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Superabsorbent polymers: On their interaction with water and pore fluid

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ABSTRACT

Superabsorbent polymers are hydrogels capable of absorbing considerable amounts of water without dissolving, and may have wide application in building materials. They were initially used in the concrete industry with high performance cement-based materials to limit the drop in internal relative humidity during the hydration process of cement. This assures the optimum development of the material properties and avoids both self-desiccation and autogenous shrinkage. The mechanisms involved in the kinetics between the hydrogel and water or pore fluid within the cement-based system are not fully understood. This paper addresses the absorption kinetics of superabsorbent polymers in water and synthetic pore solution. The physical state of particles selected from a superabsorbent polymer sample with a particle size distribution between 50 and 500 micrometers is examined by means of optical microscopy and subsequent image analysis. This method has proven to be an accurate technique for quantifying the absorption of water or fluid into the cross-linked structure of superabsorbent polymers. As a result, the size of the polymers particles has a significant effect on the absorption kinetics of these polyacrylate-based polymers. A model based on the well-known Fick's second law has been found to accurately express the physical or volumetric change within the fluid medium, after a spontaneous fluid uptake, which occurs upon submersion. An extension to this model is proposed to calculate the kinetics of absorption for a given particle size distribution.

1. Introduction

Superabsorbent polymers (SAP) are hydrogels capable of absorbing considerable amounts of water without dissolving, and may have wide application in cement-based materials. The physical or chemical characterization of superabsorbent polymers referred to in the literature is usually focused on other industrial applications rather than cement-based materials, e.g. the personal care market, which involves the main commercial interest within the development of superabsorbent polymers. The introduction of this unique material in construction materials technology may have been initially proposed by Hansen and Jensen [1], referring to the matter of water-entrained cement-based materials, which is documented in patented work. More recently, RILEM has established a special Technical Committee, the RILEM TC 225-SAP "Application of superabsorbent polymers in concrete construction" [2], whose main concern is to study and to potentially widen the use of superabsorbent polymers in building materials.

This work deals with the absorption kinetics between superabsorbent polymers and both water and cement paste pore fluid. This is particularly important, since the absorption capacity parameter is a key aspect in the superabsorbent polymer technology within most of their practical applications. In the case of cement-based materials, key issues such as the effective water to cement ratio within a water-entrained system and the porosity left by SAP particles may allow one to gain a deeper perspective, as the fresh and hardened properties of such materials highly depend on the particular kinetics of this component with the pore fluid. For example, the physical properties of superabsorbent polymers alone may significantly alter the resultant pore structure of the composite and thus affect the hardened properties of high performance concrete. Another characteristic that may be of primary interest is the time elapsed from the original state of the polymer to reach a volumetric equilibrium when submerged in a fluid medium such as fresh cement paste. If the casting of concrete into the formwork is performed before this volumetric equilibrium of the superabsorbent particles is reached, the subsequent absorption may influence the amount of free water in the system and thus induce a rheology change. Therefore, undesirable fresh behavior may be obtained. Furthermore, the knowledge developed within the following sections may be of interest in the application of superabsorbent polymers in the shotcrete market.

The definition of absorption capacity is based on the time that a certain amount of polymer takes to achieve constant weight or a stable volumetric condition. The methods usually applied for determining absorption capacity include gravimetric and volumetric measurements [3,4]. In addition, rheology experiments have

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been used with the same objective [5]. The gravimetric techniques, while giving a fast response, have a drawback on the accuracy of the measured absorption capacity. For example, the "tea-bag" technique is not capable of taking into consideration the interstitial liquid phase bonded by physical forces within the particles, even when supplemented with centrifugation. Thus, this technique will include water that is not adsorbed inside the cross-linked structure of the polymer in the measurement of absorption, viz. water adsorbed in the intermediate space between the particles. Brandt et al. [6]. proposed a colorimetric procedure by means of spectrophotometer to isolate a macromolecular dye in the swelling liquid. By measuring the concentration of dye in a known amount of solution, the researchers were able to exclude the interparticle liquid from the experimental result. However, this technique assumes that the dye is totally excluded from the swelling gel and that the chemistry of the swelling liquid is not modified by the introduction of extraneous elements. A more comprehensive description of the methods that can be applied to determine polymer absorption capacity and swelling time is given elsewhere [7]. The purpose of this paper is to explain a new technique to investigate polyelectrolyte polyacrylate-base polymers and fluid interaction with time using an optical microscope. This technique has the advantage of taking into consideration only the liquid phase that can penetrate the cross-linked structure of the polymer, leading to higher accuracy in the calculation of both maximum absorption capacity and the swelling time of unique size particles, which constitutes one of the fundamental parameters in the theoretical background [8]. Using this technique, the path between the theoretical and the experimental frameworks may be shortened.

