Cement and Concrete Research 38 (2008) 955–962

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Hydration behaviour, structure and morphology of hydration phases in advanced cement-based systems containing micro and nanoscale pozzolanic additives

A. Korpa *, T. Kowald, R. Trettin

Institute of Building and Materials Chemistry, University of Siegen, Germany

ARTICLE INFO

Article history:
Received 22 November 2006
Accepted 20 February 2008

Keywords:
Pozzolanic additive
Pyrogene oxide
Hydration behaviour
Heat of hydration
Nanostructure
Advanced cement-based systems

ABSTRACT

This paper deals with the early hydration and structure development aspects of advanced cement-based systems that contain micro and nanoscale pozzolanic additives. We have used highly reactive colloidal silica produced by pyrogenic route (pyrogene oxides) as representative of nanoscale pozzolanic additives. Colloidal silica shortens the induction period to an extent that can be qualitatively correlated to the size of its primary silica particles and the specific surface area. Colloidal silica accelerates the early hydration reactions by providing large amounts of reactive siliceous surface, which serves as a site for the early C–S–H precipitation. Additionally the use of pozzolanic additives as cement replacement smoothes and reduces the heat of hydration evolved. The high performance specimens that contain microscale additives and especially those that contain both micro and nanoscale additives are characterised by very tight structure and are made up of finer structures in closer contact than the normal performance specimen without pozzolanic additive.

1. Introduction

The properties, behaviour and performance of cement-based building materials are mainly dependent on the structure of the cementitious matrix that binds together all the material components. Therefore the knowledge of the structure and its features at the lowest scale (nanoscale) are essential for the understanding and controlling of properties, and the basis for the development of new building materials.

The structure development of a cement-based material is affected by its constituent components, their contents and the reaction and processing conditions.

The approach for the development of new, advanced building materials requires, among other things, the use of very fine mineral additives and high range water reducers (superplasticizers) that allow for the drastic reduction of the water content without negatively affecting the rheological properties [1]. The fine additives used in cement systems are being classified into reactive and "inert" substances. The so-called "inert" additives in normal processing conditions (fine quartz, limestone, dolomite etc.) are thought to contribute on strength improvements only through a physical filling effect: they fill up the void spaces remaining between the coarser particles [2]. The reactive additives (i.e. pozzolans, GGBFS etc.) act through a double mechanism: they tend to physically fill the void space between the larger particles, which is otherwise occupied by water that is not free to contribute to fluidity [3]. Additionally, with time they react chemically to produce additional material, combine some of the water in their reaction products and reduce in this way the porosity of matrix and interface transition zone [4,5]. Pozzolanic additives (components) react through the well-known pozzolanic reactions with calcium hydroxide and the other hydration phases for producing additional calcium–silicate–hydrates (C–S–H) material that contribute to strength enhancement [4,6,7]. The role of the fine additive type on the formation of micro and nanostructure and hence on the resulting material properties has to be considered individually for each type of additive. Their different contribution to the properties in hardened state can be mostly related to the differences that exist between them, considering the mineralogical and chemical composition and their content on reactive constituents; the last ones on the other hand have very different reacting potentials. Whereas, the differences on their dispersion state, particle morphology and surface characteristics have a more pronounced influence on the rheological behaviour and water retention characteristics of the paste in the fresh state. However, since the properties in the fresh state are inter-related to those in the hardened state, the pozzolan type is expected to affect the properties of the material during all its life cycle.

In a previous study we have considered colloidal silica (nanoscale pyrogene silica) and their pozzolanic reactivity to be used as ultrafine reactive additives [8]. Our investigations have revealed a very high pozzolanic reactivity for these products, much higher than that of silica fume products that are commonly used as ultrafine pozzolans for producing cementitious materials with advanced properties. It has been demonstrated by means of in-situ transmission X-ray microscopy (TXM), pH-measurements and some preliminary strength performance measurements the potential of colloidal silica to be used as highly reactive pozzolanic additives in advanced cement-

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* Corresponding author. Institut für Bau- und Werkstoffchemie, Paul-Bonatz-Str. 9-11, 57068, Siegen, Germany. Tel.: +49 2717402968; fax: +49 2717402938.
E-mail address: korpa@chemie.uni-siegen.de (A. Korpa).

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doi:10.1016/j.cemconres.2008.02.010

based systems that belong to high and ultra high performance class [8]. Besides reactivity, the knowledge of the hydration behaviour and heat evolution can be very important parameters for understanding the structure development and hardening behaviour of the cementitious material.

This paper will deal mainly with the influence of colloidal pyrogene silica known also with the name aerosil (we will shortly refer to them as “Pox” in the following part) on the development of material structure and on hydration behaviour. Other authors in the past have also investigated the hydration reactions of cement and cement phases (tricalcium silicate), in the presence of various colloidal silica.

Kurdowski et al. have reported for the hydration behaviour of tricalcium silicate with aerosil a shortening of the induction period and even an elimination of this hydration period for very high Pox additions [9]. The hydration model proposed by them was that of a quasi-stationary layer in the liquid phase supersaturated with Ca^{2+} ions surrounding the anhydrous C_3S grains. The lowering of concentration of calcium ions in solution accelerates the reaction of C_3S with water. They have used Pox in powder form and have reported a considerable increase of the first hydration peak and a reduction of the intensity of the second hydration peak.

