DETERMINATION OF CONCRETE PORE STRUCTURE PARAMETERS FROM PENETRATION TESTS WITH N-DECANE

BESTIMMUNG VON PORENSTRUKTURPARAMETERN VON BETON ANHAND DES EINDRINGVERHALTENS VON N-DECAN

DETERMINATION DE PARAMETRES DE LA STRUCTURE POREUSE DES BETONS SUR LA BASE DE LA PENETRATION DE DECANE

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SUMMARY

With the measured values of suction and infiltration tests with n-decane, which does not chemically react with hardened cement paste, the pore parameters corresponding to two cylinder capillary models were calculated for different concrete mixtures. With these experimental results, the same models can be used to predict the penetration behaviour of other liquids which do not react with concrete.

ZUSAMMENFASSUNG

Mit den Meßwerten von Saug- und Infiltrationsversuchen mit n-Decan, das mit Zementstein nicht chemisch reagiert, wurden die Porenparameter von Betonen unterschiedlicher Rezeptur nach zwei Zylinderkapillaren-Modellen berechnet. Diese experimentellen Werte ermöglichen es, mit den gleichen Modellen Erwartungswerte für das Eindringverhalten anderer Flüssigkeiten, die mit dem Beton nicht reagieren, zu berechnen.

RESUME

Avec les résultats d'essais d'absorption capillaire et d'infiltration de décane, fluide ne réagissant pas chimiquement avec la pâte de ciment durcie, les paramètres de la structure poreuse de différents bétons ont été calculés selon deux modèles basés sur des capillaires cylindriques. Ces valeurs expérimentales permettent de prédire, à l'aide de ces mêmes modèles, la pénétration d'autres liquides ne réagissant également pas avec le béton.

KEYWORDS: fluid transport, capillary suction, infiltration, capillary model

1 INTRODUCTION

Liquids which do not chemically react with concrete, penetrate into these according to the $t^{1/2}$ law. The penetration behaviour can described with cylinder capillary models with a single pore radius or with distributed pore radii [Sosoro, 1995]. The latter comes closer to the actual pore structure. The pore structure of concrete is characterised by parameters which can easily be determined experimentally: pore radius r for the simpler, or residual porosity P_R, mean pore radius $\bar{r}$, and mean square of pore radii $\overline{r^2}$ for the second model. With these parameters, a prediction of the penetration behaviour of a liquid, whose surface tension σ and dynamic viscosity η are known, is possible. The penetration behaviour of water deviates strongly from the $t^{1/2}$ law, because water reacts chemically with the hardened cement paste matrix of concrete.

The pore structure of concretes of different compositions should be characterised by means of simple tests. From the results of measurements of suction tests (i. e. fluid absorption by capillary suction) and infiltration tests (i.e. with an additional external hydraulic pressure) with n-decane, which doesn't react with the hardened cement paste, the essential parameters of pore radius distribution were calculated: pore radius r or mean pore radius $\bar{r}$ and mean square of pore radii $\overline{r^2}$. The residual porosity P_R was determined from absolute and bulk densities.

2 METHODOLOGY

2.1 Testing program and experimental setup

Concrete

The examined concretes differed by the quantities and types of cement used, the maximum aggregate size, the grading curve, the addition of silica fume and the water-cement ratio or water-binder ratio (Table 1).

Following cements were used: Portland cements CEM I 32.5 R and CEM I 42.5 R (Schwenk, Allmendingen) and blast-furnace cement CEM IIIB 32.5 NW/HS (Schwenk, Karlsruhe). The additives were from Woermann (Darmstadt): the 50% silica slurry "ELKEM MIKROSILICA (SF)", retarder LENTAN VZ 31 (VZ), and plasticiser WOERMENT FM 30 (FM). The aggregates were dried Rhine gravel and sand (Table 1).

