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Research Article

Characterization of Pore Structure of Different Hardened Cement Pastes#

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Abstract:
The goal of this study is to characterize the hardened cement paste at 1, 7 and 28 days using a combination of Mercury Intrusion Porosimetry (MIP), X-Ray diffraction (XRD), Thermal Analysis (TA). Hardened mortars are porous materials their pore structure being developed during hydration as a function of water binder ratio, the binder's chemical reactions and time. Different binder systems and as a consequence different chemical reactions will influence the pore structure. Systems such as Calcium Silicate Hydrate formation, Calcium Aluminate Hydrate formation are investigated with respect to the developing pore structure. MIP was used as a generally accepted technique for deriving porosity and pore size distribution and results correlated to those received from ESEM image analysis.
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1. Introduction

Hydration reactions are the basic processes behind the development of technological properties in cement based materials. Many of the engineering properties (as strength) are related to porosity. The results of hydration reactions are solid phases and their formation and arrangement results in changes in porosity.

Pore structure is a very important micro structural characteristic in a porous solid, because it influences the physical and mechanical properties, and controls the durability of the material. [1] Cement based materials, such as cement paste, mortar and concrete, are porous materials. The properties of porous materials are strongly affected by the characteristics of their pore system, such as porosity, pore size distribution, connectivity, etc. [2]

Sample were analysed by the following techniques:

- Strength measurement (flexural & compressive strength)
- Mercury Intrusion Porosimetry (MIP)
- X-Ray Diffraction (XRD)
- Thermal Analysis(TG-DSC).

2. Experımental

Materials and Sample preparation

The materials used in this study are Ordinary Portland Cement (*CEM I 42.5 N*), and Calcium Aluminate Cement (*SECAR 51*), Blast furnace slag cement (*CEM III B 32.5 N),* Calcium Sulfoaluminate Cement *(Calumex CSA).*Cement paste samples have been prepared with different water-cement-ratio, specifically: w/c = water demand (cf. Tab.1), w/c =0.4, w/c = 0.5. After mixing, cement pastes were cast into 40*40*160 mm prism molds and placed over water. After 24 hours, the hardened specimens were demoulded and then immersed into water. At the age 1 day, 7 days and 28 days specimens were taken out of water and crushed to a particle size of about ~2 mm for the experiments. The crushed particles were selected deliberately from the middle part of the specimens after strength testing to avoid inhomogeneity of material. The crushed samples were then put in acetone to stop the hydration process; after one hour in acetone the samples were then oven – dried at 50°C for 24 hours. [1]

Table.1 *Water demand (w/d) for the cement used in this study*

Cement	Water demand
CEM I 42.5 R	0.33
Secar 51	0.25
CSA Calumex	0.27
CEM III B 32.5 N	0.34

Characterization techniques

The *strength* of the hardened cement pastes was tested according to the German standard DIN EN 196-1.

Mercury Intrusion Porosimetry (MIP) The characterization of the pore structure of cement paste using MIP is important in understanding the mechanical and transport properties of cement paste. The pore structures obtained by mercury intrusion porosimetry can be characterized by total porosity; pore surface area and average pore diameter are calculated by measuring the amount of mercury intruded into the pore at a given pressure [1]. A PASCAL 240/440 instrument was used to carry out the measurements.

X-Ray Diffraction (XRD) Analyses were performed using a with a X'PERT Pro MPD PW 3040/60 diffractometer (PANalytical Co.) X-Ray diffraction patterns for the powdered samples were analysed with X'Pert High Score software. Quantitative analyses were made with Rietveld method.

Thermal Analysis (TG-DSC) Thermogravimetric analysis or TGA is a technique where the mass (or weight) of a material is measured as a function of temperature or time while the sample is subjected to a controlled temperature program in a controlled atmosphere [2]. Thermal analysis thermo gravimetry (TG) and DSC were conducted using a differential thermogravimetric analyzer Netzsch STA 409 PC/PG. Hydrates were estimated from the weight loss measured in the TG curve between the initial and final temperature of the corresponding DSC/TG peak. The experimental conditions involved an Argon gas dynamic atmosphere of 100 ml min^{-1}, a heating rate of 10°C min^{-1} and a platinum top-opened crucible. Alumina powder (Al_2O_3) was used as the reference material [2, 3].

3. Results

Strength measurement (flexural & compressive strength)

The strengths of four hardened cement pastes at 7days for different water to cement are shown in the Figure 1. The results show that strength decreases with increasing of water to cement ratio.