Wu et al. have also studied the hydration reaction of tricalcium silicate in the presence of different colloidal silica including also Pox [10]. They have concluded that the initial reactions depend only on the surface area of the silica in the system. Also the presence of small amounts of silica can accelerate the hydration of tricalcium silicate (C_3S), the principal constituent of Portland cement, thereby increasing the rate of early strength gain. In contrast to the results obtained by Kurdowski et al. they observed in every case the second main peak and the dormant period similarly to our results with cement systems. They have additionally reported a lengthening of the pre-induction period, but a shortening of the induction period and a renewed hydration of C_3S starting in this way earlier [10]. Their explanation was that the initial C–S–H formation would most likely be at the silica surface having specific surface area of the same order as C–S–H itself, rather than on the C_3S surface. The C_3S surface remains relatively clean until all silica particles in its vicinity have reacted. The initial rapid dissolution of C_3S will thus last longer as the ions released react with silica. The induction period according to their assumptions is shortened since $[OH^-]_{max}$ concentration is reached sooner. After the end of the induction period precipitation of C–S–H at the C_3S surface occurs normally.

Stein et al. have also used Pox for elucidating the hydration reaction mechanism. Their reports of a very early work using Pox are consistent with those of the above mentioned authors that the hydration rate is accelerated when amorphous silica is present in the hydrating system with C_3S [11]. They attributed this acceleration to the lowering of calcium and hydroxyl-ion concentrations during the first minutes of hydration and the increase of the conversion rate of a first protective hydrate layer into another less protective one. The conversion of the first into the second is accelerated by Pox through nucleus formation during the first few minutes. In a similar way their conclusions for the cement paste hydration were that not only hydration of alite but also consumption of sulphate ion is accelerated by Pox, probably through opposing formation of an ettringite layer in the first moments of hydration [11]. Based on the conclusions of the above studies and on the new insights gained by our hydration behaviour experiments we are going to propose a mechanism for explaining the hydration behaviour of cement pastes with colloidal silica. Additionally some morphology and structure development aspects of mortar specimens that contain micro and nanoscale pozzolans by some XRD and AFM examinations will be also the matter of this study.

2. Experimental

2.1. Materials

The cement used was Portland cement type PC I 52.5R HS/NA with a low C_3A content, because of its lower water demand and moderate heat development [12,13]. Its chemical composition is given in Table 1.

One of the superplasticizers (SP VP2500) of polycarboxylate-ether basis of our previous study was also used here for these experiments [8]. Some preliminary tests of cement–superplasticizer compatibility study in our laboratory have shown that the optimal content of polycarboxylate-ether superplasticizer (SP) is around 1.5–2% referring to the cement that we have used. Therefore the SP content was 1.7% referring to binder (cement + pozzolanic additive) for the pastes of the hydration behaviour experiments and the water to binder (cement + pozzolanic additive) ratio was the same for all pastes (W/C = 0.50). The superplasticizer (VP2500) was previously added to the mixing water or to the Pox dispersion, and the water content of the superplasticizer dispersion was also considered in every case. The silica fume (SF) type G983 together with fly ash (SWF) and quartz flour (Q600) with the chemical compositions and other characteristics shown in Table 1 were used as microscale pozzolanic additives. Three Pox products in dispersion form differing in primary particles sizes, specific surface area, pH-value and other characteristics were used for studying their influence on the hydration behaviour. In order to point out their influence on the hydration reactions they were used in much higher content in the hydration pastes then their real content that is employed for producing high performance concrete specimens [8].

Table 1
Some physicochemical properties of the raw materials used

Chemical composition (% mass)	Silica fume SF1 (G983)	Pyrogene silica dispersions (Pox)			FA (SWF)	PC I 52.5R	Quartz flour (Q600)
		W1226	W1714	W7520			
SiO_2	98.7	99.8	99.8	99.8	54.1	16.6	99.0
Al_2O_3	0.28				22.1	4.62	0.3
Fe_2O_3	0.1				7.71	4.13	0.05
CaO	0.23				5.11	67.1	
Na_2O+K_2O	0.3				4.22	1.04	
SO_3	0.19				2.28	3.12	
P_2O_5	0.02				0.18	0.28	
Others (LOI)	1.97	0.02	0.02	0.02	3.46	2.24	0.25
d_{50} [μm]	0.35	0.25	0.16	0.12	6.5	7.5	3.5
Spec.surf.area m^2/g (BET)	17 ± 0.5	50 ± 10	170 ± 5	190 ± 10	0.65	0.5	1.5
pH		9–10	5–6	9–10			
Disponibility form	Powder	Dispersion	Dispersion	Dispersion	Powder	Powder	Powder
Dispersion state	Aggr.-aggl.	Aggr.	Aggr.	Aggr.	Aggr.-aggl.	Aggr.-aggl.	Aggr.-aggl.

