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Development of fracture characteristics of cement pastes and causes of microcracking

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ABSTRACT: This paper deals with interesting development of hardened cement paste fracture during first year. There are very surprising changes in course of fracture in some time intervals. Some causes of the development of the fracture are discussed using roentgen diffraction analysis and differential thermal analysis.

1 INTRODUCTION

1.1 *Anomalies in mechanical properties of cement composites*

Some irregular development of mechanical, especially fracture properties of the concrete was recorded and published by some authors. The authors admit different reasons of these anomalies: autogenous shrinkage (Tazawa & Myiazawa 1997), hydration shrinkage (Lange et al. 1997), morphology development of C-S-H gel (Nishikawa & Ito 1997), delayed hydration of cement grains (Igarashi & Kawamura 1998).

Complex explanation of the development of fracture properties of concrete was proposed in Bílek (1999) and Bílek et al. (2000): the values of fracture toughness and fracture energy are closely connected with microcracks occurrence. It is necessary to explain, what is the reason of the microcracking.

In accordance with above cited papers two main mechanisms control the decrease of fracture toughness of concrete. Hardening low water/cement ratio (w/c) paste shrinks significantly (autogenous shrinkage of the paste is high). The microcracks arise around unshrinking particles as aggregates in concrete. The phenomenon is very conspicuous when the size of aggregates is large (more than 16 mm) and w/c is low (less than 0.35). From this reason the decrease of fracture characteristics is only small for mortar. For paste next mechanism can act: It is delayed hydration of cement and impossibility of new hydrates deposit in compact hardened cement paste (HCP), Igarashi & Kawamura (1998). Some different modes of microcracks self-sealing (Hearn 1998) act simultaneously and fracture characteristics of concrete increase in age 2 and 3 years. It is age of the oldest specimen, which is now studied by authors of the paper. But there are a lot of questions about the presented concept in Bílek (1999). One of the questions is development of fracture toughness of the paste and interpretation of obtained results.

1.2 *Development of fracture of hardened cement paste*

The fracture development of HCP was studied at past. Interesting results were repeatedly recorded. An example of load-deflection curves shows Figure 1.

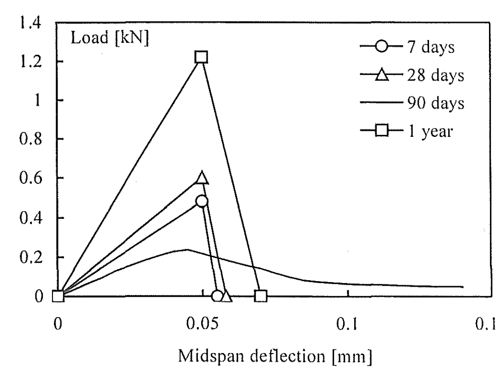

Figure 1. Development of load-deflection curves of HCP (w/c = 0.27) during first year.

There is significant difference in character of the fracture and also in values of fracture toughness. It is important to note, that specimen was sealed by PE-foils to avoiding of humidity exchange between the specimen and environment. The changes of loading curves shapes as well as values of fracture toughness were very surprising for authors, but no other physicochemical tests were perform in the time of testing of these specimen. What is the reason of this behaviour? Presented paper is intent on answering of this question.

2 EXPERIMENTAL DETAILS

New sets of specimens were prepared for purposes of present paper. The paste was prepared from cement CEM I 42.5 R, see EN 197, by using drinkable water and melamine based superplasticizer. Water/cement ratio was 0.27. The materials were mixed by obvious cement cycle, see EN 196-1. Mixture for each beams 50 × 65 × 390 mm was mixed particularly. After the mixing the beam was vibrated 2 × 30 s. Then the mould with the beam was covered by wet textile and PE-folio. Next day the specimens were demoulded and carefully wrapped by a number of layers of PE-sheet. The wrapped specimens were stored in wet air, humidity more than 95%. The beams were tested in age of 7, 14, 21, 28, 56, 90, 120, 150, 180, 240 and 365 days. Three specimens were tested in each age.

Except these beams, the beams 40 × 40 × 160 mm were prepared for testing strengths in age 7, 28, 90 and 365 days. The beams were cured by the same way as above-mentioned specimens.

Next specimens 50 × 65 × 390 mm were put into the water and this set of the specimens was fractured in age 7, 28, 90 and 365 days.

All beams 50 × 65 × 390 mm were tested in accordance with Effective Crack Model (Karihaloo & Nallathambi 1990, Karihaloo 1995). For this purpose, notch to one third of the depth of the beam was cut before testing. Time from the start to peak of loading was 2-5 minutes. Values of load and midspan deflection were recorded continuously. Effective fracture toughness was computed from two pair of the values.

Some small pieces of material from central region of cross-section of beams were stored for roentgen diffraction analysis and differential thermal analysis.

