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2006

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Citation for published version (APA):

Fagerlund, G. (2006). *Porosity and specific surface of Portland cement paste : an analysis of experimental work performed by Åke Grudemo during the years 1973-1979*. (Report TVBM; Vol. 3133). Division of Building Materials, LTH, Lund University.

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LUND UNIVERSITY

Division of Building Materials

POROSITY AND SPECIFIC SURFACE OF PORTLAND CEMENT PASTE

An analysis of experimental work performed by
Åke Grudemo during the years 1973-1979

Göran Fagerlund



Report TVBM-3133

Lund 2006

PREFACE

Mr. Åke Grudemo (1919-1994) is a part of the history of the Swedish Cement and Concrete Research Institute in Stockholm, Sweden. The Institute was established in 1942, and Mr. Grudemo was employed at the Institute already in 1944 when he still was a student at the Royal Institute of Technology in Stockholm. In the mid 1940s, the Institute was organized in five departments, and Mr. Grudemo with a M.Sc. in physics belonged to the Physical Department. He was an active researcher during four decades and under four Institute Presidents. He has published more than a dozen research bulletins and reports between the early 1950s and 1986.

Mr. Åke Grudemo's research was devoted to the microstructure of cementitious materials and he was a pioneer in using new technologies like electron microscopy. An example is his Chapter entitled "Electron Microscopy of Portland Cement Pastes" in the textbook "The Chemistry of Cement" (Academic Press, London, 1962, edited by Dr. H. F. W. Taylor).

Despite a lot of publications, much research data remain unpublished. The research money might have expired, other research projects may have needed more attention, or the research might have resulted in secondary data that were outside the scope of a certain investigation. However, experimental research is never too old. As a current representative of the Swedish Cement and Concrete Research Institute, I am grateful to Prof. Göran Fagerlund that he has taken his time to re-analyse Mr. Grudemo's research and made them public by authoring this report.

Stockholm, October 16, 2006

Johan Silfwerbrand

Professor, President of the Swedish Cement and Concrete Research Institute

FOREWORD AND ACKNOWLEDGEMENT

During his whole professional career, from the mid 1940-ies to the mid 1980-ies, Åke Grudemo was researcher at the Swedish Cement and Concrete Research Institute (CBI) in Stockholm. Åke Grudemo had his background in physics. Therefore, he quite early devoted his interest to studies of the micro-structure of cement paste, using sophisticated technique, that had practically not been used previously in cement and concrete research. Grudemo was one of the first the first to apply Transmission Electron Microscopy (TEM) for basic studies of the structure of hardening cement paste. His TEM-studies gave a new picture of the structure of cement gel. In the famous work by T.C. Powers and T.L. Brownyard from 1948 the gel was supposed to be made up of tiny spherical particles. When Åke Grudemo presented his TEM-pictures showing that the gel particles were rather thin, flat fibres or plates, Powers changed his description of the cement gel, and in writing attributed this change in view to Grudemo's work; Powers (1960). The TEM results were presented in a comprehensive report; Grudemo (1955).

Åke Grudemo also developed techniques for quantitative X-ray analysis of hydrated cement paste. Results of his studies are presented in a number of reports like Grudemo (1965, 1975B, 1977, 1986 A).

In the 1970-ies Åke Grudemo investigated structure-strength relations in cement paste and cement mortar. From 1975 to 1979 I had the privilege to collaborate with him in some of these studies and therefore obtained good insight in his work. Grudemo designed all experimental techniques and performed all experimental work. This is of high quality, and therefore the experimental results have high credibility. Some of the work -mainly the mechanical tests- was published; Grudemo (1975C, 1975D, 1977, 1979, 1982). Many results dealing with porosity and pore structure remained, however, unpublished. When Åke Grudemo retired from CBI he gave these unpublished data to me, maybe hoping that I might find them useful for some purpose. It is not until now that I have had the opportunity to make an analysis of the data. I am grateful for the confidence Åke Grudemo had in me when he gave me the data. I hope that my analysis of them should have been appreciated by him.

In the report, the Grudemo data are reported and used for tests of formulae for total and "coarse" porosity, and for determination of the specific surface of cement paste, and for determination of the structure of the cement gel. Hopefully the analysis gives some information that can be of use in future cement and concrete research.

Lund in September 2006

Göran Fagerlund

OUTLINE OF THE REPORT

The report is divided in two parts. Each part is based on its own set of experimental data obtained from the Grudemo work.

Part I deals with the porosity of cement paste and with how porosity is influenced by the composition and degree of hydration of the cement paste.

Part II deals with the specific surface and internal structure of cement paste and cement gel.

All background data are listed in two Appendices, one for each Part.

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LIST OF SYMBOLS

A	The adsorption coefficient	(-)
A_m	Surface area covered by one adsorbed water molecule	(m ²)
CH _C	Amount of calcium hydroxide as weight fraction of cement	(g/g)
CH _S	Amount of calcium hydroxide as weight fraction of solid	(g/g)
CH _{tot}	Total amount of calcium hydroxide	(g)
K	Coefficient in equation (I:7.21)	(-)
K	Coefficient in equation (II:6.8)	(m ² /kg)
M	Molecular weight of water	(18 kg/kmole)
N	Avogadro's number (6.02·10 ²⁶ molecules per kmole)	
P _{cap}	Capillary porosity	(-)
P _{coarse}	Coarse porosity (pores empty at 33% RH)	(-)
P _{coarse,meas}	Measured coarse porosity	(-)
P _{gel}	Gel porosity	(-)
P _{tot}	Total porosity	(-)
P _{tot,calc}	Calculated total porosity	(-)
P _{tot,meas}	Measured total porosity	(-)
P _{33,ads}	Coarse porosity at <i>adsorption</i> to 33% RH	(-)
P _{33,des}	Coarse porosity at <i>desorption</i> to 33% RH	(-)
Q _{dry,gel}	Dry weight of the cement gel	(g)
Q _{dry,paste}	Dry weight of the specimen	(g)
Q _{sat}	Weight of water saturated specimen	(g)
Q _{solid}	Weight of solid part of cement paste	(g)
Q ₁₀₅	Weight of specimens after drying to +105°C	(g)
Q ₁₀₀₀	Weight of specimen after heating to 1000°C	(g)
Q ₃₃	Weight of specimen in equilibrium with 33% RH	(g)
R	Amount of mineral additive as weight fraction of cement	(g/g)
S	Amount of silica gel as weight fraction of cement	(g/g)
S	Specific surface	(m ² /kg)
S _{ads}	Specific surface of the paste calculated from adsorption	(m ² /kg) or (m ² /g)
S _{ads,gel}	Specific surface of the gel calculated from adsorption	(m ² /kg) or (m ² /g)
S _{des}	Specific surface of the paste calculated from desorption	(m ² /kg) or (m ² /g)
S _{des,gel}	Specific surface of the gel calculated from desorption	(m ² /kg) or (m ² /g)
S _{gel}	Specific surface of the cement gel including Ca(OH) ₂	(m ² /kg) or (m ² /g)
S _{gel,net}	Specific surface of cement gel excluding Ca(OH) ₂	(m ² /kg) or (m ² /g)
V	Specimen volume	(cm ³)
V _{gel}	Volume of cement gel	(cm ³)
V _{paste}	Volume of cement paste	(cm ³)
V _{p,gel}	Volume of pores in the cement gel	(cm ³)
V _{p,coarse}	Volume of "coarse" pores	(cm ³)
V _{p,tot}	Total pore volume	(cm ³)
V _{p,33,ads}	Volume of empty pores at <i>adsorption</i> to 33% RH	(cm ³)
V _{p,33,des}	Volume of empty pores at <i>desorption</i> to 33% RH	(cm ³)
W _m	Amount of water in one monolayer	(kg/kg)
W _Φ	Amount of adsorbed water at equilibrium with Φ	(kg/kg)
W ₃₃	Amount of adsorbed water at 33% RH	(kg/kg)
W _{33,ads}	Amount of water at equilibrium with 33% RH at adsorption	(kg/kg)
W _{33,des}	Amount of water at equilibrium with 33% RH at desorption	(kg/kg)

$W_{33,des,gel}$	Amount of water in gel at equilibrium with 33% RH	(kg/kg)
c	Cement weight	(g)
d	Width of gel pore	(m)
k	Coefficient in equation (I:6.12)	(-)
t	Thickness of a gel particle	(m)
v_c	Specific volume of cement	(0.32 cm ³ /g)
v_w	Specific volume of water	(1 cm ³ /g)
v_{wn}	Specific volume of chemically bound water	(cm ³ /g)
W_{curing}	Amount of water sucked in during water curing	(g)
W_m	Amount of adsorbed water in one monolayer	(g)
W_n	Chemically bound water	(g)
$W_{n,max}$	Amount of chemically bound water at complete hydration	(g)
W_{sat}	Evaporable water content at saturation	(g)
W_o	Amount of mixing water	(g)
$(w/c)_o$	True water cement ratio	(-)
$(w/c)_{sat,o}$	Measured water–cement ratio including curing water	(-)
$W_{33,ads}$	Weight of pore water at <i>adsorption</i> to 33% RH	(g)
$W_{33,des}$	Weight of pore water at <i>desorption</i> to 33% RH	(g)
α	Degree of hydration	(-)
Φ	Relative humidity	(-)
Φ_m	Relative humidity corresponding to one monolayer	(-)
ρ_{CSH}	Density of cement gel particles excluding Ca(OH) ₂	(kg/m ³)
ρ_{gel}	Density of cement gel particles including Ca(OH) ₂	(kg/m ³)
ρ_{gel}'	Density of cement gel particles including Ca(OH) ₂	(g/cm ³)
ρ_{paste}'	Density of cement paste including gel pores	(g/cm ³)
ρ_w	Density of water	(1 g/cm ³)

PART I

POROSITY

SUMMARY OF PART I

The primary aim of Part I is to use data from the Grudemo investigations to find a general equation for the total porosity of Portland cement paste that can be used for any water-cement ratio and any degree of hydration. The analysis is based on 19 different air-free cement pastes. All mixes were made with one single low alkali and sulphate resistant Portland cement. The water-cement ratio was varied between 0.18 and 1.00. Measurements of porosity were made after hydration times varying from 18 hours to 30 days.

The degree of hydration was based on the weight after drying at +105 °C and the weight after ignition at 1000 °C. Equation (I:3.5) was used for the calculation.

The true water cement ratio compensated for bleeding and separation was calculated from the water-saturated weight corrected for water sucked in during hydration. Equation (I:4.6) was used for the calculation.

Total porosity

The total porosity was calculated from the water-stored weight, the weight after drying at +105 °C and the weight after ignition at 1000 °C. Equation (I:6.5) was used for the calculation.

The measured total porosity was compared with the *theoretical* total porosity based on an assumed “volume contraction” of hydrate water, and an assumed amount of water that is bound at complete hydration.

$$P_{tot} = \frac{(w/c)_0 - k \cdot \alpha}{(w/c)_0 + 0.32} \quad (\text{I:6.12})$$

where $(w/c)_0$ is the water cement ratio, α is the degree of hydration and k is a coefficient mainly determined by the “chemical contraction”, i.e. the reduction in specific volume when free water is bound chemically in the cement gel.

For $k=0.18$ à 0.19 the agreement between measured and theoretical total porosity is almost perfect over the entire water-cement ratio range 0.18-1.00, and degree of hydration range 12%-80%; see Equations (I:6.13) and (I:6.14), and Figures I:6.1 to I:6.3. This indicates that the chemical contraction is of the order 25% for all w/c-ratios and all degrees of hydration.

“Coarse porosity”

“Coarse porosity” is defined as the volume of pores filled by water at *desorption* to 33% relative humidity (RH); the “33%-porosity”. It was determined from the weight of specimens stored to equilibrium with air in vessels containing a saturated MgCl_2 -solution. Equation (I:7.3) was used for the calculation.

The measured coarse porosity was compared with “33%-porosities” calculated from “classic” desorption and adsorption isotherms determined by Powers and Brownard (1948).

The measured coarse porosity was also compared with the capillary porosity calculated by the well-known Powers formula (I:7.20).

It is shown that all these three different porosities can be described by one single formula

$$P_{coarse} = \frac{(w/c)_0 - K \cdot \alpha}{(w/c)_0 + 0.32}$$

where K is a coefficient which is different for different definitions of coarse porosity; K=0.28 or 0.31 when the “33%-porosity” is based on the Powers and Brownyard adsorption and desorption isotherms, K=0.39 for the capillary porosity.

Comparisons between the measured “33%-porosity” and the “33%-porosity” calculated from the “old” Powers and Brownyard *desorption* isotherm show good agreement for all water-cement ratios and degrees of hydration, see Equation (I:7.26), and Figures (I:7.4) and (I:7.6).

The capillary porosity deviates quite much from the measured “33%-porosity”. An analysis also shows that there is no single RH-level on either the adsorption isotherm or desorption isotherm that corresponds to the capillary porosity; see paragraph I:7.3.4.

Specific surface

The experimental data can also be used for a rough calculation of the inner specific surface of cement paste and cement gel. The calculations are shown in APPENDIX TO PART I. The specific surfaces calculated are of the same order as the more precise values given in Part II.

I:1 MATERIALS AND SPECIMENS

I:1.1 Mixing, casting and curing

A: *Cast cement paste*

Cement pastes were mixed for long time (2 hours) in a food mixer. Cement paste cylinders were cast in 75 mm long, 14 mm wide teflon moulds. Each mould was vibrated internally by a thin vibrating “needle”. After de-moulding, the specimens were stored in saturated lime water at room-temperature until the time of testing. The storage containers were sealed so as to avoid carbonation.

Mixing and casting was made in such way that practically no air-voids were entrapped. This was confirmed microscopically and by measurement of density. Thus, since the specimens were stored in water until testing, they only contained 2 phases:

1. Cement (unreacted+reacted)
2. Water (free+chemically bound)

In total 18 different mixes were produced with water-cement ratio varying from 0.25 to 1.00. Thus, a very large span in porosity was obtained

B: *Compact*

One single series was made as a “compact” where dry cement powder was dry-pressed in a mould to cylinders with diameter 12 mm and length 8 mm. After pressing the samples were placed on a moist filter-paper from which they absorbed water until they became saturated. The water absorbed corresponds to a water-cement ratio of 0.18.

I:1.2 Cement

The cement was of type low alkali, sulphate resistant Portland with the following composition in weight-percent.

C ₃ S	60
C ₂ S	18
C ₃ A	5
C ₄ AF	9
Na ₂ O	0.2
K ₂ O	0.1
SO ₃	2.4
Lime-stone filler	0

In some pastes with very high water-cement ratio, a small amount of amorphous colloidal silica gel (“aerosil”) was used for avoidance of water separation.

In order to investigate the effect of the cement fineness a certain portion of the cement was divided by sieving into a fine fraction (grains <37µm) and a coarse fraction (grains >37µm). According to Grudemo (1975D) the mineral composition determined by X-ray diffraction is about the same in both fractions.

I:1.3 Specimens

The density variation within the specimen was determined for a couple of 20 mm wide, 75 mm long cylinders of each recipe, by measuring the density of a number of 3 mm thick slices sawn from different parts of the cylinder. Results are shown in Figure I:1.1. The 40 mm long middle section of the specimens has almost constant density while the lower 20 mm had higher density indicating cement separation, and the upper 10 mm had lower density indicating water separation.

All specimens were sawn out from the part of the cylinder in which density and porosity were constant. The upper and lower ends of the cylinders were discarded.

Specimens for determination of total porosity were 20 mm long. Specimens for determination of coarse porosity and specific surface were about 3 mm thick. Several specimens were used for each type of determination.

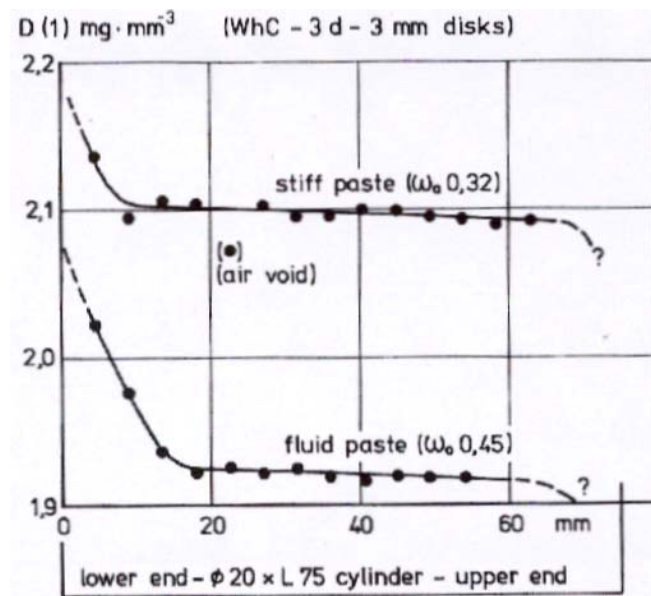


Figure I:1.1: Density variation along the specimen, Grudemo (1979). White cement was used as binder in these tests. (ω_0 is the water-cement ratio)

I:2 MEASUREMENTS

After water storage for pre-determined time, varying from less than 1 day to about 30 days, the following measurements were made:

Determination of total porosity

1. The saturated specimen was weighed (Q_{sat}).
2. The specimen was crushed and ground in ethyl-alcohol in order to stop further hydration.
3. The cement paste powder was dried at $+105^{\circ}\text{C}$ at very precise relative humidity ($x\%$) by a method developed by Danielsson (197x). The dry weight was determined (Q_{105}).
4. The dry powder was ignited at $+1000^{\circ}\text{C}$ and weighed (Q_{1000}).

Determination of coarse porosity and specific surface

1. The saturated specimen was weighed (Q_{sat}).
2. The thin specimen was placed in an evacuated vessel connected to another vessel containing a saturated solution of MgCl_2 . Drying was performed until equilibrium with the salt solution (33% RH). The weight was determined (Q_{33}). By evacuation carbonation was avoided.

The different measurements are shown in the block diagram in Figure I:2.1.

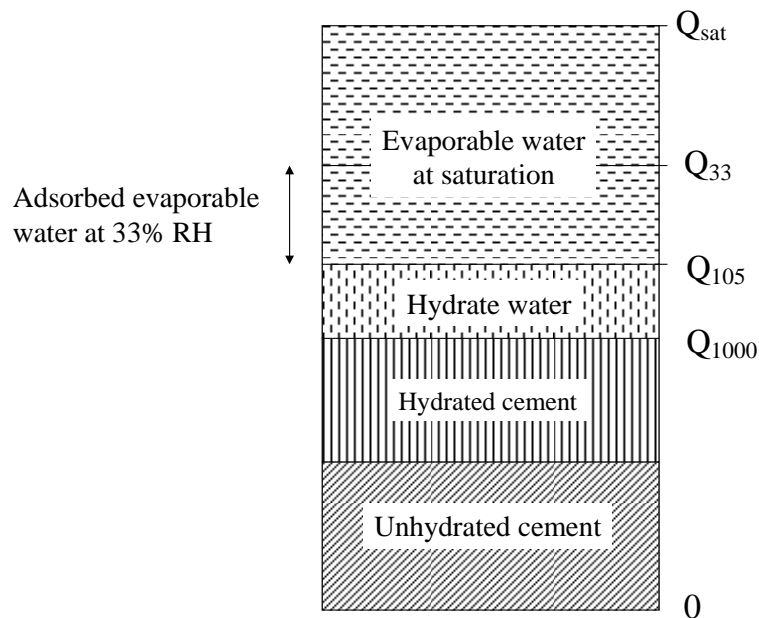


Figure I:2.1: Different phases in the cement paste specimen. Weight measurements.

I:3 DEGREE OF HYDRATION

The weight of chemically bound water in the specimen (w_n) is calculated by

$$w_n = Q_{105} - Q_{1000} \quad (\text{g}) \quad (\text{I:3.1})$$

The cement content is (assuming no carbonation)

$$c = Q_{1000} \quad (\text{g}) \quad (\text{I:3.2})$$

The amount of chemically bound water at complete hydration is supposed to be

$$w_{n,\text{max}}/c \approx 0.25 \quad (\text{I:3.3})$$

The value is somewhat different for different chemical compositions of the portland cement, Powers & Brownyard (1948).

At reaction of the pure clinker components the following amount of water in kg per kg component is bound: C₃S: 0.24 kg/kg, C₂S: 0.21 kg/kg, C₃A: 0.40 kg/kg, C₄AF: 0.37 kg/kg. For the actual cement composition these values give the water binding 0.235 kg/kg cement. In real cements other reactions also takes place, like reactions of gypsum with C₃A and C₄AF. The value 0.25, which is selected in equation (I:3.3), might therefore be afflicted with a certain error.

The degree of hydration is defined

$$\alpha = \frac{(w_n/c)}{0.25} = 4 \cdot (w_n/c) \quad 0 \leq \alpha \leq 1 \quad (\text{I:3.4})$$

Thus, the degree of hydration of the specimen is calculated by

$$\alpha = 4 \cdot \frac{Q_{105} - Q_{1000}}{Q_{1000}} \quad (\text{I:3.5})$$

All results are given in Tables IA.1-IA.5 in the APPENDIX TO PART I.

The development of degree of hydration is much slower for the coarse fraction than for the ordinary cement and for the fine fraction, as shown in Figure I:3.1.

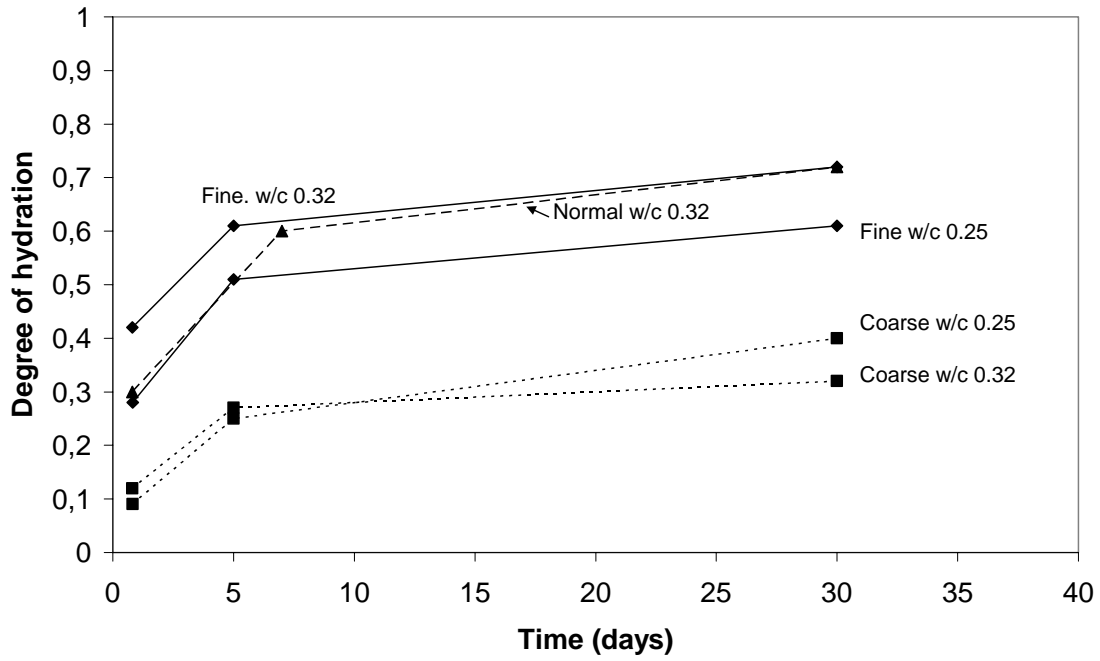


Figure I:3.1: Degree of hydration for different fractions of the cement.