2. Materials and methods

Spherical polyelectrolyte polyacrylamide superabsorbent polymer particles, with sizes of up to 500 μm, were used in the experiments. The particles were selected from the same batch, which is a suspension polymerized covalently cross-linked acrylamide/acrylic acid copolymer. Demineralised water and synthetic pore fluid were used as the liquid phase. The synthetic pore fluid is a reproduction of the liquid phase brought out from the dissolution of cement compounds in water, as determined by ion chromatographic analysis [9,10]. In the present work, the following composition is used [mmol L^{-1}]: $[Na^+] = 200$, $[K^+] = 500$, $[Ca^{2+}] = 1$, $[SO_4^{2-}] = 15$, $[OH^-] = 672$.

A stereo optical microscope NIKON SMZ-2T, equipped with a DN camera and lens C-0.38×, was used to monitor the absorption process. Polymer particles were submerged in a micro bath and digital images of 1280 × 960 pixels with 96 dpi were captured at discrete times. Magnifications of 40× and 50× were shown to be compatible with the purposes of the study. Because the scale in examination may change with time due to the particle movement in the fluid medium, either the magnification or position required to monitor the growth of the particles may change during the experiments. Therefore, a scale is attached to the micro bath, enabling the calibration of any magnified depth and movement of the system to different locations in real time. The monitoring procedure consisted of taking one frame within each minute up to the 10th minute after water or pore fluid contact. Hereafter, the image capturing frequency occurred at a rate of one frame every 10 min up to 60 min. Image analysis was carried out with a freeware software package IMAGE J [11], to determine the geometrical properties of SAP particles at each instant of time. This process essentially involves calculating the area change of the polymer particles, by calibrating the unit of pixels to the real scale of the image. Following this procedure, a simple numerical transformation was performed to derive the volume change. The tests were performed at room temperature, about 22 °C. This temperature was affected locally due to the heat generated by the illumination of the microscope. However, the light intensity was kept constant during the tests.

3. Particle size distribution and diffraction analysis

The particle size distribution of the superabsorbent polymers was analyzed in a dry state and at room temperature (see Fig. 1). Quantitative image analysis performed on digital images showed that the average size of the polymer particles was about 90 μm. The sample is composed of 180 randomly selected particles from a batch with a particle size ranging between 0 and 300 μm. More than 60% of the total number of particles were between 50 μm and 150 μm. Ideally, the sample size should consist of at least 500 particles. However, the chosen magnification enables the sizing of particles with a resolution of 10 μm. A lower magnification would allow having more particles in one sample,

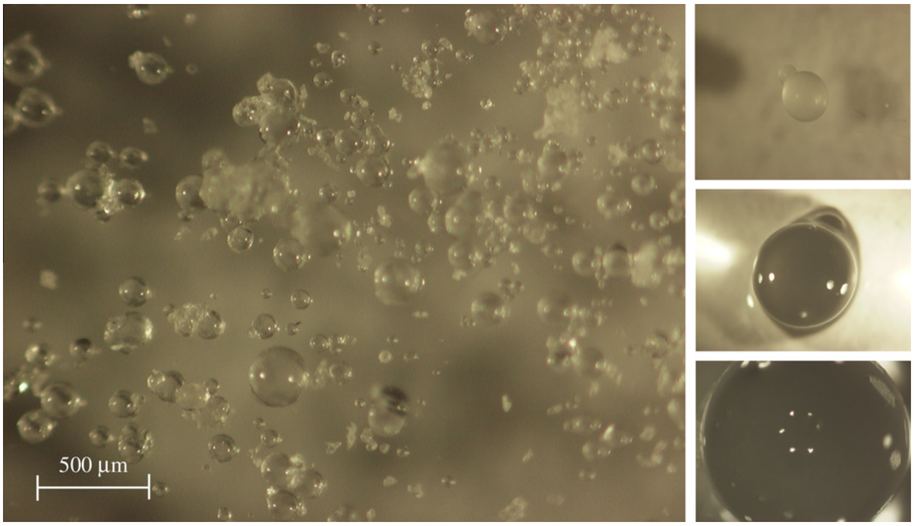

Fig. 1. Superabsorbent polymers at time zero, before water contact. The observed particle size is in the range of 0 to 300 μm. The morphology in both dry and swollen states is characterized by spherical particles. The physical change from dry to swollen state (presented in the images at the right-column) is characterized by a rapid solid to gel transition.

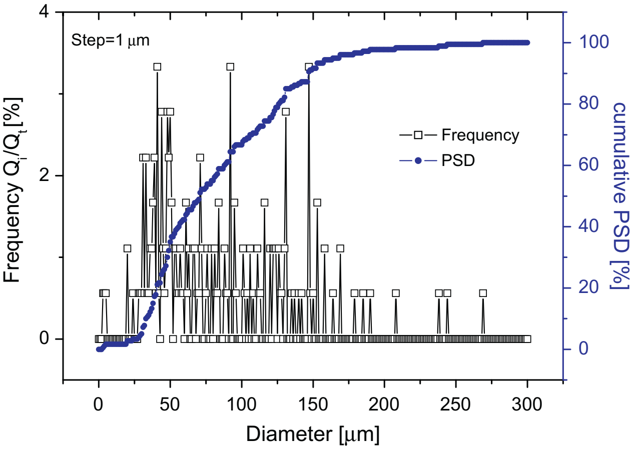

Fig. 2. Frequency chart showing the size distribution of particles of superabsorbent polymers with step size of 1 μm.

but differentiation of particles in the range of 0–100 μm would be extremely difficult.