The concretes were produced in a forced action mixer with a capacity of 150 litres according to the following mixing sequence:

- slight moistening of mixer drum
- short dry mixing of aggregates
- addition of approx. 50% of additional water, mixing for approx. 30 s
- addition of silica slurry, mixing for approx. 60 s
- adding of cement, mixing for approx. 60 s
- pouring in of remaining water during mixing
- after 1 min: admixture of plasticiser and retarder
- after 3 min: addition of plasticiser if needed to achieve required workability

The mixing time after adding the rest of the additional water was limited to a maximum of 5 minutes. Concretes without silica fume or additives were produced without the corresponding steps of the mixing sequence. The characteristics of fresh concretes are shown in Table 2.

Table 1. *Composition of concretes*

Concr.	Aggregates [kg/m³]	Grading	Cement [kg/m³]	Type of cement	W_{added} [kg/m³]	Si (solid) [kg/m³]	Re [kg/m³]	Pl [kg/m³]	$W_{tot.}$/(C+Si) -
M-Rili	1905	AB 16	320	CEM I 32,5 R	160	0	0	2,50	0,50
M1	1822	AB 16	338	CEM I 32,5 R	186	0	0	0,80	0,55
M2	1535	AB 2	467	CEM I 32,5 R	257	0	0	0	0,55
M3	1882	AB 32	309	CEM I 32,5 R	170	0	0	0	0,55
M4	1895	U 16	309	CEM I 32,5 R	170	0	0	0	0,55
M5	1677	C 16	405	CEM I 32,5 R	223	0	0	0,50	0,55
M6	1769	AB 16	485	CEM I 42,5 R	150	0	0	9,30	0,32
M7	1762	AB 16	465	CEM I 42,5 R	126	20	0	7,00	0,31
M8	1755	AB 16	445	CEM I 42,5 R	109	40	2,56	10,80	0,32
M9	1748	AB 16	425	CEM I 42,5 R	89	60	2,56	12,00	0,32
M10	1441	AB 2	615	CEM I 42,5 R	153	55	3,59	11,08	0,32
M11	1813	AB 16	338	CEM III / B	186	0	0	0	0,55
M12	1522	AB 2	467	CEM III / B	257	0	0	0	0,55

Si: silica fume Re: retarder Pl: plasticizer C: cement W: water

The composition of concrete MR corresponds to that of the reference concrete for liquid-tight concrete described in DAfStb guideline [DAfStb, 1996].

Table 2. *Properties of fresh concretes and compressive strength after 28 days*

Mix	PROPERTIES OF FRESH CONCRETE			COMPRESSIVE STRENGTH AFTER 28 DAYS			
	workability[1], flow [cm]	density of fresh concrete [kg/dm³]	air content [%]	density of hard. concr.[2] [kg/dm³]	Compressive strength smallest value [N/mm²]	Compressive strength mean value [N/mm²]	class
MR/1	41,8	2,34	1,8	2,35	52,3	53,8	B 45
MR/2	44,8	2,33	1,2	2,36	51,5	53,2	B 45
M1/1	46,5	-	-	2,33	41,8	44,0	B 35
M1/2	46,5	2,35	1,5	2,33	45,4	46,2	B 35
M2	43,5	2,16	3,6	2,19	41,8	43,1	B 35
M3/1	44,5	2,39	0,9	2,37	42,5	43,6	B 35
M3/2	46,5	2,39	0,4	2,35	42,2	43,0	B 35
M4	46,5	2,40	0,3	2,38	47,5	49,0	B 35
M5	43,8	2,28	1,8	2,18	38,2	38,8	B 25
M6	43,0	2,40	1,75	2,39	75,2	77,2	B 65
M7	48,3	2,37	1,4	2,41	80,9	84,3	B 75
M8/1	42,0	2,37	1,5	2,40	88,0	90,5	B 85
M8/2	44,8	2,37	0,7	2,40	85,1	86,2	B 75
M9	44,0	2,38	1,6	2,38	85,4	88,9	B 75
M10	44,5	2,22	2,8	2,24	77,2	78,9	B 65
M11/1	47,5	2,36	0,55	2,35	40,9	43,0	B 35
M11/2	46,5	2,35	0,45	2,34	45,5	46,0	B 35
M12	51,0	2,36	1,4	2,19	33,8	35,6	B 25

[1] workability: average diameter of the spread concrete body, determined by the german flow table test

[2] determimed on the cubes for the measurement of compressive strength

Production of samples

Up to a maximum aggregate size of 16 mm, cylinders with a diameter of 10 cm and a height of approx. 40 cm were cast for the penetration tests, and cubes with 10 cm edge length for the determination of compressive strength. For concrete M 3, due to the maximum aggregate size of 32 mm, cubes with edge lengths of 15 and 20 cm were cast for the determination of compressive strength and for penetration tests respectively. After 24 h, cylinders and cubes were stripped from the formwork.

