PORE STRUCTURE CHARACTERISATION OF SODIUM HYDROXIDE ACTIVATED SLAG PASTE

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Introduction

The alkali-activated slag (AAS) material addresses the energy and environmental concerns associated with Portland cement production without compromise on the properties and performance[1]. Pore structure, as an essential component of AAS material, its volume (the total porosity), shape, size and tortuosity determine water and ionic transport. And thus, they govern the durability of AAS materials. Mercury intrusion porosimetry (MIP) has been widely used to study the pore structure in cement-based materials. However, the standard MIP test method cannot reveal the real pore structure because MIP test results show underestimation of large pores and overestimation of small pores due to ink-bottle pore effect. In order to overcome the ink-bottle pore effect, a recently developed pressurisation-depressurisation cycling mercury intrusion porosimetry (PDC-MIP) testing method was used[2].

In this study, the pore structures of AAS specimens activated with sodium hydroxide in terms of different dosages of Na_2O and cured up to 1 year were tested using PDC-MIP and compared with standard MIP. Through the PDC cycles the throat pore size distribution and ink-bottle pore size distribution were determined. The influence of Na_2O dosage as well as curing age on pore structure were discussed.

Materials and Methods

Materials and mixtures

The chemical composition of the blast furnace slag used in this study is 32.91% SiO_2, 40.96% CaO, 11.85% Al_2O_3, 9.23% MgO, 0.46% Fe_2O_3, 1.61% SO_3, 0.33% K_2O and 1% TiO_2. Three contents of sodium hydroxide were selected with Na_2O/slag=4%, 6% and 8%. A water/slag ratio of 0.4 and sealed curing condition (20°C) were used for all mixtures. According to the content of Na_2O, the samples can be denoted as Na_2O_4%, Na_2O_6% and Na_2O_8% in the following text.

PDC-MIP

The PDC-MIP measurement is conducted following a unique mercury intrusion procedure as described in details by[2]. The applied pressure is increased by repeating pressurisation-depressurisation cycles. Within each pressurisation-depressurisation

cycle, the mercury intrusion volume (V^{in}) and extrusion volume (V^{ex}) are recorded. The mercury extrusion volume can be regarded as the throat pore volume (V^{th}, Equation (1)) and the difference between mercury intrusion and extrusion volumes can be regarded as the ink-bottle pore volume (V^{ink}) in this cycle. Since the pore size distribution of ink-bottle pores is not able to be determined, it is assumed that the size distribution of the ink-bottle pores is equal to that of the pores with the diameter larger than the corresponding throat pores. In this way, the calculated ink-bottle pore in each pressurisation-depressurisation cycle is redistributed to the pores with larger pore size than the throat pore size in the current pressurisation-depressurisation cycle using Equation (2).

$$V_{j,j}=V_j^{th} \quad (1)$$

$$V_{i,j}=V_{i,j-1}\times(1+(V_j^{in}- V_j^{ex})/(V_{1,j-1}+ V_{2,j-1}+\cdots+ V_{j-1,j-1})) \qquad (i<j) \quad (2)$$

Where $V_{i,j}$ is the volume of the pores with the diameter of D_i calculated at j-th pressurisation-depressurisation cycle.

PDC-MIP testing sequence started with a continuous pressurisation from 0.004 MPa to 0.50 MPa. Then fifty-four pressurisation-depressurisation cycles were repeated and pressure was increased to 210 MPa. The advancing contact angle and the surface tension were taken as 138° and 0.485 N/m respectively.