The frequency distribution of each diameter in the sample is shown in Fig. 2. Different frequency plots may be drawn, by assuming an average size in each range of increasing steps of 1, 10, 20 and 50 μm, whereby the effect of choosing one step on the frequency plot can be seen. The cumulative particle size distribution seems to be independent of the step size. Thus, a probability density function based on Gaussian or Rosin–Rammler equations, which are commonly used to express the distribution of granular matter, may apply to the present case.

An expression may be drawn to describe a specific physical attribute with respect to the dispersion of particles in the system:

$$f(\xi) = \frac{1}{s_c} \cdot \int_0^\infty Q(\xi) \cdot \xi \cdot d\xi \tag{1}$$

where ξ represents a physical attribute that depends on the diameter of the particle, $Q(\xi)$ is the quantity of particles of equal cluster, viz. diameter, and s_c is the step size. On the other hand, in order to find a mathematical agreement in compliance with a specific physical attribute of the polymer particles, e.g., a physical dimension such as diameter, area or volume in each cluster, it is necessary to properly define the measurement accuracy. The error of evaluating a sum of diameters according to Eq. (1) in a given collection of particles would increase by 30% when choosing the step size of 50 μm as opposed to a step size of 1 μm. Using the previous value to measure the water absorption from each size would produce an error of an order of magnitude in relation to their real absorption. Therefore, in order to establish a continuous function that describes a physical dimension within the particle size distribution of the polymer, a step size of 1 μm seems more reliable and is preferred in relation to the previous approaches. This expression forms the basis for the study of the absorption kinetics of a group of particles. In the following section of this paper, this expression will be combined to monitor the superabsorbent polymer expansion in time.

4. Absorption capacity versus swelling time

Absorption capacity refers to the maximum volume that a given universe of polymer particles can achieve when submerged in a fluid medium. In the case of cement-based materials, this corresponds to the uptake of pore fluid from the dry state, which may be considered metastable at 20 °C and at a reduced vapor pressure. The time between the initial volume in a dry state and the final volume at the swollen state constitutes the swelling time. It is fundamental to know the influence of each particle size on the absorption and desorption kinetics, as it may play a central role in the water movement during the early stages in the hydration of water-entrained cement-based materials. Fig. 3 shows one instant of time within the discrete analysis on the growth of polymer particles while submerged in pore fluid, as taken by optical microscopy.

It is clear that it is possible to identify different growing diameters with this technique. Therefore, different particles were

