THE EFFECT OF WATER RATIO ON MICROSTRUCTRE AND COMPOSITION OF THE HYDRATION PRODUCTS OF PORTLAND CEMENT PASTES

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The study was concerned with examining the effect of the water-to-cement ratio over the range of 0.19 to 0.50 on the composition and morphology of hydrated cement pastes. The strength after setting increases with decreasing w/c while the content of hydration products decreases. At the same time the homogeneity of the hydration products tends to increase and the occurrence of crystalline hydrates (particularly that of portlandite) decreases. At the lower w/c values, higher-calcium forms of the C-S-H phase, in which $Ca(OH)_2$ is dispersed, arise at the lower w/c values. Crystalline portlandite exhibits a preferential direction of fracture, thus creating conditions for potential ready crack propagation and therefore also for a possible lowering of strength. Crystalline $Ca(OH)_2$ is then the weakest part of the set system and represents a limit of its mechanical properties. The differences in the content and form of $Ca(OH)_2$ present in set materials based on Portland cement may have unexpected effects on their performance properties.

INTRODUCTION

The properties of cement-based materials depend on the properties of the matrix (i.e. those of the hydrated cement), on the strength of the aggregate, on the strength of the interstitial zone, also on the amount of defects and in particular on porosity. In agreement with Griffith´s theory, the strength of materials is given by the length of the critical crack, and is related to the modulus of elasticiry and the surface energy. These values are little affected by the chemical composition of cements and by the conditions of hydration. A significant possibility of changing the mechanical properties of cement-based materials is provided by reduction of the water-to-cement ratio (hereinafter w/c). W/C influences strength, overall porosity, permeability, modulus of elasticity and shrinkage which is due to drying out of setting mixes. Reduction of w/c is at present one of the main possibilities how to improve the properties of cement-.based materials (high-performance concrete, HPC). The w/c can be reduced with the use of fluidizers (superplasticizers) or by adjusting the mix composition (using additions of microfillers DSP) [1,2]. Another possibility asociated with the reduction of w/c is provided by the elimination of macrodefects (MDF cements) [3,4,26]. The effect of w/c is primarily associated with porosity and setting strength. The relationship between strength and porosity has been described by a number of formulas that depict reasonably well the properties of cement-based materials over the range of "ordinary" w/c.

The literature presents relatively little information on the effect of w/c on the composition and morphology of the hydration products of Portland cements. This fact is somewhat surprising in view of the wide attention paid to the properties of concrete prepared over a wide range of w/c values. The present study is aimed at studying the composition and morphology of hydration products of Portland cements over the range of w/c = 0.19-0.50 [5].

EXPERIMENTAL

The effect of w/c on the hydration of cements was studied on five systems based on Portland cement clinker taken from the standard production of the Prachovice Cement Works (Czech Republic). The clinker had the composition CaO 63.2, SiO_2 20.8, Al_2O_3 5.8, Fe_2O_3 3.3, MgO 3.6, CaO_{free} 0.88, $Na_2O + K_2O$ 0.8, SO_3 0.8 wt.%. The clinker was processed into gypsum-free Portland cement (hereinafter BS cement) with a speci-

fic surface area of 580 m²/kg by grinding in the absence of gypsum with the use of Abeson TEA grinding aid (sodium alkylaryl sulphonate). BS cement allows freely flowing pastes at low *w/c* of 0.20 to 0.21 to be prepared [6, 7]. The BS cement pastes were prepared with additions of 0.8 wt.% Zewa SL (sodium lignine sulphonate, Sarpsborg, Norway) and 2.5 wt.% Na₂CO₃, both dissolved in the mix water. Tests were also carried out with standard Portland cement CEM I 42.5 R made of the same Prachovice clinker. To improve the rheological properties of the PC pastes so as to achieve low *w/c* values at acceptable workability, use was made of an addition of 0.4 wt.% superplasticizer FM62 (Na naphthalene sulphonate, Adiment, Heidelberger Zement, Germany). Silica fume (Elkem, Norway) containing more than 97.5 wt.% SiO₂, was used as an additional admixture to both the PC and BS cement pastes. The concentrations of the additives to the PC and BS mixes were chosen on the basis of previous optimizing aimed at attaining optimum rheological properties at the low *w/c* values. The designation of the individual systems studied is listed in table 1.

