Micronized Sands as Cement Replacement

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ABSTRACT

The focus of this study is on how the presence of the micronized sand in cement paste changes the porosity and influences water permeability of cement paste. Porosity and permeability are generally considered as decisive factors with regard to the durability of concrete. Non-evaporable water test is carried out to calculate the degree of hydration of cement. By means of mercury intrusion porosimetry measurements of the pore structure of different specimens of hardened cement paste with or without micronized sands has been studied. Parameters including the amount and fineness of micronized sand and the curing time were considered. The results show that the presence of micronized sand in the material will increase the degree of hydration of cement and also influence on the porosity and water permeability.

INTRODUCTION

Concrete is one of the most widely used building materials in the construction of the nation's infrastructure [Mehta 1986]. The production of cement consumes much energy and produces a huge amount of undesirable products, which affect the environment in a negative way. From the Netherlands Environmental Assessment Agency, in the second half of 2008, half of the annual increase in global emission of carbon dioxide (CO_2) is from fossil fuel use and from cement production. Cement clinker production contributes about 4% of global total CO_2 emission from fuel use and industrial activities. The demands of the modern building industry require development of new types of binder material with reduced CO_2 emission. In order to reduce energy consumption and CO_2 emission and to increase the performance, attempts are made to mix or intergrind cement with mineral additions, such as limestone filler, fly ash and quartz sands. In cementitious material a substantial fraction of the cement particles remains unhydrated, acting as rather expensive fillers. A question is whether it is possible to reduce the use of cement by adding other fillers [Bentz 2005, Bonavetti 2003, Darweesh 2004, Justnes 2005]. In this study, micronized sand is used, which is made by selected quartz sand and is purified both mechanically and chemically after extraction. This material is considered as inert filler, which can not react with water or hydration products. This substitution can not only reduce the cost but also cut down the emission of CO_2. If that is workable and the performance of this material is without significant loss, this material can be used in cement industry to produce environment friendly products.

Among the material properties, long term properties are in the centre of interest of most researchers. The durability of concrete is essentially influenced by processes that involve the interconnectivity, into or through the material, of ions or molecules in the form of liquids and

gases. The service life will depend on the rate at which these species may move into the concrete. The passage of these potentially aggressive agencies is primarily influenced by the permeability of the concrete [Richardson 2002]. The permeability for potentially aggressive media of a cementitious material is greatly influenced by the pore structure of the material. As the pore structure might be different when replacing cement with micronized sands in comparison with traditional concrete, some changes in durability behavior might occur. Therefore, in this paper the first item that should be addressed is how the presence of the micronized sand in cement paste changes the microstructure and influences long term properties. Non-evaporable water test is applied to calculate the degree of hydration of cement. By means of mercury intrusion porosimetry (MIP) measurements, the pore structure of several mixtures of hardened cement paste, with and without micronized sands, have been studied. At the same time, the results of water permeability tests are also presented here. How the presence of micronized sand influences the water permeability is analyzed as well.

EXPERIMENTAL

Material.

Portland cement CEM I, 42.5N (OPC) and micronized sand produced by a Belgian company were used. Three types of micronized sands were used in this research, named M6, M300 and M600. The physical and chemical properties are stated in table 1. They are products which have a very high purity (>99% of SiO_2 content) from the mineral processing industry. The difference among these three types of sands is the fineness. For instance, M600 has extremely high fineness and around 90% of the sand particles are under 9 μm. Only M6 has lower fineness than OPC. The mixture proportions are given in table 2. No superplasticizer or other additives were used.

Table 1. Material Information of Different Micronized Sands.

Type	Density (g/cm^3)	Fineness* (cm^2/g)	Mean Size (μm)	SiO_2 (%)
M6	2.65	2400	30	99.5
M300	2.65	4000	17	99.5
M600	2.65	13000	4	99.2

*Fineness of OPC is 2870 cm^2/g.

Table 2. Mixture Proportion.