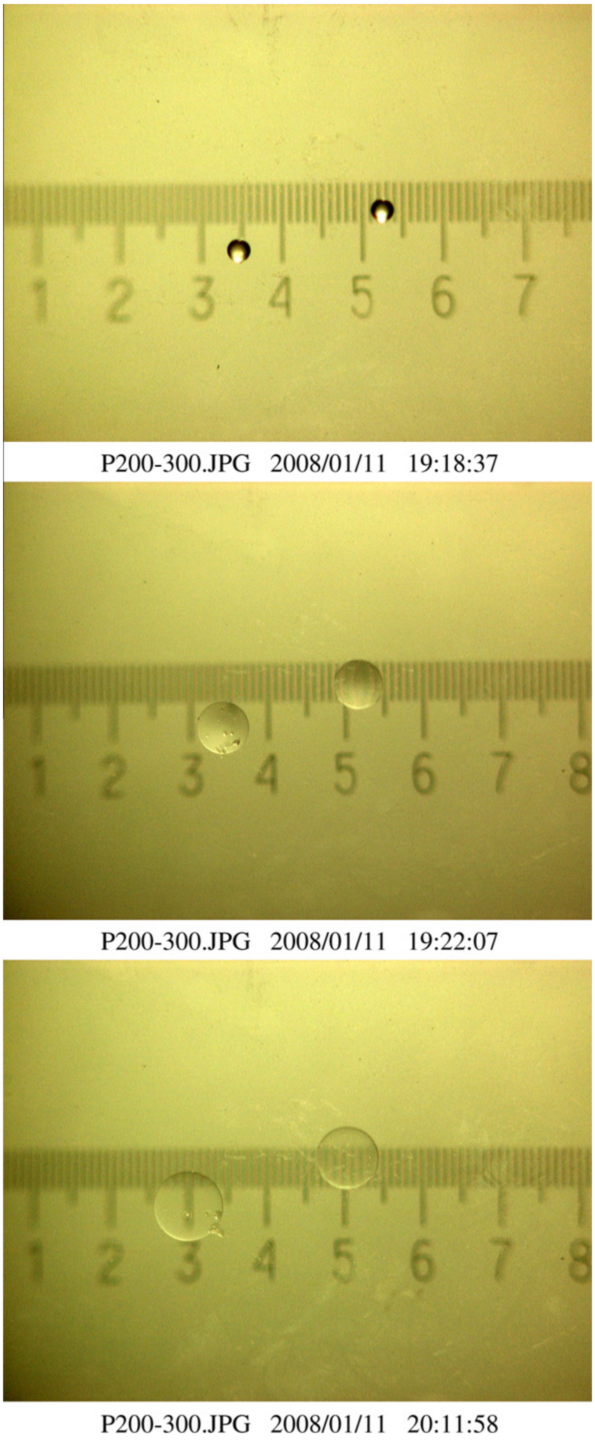

Fig. 3. Image acquisition of polymer particles with expanding size during absorption in synthetic pore solution. Numbers refer to mm.

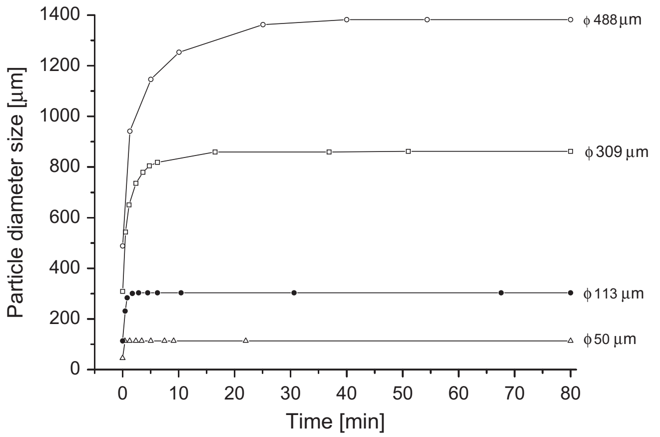

Fig. 4. Growth of individual polymer particles expressed by their diameter change as a function of time. The interaction medium is synthetic pore fluid.

selected to follow their volume change in time. From the image analysis, it was possible to follow the diameter change of different particle sizes, as presented in Fig. 4.

Within the size range in the study (particles lower than 300 µm), the volumetric equilibrium is achieved in about 10 min after immersion in synthetic pore fluid. However, for particles with larger diameters, longer times are necessary, for example 15 min for a 309 µm particle and 25 min for a 488 µm particle. In either case, it is convenient to transform the previous data into a normalized volume, to facilitate the study of the absorption kinetics in the different particle-based systems. The volume change may be expressed according to Eq. (2).

$$\Delta V(t) = \frac{V(t) - V(t_0)}{V(t_0)} \qquad (2)$$

where $\Delta V(t)$ expresses the change in volume during time t [unit-vol. unit-vol.$^{-1}$], $V(t)$ is the volume at the time t and $V(t_0)$ represents the volume at the time zero, corresponding to the volume of the particle at the dry state.

The absorption rate may be obtained as the quotient between the change in volume by the ultimate volume change that a particle can take with respect to the original volume, i.e. $\Delta V(t_\infty) = \lim_{t\to\infty} \Delta V(t)$. By rearranging the data sets to reflect the previous arguments, the results displayed in Figs. 5 and 6 are obtained.

These figures demonstrate that the particle size of the polymer particles greatly influences the absorption rate of the fluid phase. The lower the particle size, the faster is the absorption process. The particle D_{50} (superabsorbent particle with diameter of 50 µm) achieves volumetric equilibrium in less than 1 min. For particles greater than 125 µm, the full absorption process takes more than 5 min and may even be extended up to more than 20 min, in the case of particles greater than 300 µm.

Absorption capacity is shown in Fig. 6 in mL of cement paste pore fluid per gram of dry polymer, by assuming that the density of the polymer is 1.4 g/cm^3. It can be observed that the particle size of the polymer particles influences the maximum amount of liquid phase absorbed. The absorption capacity varies from about 10–16 mL per gram of dry polymer, for particle sizes between 50 and 500 µm. In previous research work, without isolating the particle size effect on the absorption capacity of this superabsorbent polymer, a value of 12.5 mL/g was registered [12], in good agreement with the present experimental results.

Thus, it is concluded that the absorption capacity is also diameter-dependent: the bigger the particle is the more pore fluid is absorbed into the cross-linked structure by its original mass. This may suggest that the cross-linked structure is changing depending on the size of the particles. According to Jensen and Hansen [12], the small particles absorb less because the surface zone is less active than the bulk of the SAP, and small particles will have a proportionally larger surface zone and a small nucleus. Thus, the particle size effect may also be manifested in the density of the polymer. In the present case, the density was taken as a constant value. Nevertheless, the previous observations would not change by considering the last statement. Thus, if the results were shown