The cement pastes prepared from the individual systems had *w/c* values ranging from 0.19 to 0.50. The lower *w/c* limit of 0.19 to 0.25 used in the experiments was chosen so as to allow the pastes with the *w/c* values to be compacted by standard methods (i.e. by vibration at 50 Hz). No special ways of compacting such as compression were employed. The pastes were formed into specimens 2×2×2 cm in size, placed for 24 hours in an environment of 95% R.H. and then up to 28 days in water at 20°C. The compressive strength was determined by destructive tests after one day and after 28 days respectively. The fragments of test specimens were used in studying the composition of the hydration products. The composition of the hydration products was examined by GTA (Mettler, Germany) over three regions, namely: by determining the loss in weight up to 450°C (content of C-S-H and C-A-H phases), over the 450 to 550°C range (content of Ca(OH)₂) and over the 550 to 800°C range (content of CaCO₃). X-ray diffraction analysis (Seifert, Germany) was used to determine the changes in Ca(OH)₂ and C₃S (alite) content. The morphology of the fracture surfaces was studied on SEM using ED spectrometer (JEOL Superprobe, Japan). Quantitative point analysis, combined with ZAF

correction, was carried out at selected points of the fracture surfaces for the purpose of determining the content of CaO/SiO₂ and C₃S (alite). The porosity of specimens after setting was determined by high-pressure Hg porosimetry (Micromeritics, USA).

RESULTS AND DISCUSSION

In agreement with the literature [3], the increase in strength in terms of decreasing *w/c* tends to be linear over the range of higher *w/c* values, while approaching an exponential dependence in the region of lower *w/c* values (figure 1 and 2). BS cement appears optimal for attaining a high early strength, which is almost double compared to that of Portland cement, as supported by the results of studies [6,7]. The results of porosity measurements are in agreement with the generally acknowledged rule that decreasing porosity (resulting from decreasing *w/c*) brings about increasing strength of hardened pastes of the systems in question.

Figures 3 through 7 show the results of GTA and X-ray diffraction analyses that characterize the content of hydration products in the systems. A comparison of relative intensities of portlandite and alite diffractions and GTA results demonstrate trends according to which reduction of the water ratio reduces the content of hydration products due to a relative increase in the content of residual (non-hydrated) phases. With respect to these trends there occur differences between the individual systems, the greatest ones between the PC and BS cements, where the effects of superplasticizer and that of silica fume were relatively small. X-ray analysis

Table 1. The designation of studied individual systems.

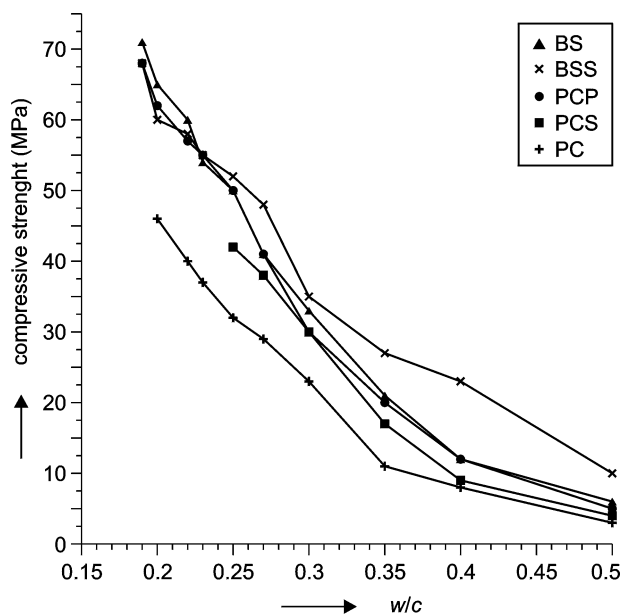| Des.	Composition of the system
PC	PC CEM I 42.4R
PCS	PC CEM I 42.4R+2 wt.% SF+0.4 wt.% Adiment FM 62
PCP	PC CEM I 42.4R+0.4 wt.% Adiment FM 62
BS	BS cement, 0.8 wt.% Zewa SL+2.5 wt.% Na₂CO₃
BSS	BS cement+2 wt.% SF, 0.8 wt.% Zewa SL+2.5 wt.% Na₂CO₃
Des. - designation	

