

The Early Stage of Cement Hydration: Measurement of the Particle Size Distribution at Different Times

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Abstract

During the hydration of Portland cement basic changes in the properties of the whole system occur. Besides the extensive research results concerning macroscopic, microscopic and chemical properties of Portland cement comparatively little are known about changes in the particle size distribution of the cement within the stages of hydration.

Due to the formation of hydration product layers on the particle surface as well as to other effects, major changes in the particle size distribution of the hydrating Portland cement are detectable. This paper deals with changes in the particle size distribution of Portland cement in the early stage of hydration, which are verified via in-situ granulometric measurements.

The influence of measuring technique, especially the sample preparation on the result of the measurement will be shown. Further investigations comprise the impact of different measuring times and concrete admixtures on the particle growth.

In order to evaluate existing simulation programs for cement hydration processes, functional dependencies between given parameters are discussed.

Particular conclusions drawn by other authors are evaluated on the basis of the achieved results.

1. Introduction

Inorganic binders such as gypsum, lime and Portland cement usually are worked up in powder form. From the macroscopic point of view, without using tools, there are only few distinctions possible regarding the granulometric properties of the powder. A powder is a composite of a large number of particles, which differ in shape and size. In dependence on the particle size distribution, final properties of the whole powder can be influenced, even if the chemical composition is unchanged. Therefore, granulometric information about the powder is needed to assess the resulting properties. The analysis of a sufficient big enough powder sample provides such information for technical and scientific demands. The methods of analysis cover a wide range of possibilities, depending on the objective and the available technique. Today most of the

measurements on powder generate granulometric variables. The complexity of the possible measurements is wide spanned, too. Simple techniques such as sieving demand low specialized knowledge as well as low cost equipment. More complex techniques have developed in the last decades. One of these techniques comprises the use of laser light for measuring the particle size distribution.

With the help of the newly developed technique combined with computer-based data processing high resolution granulometric measurements in few-minutes-cycles are accessible.

Most of past research in the field of granulometry was done on material, which did not undergo a chemical reaction during or immediate before the measurement. Thus, the majority of granulometric analyzed binders has been in the non-hydrated state. The share of granulometric in-situ-measurement, which is applicable to just hydrating hydraulic binders, is still humble.

The analysis of hydrating Portland cement and the changes in its particle size distribution during the early stage of hydration is subject of this paper.

2. Experimental

2.1 Instrument

The granulometric measurements were carried out using a COULTER LS 230 laser granulometer. The range of the measurable particle size is defined by 0,04 μm (lower limit) and 2000 μm (upper limit). The particle size distribution output is composed of 116 size channels, whose respective limits follow a logarithmic grading.

In the above mentioned instrument, the measuring principle is a chaining of two basic principles. Measured particle sizes smaller than 0,4 μm are based on the Mie-theory and patterns of scattered white light. Measured sizes above 0,4 μm are based on the Fraunhofer-diffraction.

The powder to be measured is dispersed in a diluent. This fluid runs in a closed loop within the laser granulometer. The nature of the fluid can be varied in dependence on the analyzed material. The common fluid is demineralised water, but also possible are organic fluids. For this purposes, isopropanol as fluid is used. Therefore, the special hazardous fluids module (hfm) of the laser granulometer was used.

2.2 Procedure

The whole measuring procedure includes repeated single steps of sampling and run cycles and lasts up to 4 hours altogether. Before starting a new procedure, the preparation of the sample has to be made and the readiness of the instrument has to be established.

The readiness of the instrument comprises starting the flow of the diluent, and, amongst others, accomplishing offset, alignment and background-scanning of the optical bench. These actions are adjustable by the control program, a Windows®-based software delivered with the instrument.

After weighing the constituents, the mixing of the solids and the addition of the water can be done. After adding water and mixing the sample, the particle size distribution is measured at defined times during the early hydration stage. The zero-point of hydration time is fixed by the addition of water. The “zero-size” of the particle size distribution is defined by the distribution of the unhydrated cement.

Each measuring point requires a complete run-cycle of the instrument. Therefore at each measuring point a portion is taken from the hydrating “mother” sample. During the intervening period the sample is protected against desiccation by covering the container with a wet cloth.

2.3 Special features

The special features given below are typical for the unique measuring technique. They base upon the sophisticated measurements described by Stark et al [1], which have been advanced and specified. Very important for obtaining reliable results is a standardized procedure to keep the personal bias within a close tolerance. In the case of different operators this means, comparative studies between the operators are indispensable to detect potential systematic errors.

The sampling of portions at particular times should be done carefully to avoid perturbation of the hydration and to ensure a representative sampling. Attention should be paid, if bleeding occurs. Then the whole hydrating sample must be briefly homogenized by hand.