I:4 WATER-CEMENT RATIO

In most cases the water-cement ratio can be obtained from the recipe. There might be some separation, however, making the real water-cement ratio a bit different, normally it is lower. The *true* water-cement ratio can be calculated from the measured total water content of the saturated specimen (free+chemically bound) reduced by the curing water sucked in during water storage, the suction being caused by the “volume contraction” when water is chemically bound. Thus, the amount of mixing water (w_o) can be calculated by

$$w_o = (Q_{\text{sat}} - Q_{1000}) - w_{\text{curing}} \quad (\text{g}) \quad (\text{I:4.1})$$

The volume of the curing water corresponds to about 25% of the amount of chemically bound water w_n , Powers (1960). Using the specific volume of water $1 \text{ cm}^3/\text{g}$ gives

$$w_{\text{curing}} = 0.25 \cdot w_n = 0.25 \cdot (Q_{105} - Q_{1000}) \quad (\text{g}) \quad (\text{I:4.2})$$

Then, the amount of mixing water becomes

$$w_o = (Q_{\text{sat}} - Q_{1000}) - 0.25 \cdot (Q_{105} - Q_{1000}) \quad (\text{g}) \quad (\text{I:4.3})$$

The water-cement ratio becomes

$$(w/c)_o = [(Q_{\text{sat}} - Q_{1000}) - 0.25 \cdot (Q_{105} - Q_{1000})] / Q_{1000} \quad (\text{I:4.4})$$

The measured “water-cement ratio” of the saturated specimen before the correction for curing water is

$$(w/c)_{\text{sat},o} = (Q_{\text{sat}} - Q_{1000}) / Q_{1000} \quad (\text{I:4.5})$$

The relation between the true water-cement ratio $(w/c)_o$ and the measured $(w/c)_{\text{sat},o}$ is obtained by combining equations (I:4.4) and (I:4.5) and introducing equations (I:3.4) and (I:4.2)

$$(w/c)_o = (w/c)_{\text{sat},o} - 0.25(w_n/c) = (w/c)_{\text{sat},o} - 0.25 \cdot 0.25 \cdot \alpha \quad (\text{I:4.6})$$

$$(w/c)_o = (w/c)_{\text{sat},o} - 0.0625 \cdot \alpha \quad (\text{I:4.6'})$$

Example I:4.1

The following weights were obtained for a certain cement paste:

$$Q_{\text{sat}} = 203 \text{ g}$$

$$Q_{105} = 139 \text{ g}$$

$$Q_{1000} = 121 \text{ g}$$

The water-cement ratio becomes; equation (I:4.4)

$$(w/c)_o = [(203 - 121) - 0.25 \cdot (139 - 121)] / 121 = 0.641$$

Note: If no correction for curing water is made the calculated water-cement ratio should instead be $(w/c)_{\text{sat,o}}=(203-121)/121=0.678$

Note: The true water-cement ratio can also be calculated by equation (I:4.6)

The degree of hydration is, equation (3.5): $\alpha=4\cdot(139-121)/121=0.595$

Equation (I.4.6) gives: $(w/c)_o=0.678-0.0625\cdot0.595=0.641$

I:5 DEFINITION OF POROSITY

Total porosity is based on the dry weight after drying to equilibrium at +105°C in an oven with fixed vapour pressure corresponding to x% relative humidity. The method was developed by Danielsson (1974). The dry weight obtained in this way is about the same as after so-called D-drying; defined in Powers (1960). Total porosity, P_{tot} , is the difference in water volume between full saturation and the dry state.

33% porosity (“*capillary porosity*”) is based on the weight after drying to equilibrium in 33% relative humidity. Drying is made in a vessel containing a saturated CaCl₂-solution and CO₂-free air. 33% porosity is the difference in water volume between full saturation and the water volume at equilibrium with 33% RH. The 33% porosity is not exactly the same as capillary porosity, see below.

In calculating these water volumes the *weight* of water is used, whereby the density of all pore water is assumed to be 1g/cm³.

I:6 TOTAL POROSITY

I:6.1 Total porosity-experimentally

The water content (w_{sat}) at full saturation is

$$w_{\text{sat}} = Q_{\text{sat}} - Q_{105} \quad (\text{g}) \quad (\text{I:6.1})$$

The volume of water at saturation is equal to the total pore volume ($V_{\text{p,tot}}$), i.e.

$$V_{\text{p,tot}} = v_w \cdot w_{\text{sat}} = 1 \cdot w_{\text{sat}} \quad (\text{cm}^3) \quad (\text{I:6.2})$$

Where v_w is the specific volume of water ($1 \text{ cm}^3/\text{g}$).

The specimen volume (V) is (assuming no air-pores)

$$V = v_w \cdot w_o + v_c \cdot c = 1 \cdot w_o + 0.32 \cdot c \quad (\text{cm}^3) \quad (\text{I:6.3})$$

Where w_o is the amount of mixing water (g), v_c is the specific volume of cement ($\approx 0.32 \text{ cm}^3/\text{g}$), and c is the cement weight (g).

The total porosity (P_{tot}) is

$$P_{\text{tot}} = V_{\text{p,tot}}/V = (Q_{\text{sat}} - Q_{105}) / (w_o + 0.32 \cdot c) = (Q_{\text{sat}} - Q_{105}) / \{c \cdot [(w/c)_o + 0.32]\} \quad (\text{I:6.4})$$

$(w/c)_o$, the water-cement ratio, is given by equation (I:4.4). c is given by equation (I:3.2). Inserting these equations gives

$$P_{\text{tot}} = \frac{Q_{\text{sat}} - Q_{105}}{(Q_{\text{sat}} - Q_{1000}) - 0.25(Q_{105} - Q_{1000}) + 0.32 \cdot Q_{1000}} \quad (\text{I:6.5})$$

Example I:6.1

The same cement paste as Example I:4.1.

$$P_{\text{tot}} = (203 - 139) / [(203 - 121) - 0.25 \cdot (139 - 121) + 0.32 \cdot 121] = 0.551 \quad (55.1\%)$$

Note: if no correction for curing water was made the calculated porosity would be

$$P_{\text{tot}} = (203 - 139) / [(203 - 121) + 0.32 \cdot 121] = 0.530 \quad (53\%)$$

The reason why the last porosity is erroneously low is that the specimen volume is assumed to be too high since all water in the specimen is supposed to come from the mixing water. In reality some of the water (curing water) is sucked into the specimen and does not contribute to the specimen volume.

I:6.2 Total porosity-theoretically

The total volume V is given by equation (I:6.3).

The total pore volume ($V_{p,tot}$) is given by

$$V_{p,tot} = w_o - v_{wn} \cdot w_n \quad (\text{cm}^3) \quad (\text{I:6.6})$$

Where v_{wn} (cm^3/g) is the specific volume of chemically bound water.

w_n can be expressed in terms of degree of hydration α using equation (I:3.4). Inserting this in equation (I:6.6) gives

$$V_{p,tot} = w_o - v_{wn} \cdot 0.25 \cdot \alpha \cdot c \quad (\text{cm}^3) \quad (\text{I:6.7})$$

The specific volume v_{wn} is of the order 0.75, Powers (1960). Thus, bound water “occupies” smaller volume than free water. The value 0.75 can be interpreted as a volume reduction of 25% when water is bound, (see also equation (I:4.2)). Inserting this value gives

$$V_{p,tot} = w_o - 0.75 \cdot 0.25 \cdot \alpha \cdot c = w_o - 0.188 \cdot \alpha \cdot c \approx w_o - 0.19 \cdot \alpha \cdot c \quad (\text{cm}^3) \quad (\text{I:6.8})$$

The equation is based on the assumption that no volume change (contraction) of the specimen occurs during hydration. Thus, the 25% volume reduction of chemically bound water does not cause any contraction. Instead air-filled space appears. This absorbs water when the specimen is stored in water, which is the reason why the fictitious water/cement ratio of the water-stored specimen $(w/c)_{\text{sat},o}$ is bigger than the true water-cement ratio $(w/c)_o$.

The total porosity is obtained by division of V_p by V , i.e. division of equation (I:6.8) by equation (I:6.3). The result is

$$P_{tot} = (w_o - 0.19 \cdot \alpha \cdot c) / (w_o + 0.32 \cdot c) \quad (\text{I:6.9})$$

Division by the cement content c gives

$$P_{tot} = \frac{(w/c)_o - 0.19 \cdot \alpha}{(w/c)_o + 0.32} \quad (\text{I:6.10})$$

A more general expression is

$$P_{tot} = \frac{(w/c)_o - v_{wn} \cdot (w_n/c)_{\text{max}} \cdot \alpha}{(w/c)_o + 0.32} \quad (\text{I:6.11})$$

Where $(w_n/c)_{\text{max}}$ is the amount of chemically bound water at complete hydration, $\alpha=1$, $(w_n/c)_{\text{max}}$ in equation (I:6.9) and (I:6.10) is assumed to be 0.25.

Equation (I:6.11) can also be written

$$P_{tot} = \frac{(w/c)_o - k \cdot \alpha}{(w/c)_o + 0.32} \quad (\text{I:6.12})$$

Where k is a coefficient including both “chemical contraction” of water (v_{wn}) and chemically bound water at complete saturation ($(w_n/c)_{max}$).

Example I:6.1

A cement paste with water-cement ratio 0.82 and 86% degree of hydration. Equation (I:6.10) gives

$$P_{tot} = (0.82 - 0.19 \cdot 0.86) / (0.82 + 0.32) = 0.576 \text{ (57.6\%)}$$

Example I:6.2

The same cement paste as example I:6.1, but the parameter $(w_n/c)_{max} = 0.20$ and the parameter $v_{wn} = 0.70$. Equation (I:6.11) gives

$$P_{tot} = (0.82 - 0.70 \cdot 0.20 \cdot 0.86) / (0.82 + 0.32) = 0.614 \text{ (61.4\%)}$$

I:6.3 Total porosity - results of measurements

The results of all measurements of the degree of hydration and the saturated water content $(w/c)_{\text{sat},o}$ are shown in Tables IA.1-IA.5 in the APPENDIX TO PART I. Also the true water-cement ratio $(w/c)_o$ calculated by equation (I:4.6) is shown in the tables.

The following comments can be made:

1. For cement pastes without aerosil and with high water-cement ratio the difference between the real water-cement ratio $(w/c)_o$ of the hardened paste and the water-cement ratio at mixing w_o/c is considerable which depends on separation.
2. With a small amount of aerosil almost no separation occurred even at water-cement ratio 1.
3. The spread in calculated true water-cement ratio $(w/c)_o$ between specimens of different age is very small for all initial water-cement ratios, indicating low variation within specimens from the same mix. The almost constant values of $(w/c)_o$ for different concrete age also strengthens the validity of equation (I:4.6).

Note, the value of the fictitious water-cement ratio $(w/c)_{\text{sat},o}$ increases with increased degree of hydration, which is a consequence of time dependent water absorption in “contraction pores” formed by chemical shrinkage.

I:6.4 Comparison between measured and calculated total porosity

All measured and calculated porosities are plotted in Figure I:6.1. The agreement is almost perfect. The following regression line is obtained

$$k=0.19: P_{tot, calc} = 0.003 + 0.982 \cdot P_{tot, meas} \quad r^2=1.00 \quad (I:6.13)$$

The correlation coefficient is remarkably high, considering that the data include cement pastes with water-cement ratio from 0.18 to 1.00, and degrees of hydration from 9% to 81%. Thus, the relation covers all cement pastes that are of practical interest.

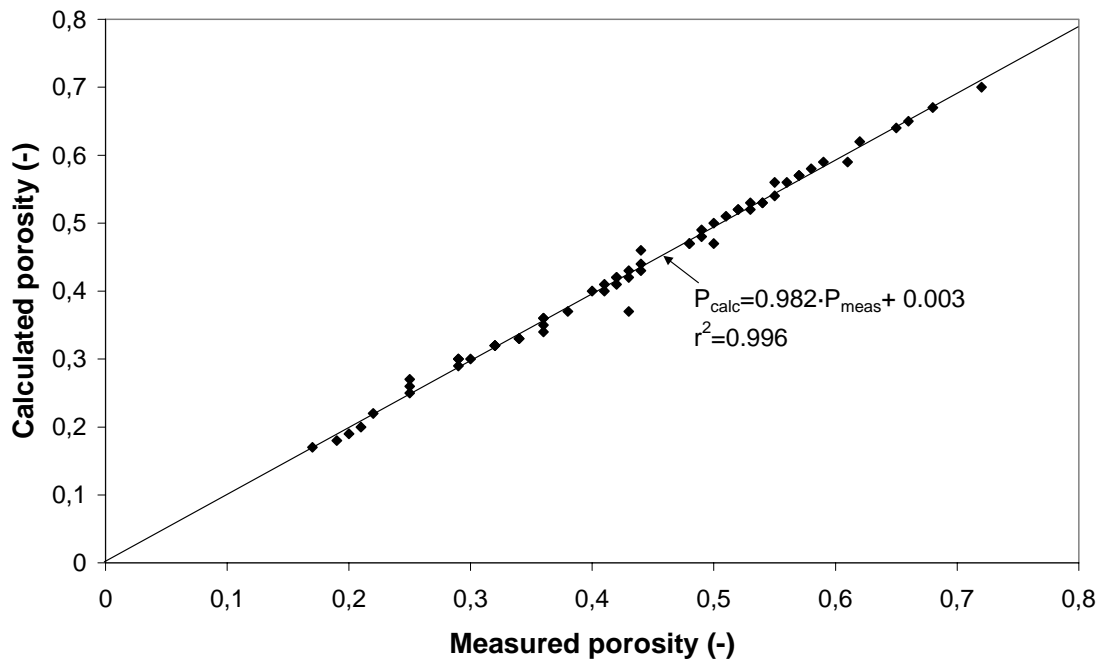


Figure I:6.1: Relation between the measured total porosity and the total porosity calculated by equation (I:6.10). ($k=0.19$).

The small deviation between measurement and calculation can be explained by an error in the coefficient selected for the parameters v_{wn} and $(w_n/c)_{max}$. In equation (I:6.10) the product of these was supposed to be 0.19 (rounded off value from the calculated value 0.188).

If instead $k=0.18$ inserted in equation (I:6.12) the relation between measured and calculated porosity will be:

$$k=0.18: P_{tot, calc} = 0.012 + 0.978 \cdot P_{tot, meas} \quad r^2=1.00 \quad (I:6.14)$$

The relation is shown in Figure I:6.2 together with measured and calculated porosities.

The two relations (I:6.13) and (I:6.14) are very similar. The correlation coefficient is the same for both relations and very high. Therefore, the analysis shows that anyone of the following relations can be used for calculation of total porosity

$$P_{tot} = \frac{(w/c)_o - 0.19 \cdot \alpha}{(w/c)_o + 0.32} \quad (I:6.10)$$

$$P_{tot} = \frac{(w/c)_o - 0.18 \cdot \alpha}{(w/c)_o + 0.32} \quad (I:6.15)$$

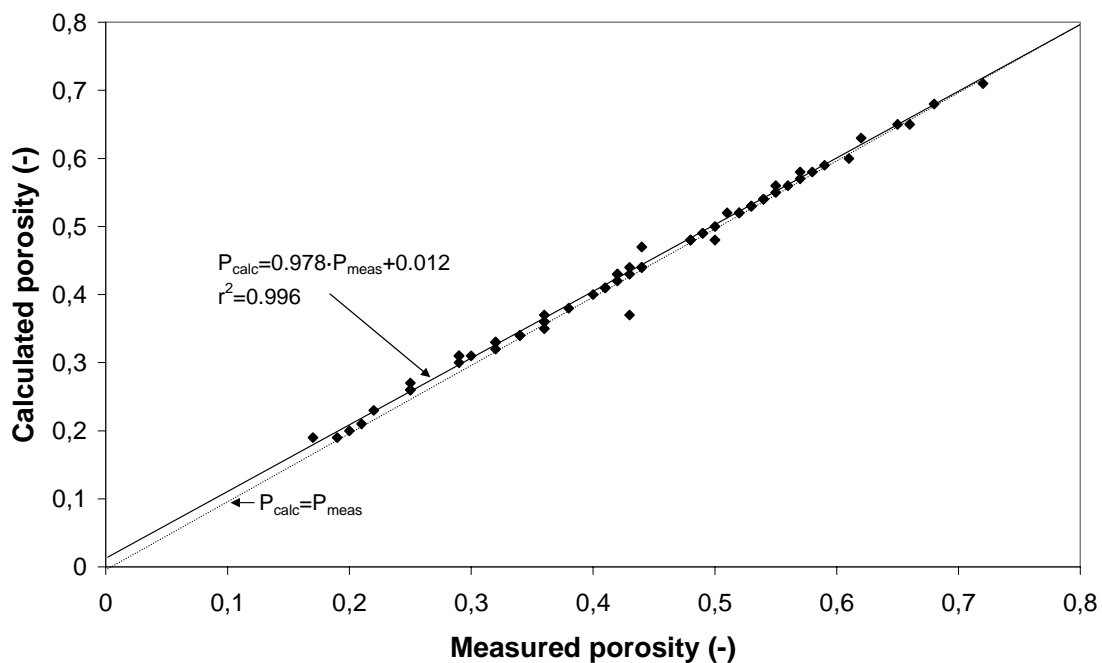


Figure I:6.2: Relation between the measured total porosity and the total porosity calculated by equation (I:6.15). ($k=0.18$).

The error in calculated porosity is quite low for both expressions as shown in Figure I:6.3. Equation (I:6.10) gives almost perfect agreement at low porosities, but it will always somewhat underestimate the porosity. For high porosities, frequently occurring in practice (60%), it underestimates the porosity by about 0.6%. Equation (I:6.15) on the other hand gives perfect agreement at about 50% porosity. For lower porosities it overestimates the porosity by maximum 0.7%, and for higher porosities it underestimates the porosity by maximum 0.3%.

Example I:6.3

A cement paste with w/c-ratio 0.35 and 50% hydration.

P_{calc} equation (I:6.10): $(0.35 - 0.19 \cdot 0.5) / (0.35 + 0.32) = 0.381 = 38.1\%$

P_{calc} equation (I:6.15): $(0.35 - 0.18 \cdot 0.5) / (0.35 + 0.32) = 0.388 = 38.8\%$

The difference in porosity is 0.7%

Example I:6.4

A cement paste with w/c-ratio 0.80 and 20% hydration.

$$P_{\text{calc}} \text{ equation (I:6.10): } (0.80-0.19 \cdot 0.2)/(0.80+0.32)=0.680=68.0\%$$

$$P_{\text{calc}} \text{ equation (I:6.15): } (0.80-0.18 \cdot 0.2)/(0.80+0.32)=0.682=68.2\%$$

The difference in porosity is only 0.2%.

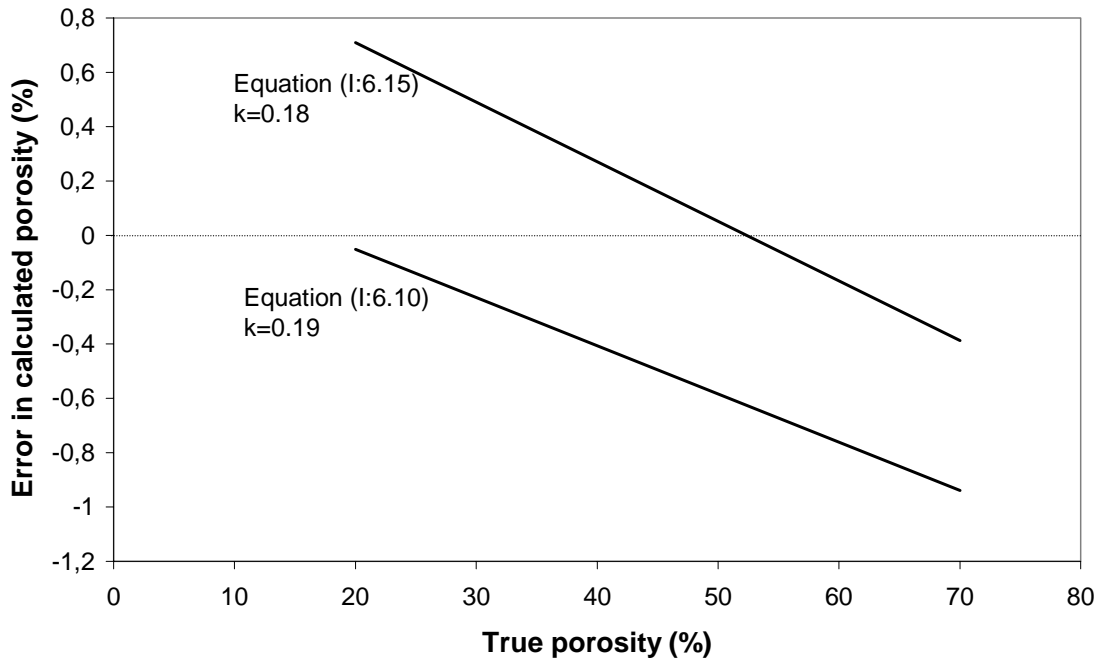


Figure I:6.3: Error in calculated porosity calculated by equations (I:6.10) and (I:6.15).

I:7 COARSE POROSITY

I:7.1 Definition of coarse porosity

By “coarse porosity” is, in this report, meant pore volume that is not water-filled when the material is at equilibrium with 33% relative humidity (RH). According to the Kelvin law for capillary condensation (probably not valid for a relative humidity as low as 33%, however) water-filled pores at 33% RH are pores containing a water meniscus with radius of about 10Å (corresponding to the thickness of about 3 water molecules stacked on top of each other). The pore size is somewhat bigger since also an adsorbed layer is present. The thickness of this corresponds to about 1 to 1.5 molecules adsorbed water, i.e. about 2.9 to 4.4 Å. Thus, pores that are water-filled above 33% RH have radii above about 13 Å to 14Å (1.3 to 1.4 nm).

The coarse porosity defined in this way is not the same as, but similar to, the “capillary porosity” as defined by Powers (1960). Therefore, it is interesting to compare the experimentally observed coarse porosity with the calculated capillary porosity. The method is described below in paragraph I:7.3.3. The coarse porosity can also be calculated from the sorption isotherm at 33% RH. The method is described below in paragraph I:7.3.1 and I:7.3.2.