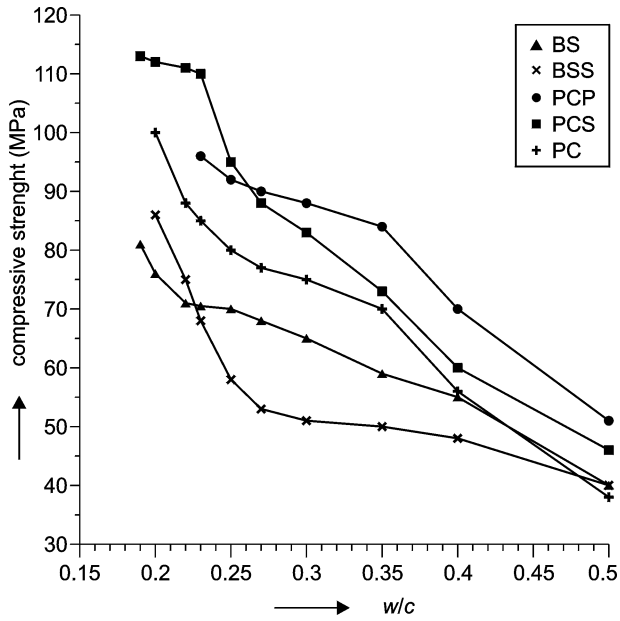Figure 1. Compressive strength of cement pastes after 1 day of hydration vs. water-to-cement ratio (*w/c*).

Figure 2. Compressive strength of cement pastes after 1 day of hydration vs. the water ratio.
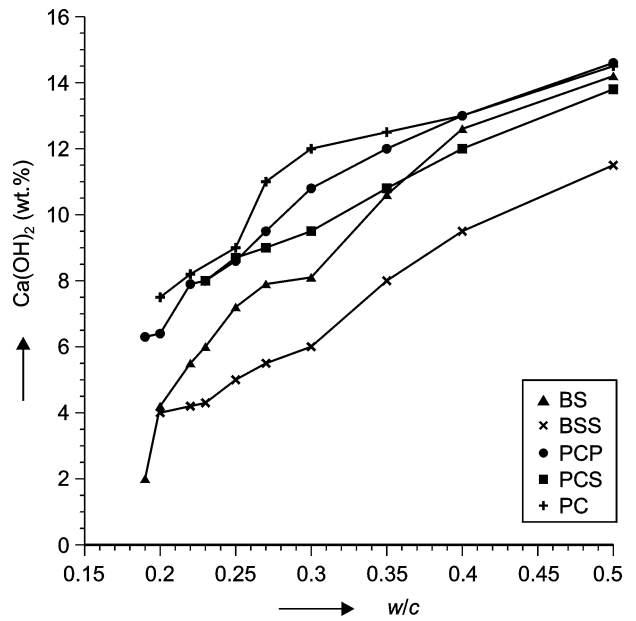

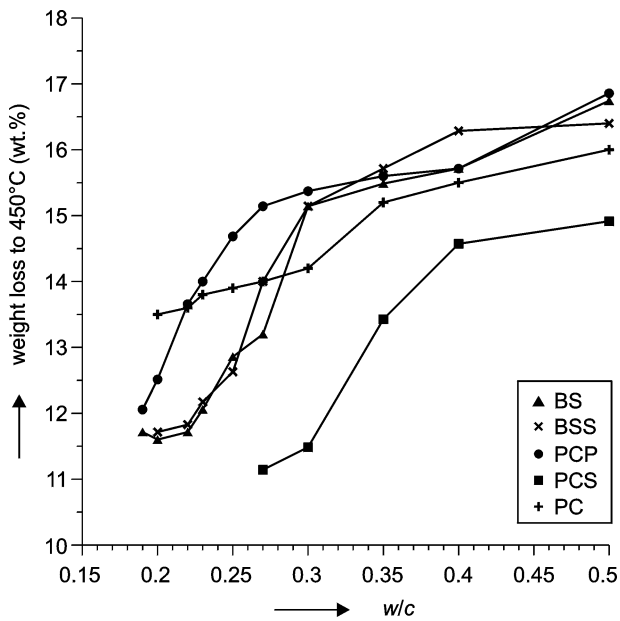Figure 4. Content of $Ca(OH)_2$ (GTA) in hardened pastes after 28 days of hydration in terms of the water ratio.