	Subset	OPC (%)	Micronized sand (%)	Sand/Powder* s/p	Water/Powder* w/p
Ref	---	100	0	0	0.4
Cement with Micronized sand	a	90	10	0.1	0.4
	b	80	20	0.2	0.4
	c	70	30	0.3	0.4

*Powder: OPC+Filler

Method.

In this study, the degree of hydration of cement in paste sample was obtained by determining the non-evaporable water content, W_n/c. W_n/c is defined as the mass loss per gram of original cement, measured between the temperatures of 105 ^{o}C and 1000 ^{o}C [Copeland, 1953]. After achieving the required age, samples for the non-evaporable water content (W_n/c) determination were ground to powder using a mortar and pestle. To determine W_n/c content, 3 crucibles with around 1.1g hydrated sample were dried in an oven at 105 ^{o}C for at least 12 hours, and were then ignited at 1000 ^{o}C in a furnace for 3 hours. The mass of the crucibles and samples were measured before and after placing them in the furnace, respectively. The degree of hydration was then determined as the ratio of the measured non-evaporable water content per gram of cement to the amount at full hydration. The W_n/c content of hydrated pastes on the ignited sample was calculated by Eq (1)

$$\frac{W_n}{c}(\%) = 100 \times \frac{\text{dried weight of paset-ignited weight of paste}}{\text{ignited weight of paste}} \tag{1}$$

To convert the measured non-evaporable water content into degree of hydration, the content of non-evaporable water for complete hydration $(W_n/c)_{complete}$ is used [L. Molina, 1992]. Based on the compositions of the plain Portland cement, the values of 0.26 g H_2O/g cement was determined for cement. The degree of hydration of cement (α) in paste sample is calculated by Eq (2):

$$\alpha(t) = [\frac{W_n(t)}{c}]/[(\frac{W_n}{c})_{complete}] \tag{2}$$

The data of the degree of hydration will also be used to calibrate the HYMOSTRUC simulation.

The typical method used to measure total porosity and pore size distribution is mercury intrusion porosimetry (MIP). Figure 1 shows the total and effective porosity can be induced by the MIP measurements. Scanning electron microscopy (SEM) has also been used extensively to observe the microstructure of cement-based material. In conjunction with a backscattering detector, the phase composition of the cement paste is represented in the images by gray level variation. Pores appear very dark and unhydrated cement particles appear very bright, which allow them to be distinguished and quantified by image analysis of the 2-D sections [Scrivener 1989]. The cement paste used for MIP and SEM measurements was mixed with tap water. After 1 minute of mixing at low speed and 2 minutes of mixing at high speed, the pastes were poured into plastic bottles. Curing periods of 1, 7 and 28 days were considered. At the end of each curing period, the plastic bottle was broken, and the sample was removed from the bottle and split into small pieces of about 1 cm^3. The hydration process was stopped by immersing the sample into liquid nitrogen for three minutes. After stopping hydration the samples were exposed to freeze-drying. The whole drying procedure was the same as suggested by Gallé [Gallé 2001]. The detailed information can be obtained in [Ye 2003] as well.
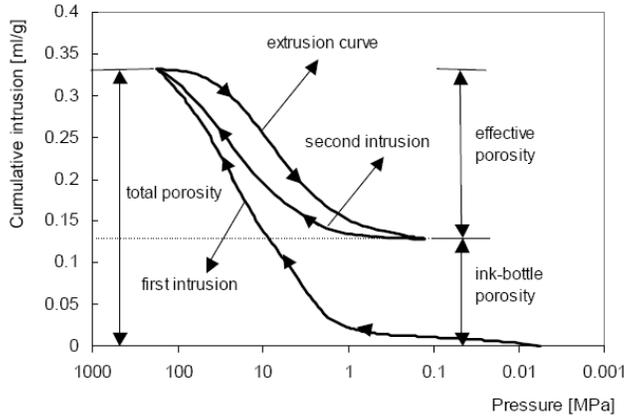
Fig. 1. Mercury Intrusion and Extrusion Hysteresis [Ye 2003]