Table 2
The simple RPC formulation (adapted)

Portland cement I 52.5R	1
Silica fume G983	0.25
Quartz sand 125–500 µm	1.1
Superplasticizer (polycarboxylate-ether)	0.015
Water	0.2
Temperature	20 °C

Some of the Pox main physicochemical properties supplied from the producer (Degussa, Germany) are shown in Table 1. The AFM examinations were carried out for the following specimens (mix formulation shown in Tables 2 and 3):

Normal mortar with W/C=0.45	(quartz aggregates <2.0 mm)
Simple RPC (HPC) with 25% SF1 G983	(quartz aggregates <0.6 mm)
HPC specimen with SF1 (G983) 20% and W1226 3.55%	(quartz aggregates <0.6 mm)
(Contents are in mass percent referred to cement)	

2.2. Methods and equipment

For the hydration behaviour a heat flow calorimeter equipment supplied by “ToniCAL, RK Toni Technik” was employed. The reacting components were firstly tempered until an “equilibrium state” (temperature equilibrium) was reached. The liquid components (water–superplasticizer or water–superplasticizer–Pox) were added to the powder mixture after the equilibrium state was reached and the heat of hydration reaction was measured continuously for the specified time interval. Some hydration reactions were additionally followed in-situ by using the XRD method and a X'Pert Pro diffractometer with Bragg–Brentano geometry, Cu $K_{\alpha 1,2}$ radiation (1.54178 Å), 45 kV and 40 mA, equipped with a RTMS-Detector (X'Celerator, PANalytical). The parameter configuration of the XRD equipment is shown in Table 4. After adding water and mixing, the pastes were poured into a special specimen holder by back loading against a plain surface. This specimen holder is a closed system that prevents the specimen from drying and carbonation during the measurement. The top of the specimen is covered by an X-ray transparent polyimide foil which gives no additional reflections in the diffraction pattern. After the preparation the specimen was installed in the measurement chamber. After 4 min of mixing with water the first measurement could be started and then was continuously measured with a scanning time of 3 min over a 2-theta range from 5 to 65°. The hydration reactions were followed on-line during the first 24 h by recording the diffraction patterns of the formed crystalline phases. The measured peak widths of the diffraction peaks represent a convolution of the instrumental broadening and the specimen contribution. To determine the instrument broadening a silicon standard material that does not represent additional size and strain broadening was employed by using exactly the same setup as for the in-situ experiments. The size broadening of the specimen is calculated with respect to the standard. For the examinations of the nanostructure an atomic force microscope (AFM “JSPM-5200, JEOL” type) available in our laboratory was employed.

Table 3
The mix formulations microfiller–Pox dispersion

Portland cement I 52.5R	1
Microfiller	0.2 (0.15[a])
Aerosil dispersion	Varying
Quartz sand 125–500 µm	1.1
Superplasticizer (polycarboxylate-ether)	0.02
Water	0.22
Temperature	20 °C

[a] Only for the cristobalite flour.

Table 4
Parameter configuration for the XRD measurements

Diffractometer type	Bragg–Brentano, Theta-Theta-Goniometer
Generator settings	45 kV, 40 mA
Anode material	Cu
Primary and secondary soller	0.02 rad
Detector type	RTMS-Detector, X'Celerator, PANalytical
Sample rotation	1 r/s
2 Theta scanning range	7–70°
Step size	0.017°
Step time	29.8 s
PDS	12 mm
K_β-Filter	Ni

2.3. Preparation of specimens for the AFM examinations

The specified Pox dispersion quantities were first mixed with the extra water and half of the superplasticizer quantity. The liquid mixture was sonicated for 5 min and added to the powder mixture and then mixed again. The water content of the Pox and superplasticizer dispersions was also considered for the total water content. After the specified mixing time (remarkably longer then that for normal mortar) the fresh mortar was filled in the mould (1.5×1.5×6 cm) in two layers and vibrated for 2 min. The prism-shaped specimens were demoulded after 24 h of hydration time and then stored in a climate chamber (20 °C and 95% r.h.) for the rest of the specified curing time. The AFM examinations of the nanostructure were carried out in polished surfaces of 3 specimens (see Section 2.1). Prior to the polishing the specimen was embedded into an epoxy resin substrate. After 2 days of substrate hardening the samples were carefully polished using papers with different coarseness and isopropanol as lubricant. At the last step of polishing diamond spray with a particle size of 1 µm had been used and afterwards the specimen was carefully cleaned with ethanol.

3. Results and discussion

The results reported consist of a comparison of heat flow calorimetry responses for 10 cement pastes containing various combinations of pozzolanic additives and superplasticizer (paste nr. 1 in Table 5 contains no superplasticizer); an XRD study of the development of crystalline calcium hydroxide in three pastes with and without additives; and separately, three AFM examinations of nanostructure on polished surfaces of mortars with and without additive.

Table 5
The evolved heat of hydration

	Paste	Heat of hydration [J/g binder] (0–48 h)	Heat of hydration [J/g cement] (0–48 h)
1	Cem–H_2O	306	306
2	Cem–H_2O–SP	229	229
3	Cem 75%–SF 25%–H_2O	209	278
4	Cem 75%–SF 25%–H_2O–SP	205	273
5	Cem 75%–FA 25%–H_2O–SP	200	266
6	Cem 75%–Q600 25%–H_2O–SP	194	258
7	Cem–W1714–H_2O–SP(*)	178	237
8	Cem–W7520–H_2O–SP(*)	129	172
9	Cem–W1226–H_2O–SP(*)	182	242
10	Cem 75%–SF 20%–W1226 4.9%–H_2O–SP(**)	92	123

(*) — The same cement content as in pastes (3–6).
(**) — Cement content the same as in pastes (3–6), whereas Pox W1226 replaces partially silica fume.