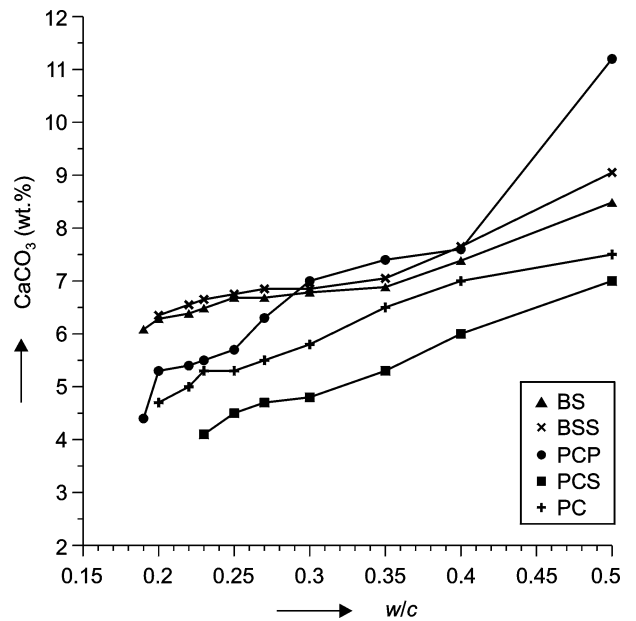Figure 3. Content of hydrates (loss in weight up to 450°C) in terms of the water ratio.

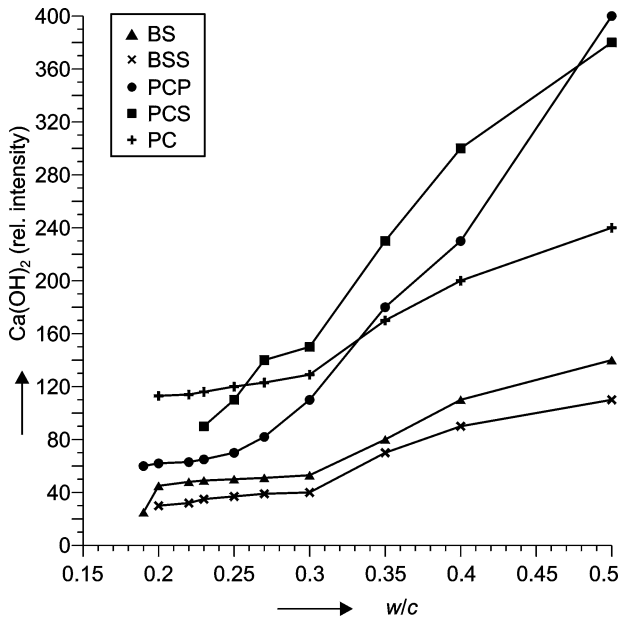Figure 5. Content of $CaCO_3$ (GTA) in hardened pastes after 28 days of hydration, in terms of the water ratio.

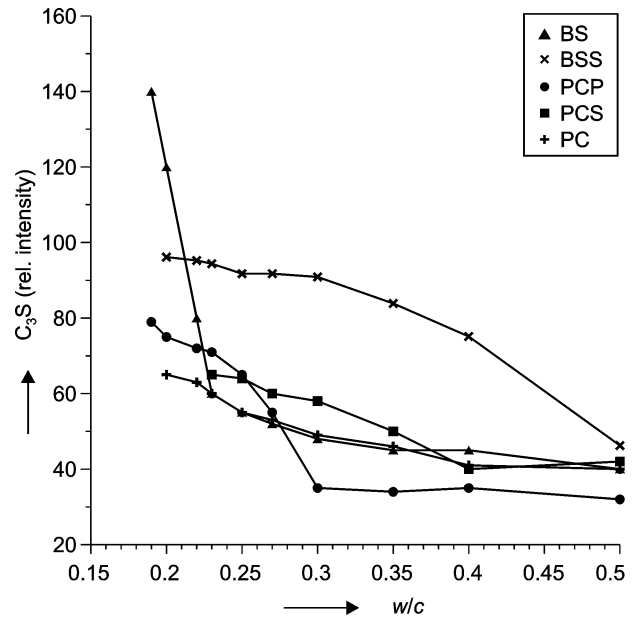Figure 6. Content of Ca(OH)$_2$ (XRD) in hardened pastes after 28 days of hydration, in terms of the water ratio.

