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The Influence Of Solvent Exchange On Porosity Of Cement Pastes Identified By Mercury Intrusion Porosimetry

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***Abstract*—Before the composition and micro structure of any hardened cement pastes can be studied at a defined period of time, the ongoing hydration must be arrested. The removal of water from hardened cement paste for analysis has been reported to affect the composition of hydrated phases and micro structures. Hydrated pastes of CEM I 42.5 R and CEM III/B 32.5 N of water/cement (w/c) ratio 0.3 and 0.45 by weight was analyzed. The effect of curing on pore structure was also studied. The solvent exchange technique using several alcohols and other organic solvents may reduce the amount of change to the pore structure during removal of water but in this technique it is difficult to differentiate between the various type of water that are replaced.**

This paper will describe pore structure examination by the application of several techniques on hydrated cement pastes.

Keywords—solvent exchange, mercury intrusion porosimetry, CEM I 42.5 R, CEM III/B 32.5 N, pore size.

I. INTRODUCTION

Concrete is a heterogeneous material in which aggregates are held in place by a hardened cement paste binder. The properties of this binder are, therefore, critical to the performance of the concrete as a whole. The better understand the properties of the binder, it is necessary to study the paste microstructure and to see how it is affected by different mixing proportions of water/cement ratio and how the microstructure is affected as the reaction of cement with water proceeds over time. The technique used to study the microstructure of hardened, cement pastes in mercury intrusion porosimetry [1-5].

Due to its simplicity and versatility, it has been employed in the determination of the pore-size distribution curves of a wide variety of porous material. This technique is based on the simple phenomenon of the capillarity depression of mercury; however, the main disadvantage in applying this principle is the oversimplification of the complex pore geometry of most materials. Various models and different methods of interpretation have been proposed so that realistic picture of pore structure of samples can be obtained by mercury intrusion porosimetry.

II. METHOD

A. *Mercury intrusion porosimetry*

With mercury intrusion porosimetry (MIP), porous samples are introduced into a chamber, the chamber is evacuated, the samples are surrounded by mercury, and pressure on the mercury is gradually increased. As the pressure increases, mercury is forced into pores on the surface of the sample. If the pore system is continuous, a pressure may be achieved at which mercury can penetrate the smallest pore necks of the system and penetrate the bulk sample volume. If the pore system is not continuous, mercury may penetrate the sample volume by breaking through pore walls. By tracking pressures and intrusion volumes during the experiment, it is possible to get a measure of the connecting pore necks of a continuous system or a break-through pressure is known as the “threshold”, “critical”, or “percolation” pore width. After achieving this highest rate of intrusion, mercury has been shown to penetrate the interior of the sample [3]. Using the technique, one also obtains a measure of the total porosity in the sample as that corresponding to the volume of mercury intruded at the maximum experimental pressure divided by the bulk volume of the unintruded sample.

B. *Limitation*

Because mercury must pass through the narrowest pores connecting the pore network, MIP cannot provide a true pore size distribution [6,7]. The threshold pore width, however, may provide a better indicator of material durability as it has an important influence on the permeability and diffusion characteristics of the cement paste [8]. Total porosity values by mercury porosimetry also differ from those obtained by other techniques. Mercury porosimetry will indicate smaller than actual porosity values where pores are too small or too isolated to be intruded by mercury. On the other hand, MIP porosities may be closer to actual values than those indicated by other techniques where mercury pressures can collapse small pores or break through to isolated pores [9,13].

C. *Materials*

Cement pastes were made from CEM I 42.5 R and CEM III/B 32.5 N and saturated water.

D. *Sample preparation, curing period and drying*

Cement pastes of 0.3 and 0.45 were prepared by mixing cement with water at the mixer for 90 seconds at the first speed level and after that with a stained steel spatula mixing by hand for 30 seconds and in the end mixing again for 90 seconds at the second speed level. After the mixing we put the fresh paste into prisms molds, 160x40x40 mm size and put them into the curing room with high relative humidity for 24 hours.
After being cured for 23.7 to 24.0 h, the hardened paste prisms were removed from the molds and stored in saturated water 23.0 ± 1.9°C so that total, nominal, curing periods of 2, 7, 28, 180 and 360 days were achieved, including the 1 day of curing in the room with RH 100%.
At the end of each curing period, we put the samples in solvent exchange for drying for the period of 4 days in acetone, ethanol and isopropanol, and after 3 days in oven [6,17].

III. RESULTS AND DISCUTIONS

Mercury intrusion porosimetry has been used in the investigation of the pore-size distribution of hardened cement pastes. Different aspects of the problem have been investigated on the pastes prepared with various methods using different water-cement ratios, mixing procedures, curing periods. Mercury intrusion porosimetry results have been compared for different drying methods.

Throughout this study, Washburn equation was used in converting the test data pore-size distribution curves. One reason for making this choice, is that Brunauer and associates concluded that cylindrical pore shape idealization gives better results than spherical geometry in evaluating capillary condensation data of hardened cement pastes [18].

The second reason for using Washburn equation is that the results are used for comparative purposes in this study. If the pores in hardened cement pastes are conical with characteristic α angle, the pore-size distributions will shift to larger pore sizes for all pastes; hence, the comparison will not be affected.