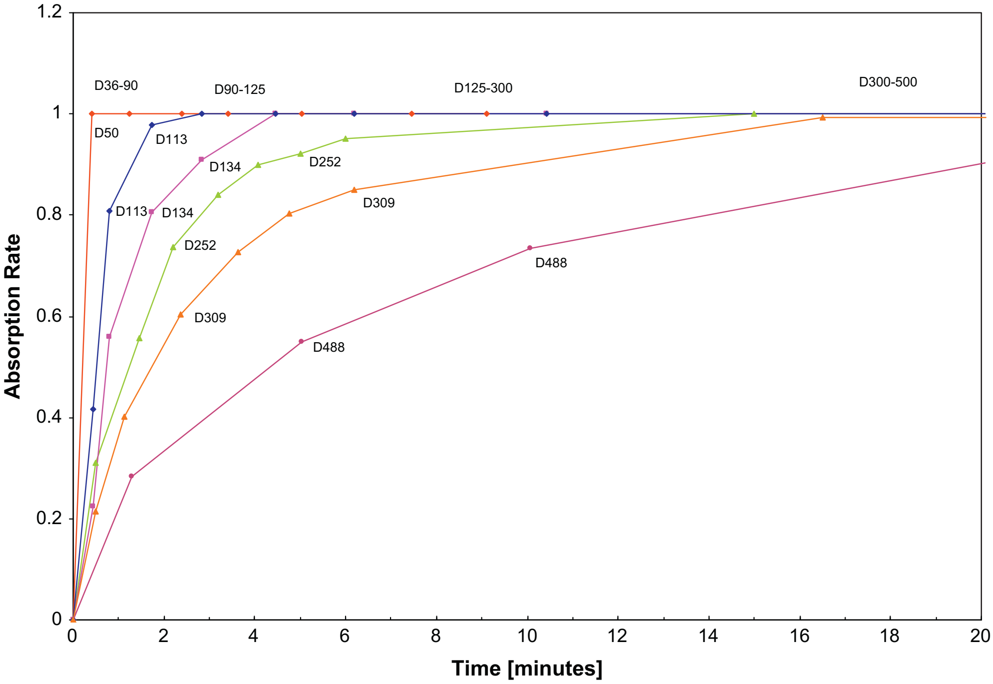

Fig. 5. Absorption rates of individual polymer particles with different particle size, viz., different diameter (D_i), the index i referring to the size of the particle in (µm). The interaction medium is synthetic pore fluid.

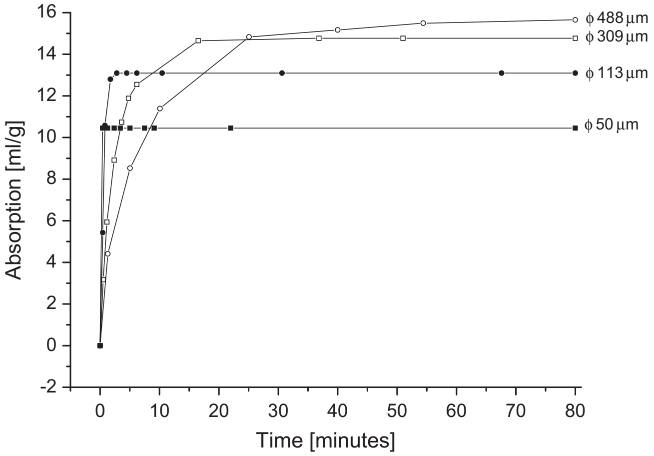

Fig. 6. Absorption capacity of individual polymer particles with different particle sizes, expressed as mL of pore fluid per gram of dry polymer with the same chemical composition. The interaction medium is synthetic pore fluid.

as function of the diameter change, rather than being shown in grams of liquid per gram of dry polymer, the observations and conclusions taken from the experimental data would still be valid. In addition, the chemical composition of the particles is assumed to be constant. Therefore, the overall absorption capacity will mainly depend on the concentration of the different particle clusters. This issue is described in more detail in the following sections.

5. Mechanism of absorption: assumptions and modelling

The mechanisms of fluid absorption by superabsorbent polymers referred to in the literature [7] are usually focused on only a few parameters; the density of the cross-linked structure, the liquid phase in relation to the presence of salts in the solution, and hydrostatic pressure constitute the usual variables in the problem. Although all of these factors have their own influence on the diffusion, osmotic pressure may be of primary interest in the study of the absorption rate [13,14]. On the other hand, it is important to express the measured data so that it is possible to predict the absorption rate of a specific collection of particles. In the following, a model to predict the pore fluid absorption, typically found in cement-based materials, is proposed. The following assumptions are made: the swelling process is controlled by a diffusion process, after an initial spontaneous up-take of the liquid phase. The hydrostatic pressure is considered constant and the fundamental physical parameter affecting the absorption rate is the particle size of the polymer particle, thus, a physical dimension related with the cross-link structure of the different particles.