The cubes for the measurement of **compressive strength** were then stored in a climatic chamber with 20°C and 95% relative humidity for 6 days, and 20°C/65% r.h. for further 21 days. At the concrete age of 28 days, compressive strength was determined according to [DIN 1048, T.5] and converted to the compressive strength $ß_{W200}$ of a cube with 200 mm edge length according to the DAfStb guideline for high-strength concrete [DAfStb, 1995]. The results of compressive strength tests are summarised in Table 2.

The samples for **penetration tests** were packed hermetically immediately after stripping and stored at 20°C for 6 days. At the concrete age of 7 days, two cylindrical specimens with a height of 15 cm were sawed from each cast cylinder. For concrete M3, cores with 10 cm diameter were drilled from the 20-cm cubes and 2.5 cm sawed off each end. All end faces were sawed in order obtain even surfaces and ensure the same pore structure as inside the sample.

In order to dry concrete without damaging the crystalline structure, the samples for the penetration tests were dried in an oven at 65°C until constant weight. The residual concrete moisture was determined by the density of samples dried at 105°C until constant weight was reached again.

Preparation of specimens

The lateral surfaces of specimens for **capillary suction tests** were coated several times with a transparent epoxy resin resistant to the test fluids in order to prevent lateral evaporation and obtain unidimensional flow.

The samples for **infiltration tests** (i.e. with additional hydraulic pressure) were produced in accordance with DAfStb guideline [DAfStb, 1996]. With epoxy resin, glass funnels were glued to the cylinders; afterwards cylinders and the lower part of the funnels (approx. 3 cm) were coated several times with the same resin.

Samples for both tests are shown schematically in Fig. 1.

Test fluids

Water and n-decane were used to perform both suction and infiltration tests on each concrete. The test results for n-decane were used to determine the parameters r (pore radius), respectively $\bar{r}$ and $\overline{r^2}$ (mean pore radius, mean square of pore radii) of pore structure used in the considered model. The physical values governing the examined transport processes, surface tension σ and dynamic viscosity η are given in Table 3. The values for cyclohexane are contained in it too, as a few tests were performed with this fluid (Fig. 2).

Table 3. *Physical values of fluids at 20°C*

Fluid	Formula	Density ρ [kg/dm3]	Surface tension σ [mN/m]	Dynamic viscosity η [mN.s/m²]	$(\sigma/\eta)^{0,5}$ [$m^{0,5}/s^{0,5}$]	Vapour pressure p_D [hPa]
n-decane	$C_{10}H_{22}$	0,73	23,9	0,88	5,21	19
water	H_2O	1,00	72,8	1,00	8,53	23
cyclohexane	C_6H_{12}	0,78	25,2	0,94	5,18	104

Experimental procedure

For **suction tests,** specimens were placed into the test fluid. The samples rested on glass rods to allow free access of the testing fluid to the inflow surface. The fluid level was approx. 10 mm above the base of the specimen. Penetration occurred by capillary forces acting against gravity.

The experimental setup for **infiltration tests** described in DAfStb guideline [DAfStb, 1996] was slightly modified. Preliminary tests had proven that the pressure head of 40 (+/- 5) cm specified there was too small to obtain measurable differences to capillary suction tests for high performance concretes. The required external pressure was estimated by calculation from the pore radius distributions of comparable concretes and fixed to 0,2 bar (20 kN/m^2) for all infiltration tests. This pressure was produced by a nitrogen bottle connected to the funnels on the samples by tubes.