Shrinkage of the paste was also measured using elongation indicator. Because the anomalies in development of the fracture occur at later age of the paste, the length of specimen at 7 days was taken as zero value.

Pieces of the beams were prepared for scanning electron microscopy (SEM) in mode secondary electrons (SE). For study of the microstructure in mode back-scattered electrons (BSE) imaging the pieces were impregnated with a low-viscosity epoxy resin and polished.

3 RESULTS OF TEST

3.1 *Fracture tests*

Some characteristic examples of load-deflection curves of wrapped beams are showed in Figure 2, values of initial modulus of elasticity E (measured during fracture test on notched beams), fracture toughness K_{Ic}, toughness G_c and strengths are given in Table 1.

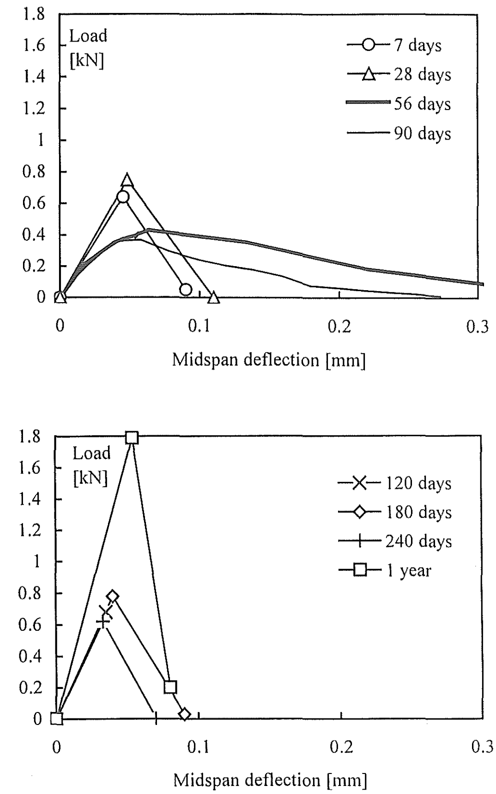

Figure 2. Typical load-deflection curves of HCP beams for ages: 7, 28, 56, 90 days (above) and 120, 180, 240, 365 days.

The differences between the curves are again very significant as well as values of mechanical properties. The 7, 14, 21 and 28 days curves are similar and their shapes answer to brittle fracture. But between 28 and 56 days some processes had to start, which evoke the change of fracture course. The shape of 56 days load-deflection curve answer to quasi-brittle fracture, similar to fracture of concrete. The peak-load value is small. Value of fracture toughness is high, because it is controlled by high deflection of increasing branch of loading curve. The quasi-brittle character of the loading curve is again observed at age 90 days. But now the peak load is still smaller in comparison of 56-days value as well as deflection. Values of mechanical properties are very low. During next month a conspicuous change of loading curve occurs. The fracture shows brittle character again. Values of mechanical properties increase. Similar situation is recorded at age of 150, 180 and

240 days. But next conspicuous change occurs between age of 240 and 365 days. Character of fracture is perfect brittle, the value of peak-load is very high and from this reason the values of mechanical properties are high too. During these last 120 days the fracture toughness increased nearly three-times, as well as modulus of elasticity and toughness. The compressive strength f_c is also the highest at this time, but bending strength f_b is the smallest.

Table 1. Fracture parameters: mean ± standard deviation.

Age	K_{Ic}	G_c	E	f_c	f_b
days	MPa m$^{1/2}$	J m^{-2}	GPa	MPa	MPa
7	0.47±0.04	11.6±1.6	19.2±0.7	82.5±4.7	8.8±0.3
28	0.57±0.01	14.6±1.7	22.7±2.3	89.0±4.0	8.2±0.2
56	0.60±0.09	22.2±5.1	16.2±1.0	-	-
90	0.40±0.01	30.0±6.0	13.7±0.9	92.0±4.0	8.0±0.2
120	0.50±0.06	11.2±2.7	22.7±0.4	-	-
180	0.53±0.02	11.1±1.9	25.7±2.4	-	-
365	1.36±0.05	44.3±3.7	41.3±0.4	106.5±3.2	6.7±0.7

In the Figure 3 there are some examples of loading curves of water curing beams. There are not recorded some changes of the fracture character. The peak-load increase in period 28 to 90 days as well as fracture toughness values. In next period a decrease of the fracture toughness occurs, but the fracture shows brittle character still. Next increase of K_{Ic} is recorded in period 90 days to 1 year.