In this research, the water permeability is calculated according to Darcy's law [Powers 1955]. The water permeability coefficient k_w (m/s) can be determined by [Neville 1995, Muskat 1937]:

$$k_w = \frac{LQ}{A_{sec}\Delta h}$$ (3)

where k_w = water permeability coefficient (m/s); L = thickness of the sample (m); Q = the volume of fluid passed in unit time (m^3/s); A_{sec} = cross-sectional area of the sample (m^2); Δh = drop in hydraulic head through the sample (m).
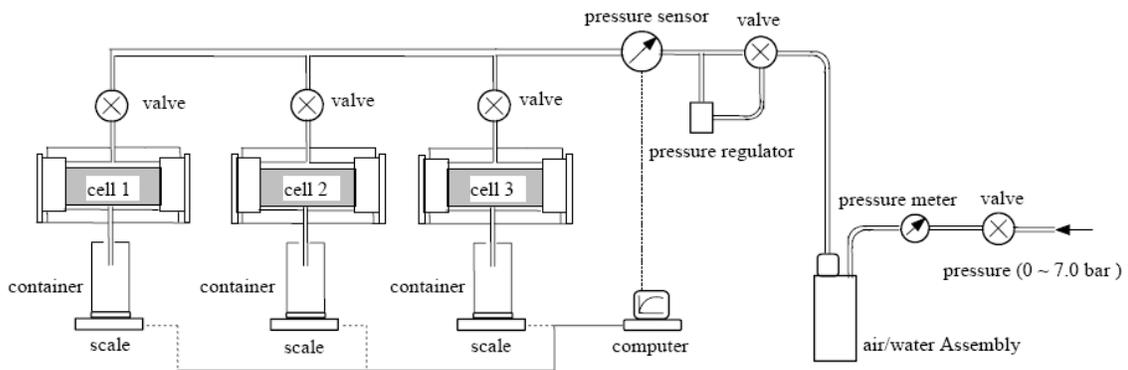

Fig. 2. Permeability Test System [Ye 2003].

The permeability apparatus is shown schematically in figure 2 [Ye 2003]. The system includes a regulated gas pressure source, a gas/water reservoir, three parallel permeability cells, a computer controlling system and appropriate valves and tubes. The mixing and curing process are the same as mentioned in the MIP and SEM tests, except the size of samples. The specimens tested are cement paste disks with a diameter of 95 mm. The thickness varies from 20mm to 40mm. The chosen pressure, 7 bars, is applied at the top of the specimens, which enables the outflow of the water to be fast enough to pass the samples without other factors influencing the results, like ongoing hydration [Ye 2003].

RESULTS AND DISCUSSIONS

Degree of hydration of paste samples
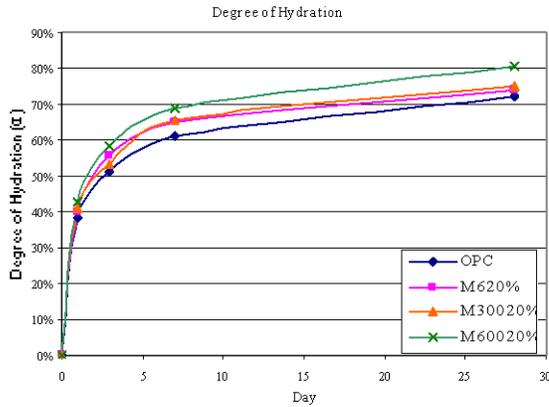
Fig. 3. Degree of Hydration of 20% Replacement Mixtures Compared with OPC Paste.
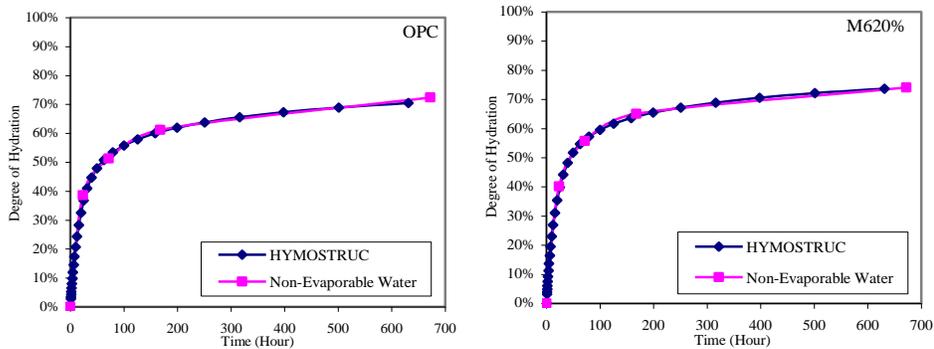
Fig. 4. Calibration of Hydration Curves: 100% Cement (left) and M620% (right).