I:7.2 Coarse porosity – experimentally

The coarse pore volume is calculated by

$$V_{p,coarse} = v_w(w_{sat} - w_{33}) \quad (\text{cm}^3) \quad (\text{I:7.1})$$

where w_{sat} (g) is the water weight at complete saturation and w_{33} (g) is the water weight at equilibrium with 33% RH. v_w is the specific volume of water ($1 \text{ cm}^3/\text{g}$).

Using the observed weights give

$$V_{p,coarse} = Q_{sat} - Q_{33} \quad (\text{cm}^3) \quad (\text{I:7.2})$$

The total volume is given by equation (I:6.3). Hence, the coarse porosity becomes

$$P_{coarse} = \frac{Q_{sat} - Q_{33}}{(w/c)_o + 0.32} \quad (\text{I:7.3})$$

Inserting equation (I.4.3) for w_o and equation (I.3.2) for c gives:

$$P_{coarse} = \frac{Q_{sat} - Q_{33}}{(Q_{sat} - Q_{1000}) - 0.25(Q_{105} - Q_{1000}) + 0.32 \cdot Q_{1000}} \quad (\text{I:7.3}')$$

I:7.3 Coarse porosity – theoretically

I:7.3.1 Calculated from the adsorption isotherm

Adsorption isotherms for Portland cement pastes were determined in the classical work of Powers & Brownyard (1948). In this work the water content at each RH was expressed in terms of the number of water molecule layers adsorbed to the pore wall predicted by the BET-theory. For adsorption in the range below about 45% RH the equilibrium water content was found to be independent of the water-cement ratio. This is seen in Figure I:7.1 showing adsorption isotherms for 3 cement pastes with different water-cement ratios.

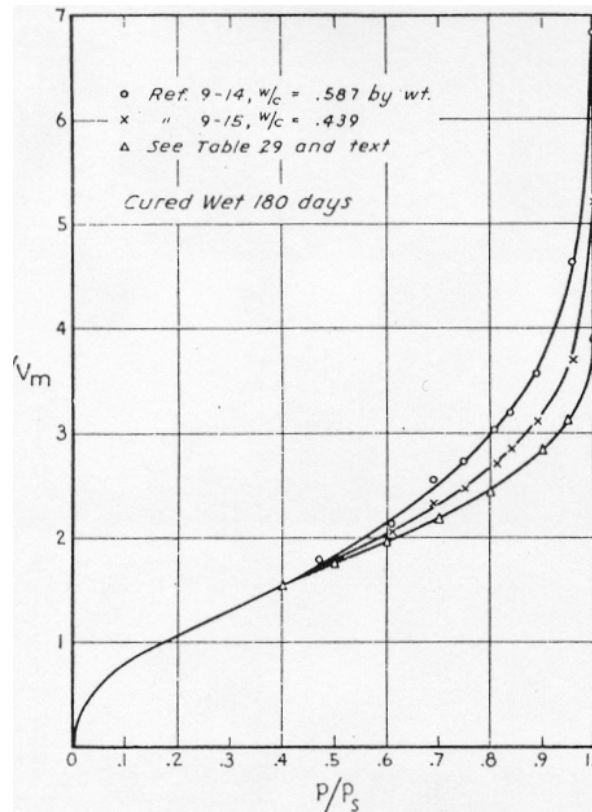


Figure I:7.1: Adsorption isotherms for Portland cement paste with three different water-cement ratios, Powers & Brownyard (1948). p/p_s is the relative vapour pressure, which is equal to the relative humidity (RH).

At 33% RH the equilibrium water content ($w_{33,ads}$) corresponds to about 1.4 molecular layers.

$$w_{33,ads} = 1.4 \cdot w_m \quad (I:7.4)$$

The monolayer capacity w_m was found to be directly proportional to the amount of chemically bound water where the proportional coefficient was found to be about 0.26 for normal Portland cements, i.e.

$$w_m = k \cdot w_n \approx 0.26 \cdot w_n \quad (I:7.5)$$

Inserting equation (I:7.4) gives

$$w_m = 0.26 \cdot 0.25 \cdot \alpha \cdot c = 0.065 \cdot \alpha \cdot c \quad (\text{g}) \quad (\text{I:7.6})$$

The adsorbed water at 33% RH becomes

$$w_{33, ads} = 1.4 \cdot w_m = 1.4 \cdot 0.065 \cdot \alpha \cdot c = 0.091 \cdot \alpha \cdot c \quad (\text{g}) \quad (\text{I:7.7})$$

The volume of the empty coarse porosity at 33% RH is

$$V_{p,33,ads} = V_{p,tot} - v_w \cdot w_{33} \quad (\text{cm}^3) \quad (\text{I:7.8})$$

Where v_w is the specific volume of water in the fine water-filled pores. This is assumed to be the same as for bulk water, i.e. $v_w = 1 \text{ cm}^3/\text{g}$. (In reality, the specific volume might be somewhat lower. The value $0.9 \text{ cm}^3/\text{g}$ was suggested by Powers (1960))

Inserting equation (I:6.8) for $V_{p,tot}$ gives

$$V_{p,33,ads} = w_o - 0.19 \cdot \alpha \cdot c - 0.091 \cdot \alpha \cdot c = w_o - 0.28 \cdot \alpha \cdot c \quad (\text{cm}^3) \quad (\text{I:7.9})$$

Division with the total volume according to equation (I:6.3) gives the coarse porosity P_{33}

$$P_{33, ads} = \frac{V_{p,33, ads}}{V} = \frac{(w/c)_o - 0.28 \cdot \alpha}{(w/c)_o + 0.32} \quad (\text{I:7.10})$$

I:7.3.2 Calculated from the desorption isotherm

The equilibrium water content at desorption is somewhat higher than at adsorption. One example is shown in Figure I:7.2.

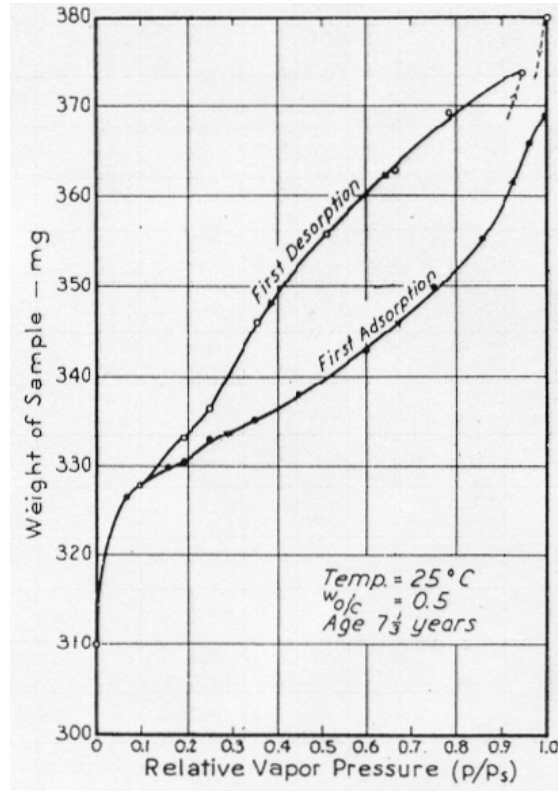


Figure I:7.2: The first desorption and the first adsorption isotherms for a cement paste with water-cement ratio 0.50, Powers & Brownyard (1948).

According to this figure the ratio between the water content at desorption and at adsorption is about

$$w_{33,des} = 1.35 \cdot w_{33,ads} \quad (I:7.11)$$

Thus, the water content at 33% RH becomes, see equation (I:7.7)

$$w_{33,des} = 1.35 \cdot w_{33,ads} = 1.35 \cdot 0.091 \cdot \alpha \cdot c = 0.123 \cdot \alpha \cdot c \quad (g) \quad (I:7.12)$$

The coarse pore volume at desorption becomes, see equation (I:6.8)

$$V_{p,33,des} = w_o - 0.19 \cdot \alpha \cdot c - 0.123 \cdot \alpha \cdot c = w_o - 0.31 \cdot \alpha \cdot c \quad (cm^3) \quad (I:7.13)$$

The coarse porosity at desorption becomes

$$P_{33,des} = \frac{V_{p,33,des}}{V} = \frac{(w/c)_o - 0.31 \cdot \alpha}{(w/c)_o + 0.32} \quad (I:7.14)$$

The only difference from the coarse porosity at adsorption is that the coefficient in front of α has been changed from 0.28 to 0.31.

I:7.3.3 Capillary porosity

The reaction products between cement and water -the cement gel- has a porosity of 28%, Powers (1960). Thus, the total gel volume is the sum of volumes of hydrated cement, chemically bound water and “gel pores”, which gives

$$V_{gel} = v_c \cdot \alpha \cdot c + v_{wn} \cdot w_n + 0.28 \cdot V_{gel} \quad (\text{cm}^3) \quad (\text{I:7.15})$$

Where v_c is the specific volume of cement ($\approx 0.32 \text{ cm}^3/\text{g}$) and v_{wn} is the specific volume of chemically bound water ($\approx 0.75 \text{ cm}^3/\text{g}$).

Inserting equation (I:3.4) for w_n gives

$$V_{gel} = (0.32 \cdot \alpha \cdot c + 0.75 \cdot 0.25 \cdot \alpha \cdot c) / 0.72 = 0.705 \cdot \alpha \cdot c \quad (\text{cm}^3) \quad (\text{I:7.16})$$

The gel pore volume is 28% of this

$$V_{p,gel} = 0.28 \cdot 0.705 \cdot \alpha \cdot c = 0.197 \cdot \alpha \cdot c \quad (\text{cm}^3) \quad (\text{I:7.17})$$

The “gel porosity” is obtained by division with the total volume described by equation (I:6.3)

$$P_{gel} = 0.197 \cdot \alpha \cdot c / (w_o + 0.32) = 0.197 \cdot \alpha / [(w/c)_o + 0.32] \quad (\text{I:7.18})$$

The capillary porosity is the difference between the total porosity given by equation (I:6.10) and the gel porosity given by equation (I:7.18)

$$P_{cap} = [(w/c)_o - 0.19 \cdot \alpha] / [(w/c)_o + 0.32] - 0.197 \cdot \alpha / [(w/c)_o + 0.32] \quad (\text{I:7.19})$$

$$P_{cap} = \frac{(w/c)_o - 0.39 \cdot \alpha}{(w/c)_o + 0.32} \quad (\text{I:7.20})$$

The coefficient 0.39 is afflicted by some uncertainties. It is a function of three material parameters, v_{wn} , $(w_n/c)_{max}$ and porosity of the cement gel. Values used in equation (I:6.10) for these parameters are $v_{wn} = 0.75$, $(w_n/c)_{max} = 0.25$ and $P_{gel} = 28\%$. A more general expression for the capillary porosity is

$$P_{cap} = \frac{(w/c)_o - K \cdot \alpha}{(w/c)_o + 0.32} \quad (\text{I:7.21})$$

Where K is a coefficient of the order 0.36-0.42.

I:7.3.4 RH-value corresponding to the capillary porosity

The relation between the coarse porosity calculated from the sorption isotherms and the capillary porosity is found by comparing the theoretical equations (I:7.10) or (I:7.14) with equation (I:7.20). It is directly seen by the equations that the capillary porosity is lower than the other two porosities. The only difference between the three equations is the coefficient in front of the degree of hydration. It is 0.39 for capillary porosity but only 0.28 and 0.31 for the other two porosities.

Example I:7.1

1: Low "coarse" porosity: $(w/c)_o=0.40$. $\alpha=0.7$:

$$\text{Equation (I:7.10) gives: } P_{33,ads}=0.283$$

$$\text{Equation (I:7.14) gives: } P_{33,des}=0.254$$

$$\text{Equation (I:7.20) gives: } P_{cap}=0.176$$

Thus

$$P_{cap}/P_{33,ads}=0.176/0.283=0.62$$

$$P_{cap}/P_{33,des}=0.176/0.254=0.69$$

2: High "coarse" porosity: $(w/c)_o=0.80$. $\alpha=0.4$:

$$\text{Equation (I:7.10) gives: } P_{33,ads}=0.614$$

$$\text{Equation (I:7.14) gives: } P_{33,des}=0.604$$

$$\text{Equation (I:7.20) gives: } P_{cap}=0.575$$

Thus

$$P_{cap}/P_{33,ads}=0.575/0.614=0.94$$

$$P_{cap}/P_{33,des}=0.575/0.604=0.95$$

RH-value on the adsorption isotherm corresponding to the capillary porosity

According to the Powers & Brownyard *adsorption* isotherm -Figure I:7.1- the capillary porosity should correspond to about *3.1 molecular layers of adsorbed water*, which is proven by the following analysis.

At 3.1 molecular layers, the amount of adsorbed water is (c.f. equation (I:7.7))

$$w_{33,ads}=3.1 \cdot 0.065 \cdot \alpha \cdot c = 0.20 \cdot \alpha \cdot c \quad (\text{I:7.22})$$

Then, equation (I:7.8) gives the following equation for the empty pore volume

$$V_{p,33,ads}=w_o - 0.19 \cdot \alpha \cdot c - 0.20 \cdot \alpha \cdot c = w_o - 0.39 \cdot \alpha \cdot c \quad (\text{I:7.23})$$

Dividing with the total volume gives the empty porosity

$$P_{33,ads} = [(w/c)_o - 0.39 \cdot \alpha \cdot c] / [(w/c)_o + 0.32] \quad (\text{I:7.24})$$

But, this is the same as the capillary porosity, see equation (I:7.20).

3.1 molecular layers correspond to more than 80% RH if only pure adsorption is considered; see Figure I:7.1. At such high RH there is also capillary condensation, which is seen in Figure I:7.1 by the fact that the different adsorption isotherms for different water-cement ratio when $RH > 45\%$; the higher the w/c-ratio, the higher the isotherm. Therefore, the true RH-value corresponding to capillary porosity is also dependent on the water-cement ratio. The RH-value can therefore vary between about 60% and 90% RH depending on the w/c-ratio.

RH-value on the desorption isotherm corresponding to the capillary porosity

3.1 adsorbed water layers corresponds to 90% RH on the lowest adsorption isotherm in Figure I:7.1 (the “gel isotherm” valid for a cement paste with no capillary pores; i.e a paste with no or very low capillary condensation). According to Figure I:7.2 this RH on the adsorption isotherm corresponds to about 60% RH on the desorption isotherm. This RH-value is also within the capillary condensation range which makes it impossible to find one single RH-value that corresponds to the capillary porosity.

The analysis shows that it is not possible to find one single RH-value on the adsorption or the desorption isotherm that corresponds to the capillary porosity. The value will depend on the water-cement ratio.

I:7.4 Comparison between measured and calculated coarse porosity

All results of measured and calculated coarse porosity are shown in Table IA1-IA5 in the APPENDIX TO PART I.

A: Based on the Powers & Brownyard *adsorption isotherm*

The relation between the measured coarse porosity and the coarse porosity calculated from the Powers & Brownyard *adsorption isotherm* is plotted in Figure I:7.3. The agreement is fair. The following regression line is obtained

$$P_{33,ads} = 1.02 \cdot P_{coarse,meas} + 0.016 \quad r^2=0.99 \quad (I:7.25)$$

The correlation coefficient is remarkably high considering that the data include cement pastes with water-cement ratio from 0.18 to 1.00, and degrees of hydration from 9% to 81%. The regression line passes very close to the origin. The deviation between the calculated and measured porosity is fairly small. For very high porosities the calculated porosity overestimates the real porosity. The difference is not very big, however.

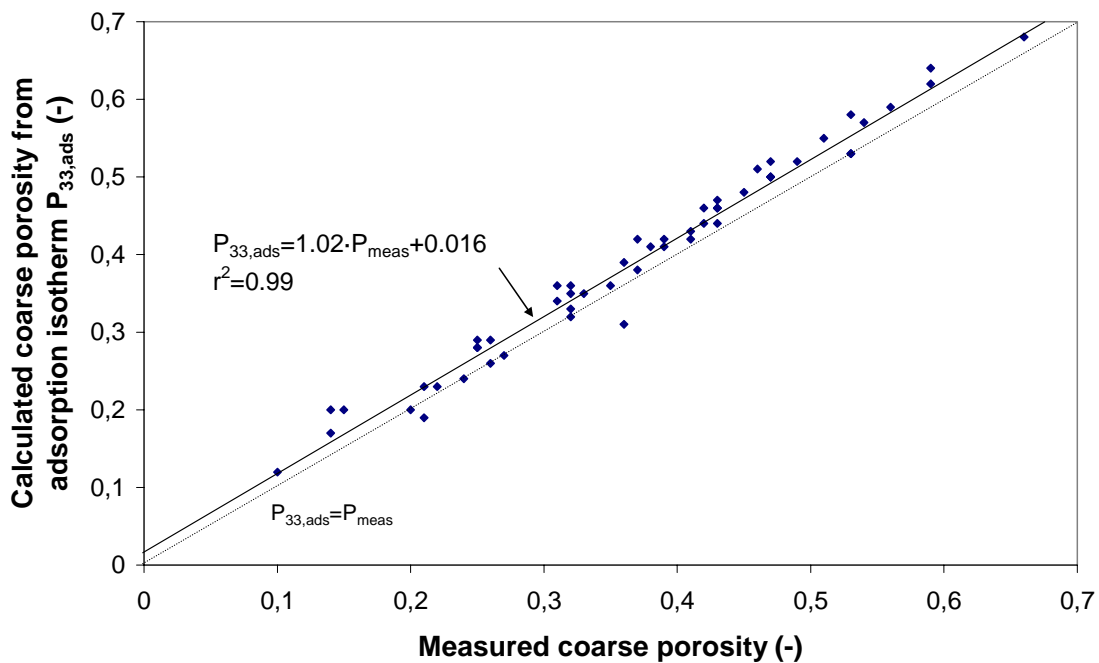


Figure I:7.3: Relation between the measured coarse porosity and the porosity calculated from the Powers & Brownyard *adsorption isotherm* for 33% RH, equation (I:7.10).

B: Based on the Powers & Brownyard desorption isotherm

The measured coarse porosity is based on desorption to 33% RH. Therefore, it is more logical to compare with porosity calculated from the desorption isotherm. Such a comparison is shown in Figure I:7.4. The agreement is good. The following regression line is obtained

$$P_{33, des} = 1.05 \cdot P_{coarse, meas} - 0.018 \quad r^2 = 0.99 \quad (I:7.26)$$

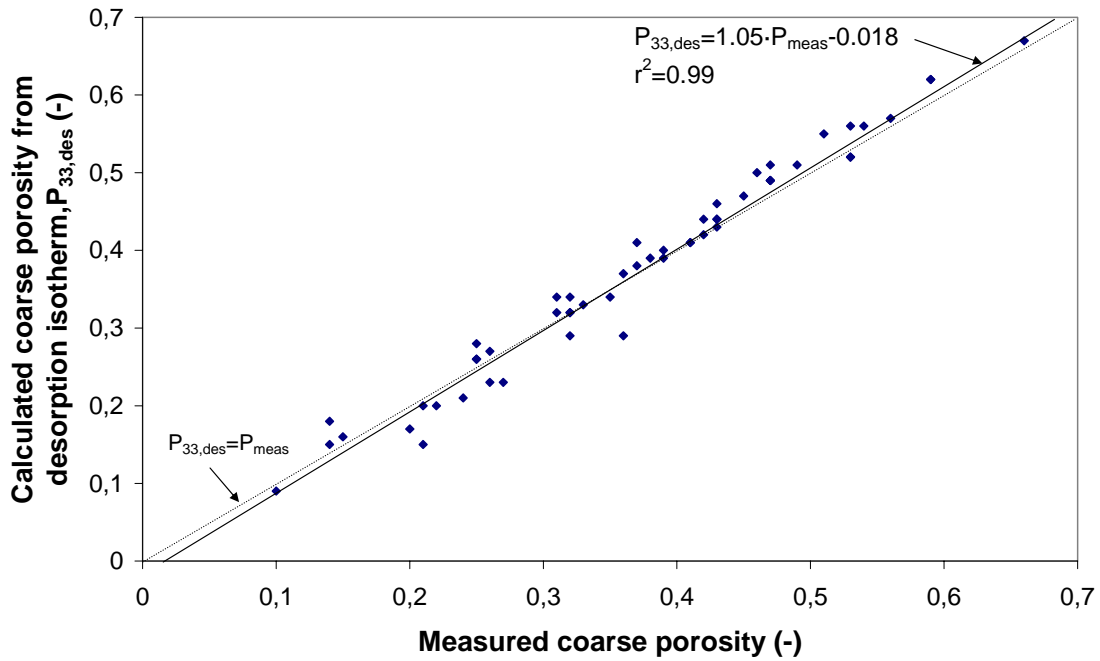


Figure I:7.4: Relation between the measured coarse porosity and the porosity calculated from the Powers & Brownyard **desorption** isotherm for 33% RH, equation (I:7.14).

C: The capillary porosity

The relation between the measured coarse porosity and the capillary porosity defined by equation (I:7.20) is shown in Figure I:7.5. The regression line is

$$P_{cap} = 1.19 \cdot P_{coarse, meas} - 0.117 \quad r^2=0.98 \quad (I:7.27)$$

This relation has a high correlation coefficient, but the rather big difference between the calculated and measured porosity, especially for low porosities, clearly indicates that the 33% RH equilibrium moisture content cannot be used as a measure of the capillary porosity.

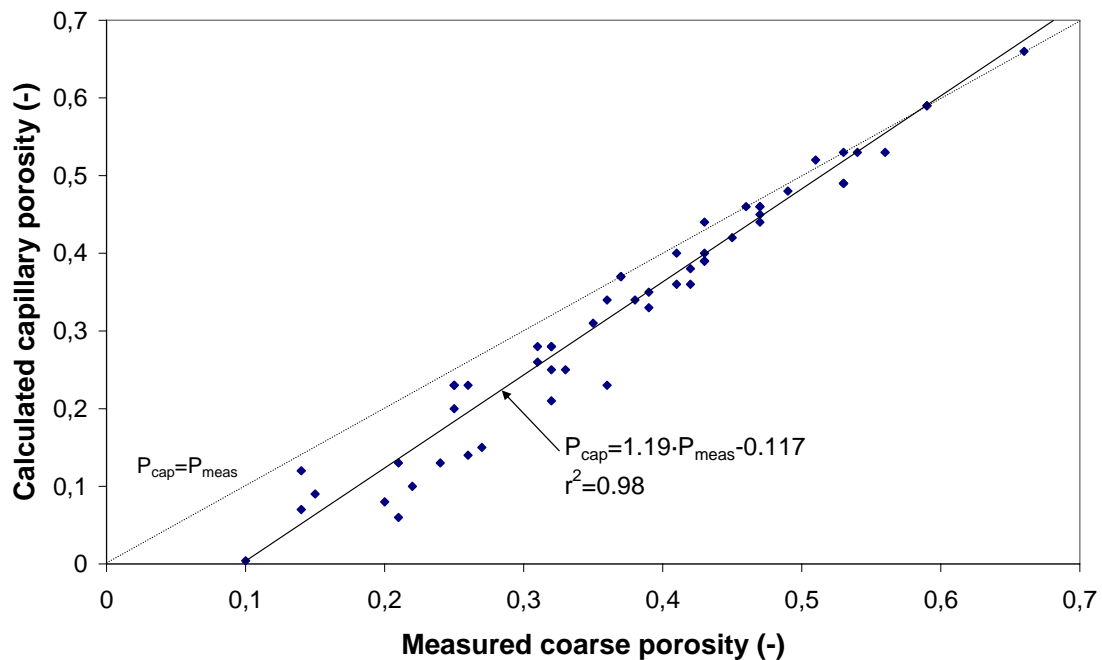


Figure I:7.5: Relation between the measured coarse porosity and the calculated capillary porosity, equation (I:7.20)

D: Discussion of errors

The error in calculated porosity is plotted in Figure I:7.6. Calculations based on the desorption isotherm according to Powers & Brownyard give the best agreement with measurement which is logical since also the measurements were made on desorbed specimens.