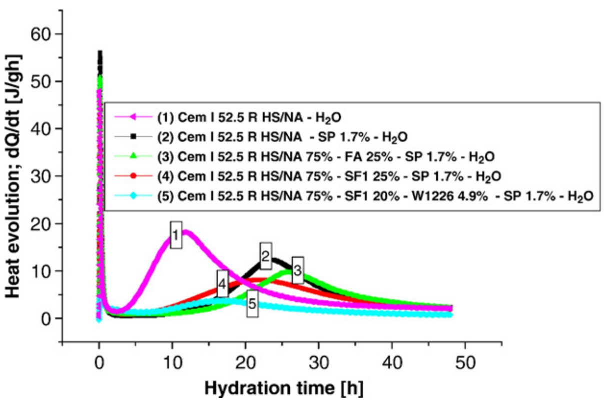

Fig. 1. Effects of microscale pozzolans and of the combination micro-nanoscale pozzolan on the hydration behaviour.

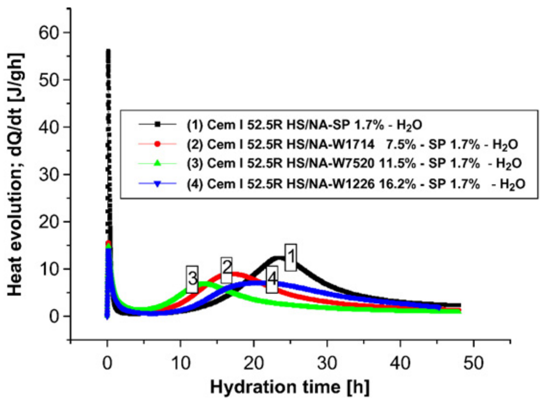

Fig. 3. Effects of various Pox dispersion products on hydration behaviour compared to the paste without Pox.

3.1. Assessment of the hydration behaviour by using the heat flow calorimetry method

Investigations of the hydration behaviour at 25 °C using the heat flow calorimeter equipment were carried out for the following pastes (W/C = 0.50, SP/C = 1.7%):

- normal cement paste (cement–water) system representative of the normal mortar specimen,
- cement–water–superplasticizer (this mixture was employed in order to assess the superplasticizer effect on hydration), and
- high performance pastes containing micro and nanoscale pozzolans.

The first two pastes namely the normal cement paste and the cement–water–superplasticizer paste were also the reference samples for these hydration behaviour studies (pastes nr. 1 and nr. 2 in Table 5 and hydration curves 1 and 2 of Fig. 1).

For these experiments the microscale pozzolan was used to partly replace cement, whereas the nanoscale pozzolan (Pox) was used as partial replacement for the microscale additive (silica fume), or was additionally given to the system by keeping constant the cement content.

Here the amount of Pox added was considerably higher than the real amount that we have used for the production of high performance specimens. The employment of lower Pox contents in the high performance pastes is conditioned by their low water to binder ratio [8]. High amounts of Pox for the hydration tests were used for the following reasons: firstly the amount of the silica fume to be compared with is also high. Secondly the theoretical amount of pozzolanic additive required for complete pozzolanic reaction lies above 20% [10]. Also the addition of high Pox amount was thought to point out its effect on the associated hydration reactions. The corresponding hydration plots are shown in Figs. 1–4 and the total hydration heat evolved during the first 48 h for all pastes is presented in Table 5. Fig. 1 shows the hydration behaviour of pastes with micro and nanoscale pozzolans and superplasticizer and the effect of superplasticizer addition. In the same figure the curves 1 and 2 represent the hydration behaviour of the reference samples namely: the normal cement paste and the cement–water–superplasticizer paste. The well-known retardation effect of superplasticizer on the hydration reaction (compared to the curve 1 without SP) is demonstrated by curves 2–5 (the hydration curve 2 represent the effect of SP addition). The affection of hydration course is different for the various pozzolans used (Fig. 1). The hydration curve 4 in Fig. 1 or curve 2 in Fig. 2 (is the same) represents the well-known acceleration effect of silica fume addition on the hydration reaction (compared to the reference sample, curve 2 in Fig. 1 or curve 1 in Fig. 2) and confirms in this way the conclusions of others in previous works [10,14,15]. Contrary to the silica fume, the addition of fly ash as cement replacement, induces a slightly longer induction period (curve 3 of Fig. 1 or curve 3 of Fig. 2) in comparison with the induction period of the paste that does not contain any pozzolanic additive (the curve 2 of Fig. 1 or curve 1 of Fig. 2). For fly ash influence on the hydration reaction contradictory observations have been reported, there were observations of both retardation [16], but also of acceleration effects [17]. The results of our study (Figs. 1 and 2) which show retardation effect on hydration are consistent with the conclusions of Chatterji, even though it should be mentioned that the effects induced by fly ash are very dependent on the fly ash product used [18]. Fly ash products have different reactivity; so that reactive ones may accelerate hydration, while less reactive ones do not [18]. In the experimenting

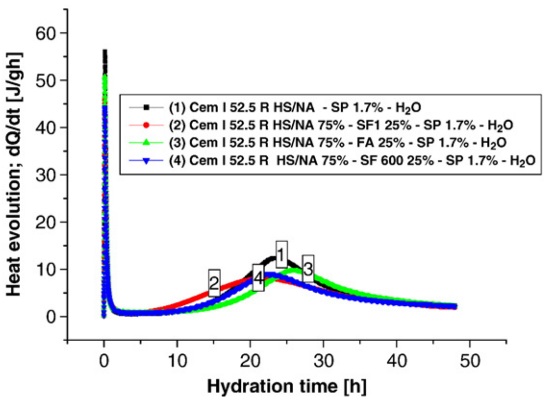

Fig. 2. Effects of various microscale pozzolans on the hydration behaviour.