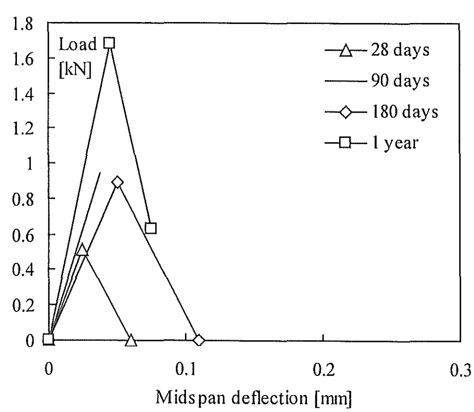

Figure 3. Typical load-deflection curves of water cured HCP beams for different ages.

3.2 *Shrinkage of the paste*

The course of shrinkage of the paste is showed in Figure 4. A quick shrinkage is recorded to 50 days. Next month the shrinkage stays on the same value. In this period the fracture showed quasi-brittle character. The delay of shrinkage occurs in this time term obviously. From age of 80 or 90 days the shrinkage starts again to increase and the new increasing continues to age of 1 year.

3.3 *Roentgen Diffraction Analysis*

Qualitative phase analysis was performed by this method. Obvious peaks of hardened cement paste were found. There are peaks of clinker minerals, portlandite, ettringite and poor peaks of C-S-H gel. Some other peaks are very weak and phase identification is uncertain. No conspicuous changes of intensity of the peaks were find by this method, except the portlandite peak (0.492 nm) intensity changes. The same phenomenon was shown in Bílek (1999), but set of results was poor at the time. Now the set is more numerous and the results have got the higher weight. Higher intensity of peak shows, that the phase is better crystallic developed or/either the amount of the phase is higher. Discussion of the problem in connection with development of mechanical properties is in section 4.

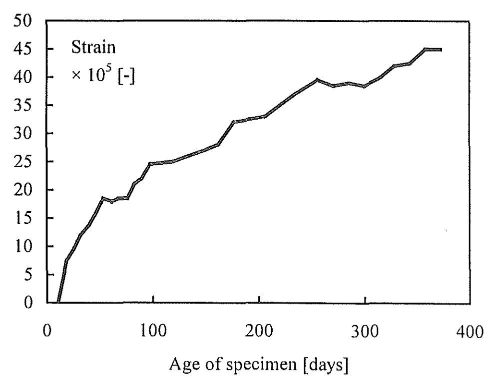

Figure 4. Shrinkage of the paste during first year of curing – foil wrapped beams.

3.4 *Differential Thermal Analysis*

The differential thermal analysis is appropriate for quantitative analysis of hardened cement paste. Unfortunately, only the portlandite decomposition is clear at the curve. Effects of other reactions interfere and it is impossible to specify precisely where C-S-H gel decomposition or decomposition of some other phase occurred. The resolution of C-S-H gel modification is not also possible.

Some inconspicuous changes of portlandite content are recorded again. An increase or a decrease of portlandite is not affect by perfect nature of its crystals, but its amount only.

3.5 *Scanning Electron Microscopy*

Scanning electron microscopy shows the same interesting details. The unhydrated cement grains are very conspicuous in BSE imaging. At the age of 90 days the unhydrated grains are good visible. The reactions rim with a crack or double-cracks around the grain occur very often around the unhydrated or partially hydrated cement grains, see Figure 5. The rims are not typical inner product. The resolution of inner and outer product of hydration is very disputable for low w/c ratio pastes. The cracks wide to neighboring hydrated mass. There are also some cracks in the grains, but their amount is not high. As the age of specimen increases (4 and 5 months) the amount of the microcracks within the partially hydrated grain also increases. The surrounding rims are still visible, but they are less conspicuous as in the age of 90 days. It can be some indication of continuing hydration. The surrounding cracks are sealed during next months (6 months) and the rims became inconspicuous. The rims and surrounding cracks are not observed at the age of 1 year.

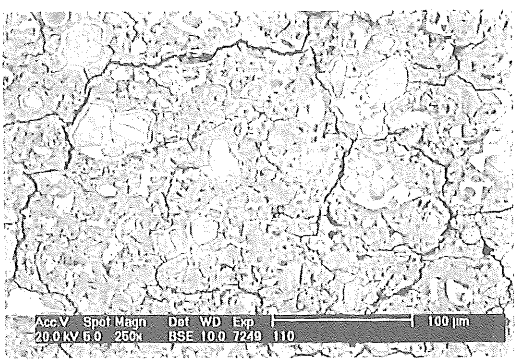

Figure 5. Micrograph of HCP, BSE imaging, 90 days.

When secondary electron imaging is used, the dense microstructure of hardened paste can be observed from 7 days to 1 year. The big crystals of portlandite are observed at each time interval as well as some needle shaped hydrates. The C-S-H gel has a short-needle or nearly spherical morphology. Very conspicuous is massive occurrence of middle length needle-shaped hydrates at age of 1 year. The EDAX of these hydrates (and results of RDA) shows, that the needles are probably formed from C-S-H with content of sulphur and aluminium.