Thus, it seems as if the “old” Powers & Brownyard desorption isotherm, as defined by equation (I:7.14) for 33% RH, in a good manner describes the experimentally determined equilibrium water content at this RH-value for cement pastes with a wide variation in water-cement ratio and degree of hydration.

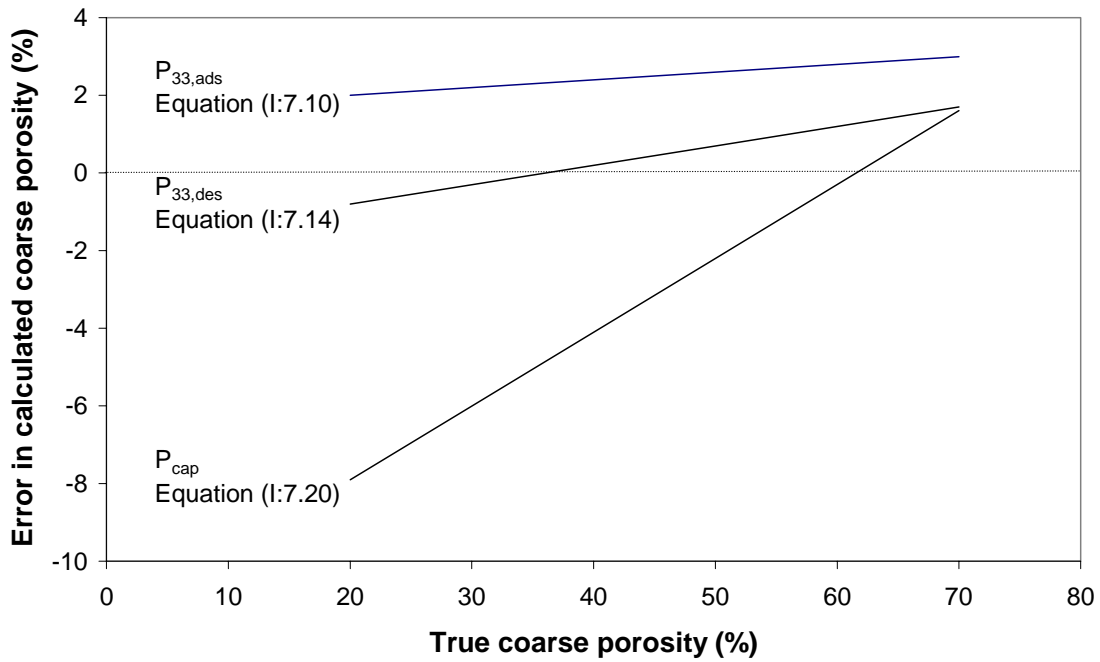


Figure I:7.6: Error in calculated porosity calculated by equations (I:7.10), (I:7.14) and (I:7.20). (“True porosity”=observed porosity)

Note: A relation between the capillary porosity and the coarse porosities defined from the sorption isotherms at 33% RH can be found by combining the “mean equations” (I:7.25) for adsorption or equation (I:7.26) for desorption with equation (I:7.27)

$$P_{cap}=1.17 \cdot P_{33,ads} - 0.136 \quad (I:7.28)$$

$$P_{cap}=1.13 \cdot P_{33,des} - 0.097 \quad (I:7.29)$$

Example I:7.2 (The same as example I:7.1)

1: Low “coarse” porosity: $(w/c)_o=0.40$. $\alpha=0.7$:

$$P_{cap}=0.176 \text{ Equation (I:7.20)}$$

$$P_{cap}/P_{33,ads}=0.66$$

$$P_{cap}/P_{33,des}=0.73$$

2: High “coarse” porosity: $(w/c)_o=0.80$. $\alpha=0.4$:

$$P_{cap}=0.575 \text{ Equation (I:7.20)}$$

$$P_{cap}/P_{33,ads}=0.95$$

$$P_{cap}/P_{33,des}=0.97$$

These relations are close to the relations calculated in example I:7.1.

I:8 SPECIFIC SURFACE

The inner specific surface of the cement paste describes the internal structure of the paste and the cement gel. The principles are described in Part II.

Some estimations of the specific surface can be made on basis of measurements in the present Part I. Data over total porosity and coarse porosity listed in Tables AI.1-AI.5 are used as input in the calculations. The precision in the data are however not big enough to give an accurate calculation. Despite this, the calculations are made and presented in APPENDIX TO PART I.

In Part II more precise calculations of specific surface and gel structure are made for a number of cement pastes based on measurements of the equilibrium weight at 33% RH and the dry weight.

PART II

SPECIFIC SURFACE AND GEL STRUCTURE

SUMMARY OF PART II

The aim of Part II is to use the Grudemo data to calculate the inner specific surface of *cement paste* as function of its water-cement ratio and degree of hydration. Another aim is to use the same data for calculation of the specific surface of the *cement gel*, and to calculate the size of gel pores and gel particles.

25 different cement pastes were included in the study. 6 of them were made with low alkali-sulfate resistant Portland cement, 18 were made with Danish white cement, 1 was a pure C₃S-paste. 3 of the white cement pastes contained 5 to 20% addition of semi-hydrate gypsum, 3 contained 5 to 20% silica gel, and 3 contained 2 to 4% ethylene glycol. The water-cement ratio was varied between 0.25 and 0.50. The age at testing in most cases varied between 1 and 28 days.

Degree of hydration

The degree of hydration was determined from the non-evaporable water content determined after drying to +105 °C and after ignition at 1000 °C. As expected the hydration rate is higher for cement with higher specific surface and for cement containing higher amount of C₃S; Figures II:3.1-II:3.2. It was also found that addition of silica gel and hemi-hydrate strongly reduced the amount of non-evaporable water for constant hydration time; Figures II:3.3-II:3.4.

Amount of calcium hydroxide (CH)

The amount of calcium hydroxide was determined by X-ray diffraction. As expected the CH content increased with increased degree of hydration; Figures II:3.5-II:3.6. Addition of silica gel reduced the amount of CH; the bigger the amount of silica gel the lower the CH-content; Figure II:3.7.

Specific surface of cement paste

The specific surface was calculated by the BET-theory using the measured equilibrium water content at the first *desorption* to 33% RH. In order to find the monomolecular capacity, which is supposed to correspond to the equilibrium water content at 17% RH, the water content at 33% RH is divided by the factor 1.38.

It was found that the specific surface of the cement paste is independent of the water-cement ratio and only dependent on the degree of hydration. This is in accordance with the Powers & Brownyard (1948) and the Powers (1960) observations. The following equation is valid:

$$S = \frac{K \cdot \alpha}{1 + 0.25 \cdot \alpha} \quad \text{m}^2/\text{kg} \quad (\text{II:6.8})$$

where K is a coefficient that is almost independent of the water-cement ratio and degree of hydration. $K \approx 3.7 \cdot 10^5$ for the LA/SR-cement; $K \approx 4.1 \cdot 10^5$ for the white cement. The Powers and Brownyard (1948) desorption isotherms gives $K \approx 3.2 \cdot 10^5$

This means that the specific surface of a cement paste with 80% hydration is about 250 m²/g. This can be compared with 210 m²/g which is calculated from the Powers and Brownyard (1948) desorption isotherm shown in Figure II:7.2.

Specific surface of cement gel

The specific surface of the entire cement gel *including the non-colloidal calcium hydroxide* is found by introducing $\alpha=1$ in the equation above:

$$\begin{array}{ll} \text{LA/SR-cement:} & S_{\text{gel}} \approx 300 \text{ m}^2/\text{g} \\ \text{White cement:} & S_{\text{gel}} \approx 330 \text{ m}^2/\text{g} \end{array}$$

The specific surface of white cement gel containing silica gel is higher than for the plain cement pastes. The most plausible reason is that the amount of calcium hydroxide is lower.

$$10\% \text{ silica gel:} \quad S_{\text{gel}} \approx 375 \text{ m}^2/\text{g}$$

Specific surface of “gel particles”

The specific surface of the gel particles *excluding the non-colloidal calcium hydroxide* is higher than for the total gel. If calcium hydroxide is supposed to have negligible surface area the net specific surface of the gel particles becomes:

$$\begin{array}{ll} \text{LA/SR-cement:} & S_{\text{gel,net}} \approx 430 \text{ m}^2/\text{g} \\ \text{White cement:} & S_{\text{gel,net}} \approx 550 \text{ m}^2/\text{g} \end{array}$$

Size of gel particles

The gel particles are assumed to be thin plates. The Grudemo desorption data give an average thickness of the plates including the calcium hydroxide of about 25 Å for both cement types.

The thickness of gel particles excluding the calcium hydroxide, assuming this to have negligible surface area, is reduced to about 14 to 18 Å.

Size of gel pores

The volume of gel pores is assumed to be 28% as shown by Powers (1960). Then, the Grudemo desorption data show that the width of slit like gel pores becomes about 10 Å if calcium hydroxide is included in the gel. If calcium hydroxide is excluded the width of the gel pores is increased to about 12 Å.

Effect of drying at +105C on the specific surface

The effect of drying is found by comparing the specific surface calculated from the first desorption isotherm on the never-dried specimen, and the first adsorption isotherm on the dried specimen. The Powers & Brownard data are used. It is found that drying decreases the specific surface by about 25% and increases the average width of the gel pore from about 10 Å to about 17 Å.

Comparison with the Powers & Brownard (1948) work

The Grudemo desorption data for a very wide spectrum of degree of hydration and water-cement ratio indicate that the specific surface of the cement paste is virtually independent of the water cement ratio. It is only a function of the degree of hydration. This is in accordance with earlier observations by Powers & Brownard (1948) and Powers (1960).

The calculated specific surface for the cement gel itself (i.e. at 100% hydration) is about 300 m²/g which can be compared with about 255 m²/g calculated from a typical Powers & Brownard (1948) first desorption isotherm, and about 210 m²/g calculated from an adsorption isotherm.

II:1 MATERIALS AND SPECIMENS

II:1.1 Mixing, casting and curing

The same procedures were used as for the specimens in Part I, see paragraph I.1.1.

Tests of the specimens were made after curing in saturated lime water for periods lasting from 1 day to 30 days (157 days for one series). An overview over curing times before testing is given in Table II.1

II:1.2 Cement

Main cement types

Three types of cements were used

- White cement (WhC)
- Low alkali, sulphate resistant Portland cement (LA/SR)
- Pure C₃S

The LA/SR-cement was the same as in Part I. Its composition is given in paragraph I.1.2.

The white cement had the following composition in weight-percent

C ₃ S	81
C ₂ S	6
C ₃ A	5
C ₄ AF	1
Limestone filler	0

Variations in cement

LA/SR-cement

A fine fraction (<37 μm) of the LA/SR-cement was also investigated. The same fine fraction was also studied in Part I.

White cement

Certain amounts of different additives were used in some mixes

1. Hemi-hydrate gypsum, CaSO₄·½H₂O (5 to 10 % added)
2. Amorphous silica gel (Aerosil) (5 to 20% added)
3. Ethylene glycol (2 to 6% added)

The aerosil and the ethylene glycol were primarily used for stabilizing the mixes against separation.

II:1.3 Specimens

The same type of cement paste specimens as described in paragraph I.1.3 were used for testing.

II:1.4 Mixes

In total 25 different mixes were studied. Characteristics of different mixes are shown in Table II:1.1.

Table II:1.1: Overview over mixes

Cement type	Additive		(w/c) _o	Age at testing days				
	Type	% ¹⁾						
LA/SR	No		0.25	1, 2, 3, 4, 6, 8, 12, 20, 28				
			0.32					
			0.40					
LA/SR Fine	No		0.32	2,4,8,16				
			0.40					
			0.50					
White cement	No		0.32	1, 2, 3, 4, 6, 8, 12, 19, 28				
			0.32	3, 9, 27				
			0.35					
			0.38					
			0.42					
			0.46					
			0.50					
			0.40	1, 2, 3, 4, 6, 8, 12, 18				
	Semi-hydrate	5 10 20	0.50	4, 8				
					Silica gel	5 10 20	0.50	1, 4, 8, 16
	5							
	5, 30							
	C ₃ S	No		0.40	2, 4, 8, 18, 157			

1) % of the cement weight

2) Including the ethylene glycol. The net w/c-ratio is 0.38, 0.36 and 0.34 respectively.

II:2 MEASUREMENTS

At terminated water curing the following procedures were undertaken (c.f. Figure I:2.1).

Determination of the degree of hydration (made on about 30 mm long specimens):

1. A cement paste specimen was crushed and ground in ethyl-alcohol in order to stop further hydration.
2. The powder was dried at +105°C by the method developed by Danielsson (1974). The dry weight was determined (Q_{105}).
3. The dry powder was ignited at +1000°C and weighed (Q_{1000}).
4. The degree of hydration was calculated by equation (I.3.5)

Determination of specific surface (made on about 3 mm thick slices):

1. The specimens were placed in a glass container connected to another glass vessel containing a saturated water solution of $MgCl_2$. The vessels were subjected to vacuum in order to avoid carbonation, and in order to decrease the time needed for the specimen to reach moisture equilibrium with air in the vessel (33% RH).
2. After moisture equilibrium had been reached the specimens were weighed (Q_{33}).
3. The specimens were dried at 105°C and the dry weight determined (Q_{105}).
4. Calculation of the specific surface was made, see equation (II:4.8) below.

In total 116 different tests were made. Furthermore, quantitative X-ray diffraction for determination of crystalline calcium hydroxide was performed on all samples except those containing ethylene glycol.

All data are listed in Tables AII.1-AII.5 in the APPENDIX TO PART II.

II:3 DEGREE OF HYDRATION. EVOLUTION OF CALCIUM HYDROXIDE

II:3.1 Degree of hydration

The degree of hydration is calculated by equation (I:3.5). The result is shown in APPENDIX TO PART II, Tables AII.1-AII.5.

The development of degree of hydration with time is plotted in Figures II:3.1 –II:3.4.

The following observations are made:

1. The hydration rate increases with increased water-cement ratio. This was also observed in Part I, see Figure I:3.1.
2. The hydration rate is higher for white cement than for the LA/SR-cement. *Example w/c=0.40*: The degree of hydration after 3 days is 0.50 for white cement and only 0.45 for LA/SR-cement. After 20 days the values are 0.65 and 0.56. The main reason is the higher amount of C₃S (and C₃A) in the white cement.
3. The hydration rate increases with increased fineness of the cement. This was also found in Part I, Figure I:3.1.
4. Addition of silica gel seems to accelerate the early hydration, but retard the long-term hydration; the higher the amount of silica gel, the bigger the long-term retardation. These conclusions might however not be correct, viz. the use of equation (I:3.5) for calculation of degree of hydration is not altogether correct for mixes containing silica gel. It was shown by Helsing Atlasi (1993) that there is no direct proportionality between the amount of chemically bound water and degree of hydration for mixes containing silica fume. The following relation for chemically bound water was given

$$w_n \approx 0.25 \cdot \alpha_C \cdot c - 0.34 \cdot \alpha_S \cdot S \cdot c \quad (\text{II:3.1})$$

Where α_C is the degree of hydration of the cement, and α_S is the degree of hydration of the silica gel. S is the amount of silica gel as weight fraction of the cement. The minus-sign in front of silica indicates that hydration of silica is a polymerization process that liberates previously bound water. This process was not known when Grudemo made his research.

Example

LA/SR-cement. w/c-ratio 0.40.10% silica gel, S=0.10. 28 days of hydration. Full hydration of silica gel ($\alpha_S=1$).

- “Believed” degree of hydration of the cement as judged by equation (I:3.5) after 28 days: $\alpha_C=0.60$ (Figure II:3.1)

-Observed amount of chemically bound water: $w_n = 0.25 \cdot 0.60 \cdot c = 0.15 \cdot c$

-Amount of water set free by hydration of silica gel: $0.34 \cdot 1 \cdot 0.10 \cdot c = 0.034 \cdot c$

-True degree of hydration of the cement calculated by equation (II:3.1):

$$\alpha_C = (0.15 + 0.034) / 0.25 = 0.74$$

The example shows that big under-estimates of degree of hydration of cement can be made if no correction for the effect of hydration of silica gel is made. The same is valid for concrete containing silica fume or reactive fly ash.

5. Addition of hemi-hydrate retards the hydration; the higher the amount of hemi-hydrate, the slower the reaction. Reactions between cement and hemi-hydrate are not considered at calculation of degree of hydration.

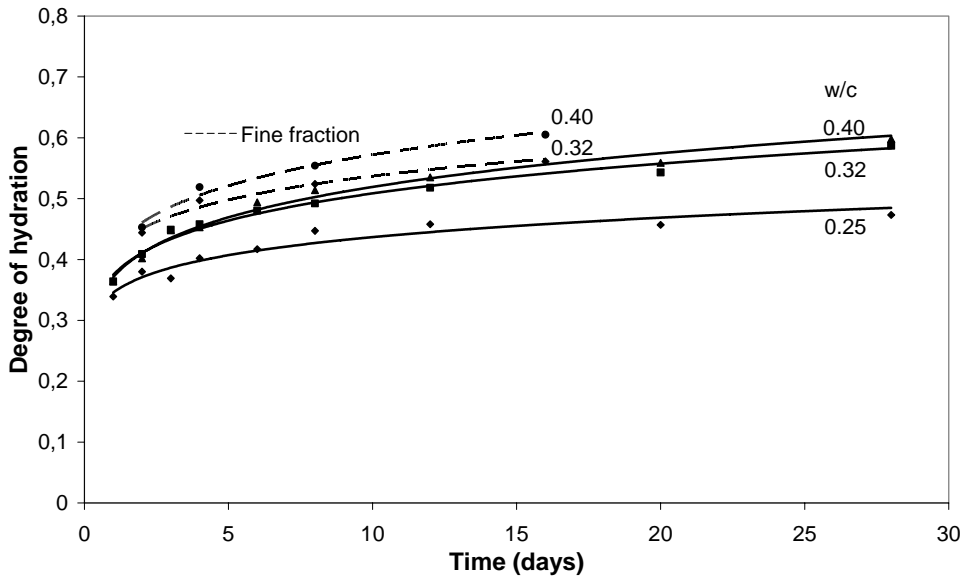


Figure II:3.1: Degree of hydration for LA/SR-cement

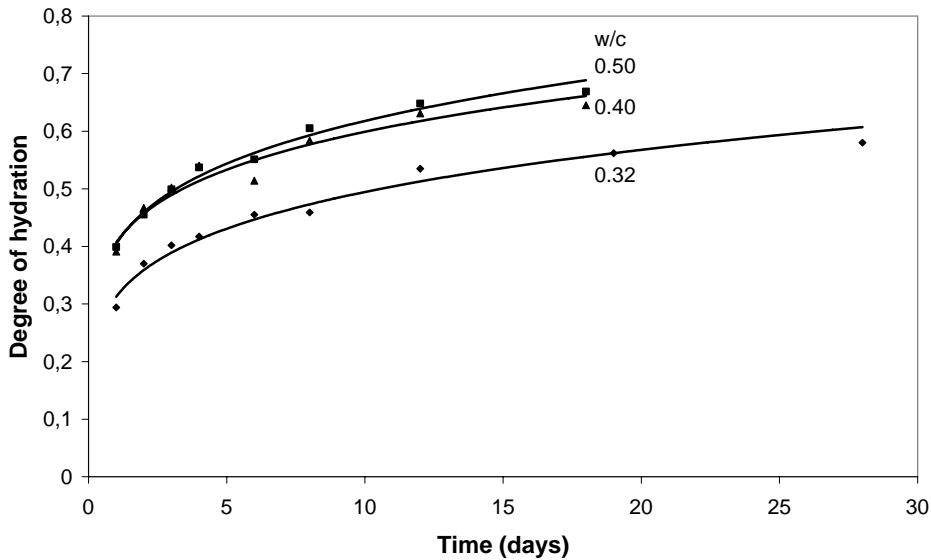


Figure II:3.2: Degree of hydration for white cement with no additives.

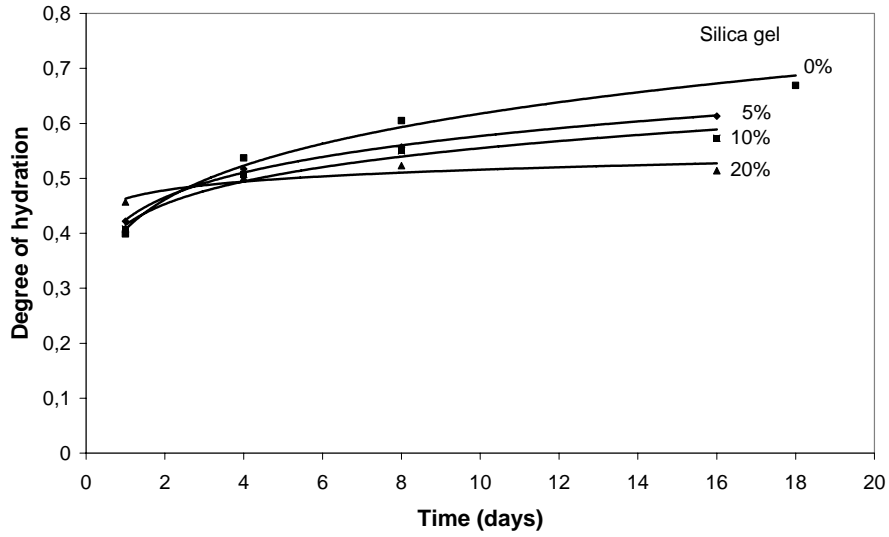


Figure II:3.3: Degree of hydration of white cement with addition of silica gel. No correction for the effect of hydration of silica gel, see above.

