ESTIMATION OF THE POROSITY OF PORTLAND CEMENT PASTES USING BACKSCATTERED ELECTRON IMAGE

MELLAS M.*, MEZGHICHE B.* & ASH J. E.**

*Laboratoire de génie civil, Université de Biskra, Algeria
**Department of civil engineering, University of Birmingham, UK

ABSTRACT

Microscopy plays an important role in the examination of cementitious materials. Electron-optical techniques allow examination of microstructural details. The increased application of scanning electron microscopy in cement and concrete investigations has brought attention to the estimation of the porosity. Backscattered Electron image has been established as a method for quantitative analysis of hardened cement paste. This paper describes work and its application to Ordinary Portland cement paste. Results show that the technique can be used to determine the porosity of Portland cement pastes. The success of these investigations is, influenced by the type and quality of specimen preparation. In particular, backscattered electron and X-ray imaging modes are influenced by the specimen surface characteristics, with the ideal surface being highly polished. The technique can be a powerful tool to determine this essential factor of durability in concrete materials.

Keys words: porosities, cement paste, strength, Scanning electron microscope, methanol exchange.

1 INTRODUCTION

It is widely recognized that the porosity of a material exerts an enormous influence on its physical properties. For hardened cement paste a large volume of pores is inherent in the set structure. This porosity is derived mainly from excess water required to ensure cement hydration and provide workability of cement paste, but can also be present due to inadequate compaction. The residue of water filled space in fresh cement paste become voids in hardened cement paste. These voids are divided in two classes, capillary pores and gel pores. The former represents the volume of the capillary pores and it depends mainly on both cement-water ratio of the mix and the degree of hydration. The latter represents the gel pores. As hydration progresses, the amount and distribution of porosity between capillary and gel pores will change. Initially all the pores are capillary pores. As hydration precedes the capillary pore volume is reduced because the capillary space becomes filled with hydration products, and the gel porosity increases. There is a net reduction in total porosity.

During the last fifteen years Mercury intrusion porosimetry which involve forcing mercury into pores of a body by application of pressure and assuming that all pores have a simple shape, has been used for determining the pore structures sizes of hydrated cement paste. This method enables a wide range of pore-size distribution to be measured between 1000µm and 30 A° depending on the pressure [Orr (1970)]. However, the application of great pressure on hydrated cement paste may cause destruction in the structure and pores below 30 A° cannot be considered [Shi D. & Winslow D N (1985)]. In addition to this method there are other investigations involving fluid replacement as methanol and helium pycnometry. The use of methanol as displacement medium for porosity measurement [Scrivener, K L & Pratt, P L (1984)], have indicated that the porosity values were equivalent to those when helium was used as displacement method. Parrot (1981) reported on the effect of drying upon the exchange of pore water with methanol. He found that the water/methanol exchange results of 0.6 water/cement ratio by weight pastes indicated that the pore volume penetration by methanol was only on average 0.7 per cent greater than that occupied by original pore water and the exchange provided reliable pore structure information.

With the application of backscattered imaging of hydrated Portland cement paste [Scrivener, K L & Pratt, P L (1984)], In a polished cement surface the anhydrous grains appear brighter than the hydration products, which have a lower atomic number due to the presence of water. It was found that in hydrated cement paste the unhydrated cement appeared bright, the area of calcium hydroxide appeared slightly darker, other hydrated products still darker, and the pores black. The use of scanning electron microscope (SEM) for cement pastes, with the application of and programming of an image store for the SEM has been applied in previous work [Mellas M et all (1993)]. Some of the work described in this paper deals with an approaches to the porosity determined by SEM and Methanol exchange.

2 MATERIALS

The cement was an Ordinary (typical) Portland cement supplied by Blue Circle Industries (Table 1). The composition was determined accurately by Gutteridge at the British Cement association (UK), and the results are quoted in Table 2.

Table 1 : Oxide composition of cement

Oxide	content (%)
CaO	64.50
SiO	20.00
Al2O3	5.30
Fe2O3	3.40
SO3	3.00
MgO2	1.20
K2O	0.78
TiO2	0.26
Na2O	0.1
P2O5	0.08
Mn2O	0.06
Loss on ignation	0.90
Insoluble residue	0.2
Free CaO	2.20

Table 2 : Phase composition by QXRD

Coumpound	QXRD (%)
C3S	53.0
C2S	25.0
C4AF	7.0
C3A	4.0

2.1 Methods of investigation

Determination of the porosity has been measured by two methods firstly by methanol exchange and then by a back scattered electron image.

