clarify its significance and possible correlation. Since the reaction was processed very slowly, the CSH and CH may cooperatively crystallize, forming the complex jag-shape interlocking microcrystalline morphology. We called this as the Rabbet Effect (RE).

2.3. RE

RE is a hypothesis proposed for describing the microstructural observation of concrete materials [9]. The transformation mechanism would be quite interesting as well as complicated. In Fig. 3(b) it can be found that a microcrystallising CSH is engulfing/invading a large piece of CH crystal. RE suggests that part of the imposed dynamic energy is dissipated, assisting the crystallographic transformation of the composing crystals. Morphological transformation observed in the SEM showing the gel-like compound composed of the CSH and CH microcrystals. The formation of the interlocking microcrystalline structure in the CSH and CH microcrystals has progressed at an extremely low rate.
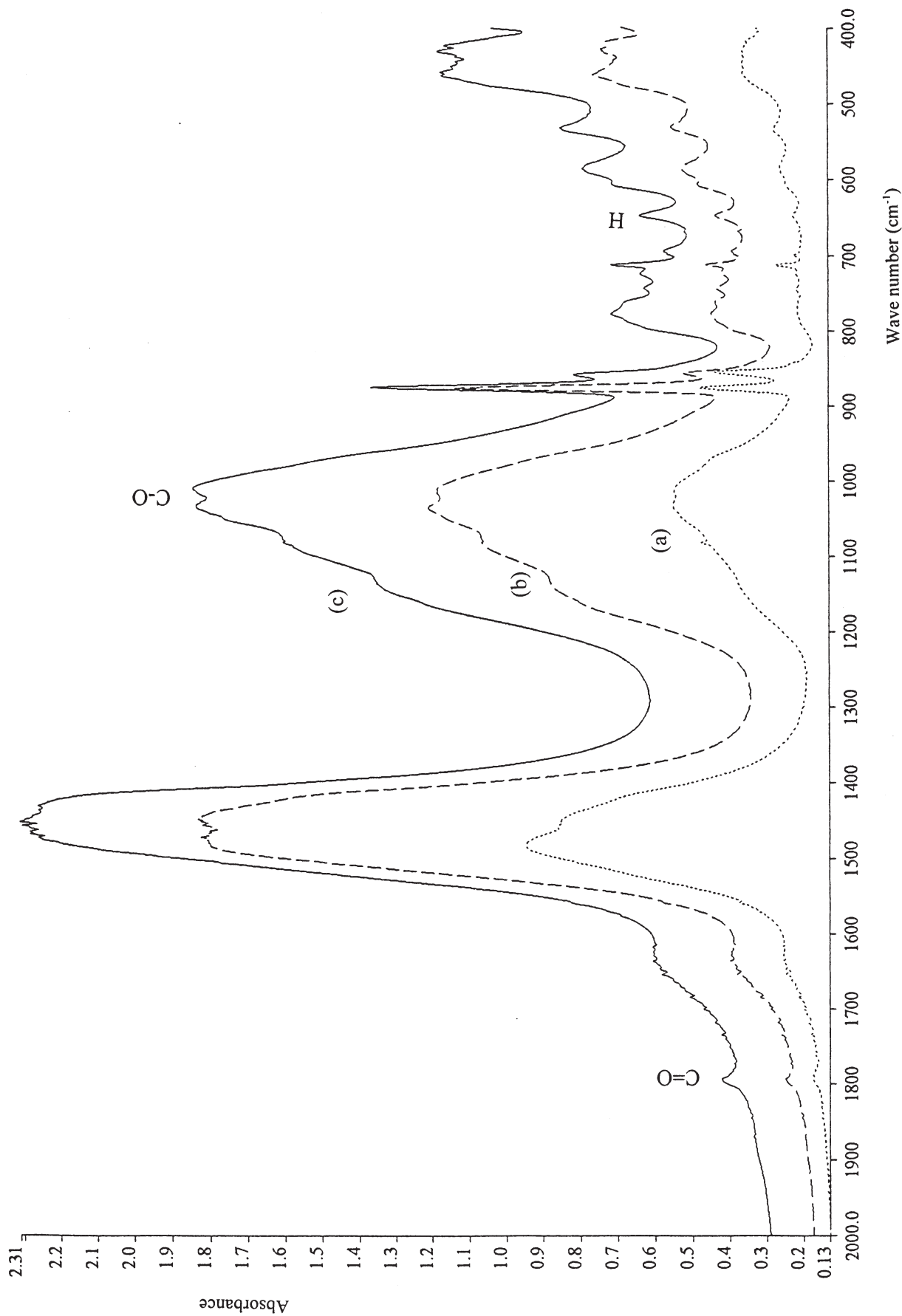
Fig. 4. The IR absorbance spectrum of the HCP samples correspond to the SEM micrographs in Fig. 2; *(a)* highest domain stresses, *(b)* medium dynamic stresses, and *(c)* lowest dynamic stresses.