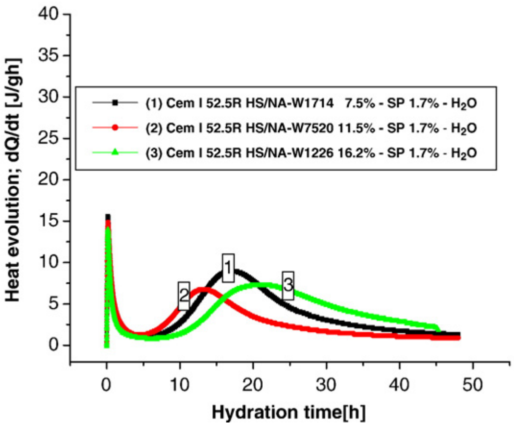

Fig. 4. Induction period dependence on primary particle size and specific surface area.

conditions of our study quartz flour (SF600) did not show any substantial effect on the hydration behaviour of the corresponding paste where it was included (curve 4 of Fig. 2). This conclusion is also in good agreement with those of others in similar works [11,19]. Similarly to the silica fume, Pox accelerate the hydration reactions (shorten the induction period), but the acceleration effect of Pox is much more pronounced (hydration curves 2–4 of Fig. 3) compared to the reference paste cement–water–superplasticizer (curve 1 of Fig. 3). This acceleration is also the reason for the higher early strengths of the pastes containing Pox [8]. The hydration curves in Fig. 4 represent the dependence of hydration reactions on the Pox primary particle size and specific surface area. Referring to this figure, a hydration behaviour dependence on Pox product that can be correlated to the size of its primary particles and specific surface area can be easily concluded. The hydration curve of the paste that contains the Pox product W7520, with the finest primary particles and the largest specific surface area, is characterised by the shortest induction period. In this way, the induction period of the paste that contains the Pox dispersion W1226, which has the lowest specific surface area among Pox products, is characterised by the longest induction period (Fig. 4). The accelerating effect depends on the Pox type and its surface characteristics (particle size and specific surface area). Also the use of Pox as partial replacement for silica fume causes a shortening of the induction period and smoothing of the heat of hydration curve (curve 5 versus curve 4 in Fig. 1 and paste nr. 10 versus nr. 3 in Table 5). Despite of the different Pox amounts used with the high performance pastes (cement–Pox–superplasticizer–water), no great difference of the hydration course that is dependent on the Pox content was observed (Fig. 4). The total hydration heat evolved during the first 48 h for all pastes is shown in Table 5. The replacement of cement by various microfillers (silica fume, fly ash and quartz flour) brings as expected and reported also by others a reduction of the total heat of hydration evolved (Table 5 and Fig. 3), [3,20]. The reason of lower heat of hydration evolved when the cement content is partially replaced by microscale additives is quite apparent: there is lower cement amount that participates in hydration reactions (the pastes nr. 3–6 in Table 5). However, the heat of hydration of the pastes cement–microfiller is higher than that of the pastes without microfiller (used as cement replacement), if one refers to the pure cement content and not to the binder content. In the case of microfiller the higher amount of the heat evolved is due to the additional pozzolanic reactions happening simultaneously to the hydration reactions. They do not “disturb” the normal run of hydration as in the case of adding high amounts of Pox. Whereas the addition of Pox as partial replacement for silica fume (the curve 5 in Fig. 4), or additionally given to the hydrating paste (Fig. 1 and Table 5), causes lowering of the peak intensity and shortening of the induction period, depending on the type of Pox product. For the lowering of the heat of hydration during the first 48 h of the pastes that contain Pox (the cement content was the same as for the pastes nr. 3–6), we assume the following main reasons: Firstly it is the lower cement content (compared with the pastes nr. 1–2) that participates in hydration, and secondly it is the presence of extremely fine nanoscale additive that “disturb” the otherwise more vigorous hydration processes and causes the smoothing of the hydration curve and lowering of the heat evolved. Because of the extreme fineness of Pox particles and the large amount added, a kind of water retention from its particles occurs. Hence this water is not available for the hydration from the first moment of mixing and considerable amount of cement remains unhydrated. This water is being given only slowly to the hydrating system during the course of hydration, resulting in this way on a considerably lower heat of hydration evolved. Probably, it seems that this water retention is more pronounced when both silica fume and Pox are simultaneously used.