The dispersing has the highest potential for systematic errors caused by the operator. As known from non-reactive powders, the dispersion technique should be powerful enough to assure the deagglomeration of the particles. The common method for this is the use of ultrasonic sound waves, which are applied to disperse the sample material in the diluent.

This dispersing method is not advisable for hydrating binder systems, since the newly formed product layers on the particle surface are blasted away due to the too high energy input. Therefore, alternative methods are possible like using a magnetic stirrer or applying turbulent flow. Finding the balance between sufficient dispersing and not-falsifying the particle size distribution led to the use of turbulent flows. Its practical implementation includes the defined variation of the pump speed of the fluid module.

For conserving the status of the particle size distribution at the measuring point the chemical reaction has to be stopped. This is done by filling the portion to be analyzed into the closed fluid loop of the granulometer, which is filled with isopropanol.

A further important factor for reliable results is to keep the table of the measuring points. Herein the in-situ-nature of the granulometric measurements shows. If the duration of a run cycle and the instrument setup exceeds the allowed time, a time delay for the following measurements occurs. This can lead to reduced or even not given usability of the results owing to not comparable measuring points.

3. Literature survey

Fundamental work regarding the changing granulometric characteristics of hydrating Portland cements and clinker phases was done several years ago. These works were strongly geared to the applicable measuring instruments. Thus, since the broad availability of laser granulometers, measuring points with narrow intervals are possible.

The first published results of hydrating cement clinker phases date back to 1985 [2]. Negro et al. analysed the main clinker phases at water/binder-ratios of 1200 ($w/b = 1200$). The focus was put on functional dependencies of the sample concentration on time. As a result, the different reactivities and morphologies of the clinker phases were researched.

Granulometric investigations by means of laser granulometer aiming directly on the early stage of cement hydration were set up by Odler et al. [3]. The water/binder-ratio was decreased to 1000. Some of Odler's measurements used $w/b = 0.3$, but only while the hydration reaction. These pastes had to be dissolved at every single measuring point for obtaining the dispersibility. The method of dispersion comprised ultrasonic sound at the begin of hydration, followed by a continuously working stirrer. The measuring range of the laser granulometer was between 1 and 190 μm . Finally, an important conclusion was, that during the early

hydration the volumetric part of particles around 20 μm increased whereas the amount of smaller and bigger particles decreased. At least the stated decrease of particles $> 30 \mu\text{m}$ is in contradiction to accepted and well-established models of cement hydration.

Lilkov et al. went on with the application of a laser granulometer [4]. The results of Odler were approved. The water/binder-ratio was kept in a normal range known by mortars and concrete.

The research at Bauhaus-University carried out by Stark as well as Brueckner and forerunners extended the knowledge of the measuring technique and of the hydration characteristics of Portland cements extremely. Besides the critical discussion of the investigations published by others (see above), some major results are [5], [1], [6]:

- Detection of typical trends and particle size ranges with increasing and decreasing respectively volume portions of particles.
- Development of an appropriate method of dispersion.
- Effect of plasticisers on hydration characteristics, which influence mean particle size and cause a retarding effect.
- Comprehensive investigations on the repeatability of test results. Specification of a minimum number of experiments to obtain reliable, statistically firm results. The required number increases from 4 to 8 per measuring point with increasing hydration time.

4. General tendencies of particle growth during hydration

The hydration characteristics of ordinary Portland cement exhibit different criteria. These criteria were detectable at all analysed Portland cements. Within these general criteria variations occur which depend on the initial particle size distribution, mineralogical composition of the cement as well as hydration constraints.

The following findings show exemplarily the behaviour of an Ordinary Portland Cement CEM I 42,5 R, see fig. 1. Starting from the initial particle size distribution (psd) of the unhydrated cement, the curve underlies some major changes. These characteristic changes are marked with the latin numbers in fig 1.