2.1.1 Methanol exchange

Determination of the porosity has been achieved by method of solvent replacement. Analar grade methanol was used which can penetrate into the microstructure without damage. The unbound water in the specimen was replaced by methanol, thus the hydration was arrested and all water eventually replaced by methanol; this is shown by a constant weight of the specimen between 3 and 14 days, (figure 1). Specimens were then dried over silica gel for 24 hours at 20 °C. The porosity was measured using methanol exchange [Parrott (1981].

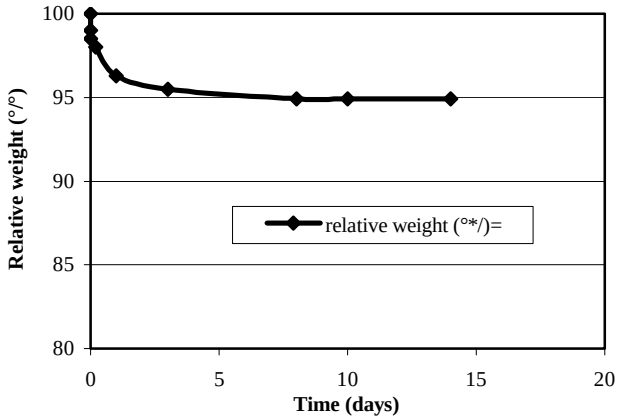

Figure 1 : Methanol exchange of cement paste, w/c=0.4 65 days old

2.1.2 Backscattered Electron Image (BEI)

Polished specimens of hardened cement paste samples was a technique developed to provide qualitative information by Backscattered Electron Image (BEI). With the application of BEI of hydrated Ordinary cement pastes, anhydrous grains appear brighter than the hydrated products, because of differences in atomic numbers [Scrivener, K L & Pratt, P L (1984)]. The unhydrated grains appear bright, area of calcium hydroxide slightly darker, other hydrated products darker and the pores black. Although quantitative measurement of BEI has been possible some time, the use of TV rate scanning without image storage usually prevents the SEM being used with the best performance in terms of contrast discrimination and beam settings, the application and programming of an image store for the SEM has been used [Hall M (1991)].

3 SPECIMEN PREPARATIONS

Several small prisms (125 x 35 x35 mm) and cubes (50 mm sides) were cast with cement ratios by weight of 0.40 and 0.45. Mixing was prolonged and intermitted to minimize the separation of water from the setting paste. Careful curing ensured no loss of water from surfaces for the first 24 hours. Following demoulding, samples were kept under wet and dry curing conditions and chosen for test at ages which provided a variation in the porosity. When selected for analysis, cubes were crushed. Prisms were cut perpendicular to the longitudinal axis with a diamond saw to yield a 3 mm thick slice. Samples were then immersed in methanol immediately in methanol to prevent carbonation and stop hydration prior to the determination of porosity.

A resin vacuum impregnation technique was developed as a means of supporting the paste microstructure during the specimen preparation, which was particularly important in the case of the weaker early age's pastes. An Araldite combination resin system consisting of 10 parts of AY18 resin and 1 part of HY 18 hardener was of low viscosity and proved to be suitable. For ease of handling during process of polishing, specimens were contained in a fast setting metaset resin. Specimen preparation is important in any microscopical technique with proper preparation methods facilitating examination and interpretation of microstructural features. Improper preparation methods may obscure features, and even create artifacts that may be misinterpreted. Scanning electron microscope (SEM) analysis using backscattered electron and X-ray imaging requires a highly polished surface for optimum imaging. Rough-textured surfaces, such as those produced using only saw-cutting diminish the image quality by reducing contrast and loss of feature definition. Specimens investigated by BEI must be plane; otherwise reflected shadows will adversely affect the image. Samples were automatically using a sequence of sand paper sizes, varying from grade 250 to Grade 1200. Satisfactory surfaces were produced when the final polishing was carried out initially with 6 µm diamond paste followed by 1 micron paste. In order to prevent the build of electron, the final surface was coated with carbon, [Bentz D P & Stutzman P L (1994)], [Stutzman P L & Clifton J R (1999)]. Proper sample preparation is absolutely vital in the study by SEM. A summary of the time required to produce one sample of hydrated cement paste is given below, where the term in brackets the time is undertaken for each operation.