The results of the degree of hydration (α) determined by W_n/c content are shown in figure 3. In this test, 20% cement material is replaced by different types of micronized sands. The α of cement paste with micronized sand is higher than that of the corresponding Portland cement at all ages. After 28 days, the α of the cement replaced by M6 and M600 is 75.2% and 80.4%, respectively, compared with 72.4% in reference sample. The higher α in modified pastes can be attributed to the 'enhanced' hydration due to the relatively higher effective w/c ratio because when part of cement is replaced by micronized sands, the concentration of cement in the system is diluted, and the effective w/c ratio controlling the rate of cement hydration is relatively increased. In addition, the α is increased with the fineness of the filler increases. The finer the sands used, the higher the degree of hydration is. The improved hydration containing the finest micronized sands may be a possible result of the particles acting more easily as nucleation sites.

In figure 4, the data from non-evaporable water test was used to calibrate the HYMOSTRUC [van Breugel, 1991] simulation. The basic HYMOSTRUC model was developed for simulation of the reaction process and of the formation of the microstructure in hydrating Portland cement. In this model the degree of hydration is simulated as a function of the particle size distribution and of the chemical composition (C_3S and C_2S content) of the cement, the water/cement ratio and the reaction temperature [van Breugel, 1991]. The hydration measured with the non-evaporable water test can be well fitted with HYMOSTRUC computation. That can give useful information and result of microstructure to be applied in future simulation work.
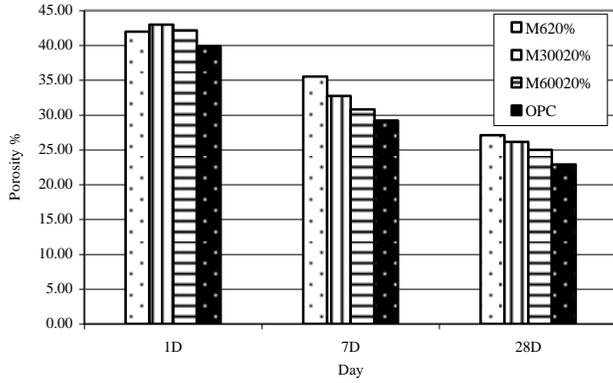
Porosity and pore size distribution

Hardened cement paste is a porous material in which the formation of the pore structure largely depends on the hydration process and the w/c ratio. A classification of pore in cement paste is presented in table 3. The gel pores are an intrinsic part of the C-S-H and they are very small. Capillary pores form because the hydration products do not fill all the available space. These capillary pores are larger than the gel pores. The capillary pores increase in amount and size with an increase in the initial w/c and decrease in amount and size as the hydration reaction proceeds [Ye 2003].

Table 3. Classification of Pores in Hydrated Cement Paste, Modified from Mindess and Young [Ye 2003].

| Designation	Diameter	Description	Affected
Capillary pores	50 nm to 0.5 μm	Large capillary	Strength, permeability
	10 to 50 nm	Medium capillary	Strength, permeability, shrinkage at high humidity
Gel pores	2.5 to 10 nm	Small capillary	Shrinkage to 50% RH
	0.5 to 2.5 nm	Micropores	Shrinkage, creep
	<0.5 nm	Micropores (interlayer)	Shrinkage, creep

