

CHARACTERISATION OF PORE STRUCTURE OF HARDENED CEMENT PASTE IN CONCRETE USING BSE IMAGE ANALYSIS AND MERCURY INTRUSION POROSIMETRY

by

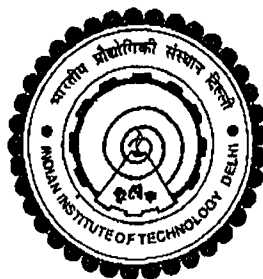
MANISH JAIN

DEPARTMENT OF CIVIL ENGINEERING

Submitted in fulfilment of the
requirements of the degree of

DOCTOR OF PHILOSOPHY

to



**INDIAN INSTITUTE OF TECHNOLOGY DELHI
HAUZ KHAS, NEW DELHI**

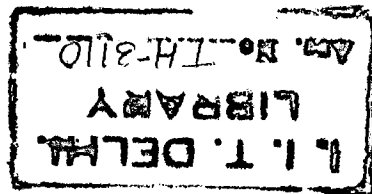
JUNE, 2002



Concrete Technology

1/06/05

TH
66.97
JH-C

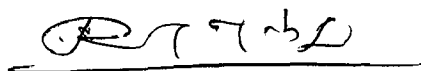


DEDICATED
TO
MY PARENTS

CERTIFICATE

This is to certify that the thesis titled “**CHARACTERISATION OF PORE STRUCTURE OF HARDENED CEMENT PASTE IN CONCRETE USING BSE IMAGE ANALYSIS AND MERCURY INTRUSION POROSIMETRY**” being submitted by **Mr. Manish Jain** to the Indian Institute of Technology Delhi, India, for the award of the degree of “**Doctor of Philosophy in Civil Engineering**” is a record of the original bonafide research work carried out by him under our guidance and supervision.

To the best of our knowledge, the thesis has reached the requisite standard. The material presented in this thesis has not been submitted in part or full to any other University or Institute for award of any degree/diploma.



(Dr. RM. Manickavasagam)

Professor and Director
Institute Instrumentation Centre
I.I.T. Roorkee
ROORKEE - 247 667 (INDIA)



Associate Professor
Deptt. of Civil Engineering
I.I.T. Delhi, Hauz Khas
NEW DELHI – 110 016 (INDIA)

ACKNOWLEDGEMENTS

I am thankful to Dr. B. Bhattacharjee, Associate Professor, I.I.T. Delhi, for suggesting a useful and contemporary research problem. It was a challenge in many ways, because it is the first time that BSE imaging technique has been used for microstructural study of concrete in our laboratory.

I am grateful to my supervisors, Dr. B. Bhattacharjee of I.I.T. Delhi and Prof. RM.Manickavasagam of I.I.T. Roorkee, for their guidance and constant encouragement at all stages of the work. It would not have been possible for me to complete this challenging task without their able support. I am also thankful to them for carefully checking the manuscript and their valuable suggestions.

The grant provided by the Central Water Commission for the purchase of equipments used in this research is gratefully acknowledged.

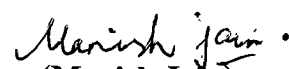
I am thankful to the staff of Concrete Laboratory and Building Materials Science Laboratory of Civil Engineering Department, I.I.T. Delhi, for their assistance. I am grateful to Ch. Badle Ram and Mr. Badan Singh, Senior Lab. Technicians, for their help in specimen preparation and testing.

I am also thankful to the staff of Institute Instrumentation Centre, I.I.T. Roorkee, for their help during my work on the Scanning Electron Microscope.

I am grateful to Dr. P.K. Garg, Associate Professor, I.I.T. Roorkee, Mr. D.S.Rathore and Dr. S.K.Jain, Scientists, National Institute of Hydrology, Roorkee, for extending their help in image processing and analysis. I am also grateful to my friend Vijay Ranjan, fellow Research Scholar, for his help.