For concluding it can be said that the results of our study agree generally well with the conclusions of Kurdowski et al. with both the hydration acceleration process and lowering of the intensity of the second heat of hydration peak [9]. However, contrary to their results, instead of an increase of the intensity of the first heat of hydration peak a lowering was observed in our experiments. Also we did not observe any elimination of the induction period, despite the very high amounts of Pox that we have used with our pastes. We assume that the increased intensity of the peak of hydration heat that they have measured may result due to the heat released associated to the wetting of extremely fine Pox particles. This was not the case in our experiments since we have used only Pox products in dispersion form. In our opinion the hydration model proposed by Wu et al. would better explain the results of this work obtained with cement–Pox pastes [10]. Developing further their model, we assume that the colloidal silica (silica fume and Pox), accelerates the early hydration of reactive cement phases, mainly C_3S and C_3A phases, by providing large amounts of reactive siliceous surface, which serves as a site for the early C–S–H precipitation. Initially the grains of cement phases are surrounded by the silica particles, being those of Pox, silica fume or both of them, enveloping each grain [8]. For 10% of silica fume added referred to cement content, each cement grain would be surrounded by approximately 10^8 silica particles [10]. Even higher is this number when Pox is added. Thus the slower initial rate of release for Ca^{2+} and OH^- ions by the hydrolysis of cement phases (mainly C_3S phase, which is the most abundant phase), along with the lower water quantity available for hydration, causes the lowering of the first peak of hydration heat. Upon contact with water, with time these ions have to pass through the enveloping layer of highly reactive silica to enter the bulk solution. The initial C–S–H will be mostly formed on silica surface rather than on the surface of the most reactive phases (C_3S, C_3A). The initial rapid dissolution of C_3S will last longer as the ions released react with silica. The $[OH^-]$ concentration reaches a high level at the end of pre-induction period instead of reaching its maximum at the end of the induction period [10]. Thus, since the $[OH^-]$ max is reached sooner, a fast precipitation and consumption of Ca^{2+} and OH^- from silica species will result on a shortening of the induction period. At the end of the induction period precipitation of C–S–H at the surface of cement phases occurs normally. Since the accelerating extent of hydration reactions can be correlated to the size of primary particles and specific surface area of the Pox product used, the consumption of Ca^{2+} ions from anionic silica species is rate determining factor that control the shortening of the dormant period and hydration acceleration. We assume that the consumption of Ca^{2+} and OH^- from the silica species, in addition to the diffusion of Ca^{2+} onto the silica surface as in the model of Wu et al. may be the rate controlling steps of the overall reactions. This consumption that is dependent on the solubility rate (dissolution rates maximised above pH 7) and reactivity of silica species is directly related to the size of primary particles and specific surface area. In earlier works Trettin et al. have also found out that the early hydration products are able to absorb Ca^{2+} from solution. Also the hydration of C_3S is accelerated by using an admixture that reduces the Ca^{2+} ions concentration, since this leads to a better penetrable reaction layer upon the C_3S surface that is poor in Ca^{2+} [21,22]. Thus the lowering of concentration of calcium ions in solution is the drive for the hydration reactions: its rate of consumption determines the acceleration extent.

3.2. Assessment of the size of portlandite crystals by X-ray diffraction (XRD) method

The hydration reactions were followed on-line during the first 24 h by recording the diffraction patterns of the formed crystalline phases.

Since we are treating here only the influence of pozzolanic additives on the size of portlandite crystals, only the diffractogram fragments of portlandite crystal formation during early hydration (first 24 h) are shown in Fig. 5 for the following pastes:

- paste without pozzolanic additive (paste nr. 1 Table 5),
- paste containing silica fume (paste nr. 3 without SP same table) and
- paste containing Pox product (paste nr. 10 without SP same table).

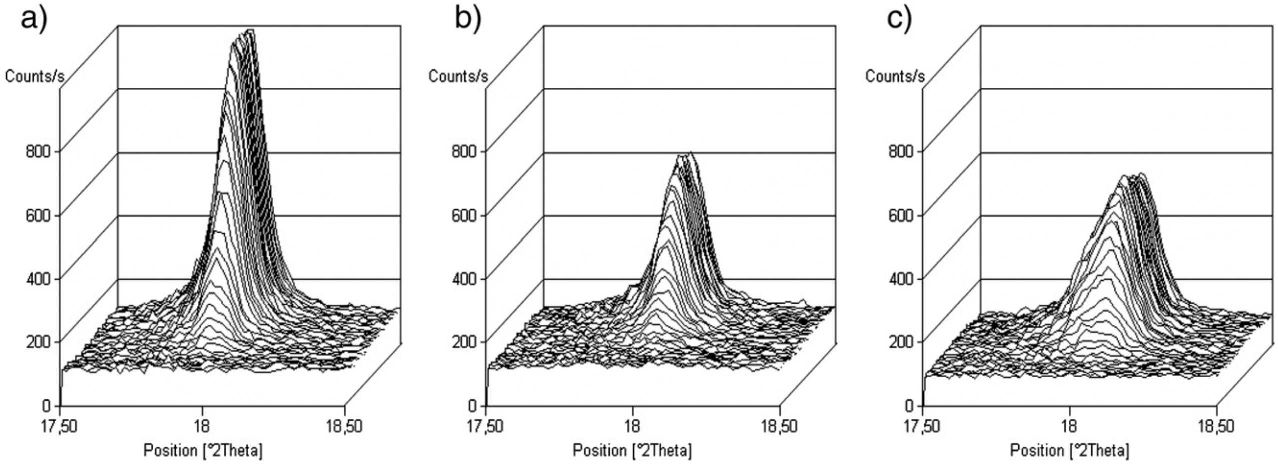

Fig. 5. Portlandite crystal formation during the first 24 h of hydration reactions (fragments of diffraction patterns).