The total porosity of samples at 1, 7 and 28 days is presented in figure 5. Obviously, with the increase of the hydration time, the total porosity decreases for all samples. Generally, micronized sand filler has significant influence on the pore structure. The total porosity of OPC is lower than the one in the paste samples with micronized sands. The difference of porosity after 28 days between cement pastes with and without micronized sand is reduced in the function of time. The results also show that the finer the sand used, the lower the porosity; this is in agreement with the development of the degree of hydration in figure 3. The higher degree of hydration results in lower porosity in cement paste with micronized sand. The higher value of α for cement particles does not imply an improvement of the volume of hydration products, because the potential cement material decreases when the particles of cement are replaced by micronized sands causing the effect commonly called dilution [Bonavetti, 2002]. There might be less hydration product to fill in the space in the mixed material. Therefore, the porosity of cement paste replaced by M600 is 25% compared with 23% in OPC, whereas the α of OPC is 11% lower.

Fig. 5. Total Porosity of Different Mixtures under the Same Replacement Percentage (20%).
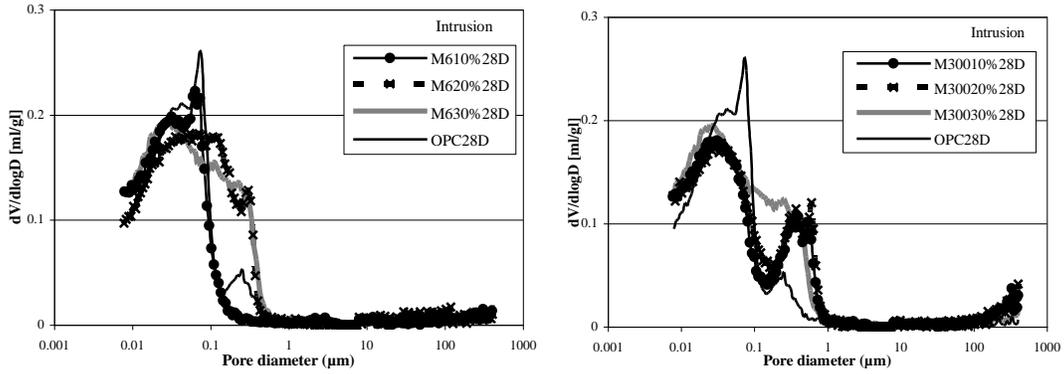
Fig. 6. Differential Pore Size Distribution under the Different Replacement Proportion after 28 Days.
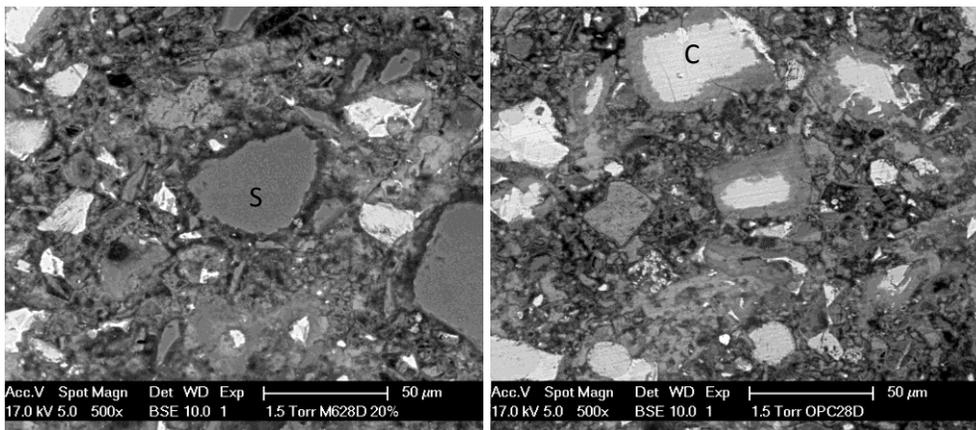
Fig. 7. BSE Images of CM6b (left) and OPC (right) after 28 Days.