I take this opportunity to express my gratitude to my parents for their blessings and constant encouragement. Also, I wish to thank my in-laws for their help and support.

Last but not the least, I would like to record my appreciation for my wife Shamina who was constantly by my side during this endeavour, and to my beautiful angel Suhani who gave my life a new meaning and helped me tide over my hurdles by her mere presence.


(Manish Jain)

ABSTRACT

In the present study, the pore structure characteristics of the *same cement pastes* in various concretes, based on Backscatter Electron (BSE) Image Analysis and Mercury Intrusion Porosimetry (MIP), are compared. The fractions of the capillary porosity and the total porosity (capillary + gel) of the hardened cement paste (hcp) in concrete, which are measured by the two techniques, are also assessed.

The theoretical estimates of the capillary porosity and total porosity of the hcp in concrete, are based on Powers Model. For this purpose, the degree of hydration of cement in the hcp must be known. The degree of hydration of cement is obtained directly from the volume fraction of unhydrated cement in the hcp, which is determined by Image Analysis technique.

Concretes with water-cement ratios, 0.40, 0.50, and 0.60 are tested for pore structure characteristics and compressive strength at the age of 7, 28, and 180 days. Some concretes are wet cured continuously till the age at test, while others are wet cured for only 7 days and then stored in air till test. Concretes are made with normal-weight aggregates and ordinary portland cement (OPC). There are no admixtures used. Concrete made with portland pozzolana cement, w/c ratio equal to 0.50 and wet cured for 7 days, has also been tested at the age of 28 and 180 days for pore structure characteristics and compressive strength.

For all concrete mixes, the aggregate content is kept constant at 65% by volume; and the maximum size of aggregate and its grading are kept the same. The influence of aggregate content and grading on the pore structure characteristics is not studied.

The samples for pore structure characterisation are selected using the 'random systematic' sampling strategy. For each concrete, twenty BSE images are acquired from three polished sections, 25x30 mm size. The digitized BSE images are acquired at 512x512 pixels, and the resolution achieved is 0.199 μm at 1000x magnification. For MIP test six samples of each concrete, 6x8x25 mm size, and six aggregate samples are tested to obtain the average intrusion curves.

The pore structure characteristics evaluated are: porosity, pore specific surface area, mean pore diameter, pore size distribution, mean distribution pore radius, pore shape factor and threshold diameter.

Most of the porosity tallied by Image Analysis is in the pore size range 0.5 μm to 10 μm , whereas essentially all of the porosity tallied by MIP is represented as occurring in pore size range 0.002 μm to 0.20 μm .

The porosity of the hcp in concrete tallied by Image Analysis is found to be half of the porosity measured by MIP. Hence, Image Analysis reveals that a significant fraction of the porosity measured by MIP is due to the pores in the size range 0.5 μm to 10 μm . MIP measurements on the *same cement pastes* record almost all porosity as though it existed in sizes below about 0.20 μm , i.e. below the threshold or percolating diameter of the bulk pore system.

It is found that the porosity of the hcp in concrete based on Image Analysis is 0.55 to 0.65 times the estimated capillary porosity, whereas the porosity of the hcp tallied by MIP is 1.1 to 1.3 times the estimated capillary porosity of the cement paste based on Powers Model.

The MIP method measures only a fraction of the estimated total porosity of the cement paste based on Powers Model. The fraction of the total porosity, measured by MIP method, is smaller in cement pastes which are more dense, i.e. pastes with lower total porosity. It has been shown that hardened cement pastes with a lower total porosity have a greater fraction of gel porosity resulting in more segmented capillary pores. Hence, mercury intrusion is restricted in dense pastes and a smaller fraction of the total porosity is recorded by MIP test.