Fig. 5. A comparison of IR absorbance spectra of the HCP samples under (*a*) highest dynamic stresses, (*b*) medium dynamic stresses, and (*c*) lowest dynamic stresses.

Hence, a stronger and better accommodate cohesion can be established in the complex crystalline structure. This represents that the strength of the concrete can be enhanced. This is in agreement with the reported experimental results of strength enhancement in concrete after multiaxial stressing [10–12].

Other consequences due to RE include the densification in terms of the lowering of the porosity and microcrystallisation of the HCP. The Van Der Waals' attractions (intermolecular forces) at the CSH=CSH and CSH-CH boundaries are increased. The increase and improvement of this secondary bonding further enhance the additive characteristics in terms of internal strength and density of the HCP. Microcrystallisation would lower the porosity of the HCP and have similar densification effects. However, microcrystallisation would also lower the fracture toughness, increasing brittleness of the material due to the significant increase in grain boundary surface.

The consequence of RE is not necessarily uniform and isotropic. This will induce the generation of internal residual stress in the composite structure, which may assist the formation and propagation of microcracks. Microcracks may further combine to form macrocracks. Therefore, the RE effect should be one of the explanations to the formation of macrocracks in concrete buildings several years after it has been built. Since the formation mechanism of the jag-shape rabbet and the effect of Rabbet phenomenon are not understood, more detailed investigations are required.

2.4. Microscopic model

Several studies have been conducted to develop the microscopic models for describing concrete materials and detailed discussion about these models can be found [12–14]. However, most of these experimental results were obtained from laboratory scale testing and the validity in the in situ concrete remains a matter of debate. Most studies are modeled on the early hydration of cement paste assuming that only limited changes would happen in the hardened state. In fact, the microstructural changes occurred inside the hardened cementitious material in the real-size building is a continuous process under the long-term influence of dynamic loading due to typhoon. Therefore, a microscopic model based on the results from IR and SEM analysis describing the HCP is suggested.
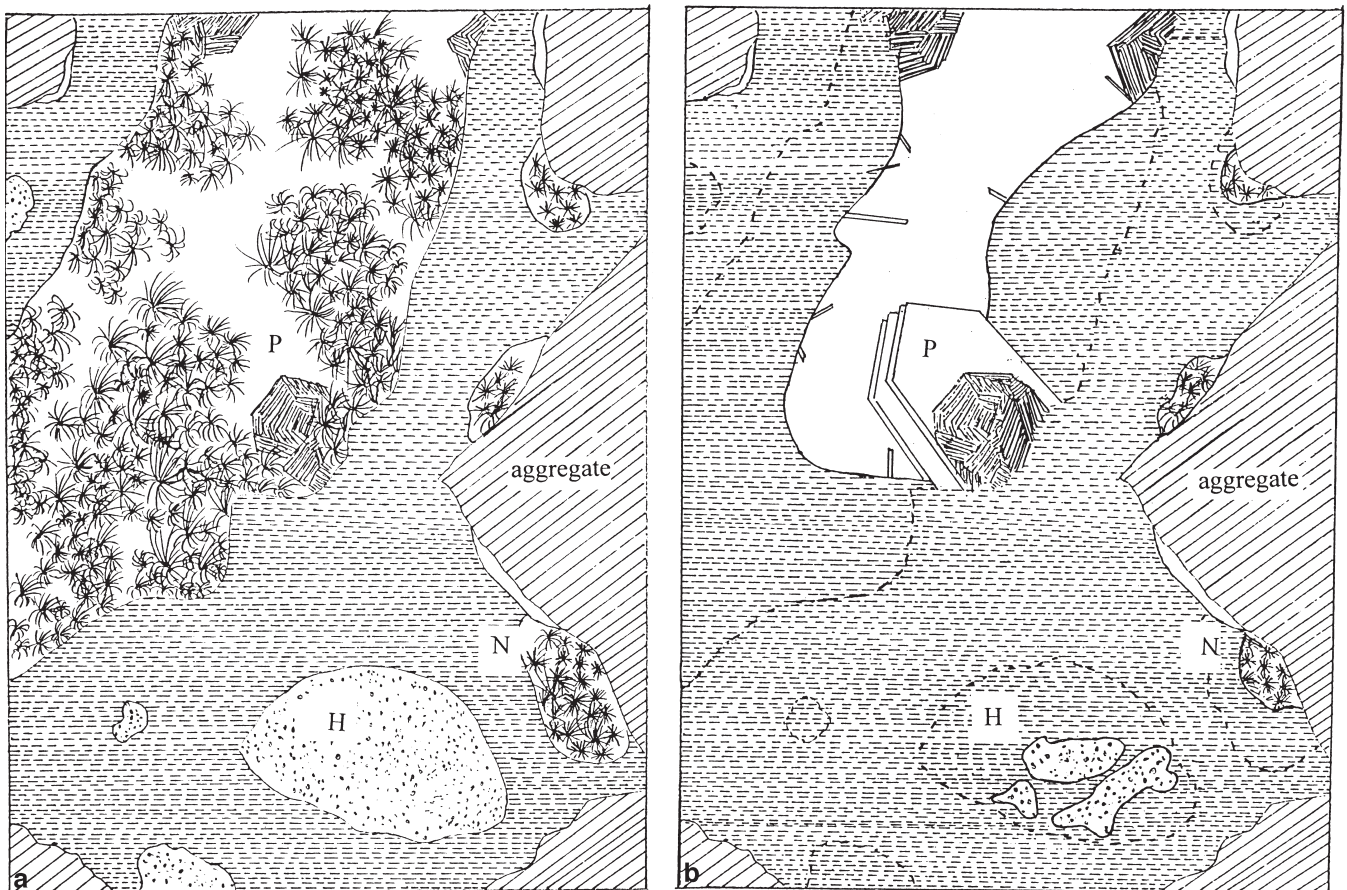