Figure 7. Content of C$_3$S (XRD) in hardened pastes after 28 days of hydration, in terms of the water ratio.

established a significantly lower content of portlandite in hardened BS cement paste compared to the PC paste. A decrease in the content of Ca(OH)$_2$ was also found by Odler [8] in his study of the system ground clinker + sodium lignosulphonate + Na$_2$CO$_3$. Down to a *w/c* value of about 0.25 the decrease of relative portlandite intensities is quite steep, whereas at the still lower *w/c* the decrease of diffractions is more proportional. A decrease in the amount of hydration products with decreasing *w/c* was also demonstrated by the evaluation of alite diffractions. The relationships of diffraction intensities of portlandite and alite diffractions for BS and PC cements after 1 and 28 days of hydration are almost identical, merely showing a quantitative shift.

Determination of the absolute content of Ca(OH)$_2$ and CaCO$_3$ by GTA established a lower Ca(OH)$_2$ content in pastes of BS cements than in those of PC (identically with the results of X-ray analysis). A decrease in the content o CaCO$_3$ likewise resulted from reducing the *w/c* but the decrease was not as significant as in the case of Ca(OH)$_2$.

A comparison of the development of strength and the content of hydration products in terms of *w/c* clearly leads to the conclusion that the setting strength increases and the content of hydration products decreases with decreasing *w/c*, as early as after one day of hydration. This paradox was already noted e.g. by Brunauer [6], Odler [8] and Locher [9]. These authors assume that the lower degree of hydration at a lower water ratio is due to a lower permeability of the gel being formed, which reduces access of water molecules to the remaining clinker grains in the cement. Also Jambor [10]

pointed out that reduction of *w/c* in C$_3$S pastes leads to a lower content of combined water and thus to promoting the bonding properties of the hydration products. However, these findings are in a certain disagreement with some hypotheses. For example, Chatterjee in his study of special and new cementitious materials [11] comes to the conclusion that one of the ways how to increase strength is provided by increasing the amount of hydration products and thus by increasing the hydration degree.

The effect of *w/c* is likewise projected to the morphology of the hydration products. Reduction of *w/c* brings about an increase in the homogeneity of hydration products and a reduction of the content of crystalline hydrates (primarily portlandite). The greatest differences in the homogeneity of the paste microstructure are demonstrated by a comparison of BS cement and PC (figures 8 and 9). Pastes of BS cement exhibit greater compactness and density, their structure does not contain crystalline formations characteristic of PC pastes (portlandite, ettringite), and the hydration products are finely dispersed. However, occurrence of crystalline plate-shaped formations of portlandite can also be observed in BS pastes at higher *w/c*. None-the-less, the structure is quite unlike the sponge-like character of PC pastes.