The differential pore size distribution of cement paste with M6 and M300 series are presented and compared with OPC in figure 6. On the left graph, the critical pore diameters represented by the peak of curve in cement paste with and without 10% M6 are almost the same, which is around 0.07 μm. However there is no clear peak in cement paste replaced by 20% M6 at 28 days. The plain paste sample showed higher differential pore volume for the finer pore diameters (<0.1 μm) accompanied with a distinctive reduction in differential pore volume for the coarse pore diameters (0.1 μm-0.5 μm). On the right graph, it can be noticed that the effect of fineness of micronized sand has an important impact on the pore structure. Adding M300 in the cement paste leads to different pore size distribution over a range from 0.1 μm-0.5 μm in comparison with left figure. According to the classification of pore size in hydrated cement paste, as explained in Table 3, large capillary pores (50 nm to 0.5 μm) can have significant influence on permeability property.

SEM observation

A clear picture about the microstructure of cement paste including the distribution of phases and the shape of pores can be obtained with the help of SEM observation. In figure 7, the BSE image of the sample, of which 20% cement is replaced by M6, is shown and compared with reference sample at 28 days (S and C are denoted as sand and unhydrated cement.). On the right side, a certain amount of cement grains remains unhydrated after 28 days, acting as an expensive filler material. On the left side, the fraction of unhydrated cement grains is relatively lower. The size of tagged M6 sand particle is similar to the tagged cement particle on the right. It is obvious that the morphology around these two particles is quite different. Around the sand particle there is less unhydrated cement grains left but a clear interfacial zone between sand particle and hydration products. The porosity in this area is higher in comparison with the bulk paste. Unlike sand particle, the inner hydration products are precipitated around the cement particle. Micronized sand, to some extent, plays a role as very fine aggregate. This higher porosity at the sand interface and the low amount of unhydrated cement grains in this area have been attributed to the "wall effect" and micro-bleeding under big sand particles. If the sand particles are smaller, they are relatively easy to embed in the hydration products or represented as nucleation sites.

Water permeability test

The water permeability tests are carried out in order to estimate how the permeability property changes when the Portland cement is partially replaced by micronized sand. The test took around one week to get results and the steady-flow can be reached after 5 days. When the resulting curve is linear over the last 10 or more readings, the steady-state flow is obtained. By using eq. 3, the water permeability coefficient (k_w) of cement samples with and without micronized sand at 28 days are presented in table 4. The results increase with the increase of replacement percentage. As has been mentioned in the previous section, adding micronized sand could lead to different pore size distribution in the cement paste and could change the permeability property eventually. Moreover, there is a clear interfacial zone between sand particle and hydration products (figure **7** left). When the replacement percentage of micronized sand increases, the interfaces around sand particles have more opportunities to connect with each other to form a continuous pore network. That makes the k_w higher when increasing the replacement percentage.

It should be noticed that the results of k_w of cement paste with and without micronized sands are in the same order of magnitude. The difference between them is not pronounced. From this point of view, micronized sand could be a promising option to replace cement material.

Table 4. Water Permeability Coefficient of Different Samples.

Specimen	k_w(m/s)
OPC28D	1.70E-12
M620%28D	1.84E-12
M630%28D	2.71E-12

CONCLUSIONS

In this study, the degree of hydration, porosity, pore size distribution and water permeability coefficient of cement paste replaced by different types of micronized sand are investigated in comparison with plain paste. The following conclusion can be drawn:

- After 28 days, almost 28% by mass of cement grains remain unhydrated, acting as an expensive filler material. The use of micronized sand could be a promising solution from the energy consumption, emission reduction and economic point of view.
- Adding micronized sand as filler has a significant influence on the pore structure of cement paste. Different pore size distribution over a range from 0.1 μm-0.5 μm, which is classified as large capillary pores, gives influence on water permeability property.
- The morphology in the material with and without micronized sands is quite different. There is a clear interfacial zone between sand particle and hydration products. The porosity in this area is higher in comparison with the bulk paste, which is supposed to be the decisive factor to influence the permeability property.
- When the replacement percentage increases, the interfaces around sand particles have more opportunities to connect with each other and form a continuous pore network. Therefore, the water permeability coefficient increases with the increase of the replacement percentage. The difference between cement paste with and without micronized sands is not great. Micronized sand could be an option to replace cement material.

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