The remarkable differences between peak intensities and peak widths of portlandite (Fig. 5) formed during the early hydration give evidence for different amounts and crystal sizes of calcium hydroxide. The detectable amounts of crystalline calcium hydroxide formed in the hydrating pastes with micro and nanoscale pozzolans are lower than the amount present in the paste that does not contain any pozzolanic additive. The amount of detectable crystalline portlandite is the lowest for the paste that contains Pox, image c. The broader portlandite peak for the paste that contains Pox accounts for smaller size of portlandite crystals formed in the presence of the nanoscale pozzolan. The measured peak widths of the diffraction peaks represent a convolution of the instrumental broadening and the sample contribution. The extra broadening of the Bragg-reflections stems from crystallite size and micro strain broadening and can be discriminated, because they vary differently in 2θ [23]. Only the two specimens (pastes) that contain pozzolans (and hence crystalline nanoscale portlandite) were employed for the determination of the crystal size. The portlandite crystals in the specimen without pozzolans represented no size broadening, as they contain µm-sized crystals (Fig. 5a). A rough estimation of portlandite crystal size by using the Scherrer algorithm for the paste that contain the microscale pozzolan gave a value of 155 nm average crystal size and for the paste that contains Pox an average size of 53 nm. Taking into consideration the relatively high errors in calculation (i.e. stacking fault, dislocation) of the absolute values and the lower quality of in-situ XRD measurements as compared to the ex-situ measurements, these values should be taken as approximate values of the crystal sizes.

In addition to the crystal size differences, the obtained results indicate that the formation of calcium hydroxide crystals detectable by XRD is accelerated along with the total hydration process in the presence of nanoscale pozzolanic additive. Thus the first detectable portlandite crystals appear after around 4 h and 36 min (for these experimental conditions) instead of 5 h and 04 min for the paste that does not contain any pozzolanic additive. The XRD measurements support in this way the results of hydration acceleration and shortening of the induction period obtained by the heat flow calorimetry method.

3.3. Atomic force microscopy (AFM) structure and morphology examinations at nanoscale

The AFM images (500 × 500 nm) were obtained on polished surfaces of 56 days old specimens. The representative area for examination was chosen by employing the optical microscope of the SPM equipment. In this way the images obtained are representative of the cementious matrix and not of the aggregate. The AFM (JSPM-5200, Japan) was operated in AC mode with a scanning speed 333.33 µs and the resolution 512 × 512 pixels. In the AC mode AFM, the cantilever is vibrated in the vicinity of its characteristic frequency (150.383 kHz), and the Z scanner is controlled so that the amplitude of the cantilever remains constant during scanning. Using the AC mode, AFM observations in the attractive-repulsion critical range become possible. The observed "topography image" of the specimen in the AC mode is the constant-force mode while keeping the cantilever amplitude constant. In this mode it is also possible to observe a "phase image" by using the phase change in the vicinity of the cantilever resonance point. Both topography and phase images are shown in Figs. 6–8 a, b for the normal mortar, the high performance specimen with silica fume and the high performance specimen with silica fume and Pox (Pox replaces partially the silica fume). The topography images (images a) show a remarkable difference of the nanostructure. There are differences of

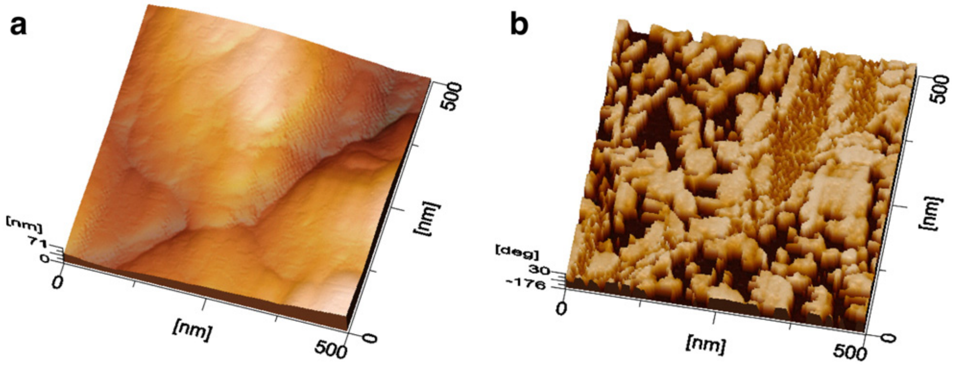

Fig. 6. a. Topography scanning image of normal mortar specimen (W/C = 0.45). b. Phase scanning image of normal mortar specimen (W/C = 0.45).

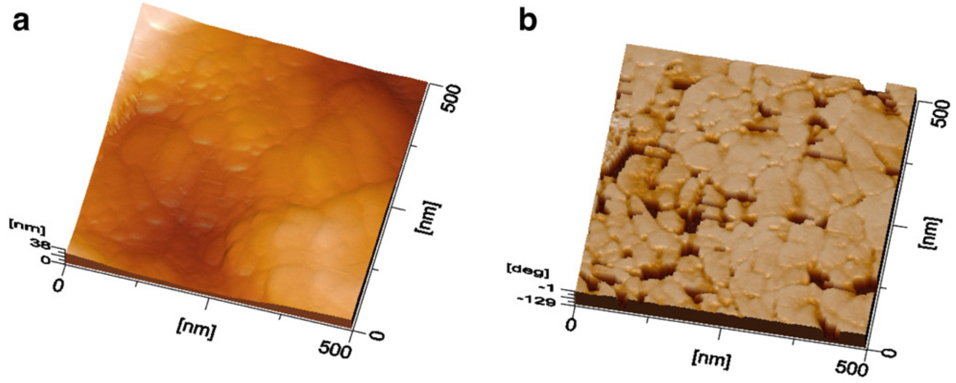

Fig. 7. a. Topography scanning image of high performance specimen with 25% SF1 (G983). b. Phase scanning image of high performance specimen with 25% SF1 (G983).