W/c has also a considerable effect on the character of Ca(OH)$_2$ (portlandite) in hardened cement pastes. Morphologically [13], Ca(OH)$_2$ has a hexagonal structure tending to form clustered platelets about 10 μm thick oriented parallel with the basal plane. The clusters are then anchored in the C-S-H phase [12]. However,
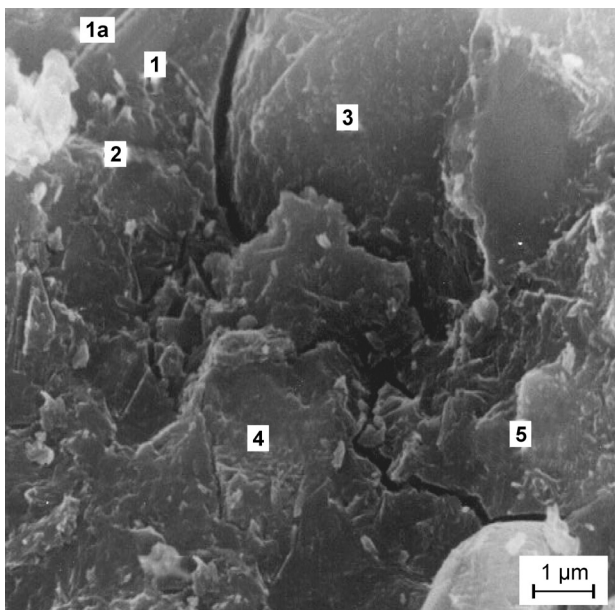
Figure 8. Fracture surface of BS cement paste, w/c = 0.21, after 28 days of hydration. ED spectrometric analysis: 1. CaO/SiO_2= = 6.1, 1a. CaO/SiO_2 = 8, 2. CaO/SiO_2 = 2.5, 3. CaO/SiO_2 = = 2.87, 4. CaO/SiO_2 = 3.4, 5. CaO/SiO_2 = 3.
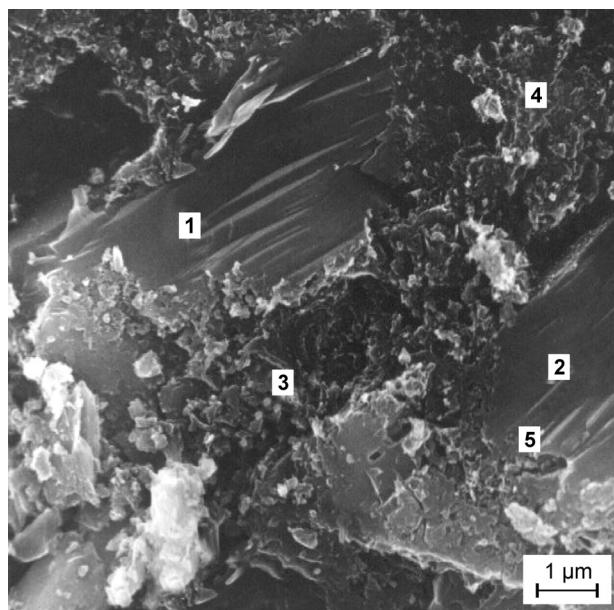

Figure 9. Fracture surface of hardened Portland cement paste, w/c = 0.40 after 28 days of hydration. ED spectrometric analysis: 1. CaO/SiO_2 > 20, 2. CaO/SiO_2 > 20, 3. CaO/SiO_2 =1.98, 4. CaO/SiO_2 = 2.1, 5. CaO/SiO_2 > 15.
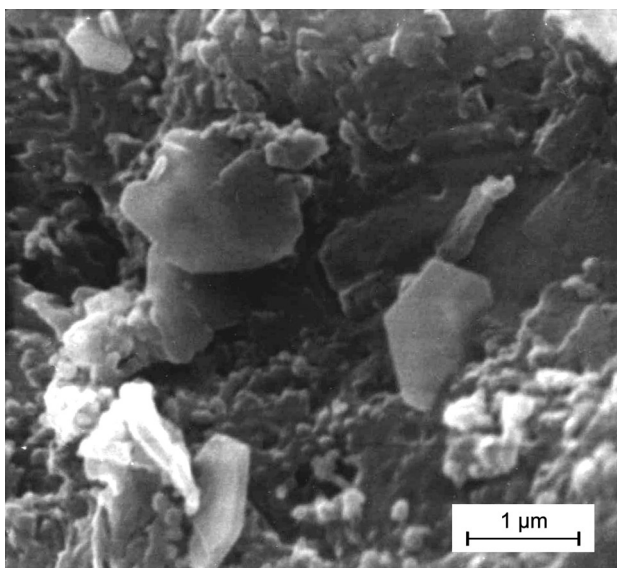