The swelling kinetics governed by diffusion may be studied by applying the first-order expression based on Fick's second law of diffusion, as given by Eq. (3).

$$\frac{dQ}{dt} = k(Q_{\max} - Q) \tag{3}$$

where $Q_{\max}$ and Q are the swelling capacities at equilibrium and at any time t, and k is the swelling constant rate, which depends on the particle size. Integrating between 0 and the maximum value $Q_{\max}$, yields:

$$Q(t) = Q_{\max}(1 - e^{-kt}) \tag{4}$$

The parameter k, expressing the swelling rate constant is diameter-dependent and is governed by the diffusion coefficient. An empirical relation may be derived from the data sets of individual particles with varying diameter:

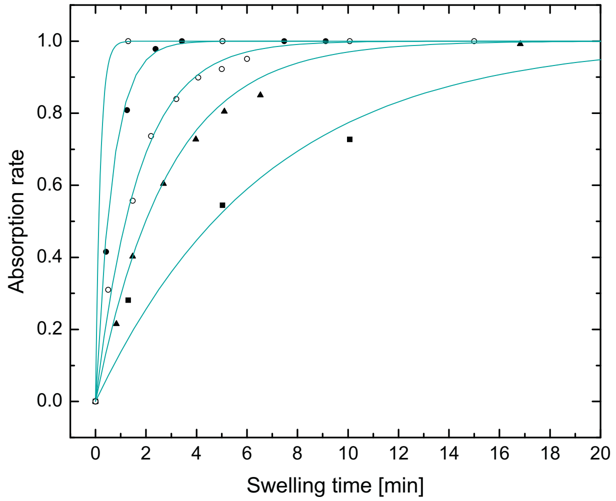

Fig. 7. Modelled absorption kinetics of hydrogels by Fick's law. Dots represent the measured data and lines illustrate the model curves arising from the direct application of Eq. (4).

$$k = 2.76 \times 10^3 \cdot \varphi^{-1567} \tag{5}$$

In Eq. (5), φ represents the diameter of the particle (µm). This expression may be applied within the geometrical interval of particles between 0 and 500 µm. For higher diameters, this expression may be expanded by assuming that the absorption rate should tend to a k-asymptotic value between 0 and 0.15. It is expected that this value may be considered constant within one order of magnitude.

Fig. 7 shows the simulation of Eq. (4) on the measured data sets. The expression accurately describes the observations of pore fluid absorption, by varying the parameter k. The approximation is more efficient for the upper range of diameters studied. There is a slight deviation when approximating the same expression for the lower range of diameters immediately at submersion. It should be noted that this experimental set up presents a limitation in the measurement during the first seconds of the absorption process due to imprecision at the time of calibration and the instant when the particles enter in contact with the fluid. Nevertheless, Fick's law may be used to model the evolution of pore fluid absorption in water-entrained cement-based materials by superabsorbent polymers.

A note should be made about the absorption medium. The expression derived for the swelling rate constant k is valid for synthetic pore fluid. The chemical properties of the fluid medium may govern the osmotic pressure, which is the driving force for the fluid uptake. In addition, there will obviously be some physical constraints that may counteract the growth of SAP in an actual cement paste that are not present in the pore solutions. The SAP particle must push away cement grains and aggregates in order to grow, which may result in reduced absorption. It would be useful to compare the absorption data obtained in this paper to results on actual cement pastes. A useful discussion about this subject will be found elsewhere [14].

6. Mathematical derivation of superabsorbent volume in time

The purpose of this section is to establish a mathematical expression capable of predicting the volume generated by the hydrogel expansion with time as a function of the dispersion of the particle size of superabsorbent polymers. The initial state may be expressed by the sum of volumes calculated from the initial particle size distribution, which relates a given collection of particles with their geometrical properties, e.g., the volume or diameter. This is valid for a general set of particles with known sizes. Then, it seems feasible to relate each particle with a growth function, which is able to augment the volume for each instant of time t. Hence, a series algorithm may be used to compute continuous cycles of Eq. (4), in order to calculate the sum of volumes at a given dimension of time. Therefore, such an expression should be both time-dependent and diameter-dependent. By combining the Fickian law with the pseudo volume distribution function arising from the PSD of the polymer, the expression may be written in the general form as:

$$F(t) = \int_0^t g(\varphi,\tau)\cdot f(\varphi)\cdot d\tau \tag{6}$$

The function f(φ) defines the sum of volumes for a given particle size distribution, and thus, is dependent on the occurrence of each diameter of a collection, as given by Eq. (1). The function g(φ,τ) translates the evolution of each volume as the pore fluid is absorbed as defined by Eq. (3). Since $Q_{\max}$ is also diameter-dependent, a relation between the size of each particle and the maximum volume of fluid uptake needs to be found. According to the experimental data, it is possible to correlate the maximum growth with the particle diameter using a power law relationship. Hence:

$$Q_{\max} = 13.462\cdot\varphi^{3.146} \tag{7}$$

At a given instant, the now designated porosity model function, referring to the SAP forming pores in the cement paste, can be set up to determine the total volume that grows in the system as the sum of volumes of each particle diameter. In the following, an example of the computations is provided.