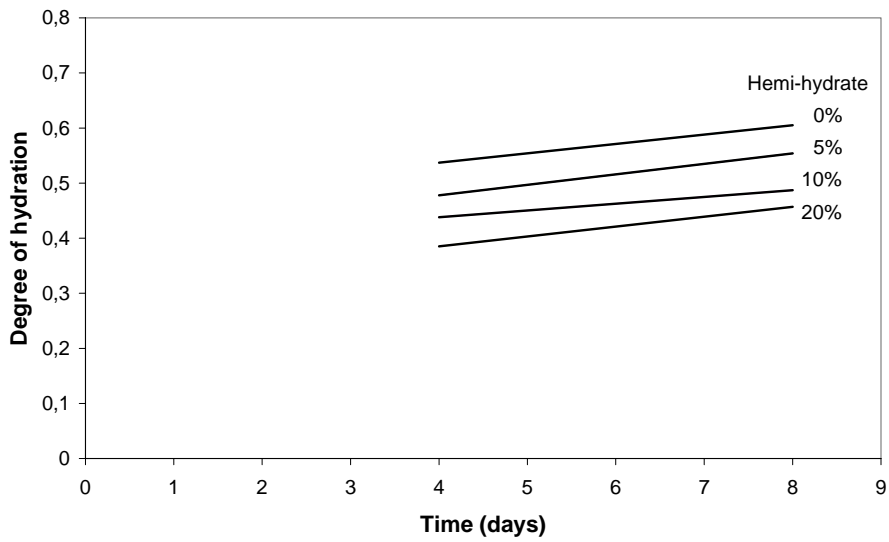


Figure II:3.4: Degree of hydration of white-cement with addition of hemi-hydrate. No correction for possible effect of “hydration” of hemi-hydrate.

II:3.2 Calcium hydroxide

The amount of crystalline calcium hydroxide (CH) was determined by quantitative X-ray diffraction on powdered samples dried at +105°C. Principles of the technique are described in Grudemo (1977).

The measurement gives the *weight fraction* of calcium hydroxide in the sample (weight-fraction of solid material). The total weight of dried solid material (with no additives) is

$$Q_{\text{solid}}=c+w_n=c(1+0.25\cdot\alpha) \quad (\text{g}) \quad (\text{II:3.2})$$

The total amount of crystalline calcium hydroxide (CH) becomes

$$\text{CH}_{\text{tot}}=\text{CH}_S\cdot c(1+0.25\cdot\alpha) \quad (\text{g}) \quad (\text{II:3.3})$$

Where the parameter CH_S is the measured amount of crystalline calcium hydroxide expressed as weight-fraction of all solid material.

The amount of calcium hydroxide as *weight fraction of the cement* becomes

$$\text{CH}_C=\text{CH}_{\text{tot}}/c= \text{CH}_S(1+0.25\cdot\alpha) \quad (\text{II:3.4})$$

For cement pastes with mineral additives equation (II:3.4) is modified to

$$\text{CH}_C= \text{CH}_S (1+R+0.25\cdot\alpha) \quad (\text{II:3.5})$$

Where the coefficient R is the amount of mineral additive as weight-fraction of cement. It is assumed that the density is the same for the additive as for the cement.

The measured amount of CH in weight-% of solid, and the calculated amount of CH as weight-% of cement, is shown in APPENDIX TO PART II, Tables AII.1-AII.5.

The amount of calcium hydroxide as function of the degree of hydration is shown in Figures II:3.5-II:3.7.

The following observations are made:

1. The amount of calcium hydroxide increases with increased degree of hydration. However, the results do not indicate a direct proportionality between CH and degree of hydration, which might depend on the rather big spread in results. One must expect that the amount of calcium hydroxide is zero at zero hydration. The trend lines do, however, erroneously predict considerable amounts of calcium hydroxide even before any hydration.
2. At equal degree of hydration the amount of calcium hydroxide is somewhat higher for the white cement than for the LA/SR-cement. The most plausible reason is the higher amount of C_3S in the white cement; more calcium hydroxide is developed at hydration of C_3S than at hydration of the same amount of C_2S .

Examples of results: 50% degree of hydration, w/c-ratio 0.40:

White cement: $CH_C \approx 0.28$.

LA/SR-cement: $CH_C \approx 0.24$.

3. At equal degree of hydration the amount of crystalline calcium hydroxide per kg cement is lower, the lower the water-cement ratio. The reason behind this observation is not completely clear. The most plausible explanation is that some calcium hydroxide is not registered at X-ray diffraction, Grudemo (19779). The fraction of non-detectable CH might possibly be higher, the lower the w/c-ratio.
4. The measured amount of calcium hydroxide is unexpectedly high. At 60% hydration the measured weight fraction of calcium hydroxide is about 25% for the LA/SR-cement and about 35% for the white cement. At complete hydration, assuming linear relations, this would lead to the weight fractions 42% and 58%. According to simple reaction formulas for Portland cements no more than about 30% and 41% should be expected at full hydration of the two cements. Probably, therefore, the quantitative X-ray diffraction used is afflicted with some uncertainties.
5. Addition of silica gel causes big reduction in the amount of calcium hydroxide. The most plausible explanation is that the silica gel reacts with calcium hydroxide and water.

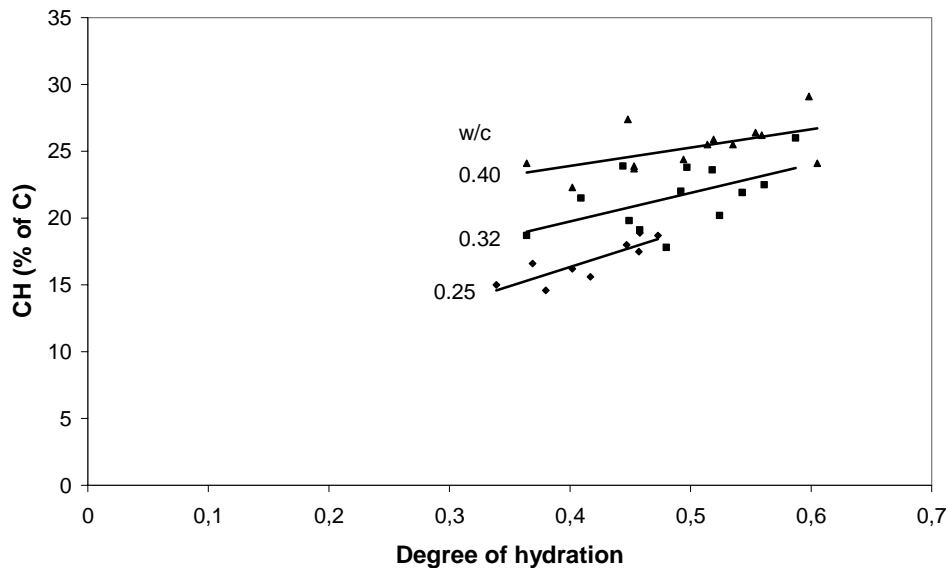
Example: 50% hydration and w/c-ratio 0.50:

0% silica gel: $CH_C \approx 0.31$

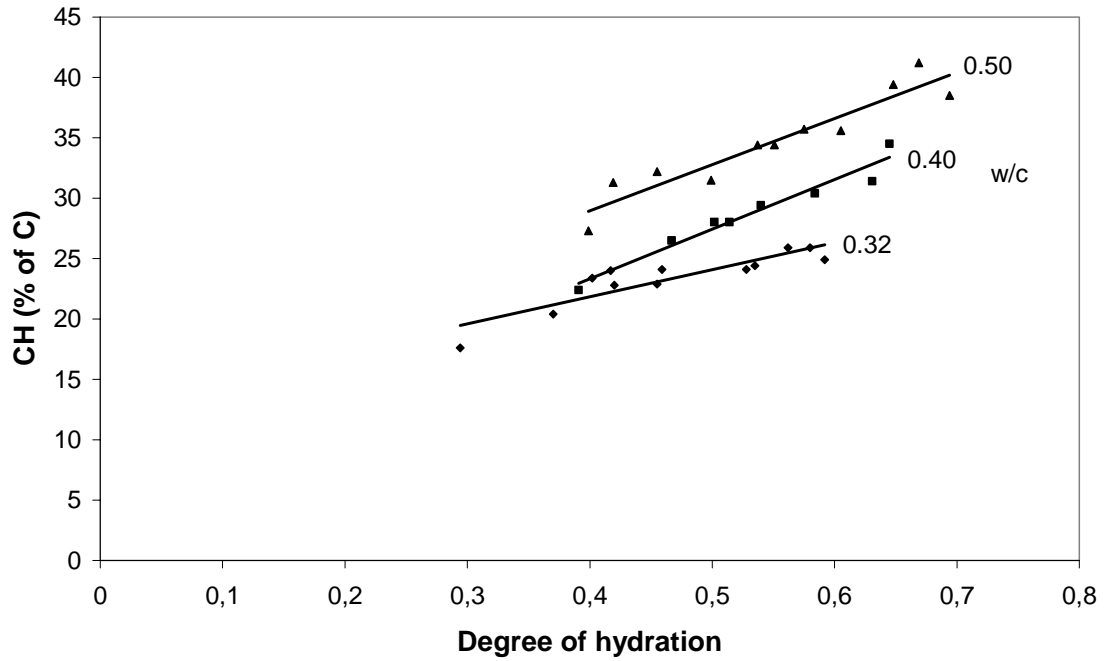
5% silica gel: $CH_C \approx 0.30$

10% silica gel: $CH_C \approx 0.24$

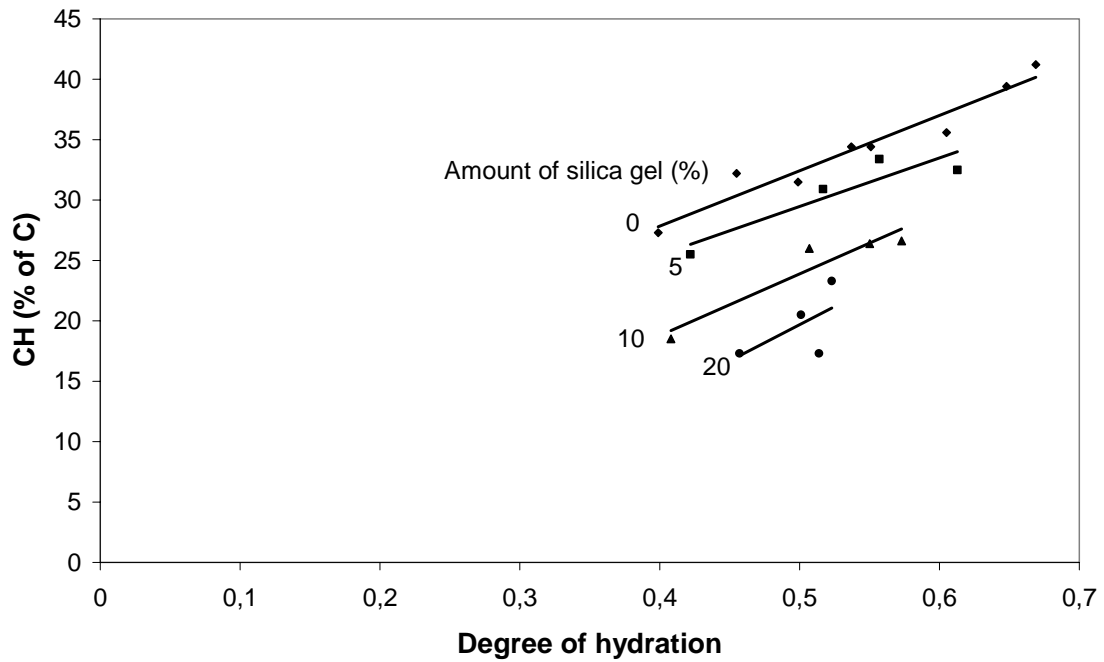
20% silica gel: $CH_C \approx 0.19$



II:3.5: LA/SR-cement. Amount of calcium hydroxide as weight-% of cement.



II:3.6: White cement. Amount of calcium hydroxide as weight-% of cement.



II:3.7: White cement with addition of silica gel. Amount of calcium hydroxide as weight-% of cement

II:4 SPECIFIC SURFACE - THE BET-THEORY

According to the BET-theory for multi-layer physical adsorption the amount of adsorbed water W_Φ (kg/kg dry material) at the relative humidity Φ (-) is

$$W_\Phi/W_m = A \cdot \Phi / \{(1-\Phi) \cdot (1+A \cdot \Phi - \Phi)\} \quad (\text{II:4.1})$$

Where W_m (kg/kg dry material) is the mono-molecular capacity, i.e. the amount of water required to completely cover the entire internal surface. A is the adsorption coefficient which depends on the affinity of water to the solid surface. The higher the value of A , the firmer is the water molecule bound to the surface. The ratio W_Φ/W_m is the number of completely filled adsorption layers. At a certain relative humidity Φ_m the ratio $W_\Phi/W_m=1$; in other words, at Φ_m the amount of adsorbed water is big enough to completely cover the entire internal surface. The value of Φ_m depends on the value of the adsorption coefficient as shown by equation (II:4.1). This gives the following relation between A and Φ_m

$$A = (\Phi_m^2 - 2 \cdot \Phi_m + 1) / \Phi_m^2 \quad (\text{II:4.2})$$

According to Figure I:7.1 one molecule layer corresponds to $\Phi_m=0.17$. Inserting this value in equation (II:4.2) gives the following value of the adsorption coefficient A

$$A = 24 \quad (\text{II:4.3})$$

Inserting this value in the BET-equation gives

$$W_\Phi/W_m = 24 \cdot \Phi / \{(1-\Phi) \cdot (1+24 \cdot \Phi - \Phi)\} \quad (\text{II:4.4})$$

The adsorbed water at equilibrium with 33% RH becomes

$$W_{33}/W_m = 24 \cdot 0.33 / \{(1-0.33) \cdot (1+24 \cdot 0.33 - 0.33)\} = 1.38 \quad (\text{II:4.5})$$

Thus, in order to obtain the monomolecular capacity the measured amount of water at 33% RH shall be divided by 1.38.

$$W_m = W_{33} / 1.38 \quad (\text{II:4.6})$$

A relation of this order has also been observed experimentally for cement paste; see Figure I:7.1. This fact indicates that the BET-equation can be used for describing adsorption of water in cement paste, indicating that adsorption in cement paste is of purely physical character. This fact was first pointed out by Powers & Brownyard (1948).

The specific surface (S m²/kg dry material) is calculated by; see Fagerlund (1998)

$$S = W_m(N/M)A_m \quad (\text{m}^2/\text{kg}) \quad (\text{II:4.7})$$

Where N is Avogadro's number ($6.02 \cdot 10^{26}$ molecules/kmole) and M is the molecular weight of water (18 kg/kmole). A_m is the area covered by 1 water molecule. Assuming close-packed molecules $A_m = 10.6 \text{ \AA}^2$. The derivation of this value is made in Fagerlund (1998).

Inserting equation (II:4.6) and the figures for all constants gives the following equation for calculation of the specific surface from the equilibrium adsorption at 33% RH.

$$S = \frac{W_{33}}{1.38} \cdot \frac{6.02 \cdot 10^{26}}{18} \cdot 10.6 \cdot 10^{-20} \quad (m^2/kg) \quad (\text{II:4.8})$$

or

$$S = 2.57 \cdot 10^6 \cdot W_{33} \quad (m^2/kg) \quad (\text{II:4.8'})$$

Note: W_{33} shall be expressed in kg per kg dry material.

II:5 SPECIFIC SURFACE OF CEMENT PASTE BASED ON ADSORPTION

According to the original BET-theory, water contents at *adsorption* shall be used. As shown in the previous paragraph -equation (II:4.8)- the following equation gives the specific surface based on the equilibrium water content at 33% RH reached by adsorption

$$S_{ads} = 2.57 \cdot 10^6 \cdot W_{33, ads} \quad (m^2/kg) \quad (II:5.1)$$

$W_{33,ads}$ was however not determined in Grudemo's work. Therefore, experimental values of specific surface based on adsorption cannot be calculated from his data.

Values of S_{ads} can be obtained from *the Powers & Brownyard (1948) adsorption isotherms*, see Figure I:7.1. The adsorbed water expressed in grams is given by equation (I:7.7)

$$w_{33,ads} = 0.091 \cdot \alpha \cdot c \quad (g) \quad (I:7.7)$$

The dry weight of the cement paste is composed of the weight of cement and chemically bound water, i.e.

$$Q_{dry} = c + 0.25 \cdot \alpha \cdot c = c(1 + 0.25 \cdot \alpha) \quad (II:5.2)$$

The water content at equilibrium with 33% RH at adsorption becomes

$$W_{33,ads} = w_{33,ads} / Q_{dry} \quad (g/g \text{ or } kg/kg) \quad (II:5.3)$$

Inserting equations (I:7.7) and (II:5.2) gives

$$W_{33,ads} = 0.091 \cdot \alpha / (1 + 0.25 \cdot \alpha) \quad (II:5.4)$$

Inserting this in equation (II:5.1) gives the following expression for the specific surface of the entire cement paste

$$S_{ads} = 2.57 \cdot 10^6 \cdot 0.091 \cdot \alpha / (1 + 0.25 \cdot \alpha) \quad (m^2/kg) \quad (II:5.5)$$

or

$$S_{ads} = \frac{2.34 \cdot 10^5 \cdot \alpha}{1 + 0.25 \cdot \alpha} \quad (m^2/kg) \quad (II:5.6)$$

Thus, according to the Powers & Brownyard (1948) work, *the specific surface based on adsorption is independent of the water-cement ratio, and only dependent of the degree of hydration*. This is logical since it is primarily the amount of *cement gel* that determines the

internal surface and not the amount of coarse pores. The volume of cement gel is independent of the water-cement ratio as shown by equation (I:7.16)

Equation (II:5.6) is shown in Figure II:6.1. When $\alpha=1$ all solid material is cement gel. Therefore, theoretically, according to equation (II:5.6) the specific surface of the cement gel is $187 \text{ m}^2/\text{g}$.

This value is of the same order as the values below values given in Powers (1960) for 4 different cement pastes. This is not unexpected since the value is calculated from an adsorption isotherm experimentally determined by Powers.

<i>Cement paste</i>	<i>Specific surface of the cement gel</i>
<i>No</i>	<i>based on the adsorption isotherm (m^2/g)</i>
1	219
2	200
3	227
4	193
<i>Mean value</i>	<i>210</i>

Note 1: All these values are the specific surface of the *entire* cement gel including non-colloidal calcium hydroxide.

Note 2: The values are valid for cement gel that has been exposed to *hard drying* before adsorption. It is not necessarily the same as the specific surface of the “virgin” (never-dried) cement paste, see the next paragraph.

II:6 SPECIFIC SURFACE OF CEMENT PASTE BASED ON DESORPTION

II:6.1 Introduction

In Grudemo's work *desorption* to 33% RH was performed. As shown in Figure I:7.2 and equation (I:7.11) the water content at desorption is about 35% higher than the water content at adsorption, Powers & Brownyard (1948). Theoretically, according to the elementary adsorption theory, there should be no hysteresis between adsorption and desorption within the RH-range from 0% to about 45%. Thus, the hysteresis observed is probably an effect of structural changes caused by the first drying. It was also shown by Powers & Brownyard (1948) that the first desorption isotherm differed from the following isotherms at repeated drying-wetting cycles. Thus, there is good reason to believe that the first desorption gives the best description of the pore structure and specific surface of cement paste used during normal climatic conditions not involving hard drying to RH below about 15%.

The specific surface can be calculated from the equilibrium water content at desorption using the following equation, see equation (II:4.8').

$$S_{des} = 2.57 \cdot 10^6 \cdot W_{33,des} \quad (m^2/kg) \quad (II:6.1)$$

II:6.2 Specific surface based on the Powers & Brownyard work

Since the amount of water at desorption to 33% RH is about 35% higher than at adsorption the specific surface can be calculated by multiplying equation (II:5.6) by the factor 1.35

$$S_{des} = \frac{1.35 \cdot 2.34 \cdot 10^5 \cdot \alpha}{1 + 0.25 \cdot \alpha} = \frac{3.16 \cdot 10^5 \cdot \alpha}{1 + 0.25 \cdot \alpha} \quad (m^2/kg) \quad (II:6.2)$$

This equation is plotted in Figure II:6.1. The specific surface of the cement gel ($\alpha=1$) becomes $253 \text{ m}^2/\text{g}$ which is 35% higher than the surface calculated from adsorption. The desorption value is most reliable since it is based on specimens that have not been exposed to hard drying which might cause structural changes in the material.

For 80% hydration the specific surface becomes $210 \text{ m}^2/\text{g}$

Alternative derivation of S_{des} :

The equilibrium water content at desorption to 33% RH is

$$w_{33,des} = V \cdot (P_{tot} - P_{33,des}) \quad (II:6.3)$$

Where V is the total volume.

It was shown in Chapters I:6 and I:7 that the total porosity can be described by the equation (I:6.10) (or alternatively by equation (I:6.15)) and the porosity after desorption to 33% RH by equation (I:7.14).

The volume is described by equation (I:6.3). Thus, the water content after desorption to 33% RH is obtained by inserting these equations in equation (II:6.3)

$$w_{33,des} \approx 1 \cdot \{[(w/c)_o - 0.19 \cdot \alpha] - [(w/c)_o - 0.31 \cdot \alpha]\} \cdot c = 0.12 \cdot \alpha \cdot c \quad (\text{g}) \quad (\text{II:6.4})$$

Where the factor 1 is the density of water (1 g/cm³).

Division by the dry weight according to equation (II:5.2) gives

$$W_{33,des} = 0.12 \cdot \alpha / (1 + 0.25 \cdot \alpha) \quad (\text{g/g or kg/kg}) \quad (\text{II:6.5})$$

Inserting this in equation (II:6.1) gives the specific surface

$$S_{des} = \frac{3.08 \cdot 10^5 \cdot \alpha}{1 + 0.25 \cdot \alpha} \quad (\text{m}^2/\text{kg}) \quad (\text{II:6.6})$$

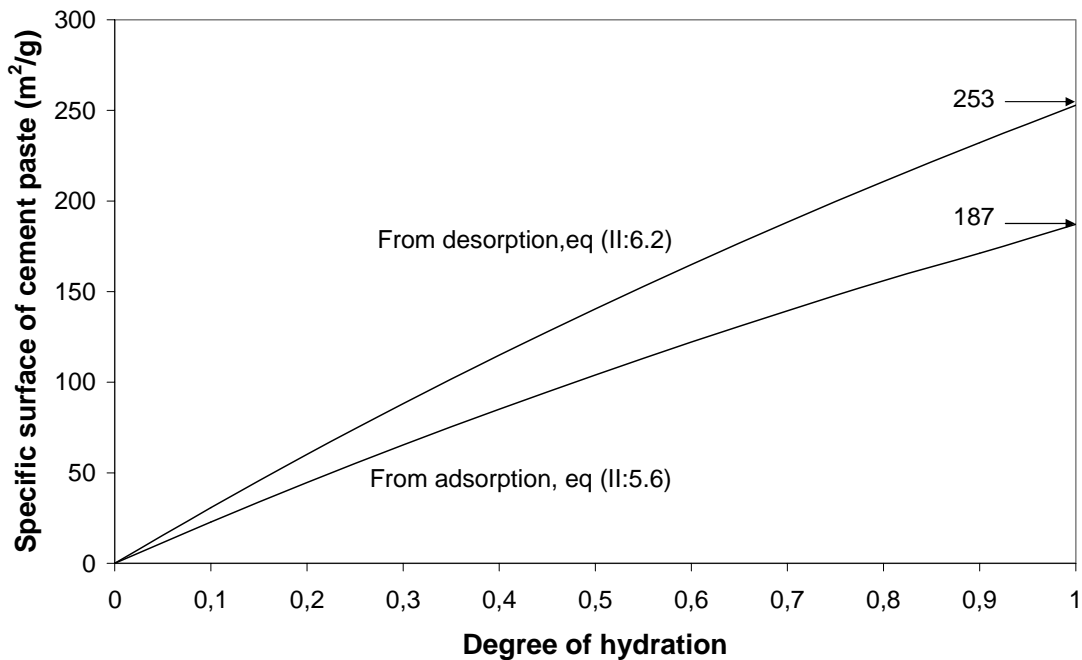


Figure II:6.1: Specific surface of cement paste based on Powers & Brownyard isotherms; adsorption, equation (II:5.6); desorption, equation (II:6.2)

The specific surface obtained from the equilibrium water content at first desorption is 35% higher than that obtained from first adsorption.