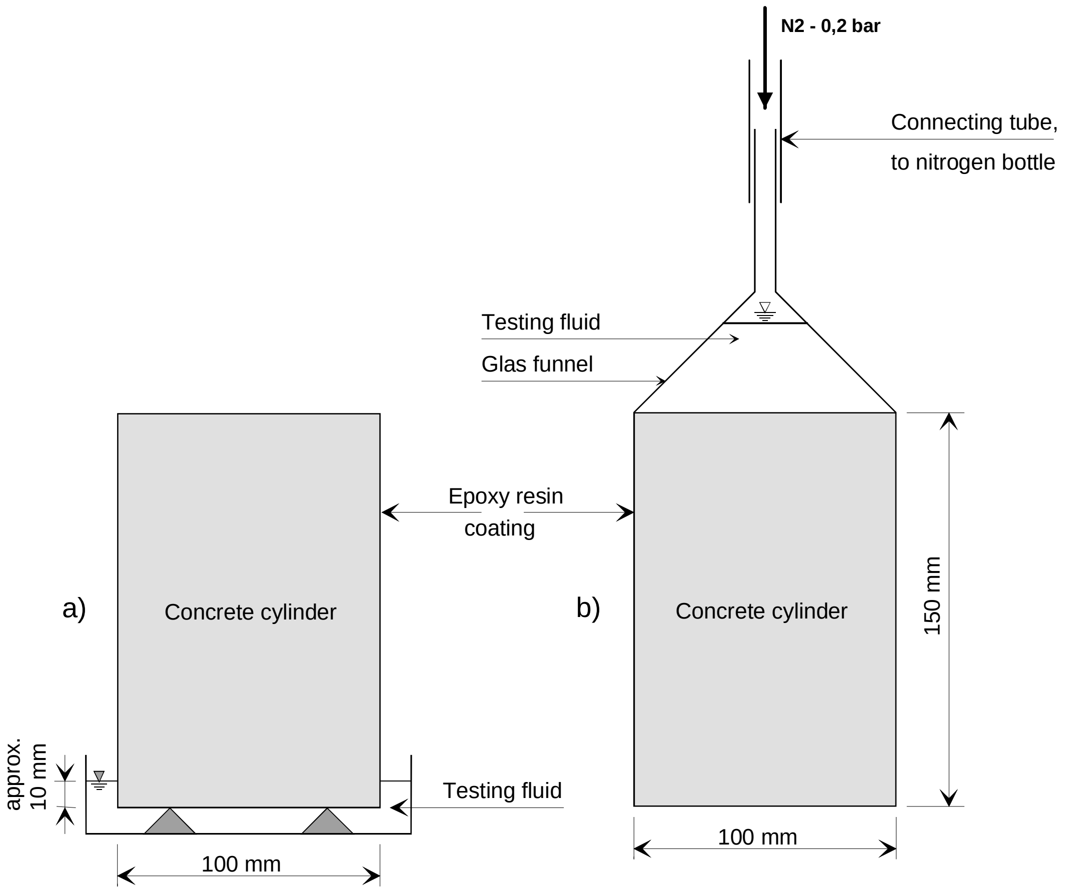

Fig. 1. *Experimental setups: a) suction test, b) infiltration test*

According to DAfStb guideline [DAfStb, 1996], the duration of penetration tests was fixed to 72 h and fluid absorption was determined by recording the increase in weight of specimens. Penetration depth was recorded as a function of time, as far as it could be seen from outside through the transparent epoxy resin coating. At the end of the tests, the specimens were split and penetration depth was determined on the splitting surfaces.