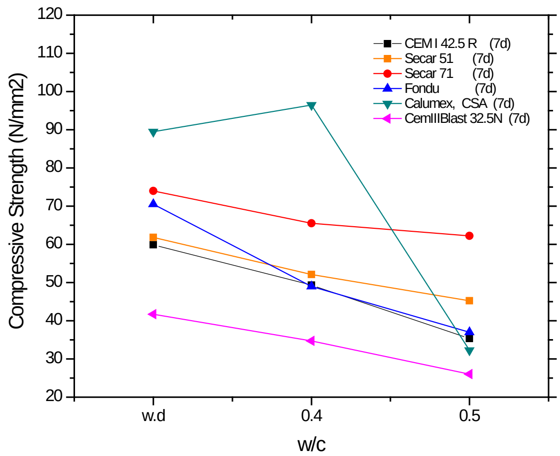

Figure 1 *The strengths of the hardened cement paste (OPC, S51)*

From the strength of each sample in Figure 1 and corresponding pore data in tab.2, it could be seen easily: though the porosity has critical effect on the strength of hardended cement paste, the differences in porosity can not exactly reveal the differences in stength.[3]

Table.2 *The pore structure of the OPC, CAC,BCF,CSA*

Hcp 7d (w/c=0.5)	**Total Cumulative volume (cc/g)**	**Total Specfic surface area (m^2/g)**	**Average Pore radius (nm)**	**Total porosity (%)**
OPC	0.182	27.69	31.71	28.81
CAC	0.131	15.77	25.46	22.36
BFC	0.224	34.43	39.64	35.74
CSA	0.086	12.56	59.13	14.79

Mercury Intrusion Porosimetry (MIP)

Corresponding pore size distributions as measured by mercury intrusion porosimetry (MIP) are depicted as cumulative distributions in figure 2 (specific volume as a function of pore radius). With increasing time of hydration the curves show for all cements a decrease in threshold radii and pore volumes.

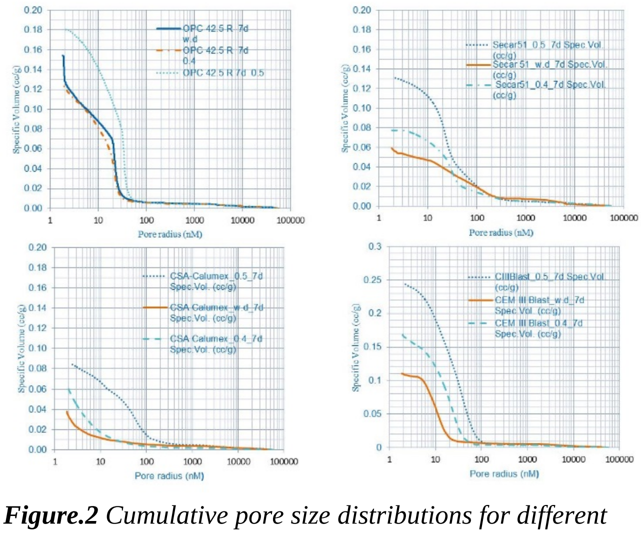

Figure.2 *Cumulative pore size distributions for different cements at 7days (w/c=0.5)*

Thermal Analysis (TG-DSC)

The test results of thermal analyses are represented in Fig.3. In each figure DSC curves are shown at the three water to cement ratios. Hydrates can be estimated from the weight loss measured in the TG curve between the initial and final temperature of the corresponding TG/DSC peak. For each curve two endothermic peaks can be observed up to about 500ºC.

The first peak at around 100-120ºC is present in each sample and can be associated to CSH and/or ettringite.

The second endothermic peak which was observed for OPC at 450ºC can be linked to CH; the one for CAC at 300ºC can be associated to CAH and/or AH_3; for BFS at 420ºC to CH and for CSA the presence of $Al(OH)_3$ at 280ºC is observed [4].

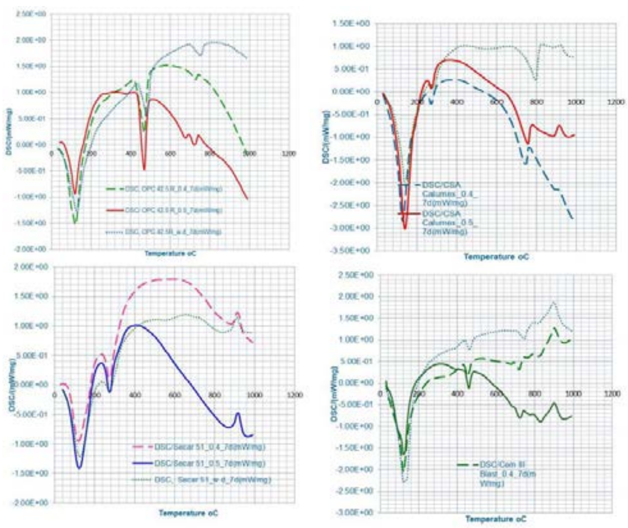

Figure.3 *DSC curves for hardened cement paste for w/d, 0.4, and 0.5 for 7days*

X-Ray Diffraction (XRD)

The hardened cement paste microstructure is examined and XRD patterns are represented respectively in figures 4.