The desorption specific surface gives the most realistic picture of the internal structure of cement paste since it is valid for the “virgin” cement paste that has not been exposed to the destructive action caused by hard drying.

II:6.3 Specific surface directly from measurements

The water content at desorption to 33% RH is

$$W_{33,des}=(Q_{33}-Q_{105})/Q_{105}=Q_{33}/Q_{105}-1 \quad (\text{kg/kg}) \quad (\text{II:6.7})$$

The specific surface becomes

$$S_{des}=2.57 \cdot 10^6 (Q_{33}/Q_{105}-1) \quad (\text{m}^2/\text{kg}) \quad (\text{II:6.7})$$

Thus, the specific surface can be calculated for each individual cement paste using the test data. These, and the calculated specific surface are shown in ANNEX TO PART II, Tables AII.1 to AII.4.

The results are shown in Figures II:6.2-II:6.7.

The following conclusions can be drawn:

1. The specific surface increases with increased degree of hydration, which is expected. The development of specific surface can be fairly well described by an equation of type (II:6.2) with the coefficient $3.16 \cdot 10^5$ exchanged for a coefficient that is different for different types of binder, and maybe also different for different w/c-ratios.

$$S_{des} = \frac{K \cdot \alpha}{1 + 0.25 \cdot \alpha} \quad (\text{II:6.8})$$

The applicability of this equation is tested by calculating values of the coefficient K for different degrees of hydration.

Example: LA/SR-cement. All w/c-ratios

$$\alpha=0.35: K=4.0 \cdot 10^5$$

$$\alpha=0.50: K=3.8 \cdot 10^5$$

$$\alpha=0.60: K=3.6 \cdot 10^5$$

Example: White cement. w/c=0.50

$$\alpha=0.40: K=3.7 \cdot 10^5$$

$$\alpha=0.50: K=3.7 \cdot 10^5$$

$$\alpha=0.60: K=3.6 \cdot 10^5$$

$$\alpha=0.70: K=3.5 \cdot 10^5$$

The value of K is fairly independent of the degree of hydration which strengthens the validity of an equation of type (II:6.8).

Values of K derived from the experimental curves (at $\alpha=0.50$) are shown in Table II:6.1. It is assumed that the coefficient 0.25 in equation (II:6.7) can be used also for cement pastes containing additives, an assumption that is not altogether correct.

Table II:6.1: The coefficient K derived from the curves in Figures II:6.2-II:6.7, and the corresponding specific surface at 80% hydration; equation (II:6.8)

Type of cement	w/c	Additive		K	Specific surface ($\alpha=0.80$) m^2/g
		Type	amount % of C		
LA/SR. Normal	0.25-0.40			$3.8 \cdot 10^5$	253
LA/SR. Fine	0.32-0.50			$3.6 \cdot 10^5$	233
White cement	0.32-0.50			$4.1 \cdot 10^5$	273
	0.32			$4.4 \cdot 10^5$	293
	0.40	$3.9 \cdot 10^5$	260		
	0.50	$3.7 \cdot 10^5$	245		
White cement	0.50	Silica gel	5	$3.9 \cdot 10^5$	260
			10	$4.7 \cdot 10^5$	313
			20	$5.9 \cdot 10^5$	346
White cement	0.50	Hemi-hydrate	5	$4.1 \cdot 10^5$	273
			10	$4.7 \cdot 10^5$	313
			20	$7.5 \cdot 10^5$	500

- The specific surface is almost independent of the water-cement ratio, which clearly indicates that the gel structure formed has the same shape irrespectively of the water-cement ratio. The very slight tendency that the specific surface is increased with decreased water-cement ratio might be a consequence of the bigger difficulty to reach moisture equilibrium during drying for cement pastes with very low water-cement ratio.
- There is no clear difference in specific surface between the normal LA/SR-cement and the fine fraction of this cement. This is of course expected since the chemical composition is the same in the two cements.
- Addition of silica gel causes a big increase in the specific surface. This can be explained by the fact that the silica gel produces more calcium-silicate hydrate gel by its reaction with calcium hydroxide.
- For all cement pastes, the specific surface is higher than the values calculated from the Powers & Brownyard (1948) desorption isotherm in Figure I:7.2, equation (II:6.2). For the LA/SR-cement it is in average 17% higher. For the white cement it is in average 25% higher. It must be considered, however, that the chemical composition of the cement used by Powers & Brownyard in their Figure I:7.2 is not the same as for the cement used in the Grudemo study.
- Addition of hemi-hydrate gypsum causes considerable increase in the specific surface. The reason is unclear.

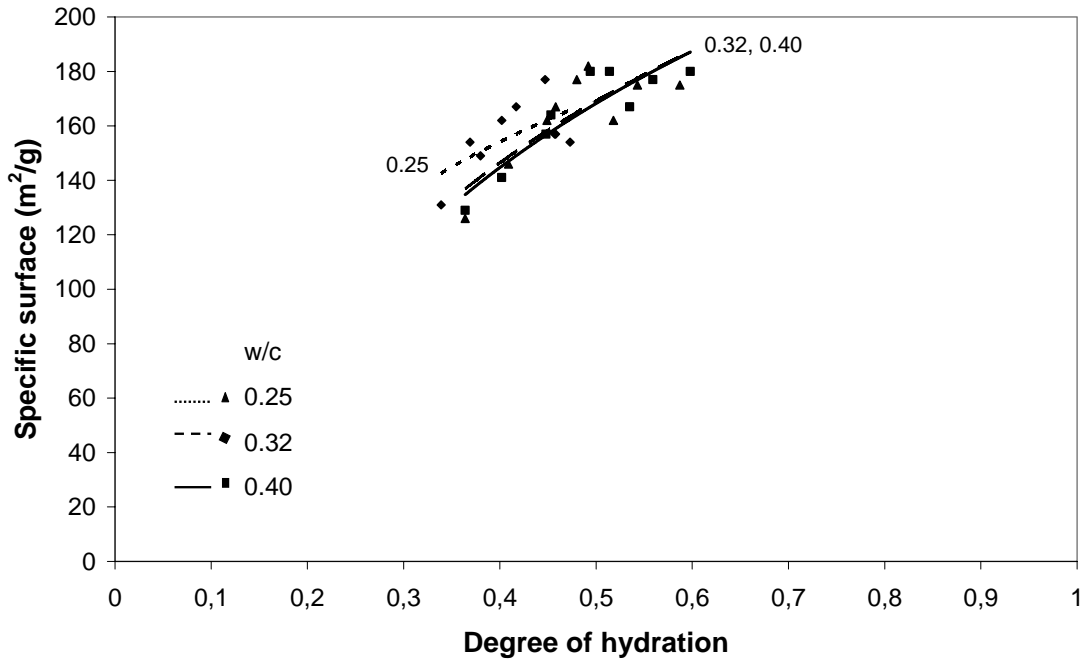


Figure II:6.2: Normal LA/SR-cement. Specific surface calculated from first desorption versus the degree of hydration.

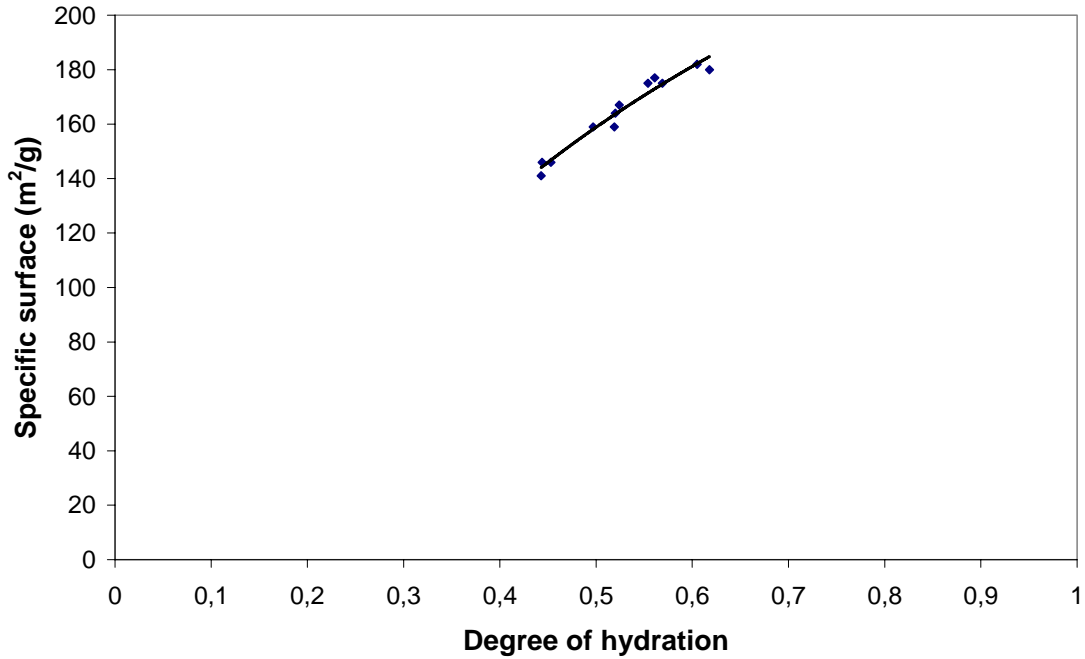


Figure II:6.3: Fine fraction of LA/SR-cement. Specific surface calculated from first desorption versus the degree of hydration.

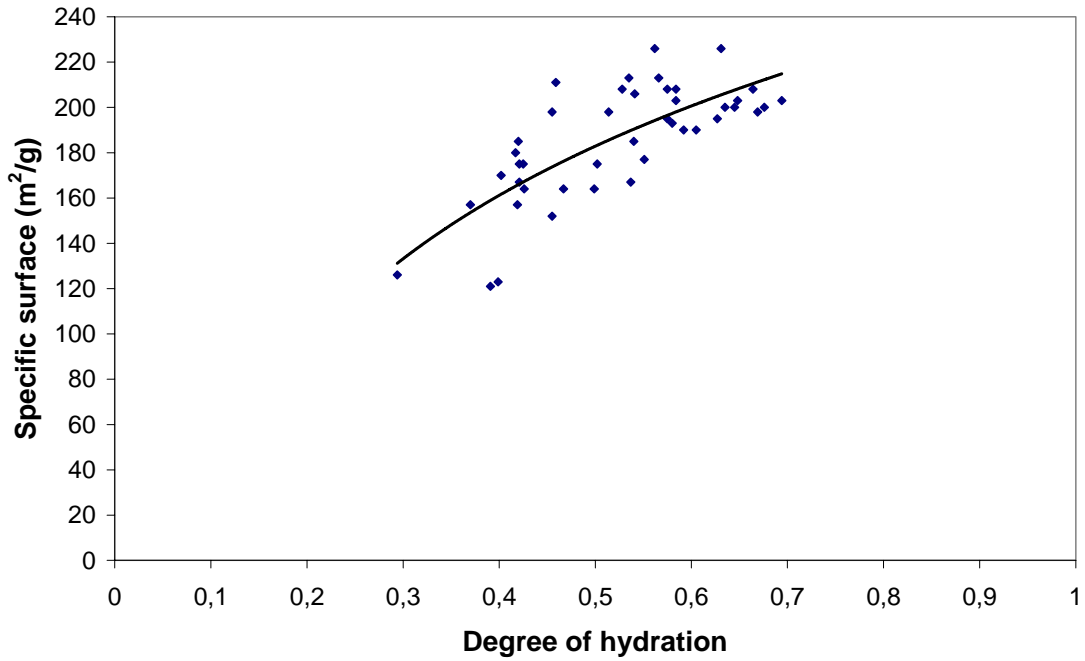


Figure II:6.4: White cement. Specific surface calculated from first desorption versus the degree of hydration. All water-cement ratios.

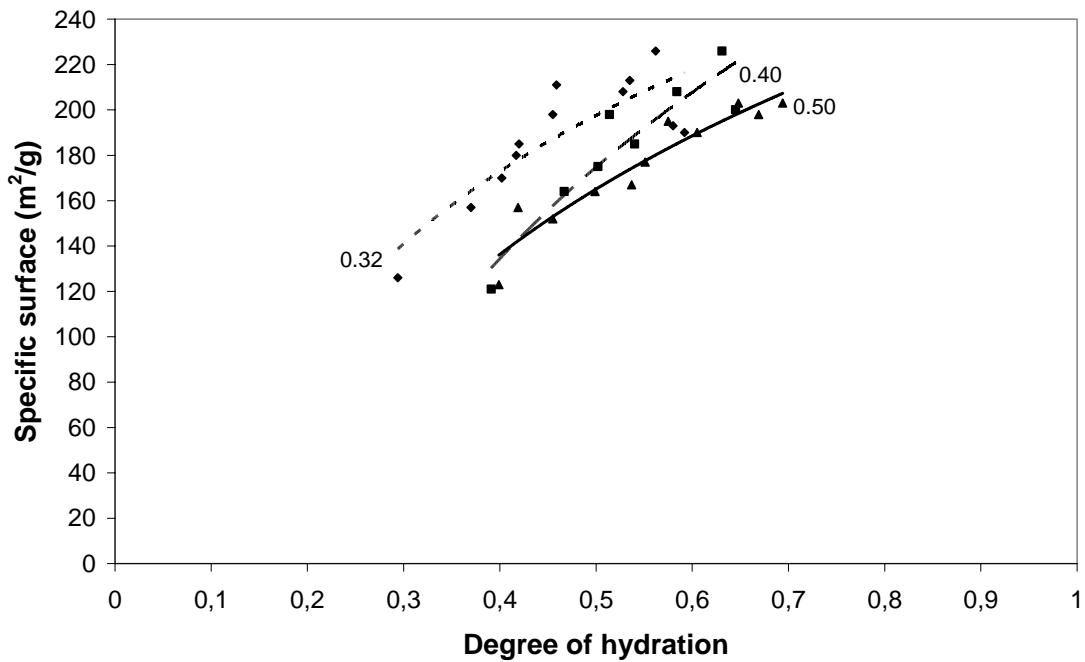


Figure II:6.5: White cement. Specific surface calculated from first desorption versus the degree of hydration. Separate water-cement ratio.

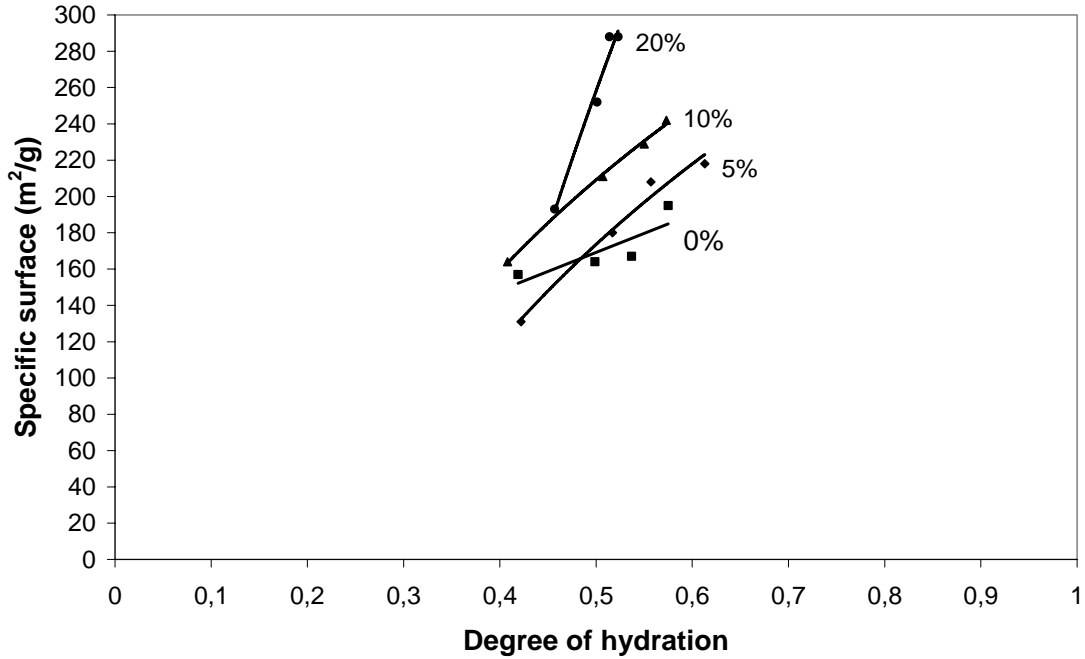


Figure II:6.6: White cement with addition of silica gel. Specific surface calculated from first desorption versus the degree of hydration. Water-cement ratio 0.50.
 Note: the values of degree of hydration are under-estimated; c.f. paragraph II:3.2.

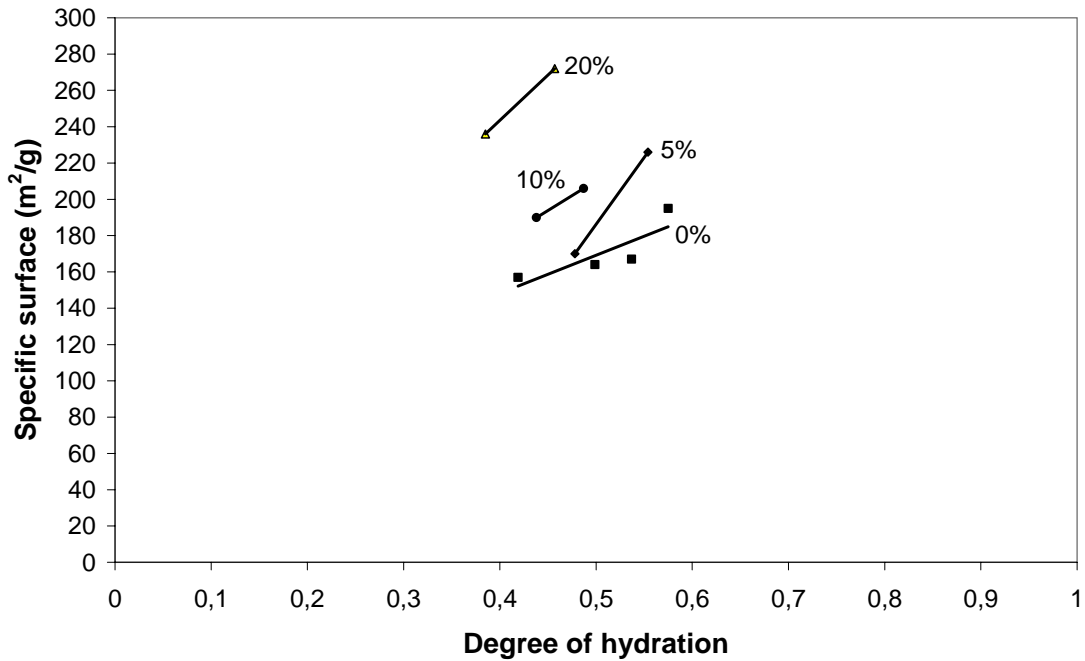


Figure II:6.7: White cement with addition of hemi-hydrate. Specific surface calculated from first desorption versus the degree of hydration. Water-cement ratio 0.50.

II:7 SPECIFIC SURFACE OF THE CEMENT GEL

II:7.1 Definition of cement gel

The “cement gel” is composed of products caused by reaction between cement and water. These products can be divided in two separate parts:

1. A fine-porous mass built up by extremely small “gel particles”, mainly consisting of calcium-silicate-hydrate, calcium-aluminate-hydrate and calcium-aluminate-ferrite-hydrate. Individual particles or aggregate of particles are separated by very fine “gel-pores”.
2. Non-porous calcium hydroxide crystals interwoven with the gel.

For each gram of fully hydrated cement about 60% to 70% consists of gel and about 30% (LA/SR-cement) to 40 % (white cement) of calcium hydroxide. These values are based on reaction formulas for hydrating cement clinker compounds. The X-ray diffraction measurements indicate higher values, but these are probably not altogether correct; see paragraph II:3.2.

The specific surface of the cement gel can be defined in two ways

1. S_{gel} . The internal surface is divided by the *total* weight of the cement gel
2. $S_{gel,net}$ The internal surface is divided by the weight of gel particles only (calcium hydroxide excluded)

The internal surface is mainly determined by the gel particles, being much smaller than the calcium hydroxide aggregates. Therefore, $S_{gel,net}$ ought to give a more representative picture of the internal surface than S_{gel} .

The relation between $S_{gel,net}$ and S_{gel} is

$$\text{LA/SR-cement:} \quad S_{gel,net} \approx S_{gel}/0.70 \quad (\text{II:7.1})$$

$$\text{White cement:} \quad S_{gel,net} \approx S_{gel}/0.60 \quad (\text{II:7.2})$$

II:7.2 Specific surface of cement gel based on *adsorption*

As shown in paragraph II:5 (equation (II:5.6) with $\alpha=1$) the adsorption isotherms determined by Powers & Brownyard (1948) give the following specific surface of the total gel.

$$S_{ads, gel} = 187 \text{ m}^2/\text{g} \quad (\text{II:7.3})$$

The net specific surface becomes

$$\text{LA/SR-cement: } S_{ads, gel, net} = \frac{187}{0.7} = 267 \text{ m}^2/\text{g} \quad (\text{II:7.4})$$

$$\text{White cement: } S_{ads, gel, net} = \frac{187}{0.6} = 312 \text{ m}^2/\text{g} \quad (\text{II:7.5})$$

In Powers (1960) the following net specific surfaces are given for 4 different types of normal Portland cement paste. They are of the same order as the value determined in this investigation for the LA/SR cement.