2.1 Calculations

Capillary model with a single pore radius

In the model with a single, mean pore radius r [Sosoro, 1995], the progression of penetration depth e as a function of time t is described by the formula:

$$\frac{e}{\sqrt{t}} = \sqrt{\left(\frac{2\sigma \cdot \cos\theta}{r} + p_a\right) \cdot \frac{r^2}{4\eta}} \qquad (1)$$

with

e	penetration depth
t	time
r	mean pore radius
σ	surface tension of the fluid
η	dynamic viscosity of the fluid
θ	contact angle between fluid and concrete
p_a	additional external pressure

The pore radius r for this model can be calculated from test results by resolving the quotient of penetration depths with and without external pressure:

$$r = \left[\left(\frac{e_{p_a}}{e_0}\right)^2 \cdot \frac{t_0}{t_{p_a}} - 1\right] \cdot \frac{2\sigma \cdot \cos\theta}{p_a} \qquad (2)$$

Capillary model with distributed pore radii

The penetration behaviour of organic liquids in concrete is described by Sosoro [Sosoro, 1995] with a model based on a better approximation of the pore radius distribution of the material. For penetration depth and absorbed fluid volume, he gives following formulas:

$$\frac{e}{\sqrt{t}} = \sqrt{\frac{2\sigma \cdot \bar{r} \cdot \overline{\cos\theta} + p_a \overline{r^2}}{4\eta}} \cdot P_R^{1,25} = B \qquad (3)$$

$$\frac{V/A_F}{\sqrt{t}} = \sqrt{\frac{2\sigma \cdot \bar{r} \cdot \overline{\cos\theta} + p_a \overline{r^2}}{4\eta}} \cdot \mu \cdot P_R^{2,25} = S \qquad (4)$$

with

- V absorbed liquid volume
- A_F area of the inflow surface
- $\bar{r}$ mean pore radius
- $\overline{r^2}$ mean square of pore radii
- $\overline{\cos\theta}$ mean cosine of the contact angle
- P_R residual porosity
- μ quotient of the pore space filled by the penetrating liquid and available porosity

B is called penetration coefficient and S the sorptivity.

The pore parameters P_R, $\bar{r}$, and $\overline{r^2}$ used in (3) and (4) can be calculated from test results. The residual porosity P_R can be calculated from absolute density ρ and bulk densities after drying at 65°C and 105°C:

$$P_R = 1 - \frac{\rho_{105°C}}{\rho} - \rho_{65°C} - \rho_{105°C} \qquad (5)$$

From the quotient of (3) and (4), μ can be calculated:

$$\mu = \frac{V}{A_F \cdot e \cdot P_R} \qquad (6)$$

The mean pore radius $\bar{r}$ can be calculated with (3) or (4) from the penetration coefficient or from sorptivity:

$$\left(\frac{B}{\sqrt{\sigma/\eta}\cdot P_R^{1,25}}\right)^2\cdot\frac{2}{\overline{\cos\theta}}=\bar{r}=\left(\frac{S}{\sqrt{\sigma/\eta}\cdot\mu\cdot P_R^{2,25}}\right)^2\cdot\frac{2}{\overline{\cos\theta}} \qquad (7)$$

The value of the mean square of pore radii $\overline{r^2}$ can be calculated from the quotient of penetration coefficients or sorptivities of both infiltration and suction tests:

$$\left[\left(\frac{B_{pa}}{B_0}\right)^2-1\right]\cdot\frac{2\sigma\cdot\bar{r}\cdot\overline{\cos\theta}}{p_a}=\overline{r^2}=\left[\left(\frac{S_{pa}}{S_0}\right)^2-1\right]\cdot\frac{2\sigma\cdot\bar{r}\cdot\overline{\cos\theta}}{p_a} \qquad (8)$$

3 RESULTS

3.1 Test results

The results of suction and infiltration tests are summarised in Table 4, the progression of fluid volume uptake is plotted in Figs. 3 to 6. The splitting surfaces of several concretes after the 72-h-suction test with water are shown in Fig. 2.