4. Conclusion

From the standpoint of strength, the water/cement ratio porosity relation is undoubtedly the most important factor because it affects the porosity of the cement paste; and we can see from the results that the compressive strength depends on porosity of the materials; we see that the strength decreases with the increasing of water to cement ratio. In addition, the thermal analyses TG-DSC can show the consecutive peaks from each system; is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere.

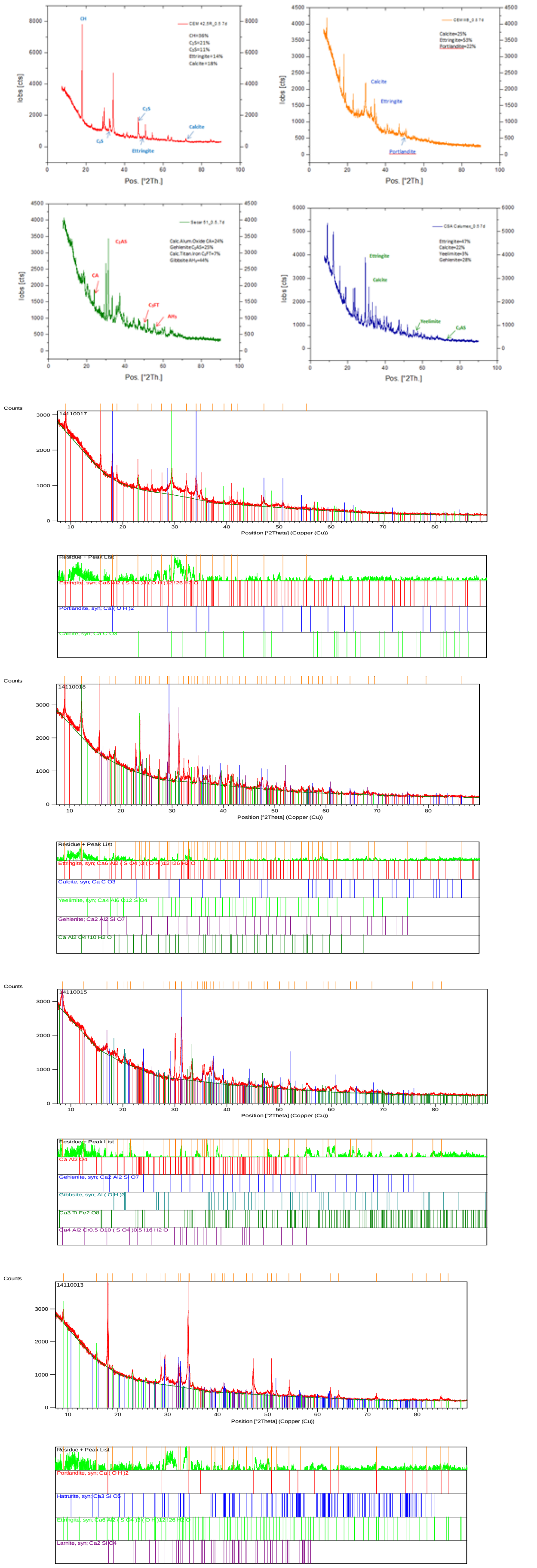

Figure.4 *XRD patterns for Cem III Blast, CSA Calumex, Secar 51, CEM I 42.5 R*

And we can compare the results from XRD pattern analyzing from High Score with TG-DSC results. TG/DSC curves (together XRD) allowed to characterize hydrates formed.

Results from MIP basically show low pore volumes with decreasing water to cement ratio for each cement paste series. However, they show very different shapes for pore size distribution curves (fingerprints) for the four different cement paste systems investigated.

Acknowledgement

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References

[1] Xudong Chen*, Shengxing Wu, Jikai Zhou, Influence of porosity on compressive and tensile strength of cement mortar, Construction and Buildings Materials 40 (2013) 869-874,

[2] Keisuke Takahashi, Effects of Mixing and Pumping Energy on Technological and Microstructural Properties of Cement-based Mortars, 2014

[3] Zh.Wensheng, L.Beixing, W.Hongxia, W.Jiangxiong, Ch.Yimin, Analysis of pore structures and their relations with strength of hardened cement paste

[4] M. Marroccoli, F. Montagnaro,Hydration Properties of Calcium Sulphoaluminate Cements made from Coal Combustion Wastes.