Fig. 6. Schematic drawings of the microstructural evolution of the transition zone in concrete *(a)* under static loading and *(b)* after static-dynamic loading. (N, needle-sharp crystals; P, platelike crystals; H, unhydrated parts).

Fig. 6 is a schematic model of the microstructural evolution of the transition zone in concrete. Under high imposed dynamic loading, three microstructural changes of the CSH will happen: (1) the volume fraction of needle-shape crystals is lower; (2) there is an increase in platelike crystals; and (3) the unhydrated parts of cementitious materials will be further hydrated.

3. Conclusion

SEM micrographs of the concrete samples obtained from a 20-year-old building demonstrate the presence of the morphologic change in HCP under external dynamic load. The needle-shape crystals have changed to platelike crystals at locations that experienced a higher dynamic stress. Evidence from IR spectrum analysis of the primary and secondary bonding shows that the concrete will undergo crystallographic changes and phase transformation according to the stress conditions. The higher the IR absorbance recorded, the lower the dynamic stresses that have been imposed. It is obvious that the transformation is facilitated by the imposed energy caused by typhoon. This is particularly important for structural concrete at the lower floors of high-rise buildings that experience the highest multiaxial stresses, both in static and dynamic sense. A schematic microscopic model based on the results from IR and SEM analyses has been established to describe the microstructural evolution of the transition zone in concrete.

References

[1] J.A. Larbi, The Cement Paste-Aggregate Interfacial Zone in Concrete. Thesis, Technical University of Delft, The Netherlands, 1991.
[2] P.K. Mehta, Concrete: Structure, Properties and Materials, Prentice-Hall, Englewood Cliffs, NJ, 1986, p. 450.
[3] O.E. Gjorv, P.J.M. Monteiro, P.K. Mehta, ACI Mats J 87 (1990) 573.
[4] J.A. Larbi, J.M. Bijen, Cem Concr Res 20 (1990) 783.
[5] C.Z. Yuan, W.J. Guo, Mat Res Symp Proc 114 (1988) 41.
[6] R.F. Feldman, J.J. Beaudoin, Cem Concr Res 6 (1976) 398.
[7] C.Z. Xiao, H.Z. Lian, X.L. Liu, Cem Concr Res 24 (1994) 1.
[8] A.P. Jeary, A Comparison of the Dynamic Behavior of Steel and Concrete Structure, BC-SDRC/96/07, City University of Hong Kong, Hong Kong, 1996.
[9] X.F. Gao, C.Y. Chung, A.P. Jeary, J.C.K. Wong, Y. An, The Effect of Typhoons on the Microstructure of Concrete in Reinforced Structure. Cem Concr Res (in press).
[10] J.K. Jiang, L.H. Fung, Strength of Concrete (1981) 58.
[11] G.J. Verbeck, R.A. Helmuth, Structure and Physical Properties of Cement Paste, Cement Association of Japan, Tokyo, 1969, p. 1.
[12] S. Mindess, J.F. Young, Concrete, Prentice-Hall, Englewood Cliffs, NJ, 1981, p. 400.
[13] F.H. Wittmanm, The structure of hardened cement paste—a basis for better understanding of the material properties in hydraulic cement pastes: Their structure and properties, Cement and Concrete Association, Slough, U.K., 1976.
[14] W. Schramli, World Cement Technology 9 (1978) 35.