Table 4. *Results of penetration tests after 72 h*

concrete	n-decane						water					
	suction test			infiltration test			suction test			infiltration test		
	t [h]	V/A_F [l/m²]	e [mm]	t [h]	V/A_F [l/m²]	e [mm]	t [h]	V/A_F [l/m²]	e [mm]	t [h]	V/A_F [l/m²]	e [mm]
MR	71,75	6,35	89	72,25	7,91	103	72	5,89	67	72	7,18	86
M1	71,75	8,93	103	72,42	11,42	125	72	8,11	75	72	7,63	85
M2	72	12,65	120	54,25	14,52	127	72	16,97	132	72,33	18,61	141
M3	72	8,49	106	72	9,43	116	72	8,37	98	72,42	9,48	104
M4	72	8,54	113	72,25	9,88	129	72	8,98	107	72,25	10,22	117
M5	72	11,69	116	74	13,48	131	72,42	12,91	114	72	15,2	131
M6	72	5,61	87	74	6,51	95	72	3,89	51	72	3,97	53
M7	72	4,68	78	72,17	5,32	85	72,42	2,77	34	72	3,22	36
M8	72	3,58	61	72,42	4,01	68	72	1,71	17	72,25	2,73	20
M9	72	3,21	63	72	4,02	76	72,42	1,8	17	72	2,01	18
M10	72	5,59	69	73	6,46	76	72,42	3,13	24	72	3,41	24
M11	72,25	9,94	115	72	11,59	129	72,25	7,01	56	72	10,88	72
M12	72	11,09	101	54,17	16,52	136	72,42	9,68	55	72	10,1	55

t: duration of test V/A_F: absorbed fluid volume per unit area   e: penetration depth

The infiltration tests with n-decane on M2 and M12 were aborted shortly after 54 hours, since the test liquid would have reached the rear side of the specimens before the next measurement, which means the tests would have reached permeation, making the test unusable in the sense of these investigations.

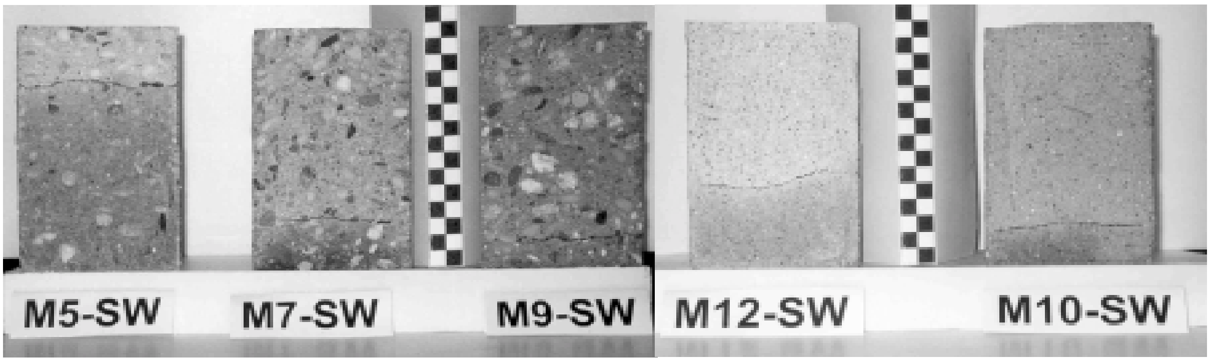

Fig. 6. *Splitting surfaces of concretes M5, M7 and M9 and mortars M12 and M10: penetration depths of water after the 72-h-suction test*