In order to investigate the effect of air-entraining on the pore structure of hardened cement pastes of various water-cement ratios and ages, the pastes shown in Table 1 were prepared by German standard DIN.

TABLE 1. THE SYSTEMS USED FOR THIS WORK

Systems	**Materials used**		
	CEM I 42.5 R	***CEM III/B 32.5 N***	***Water***
1	1600 gr		480 ml
2	1600 gr		720 ml
3		1600 gr	480 ml
4		1600 gr	720 ml

The hardened cement pastes are cured for 2 and 180 days. With MIP we are going to investigate the difference between the solvent exchange. In the following figures: Figure 1,2 we show the pore size distribution of the systems 1,2,3,4 dried in acetone and isopropanol, and after that we put for 7 days and in vacuum for 24 h.

As we see from the Figure 1, the cement paste of the system 4 cured for 2 days and after dried in acetone compared with the same system cured for 180 days is more porous. This trend can best be explained by the different curing period rather than the different mixing and molding procedures.

The pore size distribution of the hardened cement pastes listed in Table 1 are shown in *Fig. 1*. And Fig. 2.

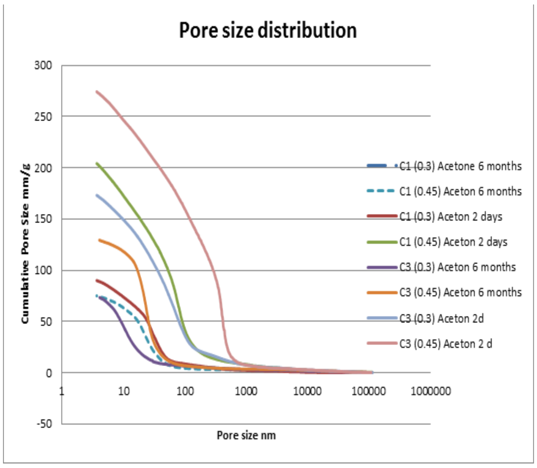

Fig.1. MIP 2 & 180 days for CEM I 42.5 R & CEM III/B 32.5 N dried in acetone

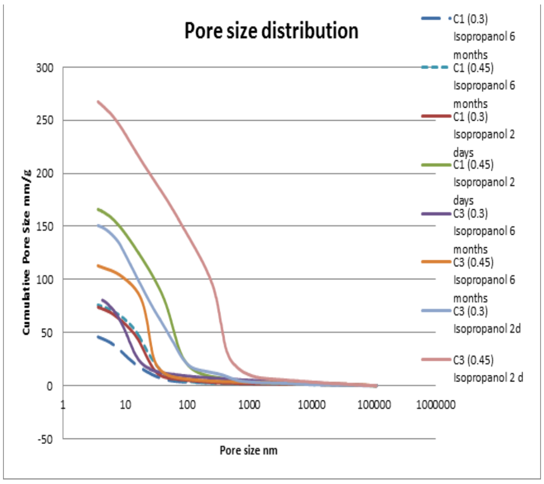

Fig.2. MIP 2 & 180 days for CEM I 42.5 R & CEM III/B 32.5 N dried in isopropanol.

We see the same trend at the Figure 2, comparing system 4 cured for 2 and 180 days dried in isopropanol.

It is seen that the uniform pore-size distribution of the pastes have similar characteristics as the first intrusion curves; i.e., with increasing age and decreasing water-cement ratio the total uniform pore volume decreases and a general reduction in uniform pore size takes place.

The second intrusion threshold diameter is equal to or smaller than the first intrusion threshold diameter. The major fraction of the difference between the total and uniform pore volumes is within a short range of diameters slightly smaller than the threshold diameter which that a large volume ink-bottle pores have entrances in this range.

The diameter of the ink-bottle pores may be much larger than the entrances; hence, it would be incorrect to state that an air-free hardened cement paste does not contain pores of sizes greater than the threshold diameter. The implication of this conclusion may be better visualized by a reference to the hypothetical specimens discussed earlier. The incremental difference between the first and second intrusion curves decreases as smaller pores are intruded which means that there is a greater volume of ink-bottle pores communicating with the outside through the pores slightly smaller than the threshold diameter.

The mercury in the spherical air voids could be ejected only after hitting the sample on the bench. This phenomenon is an experimental evidence of the theoretical statement that suction must be applied in order to withdraw mercury from a spherical pore.

IV. CONCLUSIONS

The purpose of this study was to improve mercury intrusion porosimetry testing and interpretation methods in order to gain more information about the pore structure of materials. The review of MIP theory showed that pore size and intrusion pressure can be related to each other by establishing the energy balance involved or solving the pressure differential across mercury meniscus.

Investigation of the pore structure of air entrained cement pastes utilized the improved mercury intrusion porosimetry interpretations. The analyses led to the following conclusions:

- Similar to the first intrusion, the second intrusion pore size distribution of hardened cement pastes shows a decrease in total pore volume and a reduction in uniform pore size with increasing age and decreasing w/c ratio.
- Approximately two-thirds of the total intrusion volume of an air free paste is due to uniform pores and the remaining ink bottle pores.
- Using isopropanol as drying solvent exchange because it does not react with cement, least damage to pore structure, gives finest pore size distribution.
- Sample preparation techniques affects the pore size distribution of hardened cement pastes. In order to obtain consistent and comfortable results in different studies, the mixing, curing must be standardized.

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