Figure 10. Character of $Ca(OH)_2$ particles dispersed in C-S-H phase, paste w/c = 0.25.
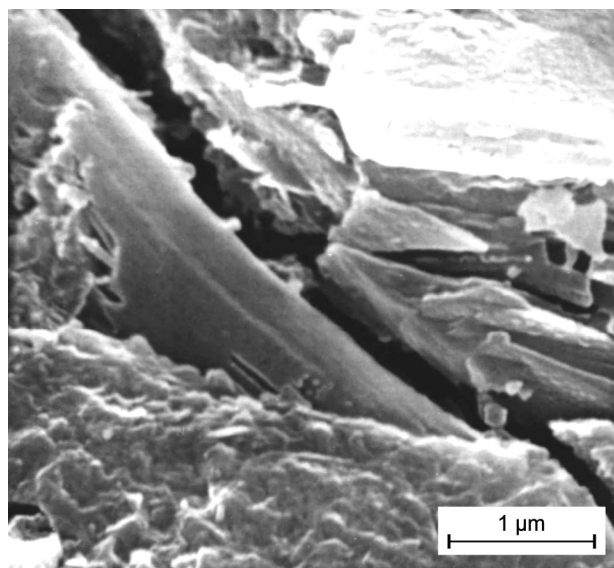

Figure 11. Character of $Ca(OH)_2$ particles dispersed in C-S-H phase, paste w/c = 0.40.

when the hydration proceeds at high w/c, the portlandite crystals grow up to sizes of about 100 µm and more. Portlandite crystals have not been determined in low-w/c materials, and are considered to be of nanometre dimensions. A mixture of the C-S-H phase with $Ca(OH)_2$ of nanometre sizes was found in hardened cement pastes with a very low w/c [14] , in some pozzolanic cements [15] and in Portland cements activated with KOH [16] . Larbi and Bijen [16] maintain that orientation of portlandite crystals at the boundary between the cement paste and the aggregate (gravel, fibres, reinforcement, and the like) is also affected by admixtures and that for instance an addition of 20 wt.% ultrafine SiO_2 may change the orientation of $Ca(OH)_2$ from almost perpendicular to almost parallel with the surface of the aggregate. However, this effect was not observed on samples prepared within the framework of the present study. This was possibly due to the lower amount of silica fume added (2 wt.%), as this was the result of optimizing for the purpose of attaining a low water ratio while ensuring the best possible workability of the pastes.

Some of the portlandite in hardened cement pastes (especially at very low w/c) may exist in nanometre dimensions, thus being obviously amorphous with respect to X-rays. The presence of a different form of $Ca(OH)_2$ in BS cement may represent an apparent contradiction between the results of GTA and X-ray analyses. The results of GTA analyses are indicative of essentially parallel trends between the $Ca(OH)_2$ content and the decreasing w/c, whereas the results of X-ray analyses show a significantly increasing content of $Ca(OH)_2$. Several other authors [7,20-23] also pointed out this discrepancy in the character of portlandite. The effect is very marked when the results for BS and PC cement pastes are compared. According to GTA, the $Ca(OH)_2$ content in hydrated BS cement is lower by only about 3% compared to standard PC, while the intensity of the strongest diffraction line of $Ca(OH)_2$ (at 0.490 nm) attains only about one seventh of the intensity of the corresponding line in hydrated PC.

The materials prepared with higher w/c were found to contain larger, rather lamellar crystals of portlandite and also their final strength was inferior. The occurrence regions of portlandite can be readily established both morphologically and analytically (ED spectrometric analysis (cf. figure 8). The occurrence regions of portlandite in samples with a low w/c are not morphologically detectable and ED spectrometric point analysis is able to determine regions with an elevated CaO/SiO_2 ratio (of more than 4-5) which could correspond to $Ca(OH)_2$ (figure 9). In such instances a higher CaO/SiO_2 ratio occurs in the material of hydrates (C-S-H) than in the hydrates of samples with a higher w/c. It may therefore be assumed that higher-calcium forms of the C-S-H phase are formed at the lower w/c in which $Ca(OH)_2$ is dispersed in nanometre dimensions in

agreement with [13]. The different character of portlandite particles in specimens with low and high w/c is illustrated by figures 10 and 11.