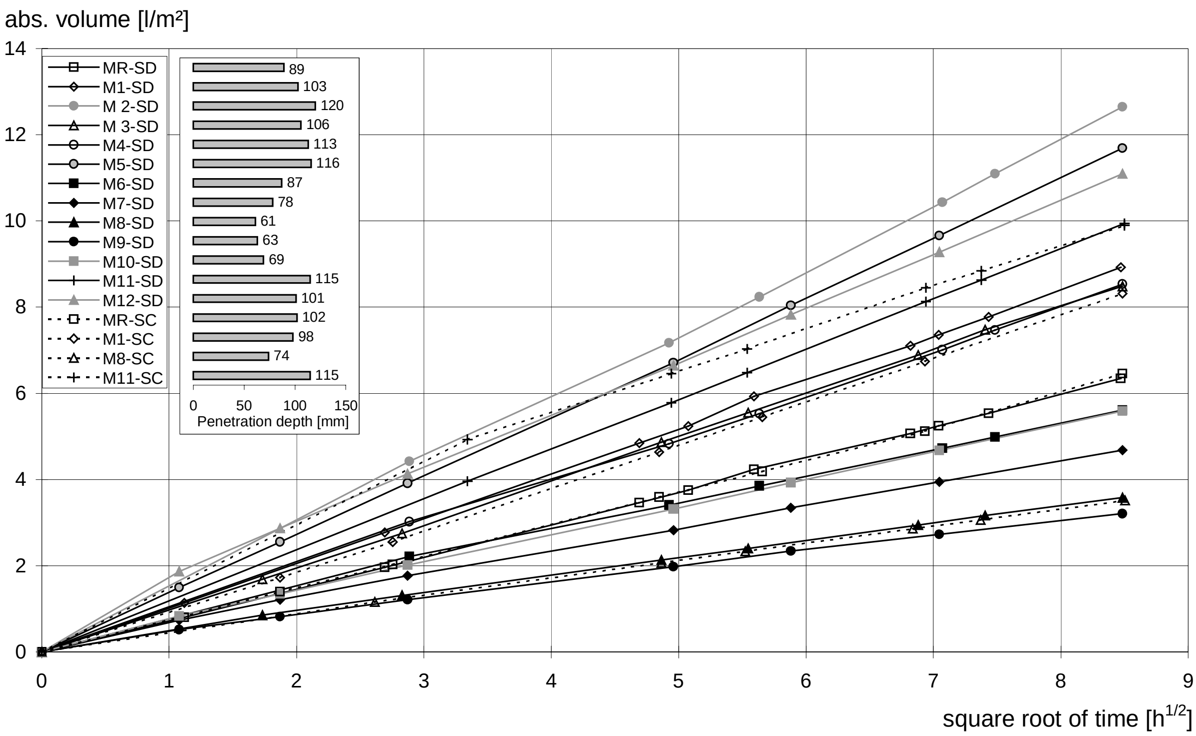

Fig. 2. *72-h-suction tests with n-decane and cyclohexane: progression of absorption, penetration depths*