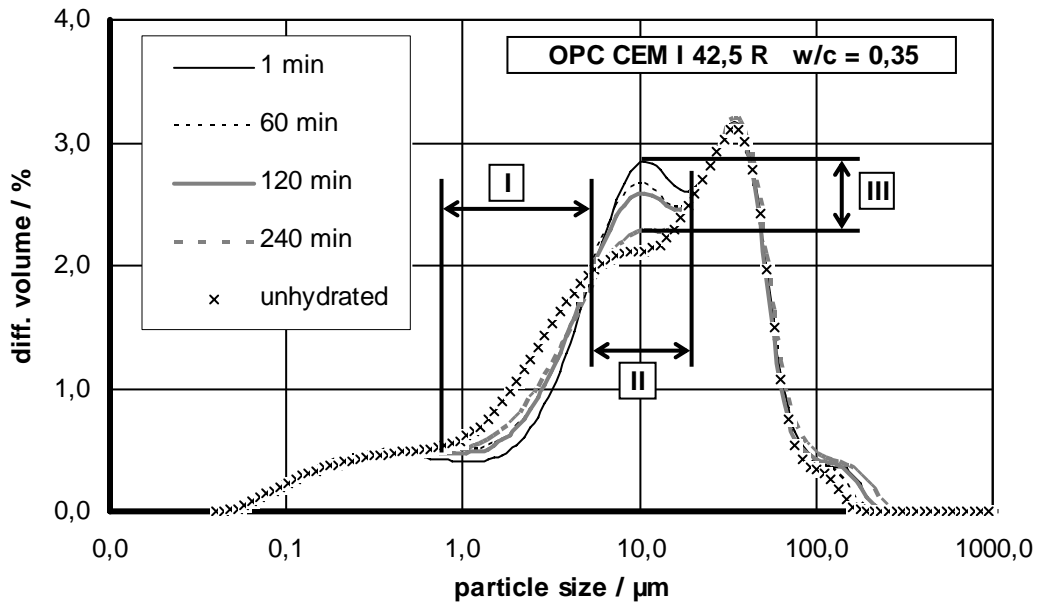


fig. 1: Particle growth of OPC during the early hydration stage

- **Area of decreasing differential volume (I):** The amount of differential volume decreases in the size range between approximately 0,7 to 5 μm . Increasing hydration time causes a slight reduction of the decrease, i.e. the psd of the hydrating binder converges slightly towards the initial psd which represents the unhydrated cement.
- **Area of increasing differential volume (II):** Subsequent to the decreasing area (I) the amount of particle volume increases between approximately 5 and 11 μm . As seen at the decreasing area, the psd-curve slightly converges to the initial psd.
- **Falling maximum (III):** The maximum in area II is decreasing. The decrease is strongly associated to the convergence of the “hydrating” psd to the “unhydrated” psd with rising hydration time. In the given example, the falling maximum is a local one. The absolute maximum at 33 μm exhibits no significant changes.
- The coexistence of two maxima is a specialty of the chosen example. Most of the analysed OPC do not have two maxima, but only one which has the described features. As an example for only one maximum, see fig 2.

Another area with both increasing and decreasing differential particle volumes can not directly be seen from fig. 2. This area comprises particles below approx. 0,4 μm and is characterized by a slight increase for hydration times greater than 10 minutes, but a decrease for hydration

times less than 10 minutes. It is assumed, that these changes in very fine particle size groups are connected with a varying chemical-mineralogical composition depending on the particle size dimension within the entire size fraction of cement

5. Results

5.1 Hydration at different w/c-ratios

The impact of different w/c-ratios is shown in fig. 2. The psd of a cement CEM I 42,5 R at w/c-ratios of 0.30 to 0.50 is represented. The mixture had no additives and consisted of demineralised water and OPC.

The impact of different w/c-ratios comprises:

- The height of the maximum is as higher, as higher the w/c-ratio is. After 60 minutes of hydration, the height of the maximum is sequenced in order of the w/c-ratios. After 1 minute of hydration this order is not developed significantly yet, but by 10 minutes.
- The w/c-ratios which are stoichiometric and beyond, form a higher maximum than the under-stoichiometric mixture of w/c = 0.30. As another influencing factor, the different consistencies due to different water contents can be considered.