<i>Cement paste</i>	<i>Net specific surface of the cement gel</i>
<i>No</i>	<i>based on the adsorption isotherm (m²/g)</i>
1	267
2	240
3	255
4	235
<i>Mean value</i>	249

II:7.3 Specific surface of cement gel based on *desorption*

II:7.3.1 Specific surface based on the Powers & Brownyard work

As shown in paragraph II:6.2 (equation (II:6.2) with $\alpha=1$) the desorption isotherm determined by Powers & Brownyard give the following specific surface of the total cement gel including $\text{Ca}(\text{OH})_2$

$$S_{des, gel} = 253 \text{ (m}^2/\text{g)} \quad (\text{II:7.6})$$

The net specific surface becomes

$$\text{LA/SR-cement: } S_{des, gel, net} = \frac{253}{0.7} = 361 \text{ (m}^2/\text{g)} \quad (\text{II:7.7})$$

$$\text{White cement: } S_{des, gel, net} = \frac{253}{0.6} = 422 \text{ (m}^2/\text{g)} \quad (\text{II:7.8})$$

II:7.3.2 Specific surface of cement gel directly from measurements

The specific surface of the cement gel is found by introducing $\alpha=1$ in equation (II:6.8). Values of the coefficient K from Table II:6.1 are used. The result is shown in Table II:7.1. No calculations of the net specific surface are made for cement paste with addition of silica gel since the amount of calcium hydroxide is uncertain.

Table II:7.1: Specific surface of the cement gel calculated from desorption to 33% RH.

Type of cement	w/c	Silica gel	K	$S_{des, gel}$ m^2/g	$S_{des, gel, net}$ m^2/g
LA/SR, normal	0.25-0.40	No	$3.8 \cdot 10^5$	304	434
LA/SR, fine	0.32-0.50		$3.6 \cdot 10^5$	289	413
White cement	0.32-0.50		$4.1 \cdot 10^5$	328	547
White cement	0.50	5%	$3.9 \cdot 10^5$	312	Cannot be calculated
		10%	$4.7 \cdot 10^5$	376	
		20%	$5.9 \cdot 10^5$	472	

The specific surface for the samples without silica gel is 20% to 30% higher than the values calculated from the Powers & Brownyard desorption isotherm. But, as said in paragraph II:6.3 the reason could be different chemical composition of the different cements.

The specific surface of the cement gel of cement pastes containing silica gel is considerably higher than for the plain cement pastes. The reason could be that these pastes contain considerably more cement gel and less calcium hydroxide.

II:8 STRUCTURE OF THE CEMENT GEL

II:8.1 Size of gel particles including calcium hydroxide

According to Powers (1960) the cement gel is composed of *plate-like crystals* separated by pores. The specific surface of such crystals is

$$S_{gel}=2/(t \cdot \rho_{gel}) \quad (m^2/kg) \quad (II:8.1)$$

or

$t = \frac{2}{S_{gel} \cdot \rho_{gel}} \quad (m) \quad (II:8.1')$
--

Where t (m) is the thickness of the particles, and ρ_{gel} (kg/m^3) the density of the particles.
 Note: S_{gel} must be expressed in m^2/kg and not in m^2/g as given by the equations above.

The weight of the cement paste is given by equation (II:5.2) expressed as

$$Q_{dry,paste}=c(1+0.25 \cdot \alpha) \quad (g) \quad (II:5.2)$$

The volume of the cement paste is composed of the total volume of hydrated cement and chemically bound water

$$V_{paste}=v_c \cdot \alpha \cdot c + v_{wn} \cdot 0.25 \cdot \alpha \cdot c \quad (cm^3) \quad (II:8.2)$$

Where v_c and v_{wn} are the specific volumes of cement and chemically bound water. $v_c \approx 0.32$ cm^3/g and $v_{wn} \approx 0.75$ cm^3/g . Inserting these values gives

$$V_{paste}=c(0.32+0.19 \cdot \alpha) \quad (cm^3) \quad (II:8.3)$$

The density of the cement paste becomes

$$\rho_{paste}'=(1+0.25 \cdot \alpha)/(0.32+0.19 \cdot \alpha) \quad (g/cm^3) \quad (II:8.4)$$

Inserting $\alpha=1$ gives the density of the gel

$$\rho_{gel}'=1.25/(0.32+0.19)=2.45 \quad g/cm^3 \quad (\rho_{gel}=2450 \quad kg/m^3) \quad (II:8.5)$$

$t = \frac{2}{S_{gel} \cdot 2450} \quad (m) \quad (II:8.1')$
--

The thickness of the gel particles are obtained by inserting the calculated specific surface from equations (II:7.3), (II:7.6), and Table II:7.1 into equation (II:8.1').

1. From Powers & Brownyard adsorption, equation (II:7.3), $S_{gel}=187 \cdot 10^3 \text{ m}^2/\text{kg}$
 $t=2/(187 \cdot 10^3 \cdot 2450)=4.4 \cdot 10^{-9} \text{ m (44 \AA)}$

2. From Powers & Brownyard desorption, equation (II:7.6), $S_{gel}=253 \cdot 10^3 \text{ m}^2/\text{kg}$
 $t=2/(253 \cdot 10^3 \cdot 2450)=3.2 \cdot 10^{-9} \text{ m (32 \AA)}$

3. From Grudemo desorption, Table II:7.1

The calculated value depends on the type of cement (as shown by Table II:6.1, it is also to a certain extent dependent on the water-cement ratio).

LA/SR-cement: $S_{gel}=304 \cdot 10^3 \text{ m}^2/\text{kg}$
 $t=2/(304 \cdot 10^3 \cdot 2450)=2.7 \cdot 10^{-9} \text{ m (27 \AA)}$

White cement: $S_{gel}=328 \cdot 10^3 \text{ m}^2/\text{kg}$
 $t=2/(328 \cdot 10^3 \cdot 2450)=2.5 \cdot 10^{-9} \text{ m (25 \AA)}$

All calculations based on desorption indicate that the mean size of gel particles are of the order 25 to 30 Å.

It seems as if drying at +105°C causes a coarsening of the gel structure. The average particle size is increased from about 25-30 Å to about 45 Å. This indicates that hard drying causes a certain “collapse” of the gel structure. The calculated increase in particle size might however be apparent, and merely depend on difficulties to re-absorb water in the very narrow gel-pores.

Note:

If the gel particles are supposed to be *spherical* the particle diameter (d) will be 3 times the plate thickness calculated above:

$$d = \frac{6}{S_{gel} \cdot \rho_{gel}} \quad (\text{II.8.1'})$$

Powers & Brownyard adsorption:	d=132 Å
Powers & Brownyard desorption:	d=96 Å
Grudemo desorption, LA/SR:	d=81 Å
Grudemo desorption, WhC:	d=75 Å

II:8.2 Size of gel particles not including calcium hydroxide

The density of calcium hydroxide is 2.24 g/cm^3 . The density of the entire gel including calcium hydroxide is 2.45 g/cm^3 . Then, the following density is valid for the CSH-particles:

$$\begin{aligned} \text{LA/SR-cement (30\% CH): } \rho_{\text{CSH}} &= 2.55 \text{ g/cm}^3 \\ \text{White cement (40\% CH): } \rho_{\text{CSH}} &= 2.61 \text{ g/cm}^3 \end{aligned}$$

Calcium hydroxide is assumed to have negligible inner surface compared to the CSH-gel. Then, the thickness of the CSH-particles becomes

$$t = \frac{2}{S_{\text{gel, net}} \cdot \rho_{\text{CSH}}} (m) \quad (\text{II:8.6})$$

The thickness of the gel particles are obtained by inserting the calculated net specific surface from equations (II:7.4), (II:7.5), (II:7.7), (II:7.8) and Table II:7.1 into equation (II:8.6). The result will depend on the type of cement.

LA/SR-cement

1. From Powers & Brownyard adsorption, equation (II:7.4), $S_{\text{gel, net}} = 267 \cdot 10^3 \text{ m}^2/\text{kg}$
 $t = 2 / (267 \cdot 10^3 \cdot 2550) = 2.9 \cdot 10^{-9} \text{ m} (29 \text{ \AA})$
2. From Powers & Brownyard desorption, equation (II:7.7), $S_{\text{gel, net}} = 361 \cdot 10^3 \text{ m}^2/\text{kg}$
 $t = 2 / (361 \cdot 10^3 \cdot 2550) = 2.2 \cdot 10^{-9} \text{ m} (22 \text{ \AA})$
3. From Grudemo desorption, Table II:7.1. $S_{\text{gel, net}} = 434 \cdot 10^3 \text{ m}^2/\text{kg}$
 $t = 2 / (434 \cdot 10^3 \cdot 2550) = 1.8 \cdot 10^{-9} \text{ m} (18 \text{ \AA})$

White cement

1. From Powers & Brownyard adsorption, equation (II:7.5), $S_{\text{gel, net}} = 312 \cdot 10^3 \text{ m}^2/\text{kg}$
 $t = 2 / (312 \cdot 10^3 \cdot 2610) = 2.5 \cdot 10^{-9} \text{ m} (25 \text{ \AA})$
2. From Powers & Brownyard desorption, equation (II:7.8), $S_{\text{gel, net}} = 434 \cdot 10^3 \text{ m}^2/\text{kg}$
 $t = 2 / (434 \cdot 10^3 \cdot 2610) = 1.8 \cdot 10^{-9} \text{ m} (18 \text{ \AA})$
3. From Grudemo desorption, Table II:7.1. $S_{\text{gel, net}} = 547 \cdot 10^3 \text{ m}^2/\text{kg}$
 $t = 2 / (547 \cdot 10^3 \cdot 2610) = 1.4 \cdot 10^{-9} \text{ m} (14 \text{ \AA})$

The particle sizes calculated above are considerably smaller than if the entire gel is looked upon as one single homogeneous phase. It must be considered, however, that the calculation might not be altogether correct. Possibly it is wrong to separate all calcium hydroxide from the gel and consider it to have negligible area.

Note:

If the gel particles are supposed to be *spherical* the particle diameter (d) will be 3 times the plate thickness calculated above, see equation (II:8.1')

II:8.3 Size of gel pores including calcium hydroxide

The porosity of the cement gel (P_{gel}) is of the order 28%, Powers (1960). The gel pores being located between individual gel particles are slit like. The specific surface of slit like pores is

$$S_{gel}=2 \cdot P_{gel} / [\rho_{gel}(1-P_{gel})d] \quad (\text{m}^2/\text{kg}) \quad (\text{II:8.6})$$

or

$$d = \frac{2 \cdot P_{gel}}{S_{gel} \cdot \rho_{gel} \cdot (1 - P_{gel})} \quad (\text{m}) \quad (\text{II:8.7})$$

Where P_{gel} is the gel porosity (-) and d (m) is the width of the pores.

Inserting $P_{gel}=0.28$ and $\rho_{gel}=2450 \text{ kg/m}^3$ gives

$$d = \frac{3.17 \cdot 10^{-4}}{S_{gel}} \quad (\text{m}) \quad (\text{II:8.7'})$$

The width of the gel pores is obtained by inserting calculated specific surface from equations (II:7.3), (II:7.6), and Table II:7.1 into equation (II:8.7').

1. From Powers & Brownyard adsorption, equation (II:7.3), $S_{gel}=187 \cdot 10^3 \text{ m}^2/\text{kg}$
 $d=3.17 \cdot 10^{-4}/187 \cdot 10^3=1.7 \cdot 10^{-9} \text{ m}$ (17 Å)
2. From Powers & Brownyard desorption, equation (II:7.6), $S_{gel}=253 \cdot 10^3 \text{ m}^2/\text{kg}$
 $d=3.17 \cdot 10^{-4}/253 \cdot 10^3=1.3 \cdot 10^{-9} \text{ m}$ (13 Å)

3. From Grudemo desorption, Table II:7.1

The calculated value depends on the type of cement (as shown by Table II:6.1, it is also to a certain extent dependent on the water-cement ratio).

$$\text{LA/SR-cement: } S_{gel}=304 \cdot 10^3 \text{ m}^2/\text{kg} \\ d=3.17 \cdot 10^{-4}/304 \cdot 10^3=1.0 \cdot 10^{-9} \text{ m} \text{ (10 \AA)}$$

$$\text{White cement: } S_{gel}=328 \cdot 10^3 \text{ m}^2/\text{kg} \\ d=3.17 \cdot 10^{-4}/328 \cdot 10^3=1.0 \cdot 10^{-9} \text{ m} \text{ (10 \AA)}$$

All calculations based on desorption indicate that the mean width of gel pores is of the order 10 Å. Thus, about 3-4 water molecule layers can be contained in gel pores.

Drying to +105°C before the adsorption isotherm is determined causes a coarsening of the pores from about 10 Å to about 17 Å. The reason might be a more or less permanent decrease in the gel porosity. Theoretically, the size of the remaining gel pores is unchanged (10Å), provided the gel porosity is reduced from 28% to 18% due to drying.

II:8.4 Size of gel pores not including calcium hydroxide

In the calculation above the total cement gel including calcium hydroxide was considered. The calculated gel pore size might become smaller if calcium hydroxide is excluded. An approximate calculation will be made.

It is assumed that all gel pores are located in the CSH-gel. Thus the porosity 28% valid for the total gel will be increased to

$$P_{CSH}=0.28/V_{CSH} \quad (II:8.8)$$

Where P_{CSH} is the porosity of the CSH-gel and V_{CSH} is the volume fraction of CSH-gel.

The porosity will be somewhat different for different types of cement

LA/SR-cement:	$P_{CSH}=0.40$
White cement:	$P_{CSH}=0.46$

The gel pore size becomes

$$d = \frac{2 \cdot P_{CSH}}{S_{gel, net} \cdot \rho_{CSH} \cdot (1 - P_{CSH})} \quad (m) \quad (II:8.9)$$

The pore width is obtained by inserting the calculated net specific surface from equations (II:7.4), (II:7.5), (II:7.7), (II:7.8) and Table II:7.1 into equation (II:8.6). The result will depend on the type of cement.

LA/SR-cement

1. From Powers & Brownyard adsorption, equation (II:7.3), $S_{gel,net}=267 \cdot 10^3 \text{ m}^2/\text{kg}$
 $d=2 \cdot 0.40 / [(267 \cdot 10^3 \cdot 2550 \cdot (1-0.40))] = 2.0 \cdot 10^{-9} \text{ m}$ (20 Å)
2. From Powers & Brownyard desorption, equation (II:7.6), $S_{gel,net}=361 \cdot 10^3 \text{ m}^2/\text{kg}$
 $d=2 \cdot 0.40 / [(361 \cdot 10^3 \cdot 2550 \cdot (1-0.40))] = 1.4 \cdot 10^{-9} \text{ m}$ (14 Å)
3. From Grudemo desorption, Table II:7.1, $S_{gel,net}=434 \cdot 10^3 \text{ m}^2/\text{kg}$
 $d=2 \cdot 0.40 / [(434 \cdot 10^3 \cdot 2550 \cdot (1-0.40))] = 1.2 \cdot 10^{-9} \text{ m}$ (12 Å)

White cement

1. From Powers & Brownyard adsorption, equation (II:7.5), $S_{gel,net}=312 \cdot 10^3 \text{ m}^2/\text{kg}$
 $d=2 \cdot 0.46 / [(312 \cdot 10^3 \cdot 2610 \cdot (1-0.46))] = 2.1 \cdot 10^{-9} \text{ m}$ (21 Å)
2. From Powers & Brownyard desorption, equation (II:7.8), $S_{gel,net}=434 \cdot 10^3 \text{ m}^2/\text{kg}$
 $d=2 \cdot 0.46 / [(434 \cdot 10^3 \cdot 2610 \cdot (1-0.46))] = 1.5 \cdot 10^{-9} \text{ m}$ (15 Å)
3. From Grudemo desorption, Table II:7.1, $S_{gel,net}=547 \cdot 10^3 \text{ m}^2/\text{kg}$
 $d=2 \cdot 0.46 / [(547 \cdot 10^3 \cdot 2610 \cdot (1-0.46))] = 1.2 \cdot 10^{-9} \text{ m}$ (12 Å)

Calculations based on desorption indicate that the mean width of gel pores is of the order 12-15 Å. This corresponds to about 4-5 water molecule layers.

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APPENDIX TO PART I

AI.1 Tables. Porosity data

Table AI.1. Porosity. Cement pastes made with the ordinary cement

(w/c) _o from recipe	Age	α	(w/c) _{sat,o}	(w/c) _o true value Eq (4.6)	Total porosity		Coarse porosity			
					Measured	Calculated Eq (6.10)	Meas.	Adsorpt. isotherm Eq(7.10)	Desorpt. isotherm Eq(7.14)	Cap. Eq(7.20)
0.80 Hand mixed	18-22h	0.37	0.61	0.59	0.57	0.57	0.53	0.53	0.52	0.49
	5d	0.42	0.61	0.58	0.55	0.56	0.46	0.51	0.50	0.46
	27d	0.60	0.62	0.58	0.52	0.52	0.42	0.46	0.44	0.38
0.80	18-22h	0.33	0.58	0.56	0.57	0.57	0.53	0.53	0.52	0.49
	5d	0.50	0.60	0.57	0.54	0.53	0.45	0.48	0.47	0.42
	27d	0.57	0.61	0.57	0.53	0.52	0.43	0.46	0.44	0.39
0.63	18-20h	0.23	0.55	0.54	0.58	0.58	0.51	0.55	0.55	0.52
	5d	0.51	0.56	0.53	0.51	0.51	0.43	0.46	0.44	0.39
	30d	0.64	0.57	0.53	0.49	0.48	0.39	0.41	0.39	0.33
0.50	18-20h	0.28	0.49	0.47	0.53	0.53	0.47	0.50	0.49	0.46
	5d	0.50	0.50	0.47	0.48	0.47	0.39	0.42	0.40	0.35
	30d	0.69	0.51	0.47	0.43	0.43	0.32	0.35	0.32	0.25
0.40	18-22h	0.33	0.41	0.39	0.44	0.46	0.37	0.42	0.41	0.37
	7d	0.53	0.42	0.39	0.41	0.41	0.31	0.34	0.32	0.26
	30d	0.72	0.43	0.39	0.36	0.36	0.27	0.27	0.23	0.15
0.40	20h	0.26	0.40	0.38	0.50	0.47	0.43	0.44	0.43	0.40
	5d	0.51	0.43	0.40	0.42	0.42	0.32	0.36	0.34	0.28
	30d	0.74	0.44	0.39	0.36	0.35	0.26	0.26	0.23	0.14
0.32	18-20h	0.30	0.33	0.31	0.41	0.40	0.35	0.36	0.34	0.31
	7d	0.60	0.36	0.32	0.32	0.32	0.24	0.24	0.21	0.13
	30d	0.72	0.36	0.32	0.29	0.29	0.21	0.19	0.15	0.06
0.32	20h	0.26	0.34	0.32	0.43	0.42	0.36	0.39	0.37	0.34
	5d	0.52	0.36	0.33	0.36	0.36	0.25	0.28	0.26	0.20
	30d	0.71	0.37	0.33	0.29	0.30	0.20	0.20	0.17	0.08

Table AI.2. Porosity. Cement pastes made with the fine cement fraction (<37 μ m)

(w/c) _o from recipe	Age	α	(w/c) _{sat,o}	(w/c) _o true value Eq (4.6)	Total porosity		Coarse porosity			
					Measur.	Calculated Eq (6.10)	Meas.	Adsorpt. isotherm Eq(7.10)	Desorpt isotherm Eq(7.14)	Cap. Eq(7.20)
0.40	18-20h	0.22	0.41	0.40	0.50	0.50	0.43	0.47	0.46	0.44
	5d	0.53	0.44	0.41	0.42	0.42	0.31	0.36	0.34	0.28
	30d	0.81	0.44	0.39	0.34	0.33	0.22	0.23	0.20	0.10
0.50	18-20h	0.24	0.49	0.48	0.55	0.54	0.49	0.52	0.51	0.48
	5d	0.53	0.51	0.48	0.48	0.47	0.38	0.41	0.39	0.34
	30d	0.81	0.54	0.49	0.42	0.41	0.32	0.32	0.29	0.21
0.32	18-20h	0.42	0.34	0.31	0.43	0.37	0.36	0.31	0.29	0.23
	5d	0.61	0.36	0.32	0.32	0.32	0.21	0.23	0.20	0.13
	30d	0.72	0.37	0.33	0.29	0.30	0.15	0.20	0.16	0.09
0.25	20h	0.28	0.26	0.24	0.34	0.33	0.26	0.29	0.27	0.23
	5d	0.51	0.27	0.24	0.25	0.26	0.14	0.17	0.15	0.07
	30d	0.61	0.28	0.24	0.22	0.22	0.10	0.12	0.09	0.004

Table AI.3. Porosity. Cement pastes made with the coarse cement fraction ($>37\mu\text{m}$)

(w/c) _o from recipe	Age	α	(w/c) _{sat,o}	(w/c) _o true value Eq (4.6)	Total porosity		Coarse porosity			
					Measured	Calculated Eq (6.10)	Meas.	Adsorpt. isotherm Eq(7.10)	Desorpt. isotherm Eq(7.14)	Cap. Eq(7.20)
0.32	18-20h	0.12	0.30	0.29	0.44	0.44	0.41	0.42	0.41	0.40
	5d	0.27	0.29	0.27	0.38	0.37	0.32	0.33	0.32	0.28
	30d	0.32	0.28	0.26	0.36	0.34	0.25	0.29	0.28	0.23
0.25	20h	0.09	0.25	0.24	0.40	0.40	0.37	0.38	0.38	0.37
	5d	0.25	0.24	0.22	0.32	0.32	0.25	0.28	0.26	0.23
	30d	0.40	0.24	0.22	0.25	0.27	0.14	0.20	0.18	0.12

Table AI.4. Porosity. Cement pastes made with the ordinary cement with aerosil added for stabilization.

(w/c) _o from recipe	Age	α	(w/c) _{sat,o}	(w/c) _o true value Eq (4.6)	Total porosity		Coarse porosity			
					Measured	Calculated Eq (6.10)	Meas.	Adsorpt. isotherm Eq(7.10)	Desorpt. isotherm Eq(7.14)	Cap. Eq(7.20)
1.00	18-22h	0.31	0.98	0.96	0.72	0.70	0.66	0.68	0.67	0.66
	5d	0.55	1.01	0.98	0.68	0.67	0.59	0.64	0.62	0.59
	30d	0.75	1.02	0.97	0.65	0.64	0.56	0.59	0.57	0.53
0.80	18-22h	0.32	0.79	0.77	0.66	0.65	0.59	0.62	0.62	0.59
	5d	0.53	0.82	0.79	0.62	0.62	0.53	0.58	0.56	0.53
	30d	0.74	0.84	0.79	0.59	0.59	0.47	0.52	0.51	0.45
0.63	20h	0.30	0.63	0.61	0.61	0.59	0.54	0.57	0.56	0.53
	5d	0.54	0.66	0.63	0.56	0.56	0.47	0.50	0.49	0.44
	30d	0.74	0.68	0.63	0.52	0.52	0.42	0.44	0.42	0.36
0.50	20h	0.28	0.50	0.48	0.54	0.53	0.47	0.50	0.49	0.46
	5d	0.53	0.53	0.50	0.49	0.49	0.41	0.43	0.41	0.36
	30d	0.73	0.54	0.49	0.44	0.43	0.33	0.35	0.33	0.25

Table AI.5. Porosity. Compact made with the ordinary cement.