4 DISCUSSION OF THE RESULTS

During first year of curing some changes were recorded: fracture toughness changes, changes of portlandite content, an irregular shrinkage of the specimens and microstructure changes in hardened paste, especially in vicinity of partially hydrated grains.

It is interesting to draw fracture toughness K_{Ic} vs. content of portlandite (CH) graph, see Figure 6.

An indirect dependence between fracture toughness and portlandite content is fought. Some other authors assume similar results. They provided those large and brittle crystals of portlandite act as concentrators of stress. It is interesting, that dependence fracture toughness – intensity 0.492 nm peak of portlandite (RDA) is closer than fracture toughness – amount of portlandite (DTA) dependence. Assuming a linear form of the dependence the correlation coefficient is 0.83 and 0.63 respectively. From this reason it can be assumed that crystal character of the portlandite is important from the viewpoint of fracture toughness.

The next question is why the portlandite content is varying. The portlandite is the first phase, which arises when cement starts hydrated. The changes of portlandite content can be interpreted as some changes in hydration processes. Can be this hypothesis supported by some other results? Maybe, the microscopic details around partially hydrating grains are the support for that hypothesis. The reaction rims and surrounding cracks can be formed by delayed hydration of cement. The rims can be some above mentioned layers of new hydrates, which have not place for their deposit and from this reason they evoke some pressure to hardened paste. It can be one of origin of microcracking of the paste.

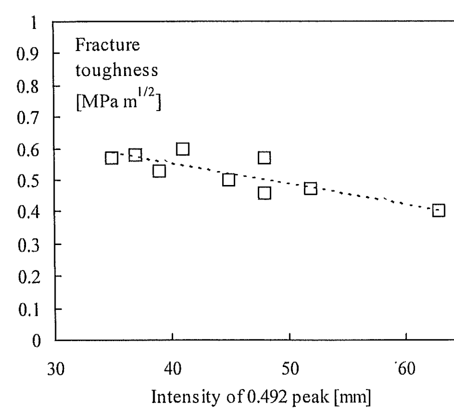

Figure 6. Fracture toughness K_{Ic} vs. amount of portlandite.

There are shrinkage stopping at the same time interval (49-77 days) as the fracture character changes and portlandite content increases. What is the reason of the shrinkage irregularity? It can be controlled by hydration development.

As the hardened paste shrinks, the unhydrated grains act as no-shrinking particles. When microcracks arise around these particles, the shrinkage is stopping. The reason of this behaviour is hydration and self-desiccation shrinkage of the paste. The above-discussed mechanism of pressure can also act.

The pressure can stop the shrinkage in some time period. By the way, the stopping of shrinkage can be indication of some microcracking. The change of fracture character in the same time supported the assumption.

Importance of different causes of microcracking can be established by comparison of the results for wrapped and water cured beams. Role of self-desiccation is reduced for the water-cured beams. In time period from 28-90 days the fracture toughness of the water curing beams increases. From this reason the self-shrinkage can be accounted as the main cause of crossing from brittle to quasi-brittle character of fracture for wrapped beams. The portlandite content does not show any significant change in the period.

The decrease of the fracture toughness between 90 and 180 days (see Figure 3) is interesting. It can be explained by water adsorption to structure of C-S-H gel (Beaudoin 1986). It is assumed, the gel is formed from sheets of SiO_4 tetrahedra. Some water molecules go into interlayer spaces, the sheets recede and mechanical properties decreases. The character of the fracture stays brittle still.

When we compare results for the paste with results for paste prepared using polycarboxylate based plasticizer, we can see that fracture toughness of the new pastes is significantly higher. It can be controlled by rapid hydration (a lot of cement grains hydrated in first time period and role of delayed hydration is reduced) and decreasing of surface tension of pore solution (decreasing self-desiccation shrinkage).

5 CONCLUSIONS

Some influences of microcracking to mechanical properties of hardened cement paste were discussed on this paper. It can be summarized:

Fracture character of hardened cement paste varying very conspicuously during first year of curing.

Self-desiccation shrinkage of the paste can act as basic mechanism of microcracking and can control the fracture change.

Some other mechanisms, as impossibility of new hydrates deposition, can also attribute to the microcracking.

Not only decrease of fracture properties occurs, but the increase is also observed in some time intervals. The reason of this increase is self-sealing of microcracks. At last time period (240-365 days) the reach occurrence of needle-shaped hydrates helps to increase of fracture toughness.

The processes can have significant effect on durability of concrete. For example when paste beams are freeze-thaw cycled, there is a big difference when the cycling start. When it starts at age 28 days, after 100 cycles the paste shows nearly the same strength and fracture properties as before cycling. When the cycling starts at age 90 days, the beams broken during first 10 cycles. Some next impacts of the microcracking to freeze-thaw resistance will be discussed in our next paper.

The next measurements are needed for better understanding of the above-discussed processes and avoiding the desirable effects of paste fracture.

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