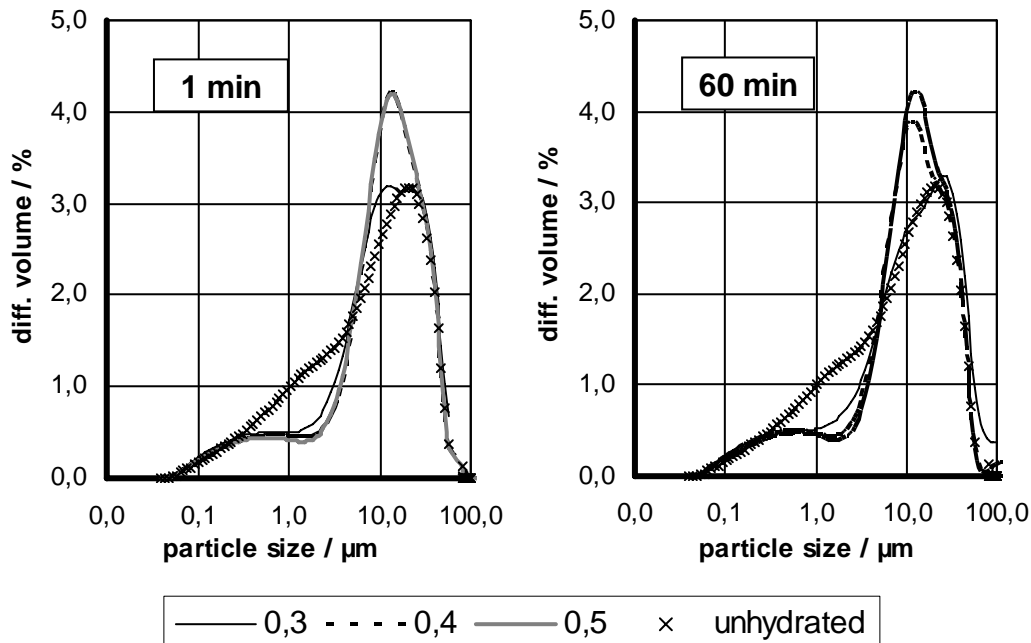


fig. 2: Influence of different w/c-ratio on the particle size distribution of hydrating CEM I 42,5 R

5.2 Effect of superplasticiser at different w/c-ratios

The addition of superplasticisers based on polycarboxylatethers (pce) leads to a liquefying and a retarding effect. Both effects exist usually in parallel. As stated elsewhere, the use of pce-plasticisers can cause an apparent constitutional change in the particle growth compared with the hydrating system free of pce [7].

The effect of superplasticisers was analysed using a commercial cement CEM I 42,5 R accordant to DIN EN 197. Some data of this cement are given in table 1.

table 1: Physical, mineralogical and granulometric data of the used cement

Spec. surface (Blaine) = 4850 cm ² /g		
Composition acc. to Bogue	C ₃ S = 55,0 %	C ₂ S = 16,3 %
	C ₃ A = 8,1 %	C ₄ AF = 8,1 %
Composition acc. to Taylor (modified Bogue-calculation)	C ₃ S = 60,1 %	C ₂ S = 12,7 %
	C ₃ A = 5,8 %	C ₄ AF = 8,3 %
Particle size	mean = 14 µm	
	median = 10 µm	

The superplasticiser was a standard product. The agent of it can be described as multicarboxylatether which acts via sterical rejection. It can be applied together with or after adding water to the mixture. For our purposes, the superplasticiser was added together with water at a dosage of uniformly 1,5 % of the cement weight.

For an advanced analysis of the experimental data, the particle size distribution of each measurement was divided into eight particle size groups, which are < 0,1 µm, 0,1 – 0,4; 0,4 – 1 µm, 1 – 5 µm, 5 – 10 µm, 10 – 20 µm, 20 – 40 µm and 40 – 70 µm. By simplifying the particle size distribution, the analysis could be arranged more concisely. Water/cement-ratios of 0,30; 0,40 and 0,50 with and without superplasticiser were analysed.

The diagrams in fig. 3 show the influence of the superplasticiser on the particle growth characteristics. The graphs are based on a normalized presentation of data, i.e. the differential volume of each particle size group of the mixture containing superplasticiser was divided by the differential volume of the particle size group of the corresponding mixture without superplasticiser. As a result, the ratio is dimensionless. A ratio of 1 means no change in volume. If the ratio is above or below 1, an increase or decrease of volume amount in the specific particle size group can be stated.