- Cutting the sample to yield 3 mm thick slices, (15 mn).
- Drying the sample by methanol exchange, (15 days).
- Resin impregnation of the sample, (1hours). Then the impreganation sample was left to be hardened, (1 day).
- Cutting the impregnated sample to yield 15 mm square, (15 mn).
- The sample was then placed into a 30 mm diameter plastic tube mould fast-setting resin and hardener, (20 mn)
- Manual polishing on sand paper through the grades 25. 400.800.1000.1200.(60mn).
- Automatic polishing on a rotating wheel using Metaserv cloths and diamound paste respectively 6 and 1 um (12 hours).
- Coating with carbon
- Study by SEM (4 hours).

4 RESULTS AND DISCUSSION

Table 3 shows results for a cement paste with a water cement ratio by weight of 0.4 and 0.45, cured under water and in air, and tested at range of ages to provide information about the porosity determined by methanol exchange and BEI.

Table 3 : Results of compressive strength and porosity of cement pastes

W/C	Ages (days)	Compressive strength porosity (MPa)	Methanol (%)	BEI porosity (%)
Water cured				
0.4	7	48.4	29.4	14.3
	14	57.9	27.6	13.1
	28	74.0	26.2	10.8
	65	77.2	24.9	7.7
45	7	41.7	35.8	15.3
	14	48.2	32.3	13.4
	28	53.8	31.1	9 .7
	65	57.8	29.4	8.8
Air cured				
0.4	7	41.0	30.1	14.9
	14	45.4	29.1	14.4
	28	46.7	28.5	13.4
	65	47.6	28.2	9.2
0.45	7	33.4	37.1	15.1
	14	39.1	31.6	13.7
	28	41.0	32.2	12.7
	65	46.5	30.7	10.5

NB: Each porosity is the average range of a ten random observations within +-1 standard deviations

The porosity by BEI is determined at 200 magnification (X200), this magnification was found adequate in the previous work, [Mellas et al (1993)], for the determination of the degree of hydration. Figure.2 shows images taken from samples with w/c= 0.4 at 28 days old, water cured where the unhydrated product are bright, area of calcium hydroxide slightly darker, other hydrated products darker and the pores black. Figure 3 shows a BEI, where the pores (in red), the hydration product (in yellow) and the unhydrated product (in blue) were selected.

Figure 4 shows the porosity of hydrated cement based upon methanol exchange as a function of various ages of different water cement ratio. Figure 5 shows the compressive strength of hydrated cement paste as a function of total porosity based upon the methanol exchange method. This illustrate clearly the increase of strength while the porosity decrease, the results are for pastes with water cement ratio of 0.4 and 0.45, tested at various ages. Figure 6 shows the compressive strength of hydrated cement paste as function of age.

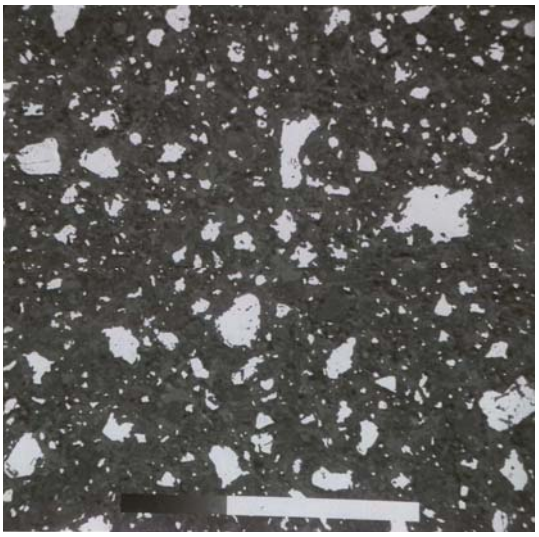

Figure 2 : BEI of a sample of hydrated cement paste with w/c=0.4, age 28 days, water cured