It is found that the mean pore diameter and the pore specific surface area increase with an increase in the porosity of the hcp in concrete. The pore shape factors, however, do not change with the porosity. The threshold diameter of an interconnected capillary network is found to lie in the range 0.10 μm to 0.20 μm for the hcp in various concretes. It is observed that the threshold diameter is smaller for concretes of low porosity which have a finer network of pores in the hcp.

It is shown that the mean pore diameter and the mean distribution pore radius, in fact, represent the same pore structure characteristic, although these are determined by two different approaches.

It is found that the experimental data in the present study fits well the strength – porosity relation proposed by Powers. Strength – porosity relation considering pore size distribution has been obtained based on Atzeni's Model.

CONTENTS

	Page No.
List of Plates	xii
List of Figures	xiii
List of Tables	xviii
 CHAPTER	
1. INTRODUCTION	1
1.1 General	1
1.2 Pore Structure of hcp in Concrete	2
1.3 Characterisation of Pore Structure	3
1.4 Objectives of Study	7
1.5 Scope of Study	8
1.6 Experimental Program	10
1.7 Thesis Format	11
 2. LITERATURE REVIEW	14
2.1 General	14
2.2 Microstructure of Concrete	15
2.2.1 Microstructure of Aggregates	16
2.2.2 Microstructure of Hardened Cement Paste	17
2.2.2.1 Microstructure of Anhydrous Cement	17
2.2.2.2 Development of Microstructure with Hydration	20
2.2.2.3 Microstructural Elements of Cement Paste	23
2.2.3 Microstructure of Interface Zone	27
2.3 Microstructural Models of hcp	30
2.3.1 Modelling Strategy	30
2.3.2 Constitutive Models	31
2.3.2.1 Powers- Brownyard Model	31
2.3.2.2 Parrott's Model	32

2.3.2.3	Feidman- Sereda Model	33
2.3.2.4	Jennings-Tennis Model	34
2.3.3	Simulation Models	35
2.3.3.1	Pixel/ Digital Model	35
2.3.3.2	Kinetic Model	36
2.4	Pore Structure of hcp in Concrete	37
2.5	Factors influencing Pore Structure of hcp	42
2.5.1	Effect of Mineral Admixtures	43
2.5.2	Pore Structure of Very High Strength Cement Pastes	46
2.6	Microstructure Investigation Techniques	46
2.6.1	Indirect Techniques	47
2.6.1.1	Fluid Pycnometry	47
2.6.1.2	Sorption Isotherms and Capillary Condensation	49
2.6.1.3	Mercury Intrusion Porosimetry	49
2.6.1.4	AC Impedance Spectroscopy	52
2.6.1.5	Small-angle X-ray Scattering	53
2.6.1.6	Small-angle Neutron Scattering	53
2.6.1.7	Nuclear Magnetic Resonance	54
2.6.1.8	Low-temperature Calorimetry	54
2.6.1.9	X-ray Diffraction Spectrometry	55
2.6.1.10	Thermal Analysis	55
2.6.2	Direct Techniques	56
2.6.2.1	Optical Microscopy	56
2.6.2.2	Electron Microscopy	60
2.6.2.3	Computer Tomography	63
2.7	Characterisation of Pore Structure	64
2.8	Strength-Porosity Relationships	68
2.9	Summary	72

3.	EXPERIMENTAL PROCEDURE	75
3.1	General	75
3.2	Choice of Parameters	75
3.3	Concrete Designations	77
3.4	Material Properties	78
	3.4.1 Cement	78
	3.4.2 Aggregate	79
3.5	Mix Proportions	80
3.6	Entrapped Air Voids	82
3.7	Compressive Strength Test	83
3.8	Sampling Procedure	84
3.9	Specimen Drying	86
3.10	Preparation of Polished Sections	88
	3.10.1 Epoxy Impregnation	88
	3.10.2 Lapping	91
	3.10.3 Polishing	92
3.11	Procedure for BSE Imaging	93
	3.11.1 Carbon Coating	93
	3.11.2 SEM Setting	95
	3.11.3 Image Acquisition	98
	3.11.4 Number of Images for Statistical Certainty	100
3.12	Procedure for MIP Test	102
	3.12.1 Description of Porosimeter	102
	3.12.2 Low Pressure Operation	103
	3.12.3 High Pressure Operation	105
	3.12.4 Test Procedure	106
	3.12.5 Penetrometer Constants and Blank Cell Correction	107
	3.12.6 Mercury Constants	108
	3.12.7 Aggregate and Concrete Samples	109
	3.12.8 Number of Samples for Statistical Certainty	110