the phase texture, morphology and size of structure building phases. Both the high performance specimens (containing silica fume and Pox) are characterised by finer phases and their nanostructure seems to be build up of much smaller units than the normal mortar specimen. The phase difference images (images b) indicate that both high performance specimens (Figs. 7b, 8b) are additionally characterised by an overall tighter structure than the normal mortar specimen. Also their phase texture is more homogeneous and the structure seems to have less "defects" present. Their corresponding phases are also in much more closer contact. These characteristics are mostly pronounced at the high performance specimen that additionally contains Pox: it has the tightest and most homogeneous structure among the three examined specimens. The information obtained by both topography and phase images are in perfect agreement with the results of porosities and pores size distributions previously obtained in these three specimens [8]. The lower porosity and the pore refinement can be attributed to the presence of phases with finer structure for the high performance specimens and especially for the specimen that contains both micro and nanoscale pozzolanic additives. Also the XRD examinations and the results about the size of portlandite crystals strongly support the findings of the AFM and gas adsorption measurements. All results correlate very well between them and indicate that the addition of nanoscale pozzolans (Pox) enables remarkable improvement of the nanostructure.

4. Conclusions

We have treated in this paper some aspects of hydration behaviour and structure development of advanced cement-based systems that contain micro and nanoscale pozzolans (Pox).

It has been observed that the hydration course is strongly affected by the kind of additive employed and its properties considering the size of its primary particles and specific surface area, among other parameters. Both silica fume and Pox accelerate the hydration reactions by providing large amounts of reactive siliceous surface, which serve as site for the early C–S–H precipitation. Pox products with much larger specific surface area and finer primary particle sizes than the commonly used microscale pozzolans, accelerate more strongly the hydration processes (shorten the induction period). The replacement of cement by microfiller results on the smoothing and lowering of the total heat of hydration (referring to the binder). For explaining the accelerating effect in the presence of colloidal silica, we have assumed that the colloidal silica, which provides large amounts of reactive siliceous surface, serves as a site for the early C–S–H precipitation. In this way the initial C–S–H will be mostly formed on silica surface rather than on the surface of the most reactive phases (C_3S, C_3A). Since the $[OH^-]$ max is reached sooner (at the end of pre-induction period instead of reaching its maximum at the end of the induction period), a fast precipitation and consumption of Ca^{2+} and OH^- from silica species will result on a shortening of the induction period (acceleration). The consumption of Ca^{2+} ions from anionic silica species, in addition to the diffusion of Ca^{2+} onto the silica surface, may be the rate controlling steps, due to the fact that the accelerating extent of hydration reactions can be correlated to the size of primary particles and specific surface area of the Pox product involved. The in-situ following of hydration reactions by means of the XRD method gives additional evidence for hydration acceleration in the presence of Pox. The detectable amount of the crystalline calcium hydroxide of the early hydration (first 24 h) for the pastes containing micro and nanoscale pozzolans (more pronounced for the paste containing Pox) is remarkably lower than that of the paste that does not contain pozzolan additives. The first detectable portlandite crystals for the Pox containing paste appear earlier (after 4 h and 36 min from the beginning of hydration) than for the paste without Pox (5 h and

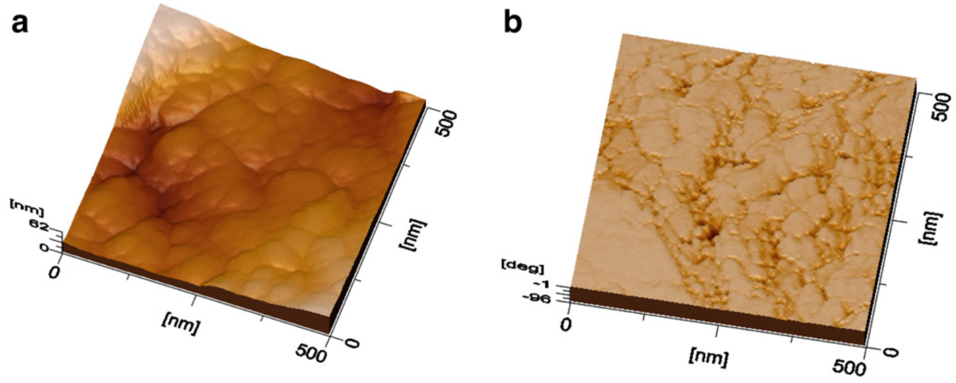

Fig. 8. a. Topography scanning image of high performance specimen with 20% SF1 (G983) and 3.55% W1226. b. Phase scanning image of high performance specimen with 20% SF1 (G983) and 3.55% W1226.

04 min) and their size seems to be much smaller in the presence of Pox.

The nanostructure examinations by means of AFM method strongly support the results of finer structure (smaller portlandite crystals) assessed by the XRD method and drastically reduced porosity and pore refinement assessed by gas adsorption for the specimen that contain micro and nanoscale pozzolans.

Acknowledgement

The authors gratefully acknowledge financial support from the company Degussa (aerosil and silanes), Germany.

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