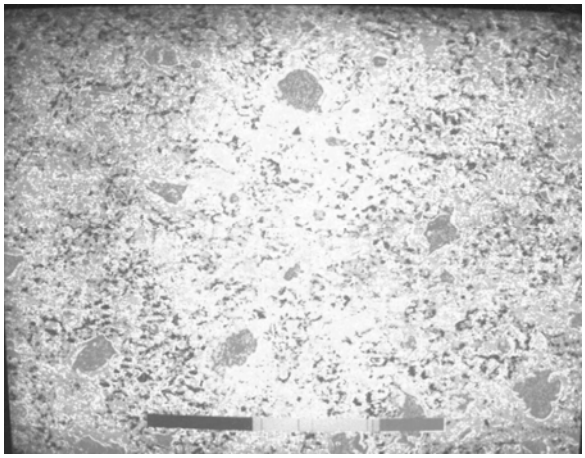

Figure 3 : a BEI oh hydrated cement, where the pores (in red), the hydrated product (in yellow) and the unhydrated cement (in blue) where selected

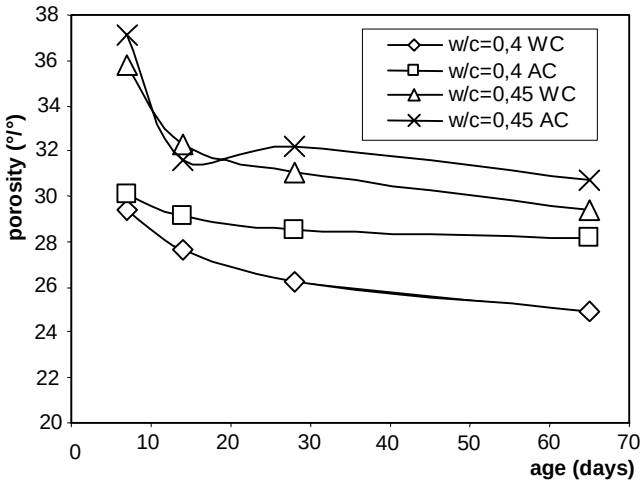

Figure 4 : Porosity of hydrated cement paste based upon methanol exchange

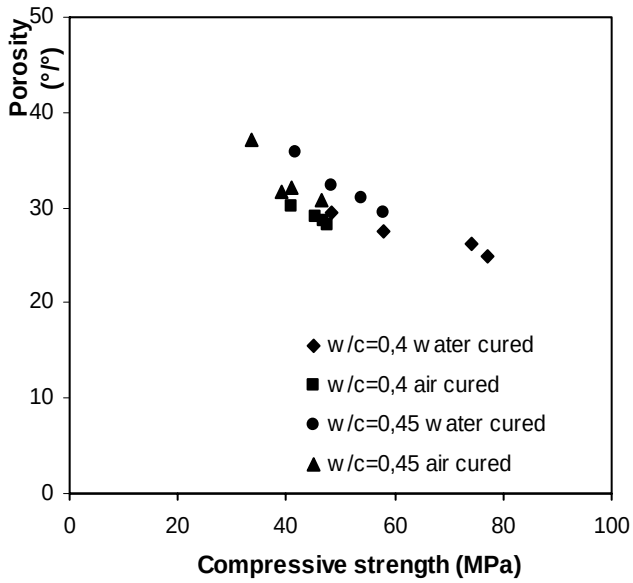

Figure 5 : compressive strength of hydrated cement paste as function of total porosity based upon methanol exchange