Let the collection of particles in the following study be defined by a system of two diameters of 50 μm and 100 μm, occurring in equal number. The total volume of this collection at the initial state is about 0.71 cm^3. The resulting particle count leads to about 1.21×10^6 particles in the system. It is interesting to note that the presence of particles of type D_{50} (superabsorbent particle with diameter of 50 μm) does not significantly affect the system physics when the volume generated by 50% of particles D_{50} is compared to the other case where it is fully constituted by particles of type D_{100}. Fig. 8 shows the results of the simulation performed on the absorption kinetics of this system during the first 20 min. The effect of the polymer concentration on the overall volume uptake can be seen with respect to the same systems composed by unique particle clusters. The presence of 50% of particles with cluster D_{50} does not significantly affect the absorption kinetics of the system in comparison to a 100% D_{100} system. If the concentration of D_{50} particles increases, the curve $D_{50}+D_{100}$ approaches the curve representing the 100% cluster D_{50}. This finding is particularly important in the study of the porosity left behind by superabsorbent polymers in cement-based materials, since the size of smaller

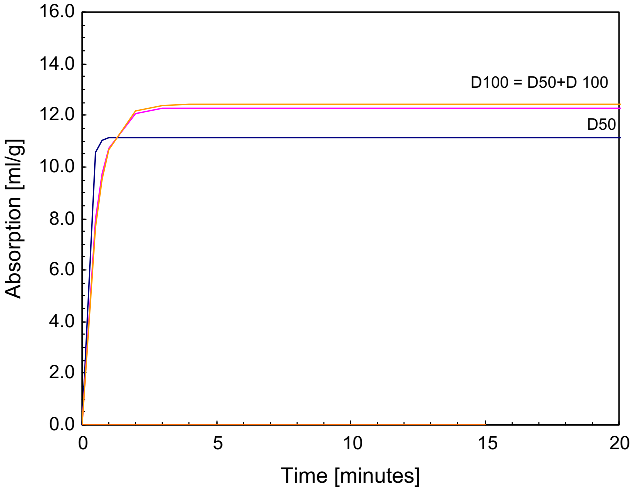

Fig. 8. Simulation of the absorption kinetics for mono and dual-sized systems. Monosized systems are fully composed of particles with a diameter of either 50 or 100 μm. The profile D50 + D100 (dual-sized system) is composed of 50% each of D_{100} and D_{50} particles.

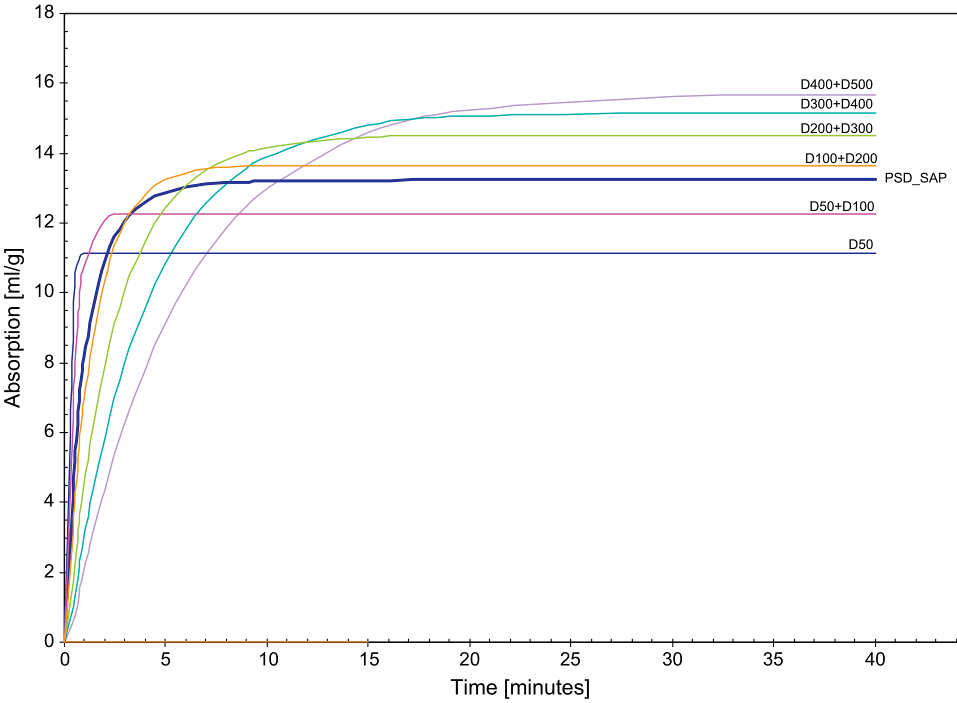

Fig. 9. Simulation of absorption kinetics for SAP systems with varying PSD, including the global PSD of the SAP, as determined in Section 1. The PSD profiles include unique particle clusters with equal frequency (distributed in the ratio of 1/1).