4.	IMAGE ANALYSIS OF HCP IN CONCRETE	111
4.1	General	111
4.2	Phase Identification	111
4.3	Image Analysis Procedures	114
4.3.1	ERDAS and ILWIS Softwares	114
4.3.2	Binary Segmentation	115
4.3.3	Feature Definition	116
4.3.4	Size Limits	116
4.3.5	Feature Analysis	117
4.4	Description of Images	117
4.4.1	BSE Images of Cement Paste	118
4.4.2	Binary Images of UH Phase	119
4.4.3	Binary Images of Pore Phase	120
4.5	Image Analysis Data	138
4.5.1	Area Fractions of Pore and UH Phases	138
4.5.2	Perimeter of Pore Phase/unit area	138
4.5.3	Pore Size Distribution	157
4.5.4	Pore Shape Factor	159
5.	PORE STRUCTURE CHARACTERISTICS OF HCP BASED ON IMAGE ANALYSIS	160
5.1	General	160
5.2	Stereology	160
5.2.1	Basic Concepts	161
5.2.2	Geometric Properties of Microstructure	163
5.2.3	Fundamental Relations	164
5.3	Statistical Analysis of Image Data	165
5.3.1	Testing Measurement Data for Normality	166
5.3.2	Precision of Estimate of Population Mean	171
5.4	Geometric Properties of 3-D Microstructure	172

5.5	Pore Structure Characteristics	173
5.5.1	Porosity	174
5.5.2	Pore Specific Surface Area	176
5.5.3	Mean Pore Diameter	176
5.5.4	Pore Size Distribution	177
5.5.5	Mean Distribution Pore Radius	197
5.5.6	Pore Shape Factor	197
5.6	Degree of Hydration based on Image Analysis	198
5.7	Capillary Porosity and Total Porosity based on Powers Model	200
5.8	Summary	203
6.	PORE STRUCTURE CHARACTERISTICS OF HCP BASED ON MIP	205
6.1	General	205
6.2	Basic Concepts of MIP	205
6.3	MIP Test Results	207
6.3.1	Intrusion Curve of Aggregate	208
6.3.2	Intrusion Curves of Concretes	209
6.3.3	Intrusion Curves of hcp in Concrete	216
6.4	Pore Structure Characteristics	223
6.4.1	Porosity	224
6.4.2	Pore Specific Surface Area	225
6.4.3	Mean Pore Diameter	226
6.4.4	Pore Size Distribution	226
6.4.5	Threshold Diameter	227
6.4.6	Mean Distribution Pore Radius	241
6.5	Summary	241
7.	DISCUSSION OF TEST RESULTS AND STRENGTH-POROSITY RELATIONS	243
7.1	General	243
7.2	Porosity	243

7.3	Pore Specific Surface Area	250
7.4	Mean Pore Diameter	253
7.5	Pore Size Distribution	256
7.6	Mean Distribution Pore Radius	264
7.7	Strength - Porosity Relations	266
7.7.1	Relation Based on Powers Model	267
7.7.2	Relation Based on Atzeni's Model	268
7.8	Summary	270
8.	SUMMARY AND CONCLUSIONS	274
8.1	Summary	274
8.2	Conclusions	277
8.3	Suggestions for Future Work	281
	REFERENCES	282
	AUTHOR'S BIO DATA	