(w/c) _o from recipe	Age	α	(w/c) _{sat,o}	(w/c) _o true value Eq (4.6)	Total porosity		Coarse porosity			
					Measured	Calculated Eq (6.10)	Measured	Adsorpt. isotherm Eq(7.10)	Desorpt. isotherm Eq(7.14)	Cap. Eq(7.20)
≈ 0.18	6h	0.18	0.20	0.19	0.30	0.30	0.27	0.27	0.26	0.23
	12h	0.32	0.21	0.19	0.25	0.25	0.20	0.20	0.18	0.13
	1d	0.42	0.21	0.18	0.21	0.20	0.15	0.12	0.10	0.03
	2d	0.48	0.21	0.18	0.19	0.18	0.13	0.09	0.06	0
	4d	0.49	0.22	0.19	0.20	0.19	0.13	0.10	0.07	0
	10d	0.53	0.22	0.19	0.17	0.17	0.12	0.08	0.05	0

**AI.2 Specific surface of *cement paste* based on porosity data in
Part I**

Based on first desorption to 33% RH

Analysis of data

The water content at desorption to 33% RH is

$$W_{33,des}=(Q_{33}-Q_{105})/Q_{105}=Q_{33}/Q_{105}-1 \quad (\text{kg/kg}) \quad (\text{AI.1})$$

The specific surface becomes -see equation (II:6.1) in Part II.

$$S_{des}=2.57 \cdot 10^6 \cdot W_{33,des} = 2.57 \cdot 10^6 (Q_{33}/Q_{105}-1) \quad (\text{m}^2/\text{kg}) \quad (\text{AI.3})$$

Thus, the specific surface can be calculated for each individual specimen. Unfortunately, however, individual data for Q_{33} and Q_{105} were not furnished to the present author.

An alternative calculation of the water content at 33% RH can be made by directly using the measured total porosity (P_{tot}) and coarse porosity from desorption ($P_{33,des}$). Data for these are known and listed in Tables AI.1-AI.5.

The water content at equilibrium with 33% RH at desorption is

$$w_{33,des}=\rho_w(P_{tot}-P_{33,des})V \quad (\text{g}) \quad (\text{AI.4})$$

Where ρ_w is the density of water (1 g/cm³). The specimen volume is

$$V=w_o+0.32 \cdot c = c[(w/c)_o+0.32] \quad (\text{cm}^3) \quad (\text{AI.5})$$

The dry weight is

$$Q_{dry}=c(1+0.25 \cdot \alpha) \quad (\text{g}) \quad (\text{AI.6})$$

The water content at equilibrium with 33% RH at desorption becomes

$$W_{33,des}=w_{33,des}/Q_{dry} \quad (\text{g/g or kg/kg}) \quad (\text{AI.8})$$

Inserting equations (AI.4) and (AI.6) gives

$$W_{33,des}=(P_{tot}-P_{33,des})[(w/c)_o+0.32]/(1+0.25 \cdot \alpha) \quad (\text{AI.9})$$

The specific surface becomes

$S_{des} = \frac{2.57 \cdot 10^6 (P_{tot} - P_{33,des})[(w/c)_o + 0.32]}{1 + 0.25 \cdot \alpha} \quad (\text{m}^2/\text{kg}) \quad (\text{AI.10})$
--

The calculation involves a subtraction of two numbers that are of similar size. The value of these numbers (P_{tot} and $P_{33,des}$) given in Tables I:A1.1-I:A1.5 are not precise enough for a reliable calculation of the specific surface of each individual cement paste, since they are only stated by two decimals. Instead the *mean relation* between the total number of observations

and the theoretical porosities are inserted in equation (AI.10). In this way the *average* specific surface for the whole population of cement pastes is obtained.

Equation (I:6.13) gives the relation between measured and theoretical total porosity. Redistribution of the terms gives

$$P_{\text{tot,meas}} \approx 1.018 \cdot P_{\text{tot,calc}} - 0.003 \quad (\text{I:6.13'})$$

Inserting the theoretical equation (I:6.10) for $P_{\text{tot,calc}}$ gives

$$P_{\text{tot,meas}} = 1.018 \left[\frac{(w/c)_o - 0.19 \cdot \alpha}{(w/c)_o + 0.32} \right] - 0.003 \quad (\text{AI.11})$$

Equation (I:7.26) gives the relation between measured and theoretical coarse porosity based on desorption to 33% RH. Redistribution of the terms gives

$$P_{33,\text{des,meas}} \approx 0.952 \cdot P_{33,\text{des,calc}} + 0.017 \quad (\text{I:7.26'})$$

Inserting the theoretical equation (I:7.14) for $P_{33,\text{des,calc}}$ gives

$$P_{33,\text{des,meas}} = 0.952 \left\{ \frac{(w/c)_o - 0.31 \cdot \alpha}{(w/c)_o + 0.32} \right\} + 0.017 \quad (\text{AI.12})$$

Inserting equations (AI.11) and (AI.12) in equation (AI.10) gives

$$S_{\text{des}} = 2.57 \cdot 10^6 \left\{ \frac{0.066(w/c)_o + 0.102 \cdot \alpha}{(w/c)_o + 0.32} - 0.020 \right\} \cdot \frac{(w/c)_o + 0.32}{1 + 0.25 \cdot \alpha} \quad (\text{AI.13}) \quad (m^2/kg)$$

This equation is not quite logical since a considerable specific surface is predicted even before any hydration.

$$\alpha=0: \quad S_{\text{des}} = 2.57 \cdot 10^6 \cdot \left\{ \frac{0.066(w/c)_o}{(w/c)_o + 0.32} - 0.020 \right\} \cdot [(w/c)_o + 0.32] \quad (\text{AI.14})$$

Example

(w/c) _o =0.40:	$S_{\text{des}}=31 \text{ m}^2/\text{g}$
(w/c) _o =1:	$S_{\text{des}}=101 \text{ m}^2/\text{g}$

This means that the specific surface is predicted to be too high for low degrees of hydration, see Figure AI.1 below. Furthermore, according to the equation, the specific surface is also a function of the water-cement ratio, which is not logical. The reason for this defect is that the coefficients ahead of $(w/c)_o$ in equations (AI.11) and (AI.12) are not exactly one, as they should have been, had there been a perfect agreement between measured and calculated total and coarse porosities. The small differences from one (1.018 and 0.952 in equations (AI.11) and (AI.12)) have big effects when introduced in the formula (AI.10) for specific surface.

Despite this defect in equation (AI.13) it is plotted in Figure AI.1.

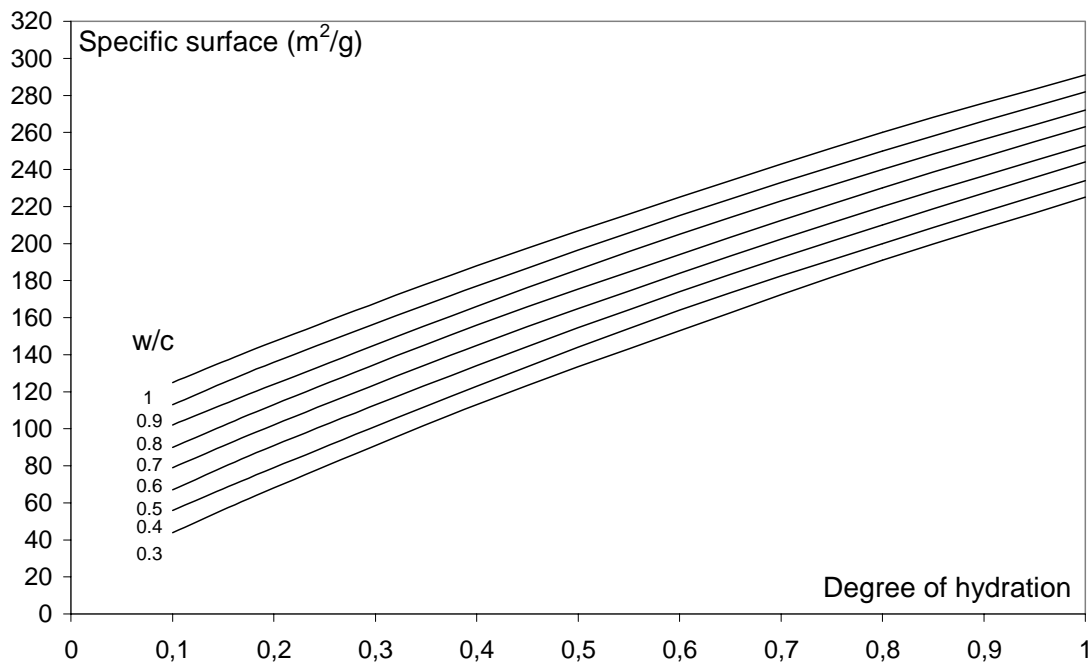


Figure AI.1: Experimental determination of the specific surface of the cement paste based on desorption. Equation (AI.13).

The results can be compared with the LA/SR-cement in Part II, Chapter II:6. Comparisons can only be made for w/c-ratio between 0.3 and 0.5 since data for other w/c-ratios are lacking in Part II. As shown by the examples below the difference is not so big water-cement ratio 0.50 but considerable for water-cement ratio 0.30 with high degrees of hydration.

Examples

w/c 0.30

Degree of hydration 40%.

Equation (AI.13):	$S_{\text{paste}} = 110 \text{ m}^2/\text{g}$
Equation (II:6.7) with $K=3.7 \cdot 10^5$:	$S_{\text{paste}} = 135 \text{ m}^2/\text{g}$

Degree of hydration 60%.

Equation (AI.13):	$S_{\text{paste}} = 160 \text{ m}^2/\text{g}$
Equation (II:6.7) with $K=3.7 \cdot 10^5$:	$S_{\text{paste}} = 195 \text{ m}^2/\text{g}$

Degree of hydration 100%.

Equation (AI.13):	$S_{\text{paste}} = 225 \text{ m}^2/\text{g}$
Equation (II:6.7) with $K=3.7 \cdot 10^5$:	$S_{\text{paste}} = 296 \text{ m}^2/\text{g}$

w/c 0.50

Degree of hydration 40%.

Equation (AI.13):	$S_{\text{paste}} = 135 \text{ m}^2/\text{g}$
Equation (II:6.7) with $K=3.7 \cdot 10^5$:	$S_{\text{paste}} = 135 \text{ m}^2/\text{g}$

Degree of hydration 60%.

Equation (AI.13):

Equation (II:6.7) with $K=3.7 \cdot 10^5$:

$$S_{\text{paste}} = 175 \text{ m}^2/\text{g}$$

$$S_{\text{paste}} = 195 \text{ m}^2/\text{g}$$

Degree of hydration 100%.

Equation (AI.13):

Equation (II:6.7) with $K=3.7 \cdot 10^5$:

$$S_{\text{paste}} = 245 \text{ m}^2/\text{g}$$

$$S_{\text{paste}} = 296 \text{ m}^2/\text{g}$$

**AI.3 Specific surface of *cement gel* based on porosity data in
Part I**

Based on first desorption to 33% RH

Analysis of data

The water content related to the dry weight of the gel is given by equation (AI.9) with $\alpha=1$.

$$W_{33,des,gel}=(P_{tot}-P_{33,des})\cdot[(w/c)_o+0.32]/1.25\cdot\alpha \quad (\text{g/g or kg/kg}) \quad (\text{AI.15})$$

Inserting this in equation (AI.3) gives

$$S_{des,gel}=2.06\cdot 10^6(P_{tot}-P_{33,des})\cdot[(w/c)_o+0.32]/\alpha \quad (\text{m}^2/\text{kg}) \quad (\text{AI.16})$$

Instead of using individual experimental values for P_{tot} and $P_{33,des}$ the mean relation for all cement pastes between the experimental values and the theoretical relations are used. These relations, (AI.11) and (AI.12), are inserted in (AI.16)

$$S_{des} = 2.06 \cdot 10^6 \left\{ \frac{0.066(w/c)_o + 0.102 \cdot \alpha}{(w/c)_o + 0.32} - 0.020 \right\} \cdot \frac{(w/c)_o + 0.32}{\alpha} \quad \text{m}^2/\text{kg} \quad (\text{AI.17})$$

As discussed in connection with equation (AI.13) this equation is not altogether logical since it predicts an effect of the water-cement ratio on the specific surface of the gel. Furthermore it predicts a big effect of the degree of hydration. According to the Powers model for gel structure the specific surface should be independent on these parameters, Powers (1960). The reason for these defects is that the mean relations between the measured total and coarse porosity, and the theoretical total and coarse porosity, did not agree completely, see equations (AI.11) and (AI.12).

It had been better to use individual values of coarse and total porosity, but as said before, the data lacked in precision since only two decimals were stated in Grudemo's raw data.

Equation (AI.17) is plotted in Figure AI.2.

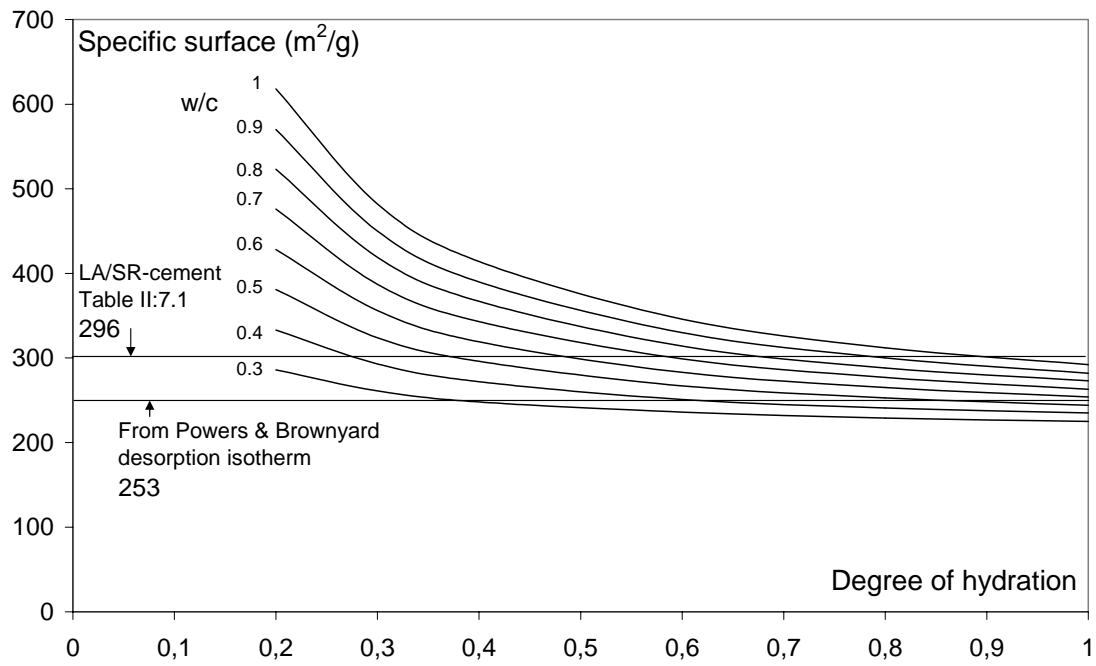


Figure AI.2: Specific surface of cement gel calculated by equation (AI.17). The gel surface based on the Powers & Brownyard desorption isotherm -Figure I:7.2, equation (II:7.6)- and the measured gel surface for LA/SR-cement according to Part II -Table II:7.1- are also shown.

APPENDIX TO PART II

Tables. Specific surface data

Table AII.1: LA/SR Cement. Ordinary size distribution. No additives.

(w/c) _o	Age days	α	Ca(OH) ₂		W _{33,des} kg/kg	S _{paste} m ² /g
			weight-% of solid	weight-% of C		
0.25	1	0.339	13.8	15.0	0.051	131
	2	0.380	13.3	14.6	0.058	149
	3	0.369	15.2	16.6	0.060	154
	4	0.402	14.7	16.2	0.063	162
	6	0.417	14.1	15.6	0.065	167
	8	0.447	16.2	18.0	0.069	177
	12	0.458	17.0	18.9	0.061	157
	20	0.457	15.7	17.5	0.061	157
	28	0.473	16.7	18.7	0.060	154
0.32	1	0.364	17.1	18.7	0.049	126
	2	0.409	19.5	21.5	0.057	146
	3	0.449	17.8	19.8	0.063	162
	4	0.458	17.1	19.1	0.065	167
	6	0.480	15.9	17.8	0.069	177
	8	0.492	19.6	22.0	0.071	182
	12	0.518	20.9	23.6	0.063	162
	20	0.543	19.3	21.9	0.068	175
	28	0.587	22.7	26.0	0.068	175
0.40	1	0.364	22.1	24.1	0.050	129
	2	0.402	20.3	22.3	0.055	141
	3	0.448	24.6	27.4	0.061	157
	4	0.453	21.3	23.7	0.064	164
	6	0.494	21.7	24.4	0.070	180
	8	0.514	22.6	25.5	0.070	180
	12	0.535	22.5	25.5	0.065	167
	20	0.559	23.0	26.2	0.069	177
	28	0.598	25.3	29.1	0.070	180

Table AII.2: LA/SR Cement. Fine fraction (>37 μ m). No additives.

(w/c) _o	Age days	α	Ca(OH) ₂		W _{33,des} kg/kg	Spaste m ² /g
			weight-% of solid	weight-% of C		
0.32	2	0.444	21.5	23.9	0.057	146
	4	0.497	21.2	23.8	0.062	159
	8	0.524	17.9	20.2	0.065	167
	16	0.561	19.7	22.5	0.069	177
0.40	2	0.453	21.5	23.9	0.057	146
	4	0.519	22.9	25.9	0.062	159
	8	0.554	23.2	26.4	0.068	175
	16	0.605	20.9	24.1	0.071	182
0.50	2	0.443	26.2	29.1	0.055	141
	4	0.520	28.6	32.3	0.064	164
	8	0.569	23.9	27.3	0.068	175
	16	0.618	26.5	30.5	0.070	180

Table AII.3: White cement. No additives.

(w/c) _o	Age days	α	Ca(OH) ₂		W _{33,des} kg/kg	S _{paste} m ² /g
			weight-% of solid	weight-% of C		
0.32	1	0.294	16.4	17.6	0.049	126
	2	0.370	18.7	20.4	0.061	157
	3	0.402	21.3	23.4	0.066	170
	4	0.417	21.7	24.0	0.070	180
	6	0.455	20.6	22.9	0.077	198
	8	0.459	21.6	24.1	0.082	211
	12	0.535	21.5	24.4	0.083	213
	19	0.562	22.7	25.9	0.088	226
28	0.580	22.6	25.9	0.075	193	
0.40	1	0.391	20.4	22.4	0.047	121
	2	0.467	23.7	26.5	0.064	164
	3	0.502	24.9	28.0	0.068	175
	4	0.540	25.9	29.4	0.072	185
	6	0.514	24.8	28.0	0.077	198
	8	0.584	26.5	30.4	0.081	208
	12	0.631	27.1	31.4	0.088	226
	18	0.645	29.7	34.5	0.078	200
0.50	1	0.399	24.8	27.3	0.048	123
	2	0.455	28.9	32.2	0.059	152
	3	0.499	28.0	31.5	0.064	164
	4	0.537	30.3	34.4	0.065	167
	6	0.551	30.2	34.4	0.069	177
	8	0.605	30.9	35.6	0.074	190
	12	0.648	33.9	39.4	0.079	203
	18	0.669	35.3	41.2	0.077	198

Table AII.3: White cement. No additives. Continued

(w/c) ₀	Age days	α	Ca(OH) ₂		W _{33,des} kg/kg	S _{paste} m ² /g
			weight-% of solid	weight% of C		
0.32	3	0.420	20.6	22.8	0.072	185
	9	0.528	21.3	24.1	0.081	208
	27	0.592	21.7	24.9	0.074	190
0.35	3	0.421	22.0	24.3	0.068	175
	9	0.541	22.7	25.8	0.080	206
	27	0.627	24.9	28.8	0.076	195
0.38	3	0.425	22.9	25.3	0.068	175
	9	0.566	26.0	29.7	0.083	213
	27	0.636	26.9	31.2	0.078	200
0.42	3	0.421	23.6	26.1	0.065	167
	9	0.575	29.9	34.2	0.081	208
	27	0.676	29.8	34.8	0.078	200
0.46	3	0.426	26.7	29.5	0.064	164
	9	0.584	30.8	35.3	0.079	203
	27	0.664	32.3	37.7	0.081	208
0.50	3	0.419	28.3	31.3	0.061	157
	9	0.575	31.2	35.7	0.076	195
	27	0.694	32.8	38.5	0.079	203

Table AII.4: White cement with additives.

Additive		(w/c) _o	(w/c) _{eff}	Age days	α	Ca(OH) ₂		W _{33,des} kg/kg	S _{paste} m ² /g
Type	Amount % of C		1)			weight-% of solid	weight-% of C		
Semi-hydrate gypsum	5	0.50	0.476	4	0.478	23.3	27.2	0.066	170
				8	0.554	33.7	40.0	0.088	226
	10	0.50	0.455	4	0.438	29.9	36.2	0.074	190
				8	0.487	29.1	35.6	0.080	206
	20	0.50	0.417	4	0.385	25.5	33.1	0.092	236
				8	0.457	26.9	35.4	0.106	272
Silica gel	5	0.50	0.476	1	0.422	22.1	25.5	0.051	131
				4	0.517	26.2	30.9	0.070	180
				8	0.557	28.1	33.4	0.081	208
				16	0.613	27.0	32.5	0.085	218
	10	0.50	0.455	1	0.408	15.4	18.5	0.064	164
				4	0.507	21.2	26.0	0.082	211
				8	0.550	21.3	26.4	0.089	229
				16	0.573	21.4	26.6	0.094	242
	20	0.50	0.417	1	0.457	13.2	17.3	0.075	193
				4	0.501	15.5	20.5	0.098	252
				8	0.523	17.5	23.3	0.112	288
				16	0.514	13.0	17.3	0.112	288
Ethylene glycol	2	0.40	0.42	5	-	-	-	0.081	208
				30	-	-	-	0.097	249
	4	0.40	0.44	30	-	-	-	0.100	257
				6	0.40	0.46	5	-	-
				30	-	-	-	0.100	257

1) (w/c)_{eff} is defined:

- For mineral additives: $(w/c)_{eff} = (w/c)_o / (1+a)$

- For ethylene glycol: $(w/c)_{eff} = (w/c)_o + a$

Where a is the additive as fraction of the cement.

Thus the mineral additive is treated as full-worthy cement (binder) while the ethylene glycol is treated as ordinary mixing water. These assumptions are of course not correct and are only used for more alternative comparisons with the pure cement pastes.