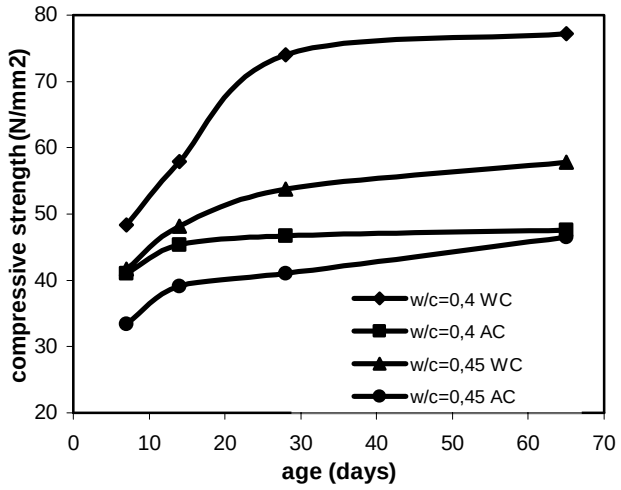

Figure 6 : Compressive strength of hydrated cement paste as function of age

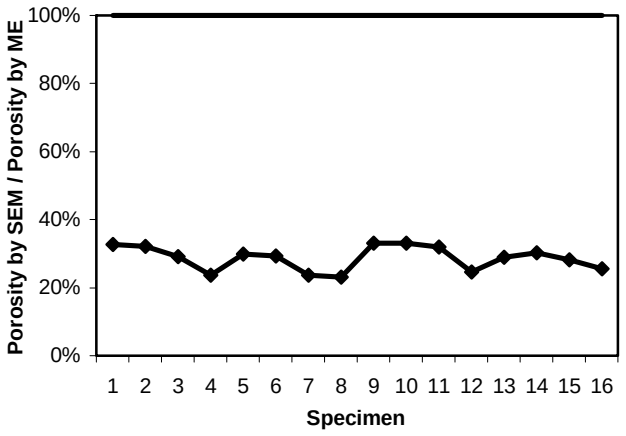

Figure 7 : Relation between the porosity obtained by SEM and that obtained by Methanol Exchange (ME)

A correlation can be made between the two methods, (figure 7). This relation shows that the porosity determined by SEM is proportional to that obtained by methanol exchange method, thus giving a difference between the different curing condition and various ages.

The significant differences between the two methods is subjected to a different factors such as

Difficulties in sample preparation for the in the SEM

Effect of magnification, the calculation of the porosity under 200 magnifications, and the area shown on the SEM represents an area of 0.5X0.5 mm^2 of the sample considered.

Random selection of a number of small area; It depends on the selection of different parts of the sample and the boundary between the compounds

Subjective analysis of the images

Rough-textured surfaces, such as those produced using only saw-cutting diminish the image quality by reducing contrast and loss of feature definition. Additionally, the lack of a polished specimen makes quantitative estimates arduous, as the surface is no longer planar. Nonetheless this method remains and can be applied for concrete materials to show the porosity of cement paste in concrete materials. Even thought the porosity obtained by the scanning electron microscope is less than that obtained by methanol, it remains the only one tools to observe and determine the porosity of cement pastes. The results obtained show clearly the variation of the porosity of different curing condition and water cement ratios.

Durability of concrete is dependant upon the porosity. Figure 6 demonstrate a wide spread of results in comparing compressive strength to the porosity. This shows that the water cement ratio has a marked and interesting effect worthy of further research.

Various authors have suggested that curing, age, degree of hydration, porosity and cement constituents will also have an effect. It is clear that, although cube compressive strengths remain as an easy, practical measure of compliance of site of concrete, adequate strength are not absolute guarantee of satisfactory durability

BIBLIOGRAPHIE

1. **Bentz Dale P**. and. **Stutzman Paul E** : SEM Analysis and Computer Modelling of Hydration of Portland Cement Particles. Petrography of Cementitious Materials, ASTM STP 1215, Sharon M. DeHayes and David Stark, Eds., American Society for Testing and Materials, Philadelphia, pp. 60-73, 1994
2. **Hall M G** ; The application and programming of an image store for the Scanning Electron Microscope; Scanning, vol 13 N° 3, 1991
3. **Mellas et al**; Estimations of degree of hydration of Portland cement pastes. Cement and Concrete Research, vol 23, pp 399-405, 1993
4. **Orr C**.: Application of mercury penetration to material analysis. Powder Technology, vol 3, 1970.
5. **Parrott , L. J**., "Effect of drying history upon the exchange of pore water with methanol and upon subsequent methanol sorption behaviour in hydrated alite paste", Cement and Concrete Research, Vol 11, 1981, p 651 – 658.
6. **Scrivener, K L and Pratt**, P L; Backscattered Electron Images of Polished Cement Section in the Scanning Electron Microscope. Proc. 6th int. Conf. On Cement Microscopy, 26 – 29,March 1984, Albubkerque , New Mexico, pp 145 – 155.
7. **Shi D. and Winslow D N**. : Contact angle and damage during mercury intrusion into cement paste. Cement and Concrete Research, vol 15, 1985
8. **Stutzman P E** & **Clifton J R**; Specimen preparation for Scanning Electron Microscopy. Proceedings of the twenty-First international conference on cement microscopy. April 25-29,1999, Las vegas, Nevada, pp 10-22,1999