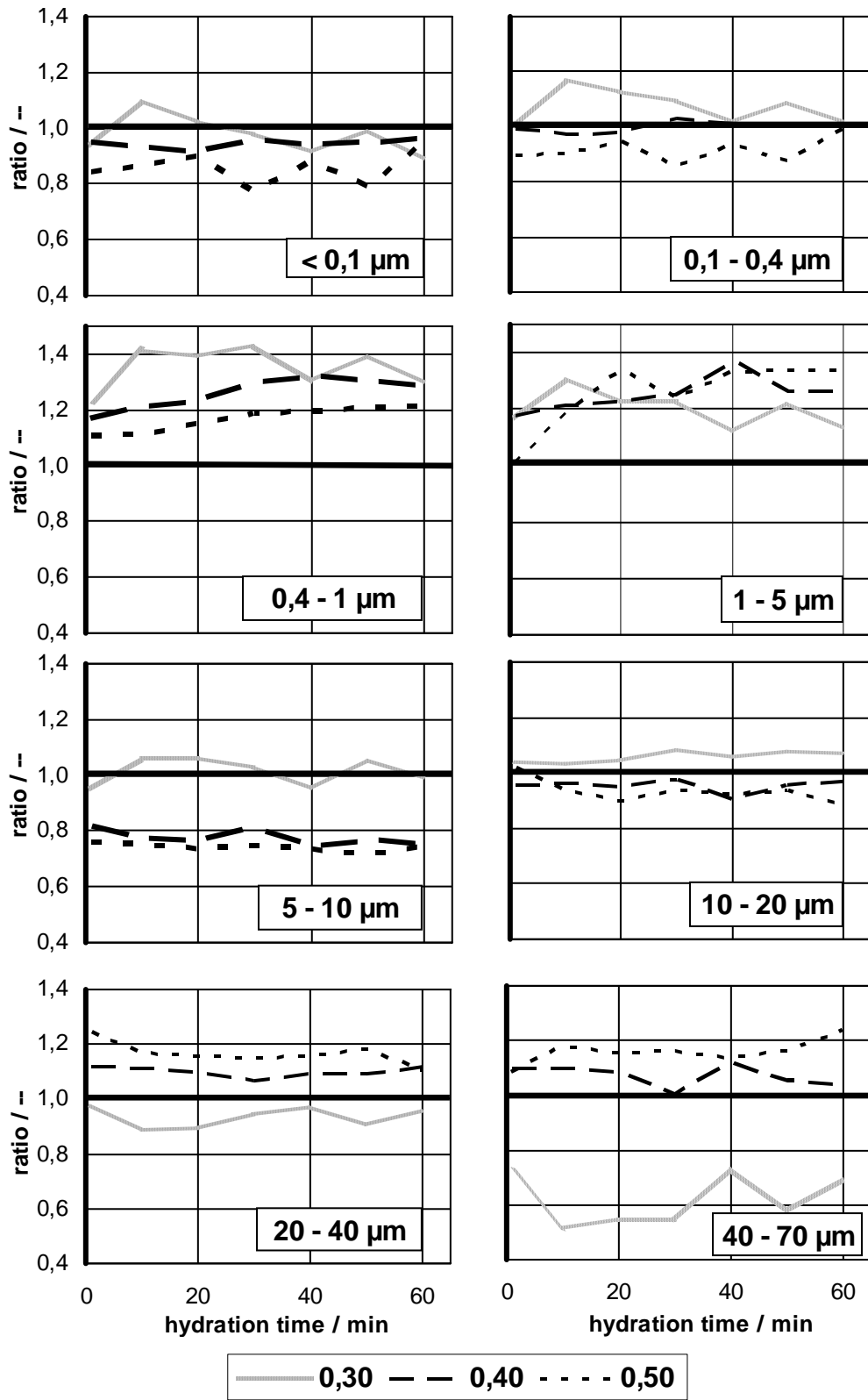


fig. 3: Influence of superplasticiser (pce) at different w/c on relative amount of particle size groups

As can be seen in fig 3, the use of superplasticisers affects the particle growth. Thus, it can be stated, that the use of superplasticiser leads to:

- The amount of the finest particles $< 0,1 \mu\text{m}$ is decreased, mostly not more than 20 %.
- The amount of particle size group $0,1 - 0,4 \mu\text{m}$ is increased (w/c = 0,30), neutral (0,40) or decreased (0,50). The change in amount does not exceed 20 %.
- The amount of particle size groups $0,4 - 1$ and $1 - 5 \mu\text{m}$ is increased. Within group $0,4 - 1 \mu\text{m}$ the graph order reflects the different w/c clearly.
- Depending on the w/c-ratio, the amount of particles of the size groups $5 - 10 \mu\text{m}$ and $10 - 20 \mu\text{m}$ is decreased. The strongest decrease (up to approx. 30 %) happens in the $5 - 10 \mu\text{m}$ fraction.
- Also depending on the w/c-ratio, the amount of particles between 20 and $70 \mu\text{m}$ of size is changed.

The effect of different w/c-ratios on mixtures including superplasticiser (pce) demonstrates as follows.

- The stated change in the amount of the particle size groups is as higher, as higher the w/c-ratio is ($1 - 40 \mu\text{m}$).
- An under-stoichiometric water content, which differs from the theoretically required one, can lead to indifferent or even contrary trends compared to higher w/c-ratios.

6. Conclusions

During the early hydration stage of Portland cement characteristic changes in the particle size distribution occur. These changes can be analysed via in-situ measurements based on a laser granulometer and a special developed technique.

Portland cement shows a characteristic, reproducible behaviour in its changes in particle size distribution. The manner of the changes differs depending on the initial properties of the unhydrated cement.

Besides the cement properties, the w/c-ratio and potential additives impact on the hydration behaviour measurable by the laser granulometer technique.

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