Results and Discussion

Testing results by first intrusion and second intrusion using standard MIP

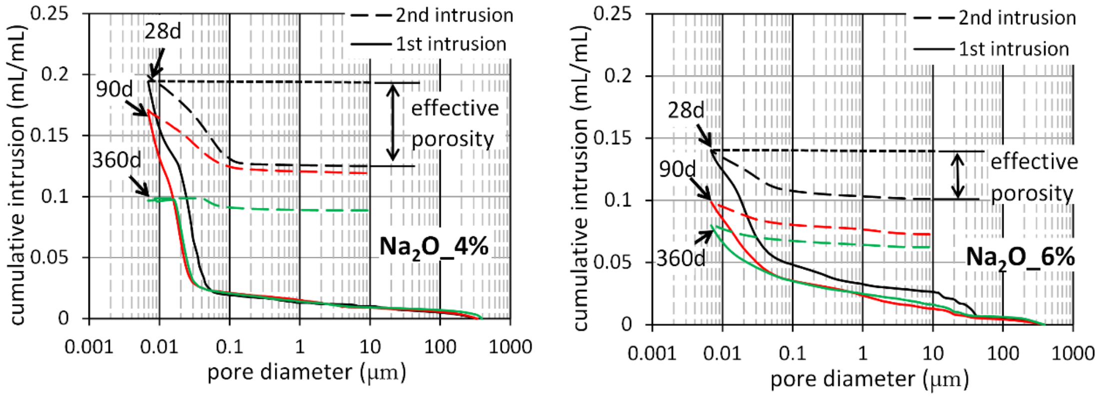

Figure 1: Pore size distribution of samples for Na_2O_4% (left) and Na_2O_6% (right)

As curing time goes from 28 days to 360 days, the pore size is reduced and moves to fine pore size region. The total porosity decreases from 19.4% to 9.7% for Na_2O_4%, from 13.9% to 8.0% for Na_2O_6% and from 14.0% to 6.7% for Na_2O_8%. When the Na_2O dosage increases from 4% to 8%, the total porosity is also reduced regardless of the curing age. This is because the higher Na_2O dosage creates pore solution

environment with higher alkalinity which accelerates the hydration of slag. When curing, age goes from 28 days to 90 days (I) and from 90 days to 360 days (II), the reduction on pore size distribution gets bigger in the first period (I) while smaller in the second period (II) as Na_2O dosage increases from 4% to 8%.

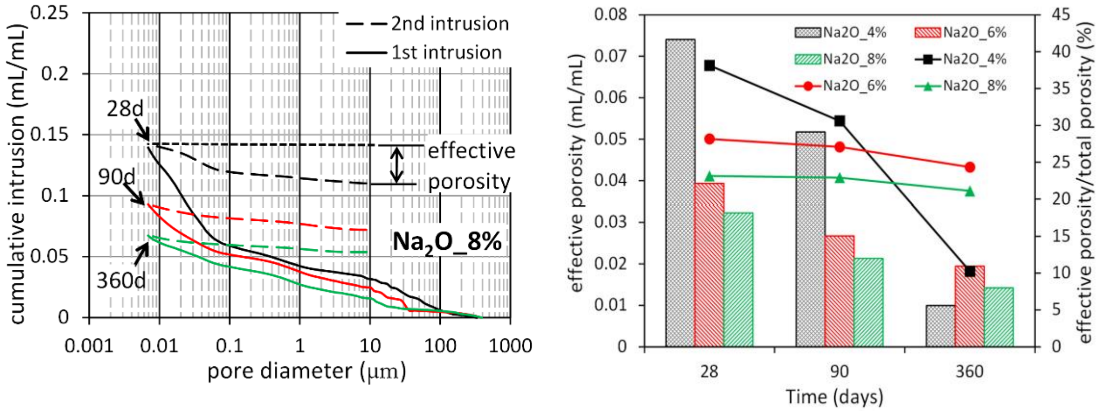

Figure 2: Pore size distribution of samples for Na_2O_8% (left) and effective porosity expressed in different terms (right)