The effect of portlandite on the strength of cementitious materials has not yet been completely explained, but for instance Berger et al. [17] assume that it acts rather as an "inclusion" whose effect may be regarded as a rather detrimental more than a useful one for the bond between aggregates and the material of hydrates (particularly the C-S-H phase). Crystalline portlandite has a preferential direction of fracture along crystalline axis c, so that with larger dimensions of its crystals favourable conditions for crack propagation and thus a possible reduction of strength may occur. High-density systems do not provide ample space for supercritical cracks, and crystalline $Ca(OH)_2$ with a preferential direction of fracture then represents the weakest part of the set system. The crystalline $Ca(OH)_2$ phase is then the controlling factor determining the maximum strength of the system. The lower porosity, the higher content of the C-S-H phase and the lower content of the $Ca(OH)_2$ crystalline phase in the cement paste and in the interstitial zone between the hydrates and the aggregates have a positive effect on transport and mechanical properties of highly resistant concretes, as pointed out by Li [24] and Xu [25] .

The differences in the content and form of $Ca(OH)_2$ in hardened materials based on Portland cements may have unexpected effects on their performance properties. Materials based on BS cements, prepared with a low w/c and having most of its $Ca(OH)_2$ in amorphous form, exhibit a much greater resistance to temperatures of up to 1200°C [20,21] . According to Ševčík [20,21] , these materials can even be used as a substitute for alumina cement with a lower Al_2O_3 content.

The effect of w/c on the properties of set materials based on hydraulic cements may include changes in the modulus of elasticity and in surface energy. This is particularly the case of hydrated cementitious materials prepared with extremely low w/c, whose strength approaches that of ceramic materials [2]. Continuing material research in the field is necessary, because knowledge of the dependence of strength vs. porosity or that of strength vs. w/c is no longer sufficient in view of the newly emerging materials of the types MDF, DSP, alkali-activated geopolymers and others.

CONCLUSION

1. A comparison of the development of strength and the content of hydration products in terms of w/c shows that with decreasing w/c the set hardness increases while the content of hydration products decreases.
2. With decreasing w/c the hydration products tend to become more homogeneous and to contain less crystalline hydrates (particularly portlandite). In hardened

cement pastes, especially in those with very low *w/c*, some of the portlandite may occur in nanometre dimensions and these forms of portlandite are obviously X-ray amorphous. High-calcium forms of the C-S-H phase containing dispersed $Ca(OH)_2$ are formed at low *w/c*.

3. The presence of a different form of $Ca(OH)_2$ in hydrated BS leads to an apparent contradiction between the results of GTA and X-ray analyses. Crystalline portlandite exhibits a preferential direction of fracture, thus providing space for potential crack propagation and therefore possible reduction of strength. The high-density systems do not provide space for the formation of overcritical cracks and crystalline $Ca(OH)_2$ is then the weakest point of the hardened system and limits its mechanical properties.

4. The different content and forms of $Ca(OH)_2$ in hardened materials based on Portland cements may have a considerable effect on their performance properties.

Acknowledgement

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VLIV VODNÍHO SOUČINITELE NA MIKROSTRUKTURU A SLOŽENÍ PRODUKTŮ PŘI HYDRATACI PORTLANDSKÉHO CEMENTU

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V práci byl sledován vliv vodního součinitele v rozmezí 0,19 až 0,50 na složení a morfologii hydratačních produktů cementových kaší. S klesajícím *w/c* vzrůstají pevnosti po zatvrdnutí a současně klesá obsah hydratačních produktů. Současně se projevuje se tendence ke zvyšování homogenity hydratačních produktů a k omezování výskytu krystalických hydrátů (zejména portlanditu). Při nižších *w/c* se vytvářejí výše vápenaté formy C-S-H fáze v níž je rozptýlen $Ca(OH)_2$. Krystalický portlandit má přednostní směr lomu, čímž vzniká prostor pro potenciální dobré šíření trhlin, a tím i možné snížení pevností. Krystalický $Ca(OH)_2$ je pak nejslabší částí zatvrdlého systému, který limituje mechanické vlastnosti. Rozdílný obsah a forma $Ca(OH)_2$ v zatvrdlých materiálech na bázi portlandských cementů může mít neočekávaný vliv na jejich inženýrské vlastnosti.