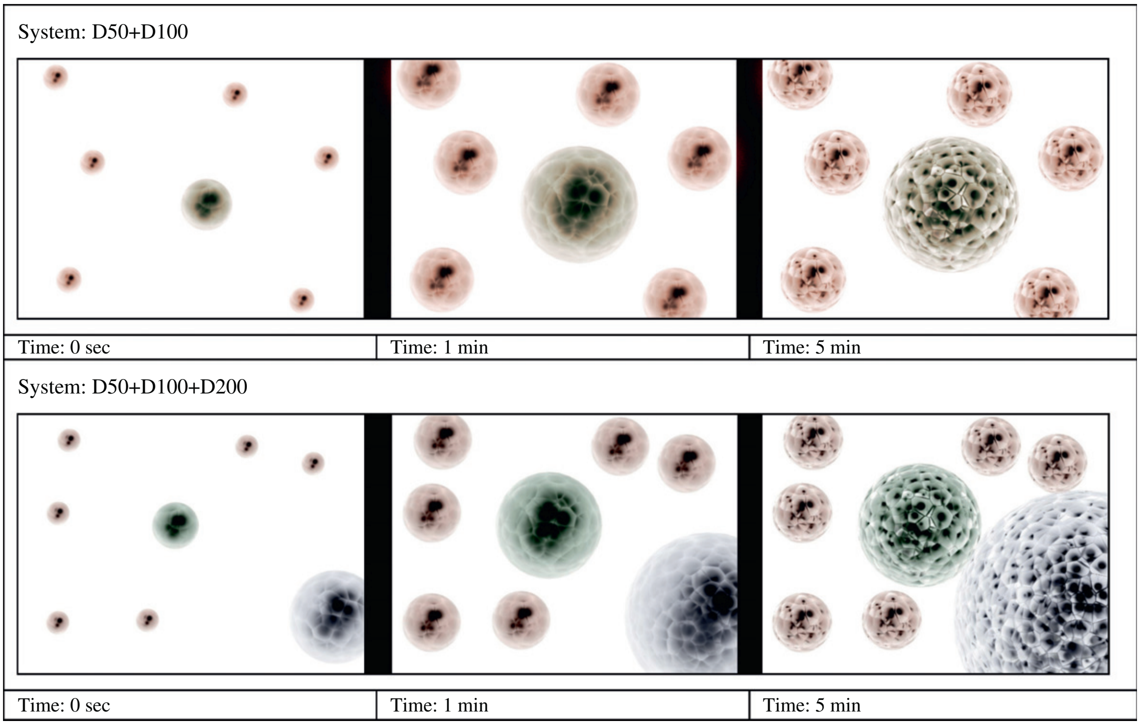

Fig. 10. Simulation on the absorption kinetics performed on different systems, shown in augmented reality.

particles may be of less significance if a low concentration of higher diameter particles exists in the system.

In either case, it is now possible to predict the superabsorbent expansion for specific particle size distributions, which may be useful in a number of applications. For example, if is assumed that the swelling occurs without any hindrance by the mineral grains of the matrix, the proposed model may be used to predict the initial porosity left by the superabsorbent polymers in cement-based materials at early-age. In Fig. 9, various PSD profiles, including the PSD presented in the first section, are plotted against time. In addition, Fig. 10 depicts a simulation of the absorption kinetics of two systems performed in augmented reality. This essentially consists of randomly placing spheres in space to represent the real spacing of particles in a formal volume, and running the growth functions in a geometrical scale basis. This simulation enables the representation of individual particles and the tracking of the volume change within a reduced time scale. As a consequence, a porosity algorithm could be established to derive the initial microstructure that describes the SAP-porosity of a water-entrained cement-based system.

7. Final remarks

The method proposed for the determination of superabsorbent polymer absorption may be used to quantify the absorption of specific liquid phases by the cross-linked network of hydrogels. The measurement accuracy has been improved in relation to previous techniques used to describe the absorption kinetics of superabsorbent polymers. Because gravimetric techniques may erroneously take into account the water that is physically adsorbed at the inter-particle interstitial spaces, these methods may lead to higher inaccuracies. In addition, the lower the particle size of the polymer particles, the more that the surface zone will be exposed to Van der Waals forces, inducing a higher uncertainty in the quantity of absorbate that was actually absorbed by the polymer particles.

Fick's law of diffusion may be applied to describe the kinetics of SAP absorption. A note should be made about the expressions derived for pore fluid. In the experiments, synthetic pore fluid was used to follow the volume change. The chemical formula of the real pore fluid is highly dependent on the cement-based system and especially on the dissolution of substances in the first few minutes after water addition. The amount of water added to the system will determine the concentration of the different ions for a given cement type.

From the findings, it is clear that the particle size influences the rate of absorption and the maximum absorption capacity, which were shown to have a non-linear relationship with the particle diameter. The absorption capacity is higher for increasing particle diameters.

The knowledge that was developed in this work may provide some insight with respect to the applications of superabsorbent polymers in cement-based materials. For example, the use of small particles should favor the rheology change of the cement paste fraction through fast absorption kinetics. This can be used in applications such as shotcrete, among others. On the other hand, for applications where a freeze–thaw resistance is required, bigger SAP particles should be used in order to produce larger (polymer vacated) air voids, which can be precisely foreseen.

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