The effective porosity can be obtained from the second intrusion curves as shown in Figures 1 and 2. Figure 2 (right) shows the effective porosity and its proportion (%) in total porosity for Na_2O_4%, Na_2O_6% and Na_2O_8% at different curing ages. The effective porosity decreases from 7.4% to 1.0% for Na_2O_4%, from 3.9% to 1.9% for Na_2O_6% and from 3.2% to 1.4% for Na_2O_8% when curing age increases from 28 days to 360 days. As hydration of slag progresses, the porosity no matter total porosity or effective porosity should decrease with time. These experimental results are consistent with the research expectation. When the effective porosity is expressed against the total porosity, it can be seen that the effective porosity consists less than 50% of total porosity and decreases with time. In other words, the ink-bottle pores consist more than 50% of the total porosity. Therefore, it's of great importance to know the size distribution of ink-bottle pores.

Testing results by PDC-MIP

Taking Na_2O_4% as an example, the testing results by PDC-MIP are presented. The throat pore size distribution as well as the ink-bottle pore size distribution can be obtained as shown in Figure 3 (left). The ink-bottle pore size distribution doubles or even triples the throat pore size distribution. The volumes of ink-bottle pore as well as throat pore at different pore sizes especially at fine pore sizes are greatly reduced as curing time goes from 28 days to 360 days. By adding the ink-bottle pore size distribution and throat pore size distribution together, the total pore size distribution can be obtained as shown in Figure 3 (right). Comparing to the pore size distribution obtained by standard MIP, the pore size distribution obtained by PDC-MIP shifts to the coarse pore sizes, which illustrates the reduction of influence of overestimation of small pores and underestimation of large pores by using PDC-MIP.

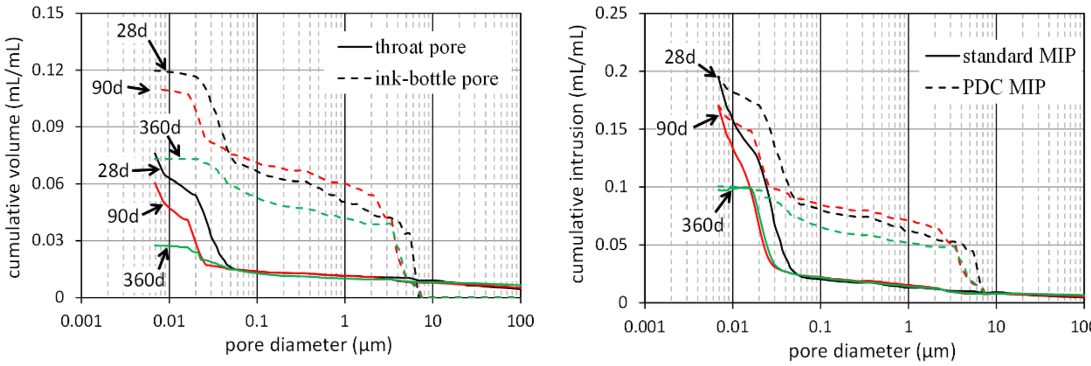

Figure 3: Pore size distribution of samples for Na_2O_4% using PDC-MIP: throat pore and ink-bottle pore size distribution (left) and total pore size distribution (right)

Conclusions

The AAS samples activated with sodium hydroxide were tested using standard MIP and modified PDC-MIP at different curing ages up to one year. The testing results by standard MIP show that the total porosity decreases from 19.4% to 6.7% and the effective porosity decreases from 7.4% to 1.0% as curing age increases from 28 days to 360 days. The effective porosity consists less than 50% of total porosity and decreases with the increasing of curing time. The modified PDC-MIP enables the determination of size distributions of throat pores and ink-bottle pores. The calculated pore size distribution by PDC-MIP shifts to the coarse pore sizes when compared to the pore size distribution measured by standard MIP. After removing the ink-bottle pore effect, the characterisation of pore structure by PDC-MIP will help to improve the interpretation of the properties of AAS materials.

Acknowledgement

Microlab in Delft University of Technology (TUD) is greatly acknowledged and the first author thanks China Scholarship Council (CSC).

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