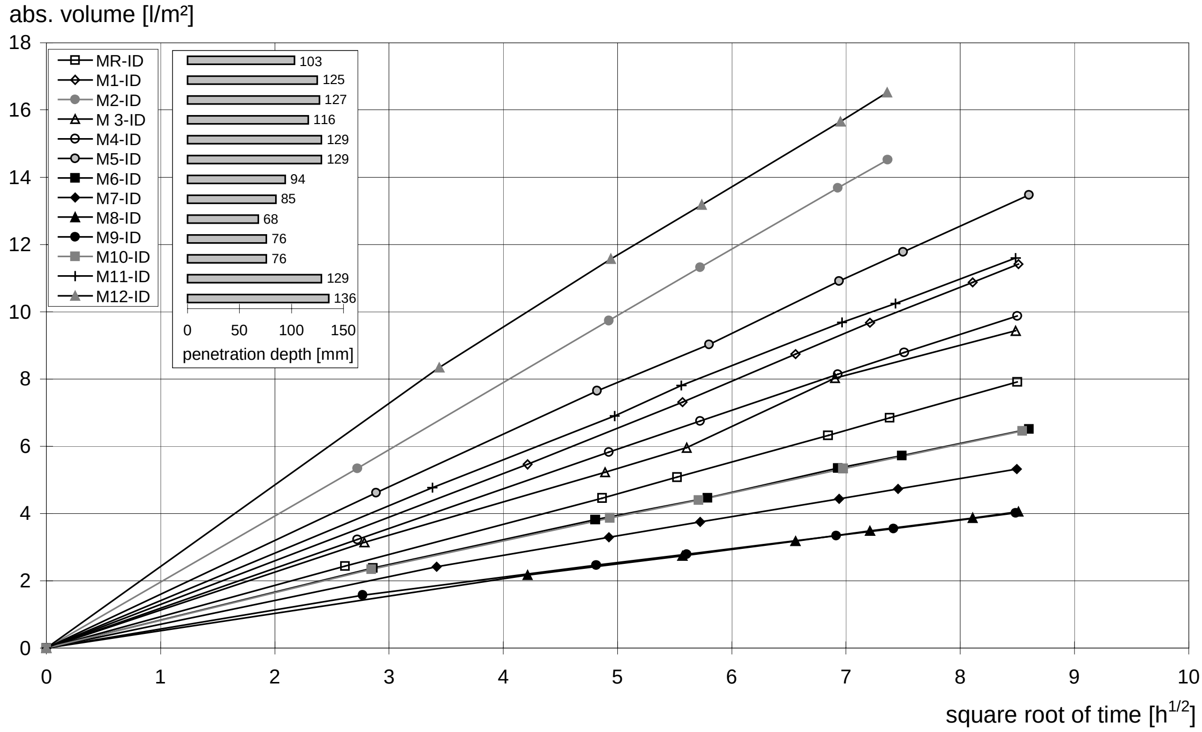

Fig. 3. *72-h-infiltration tests with n-decane: progression of absorption, penetration depths*

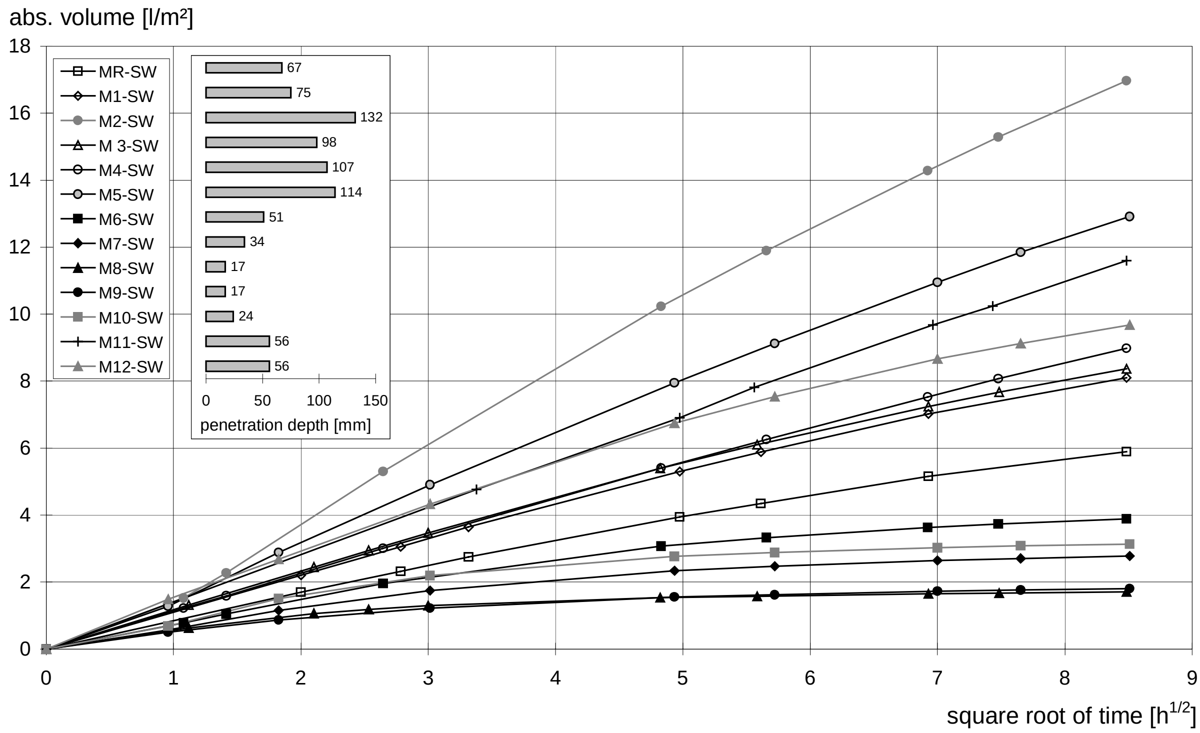

Fig. 4. *72-h-suction tests with water: progression of absorption, penetration depths*

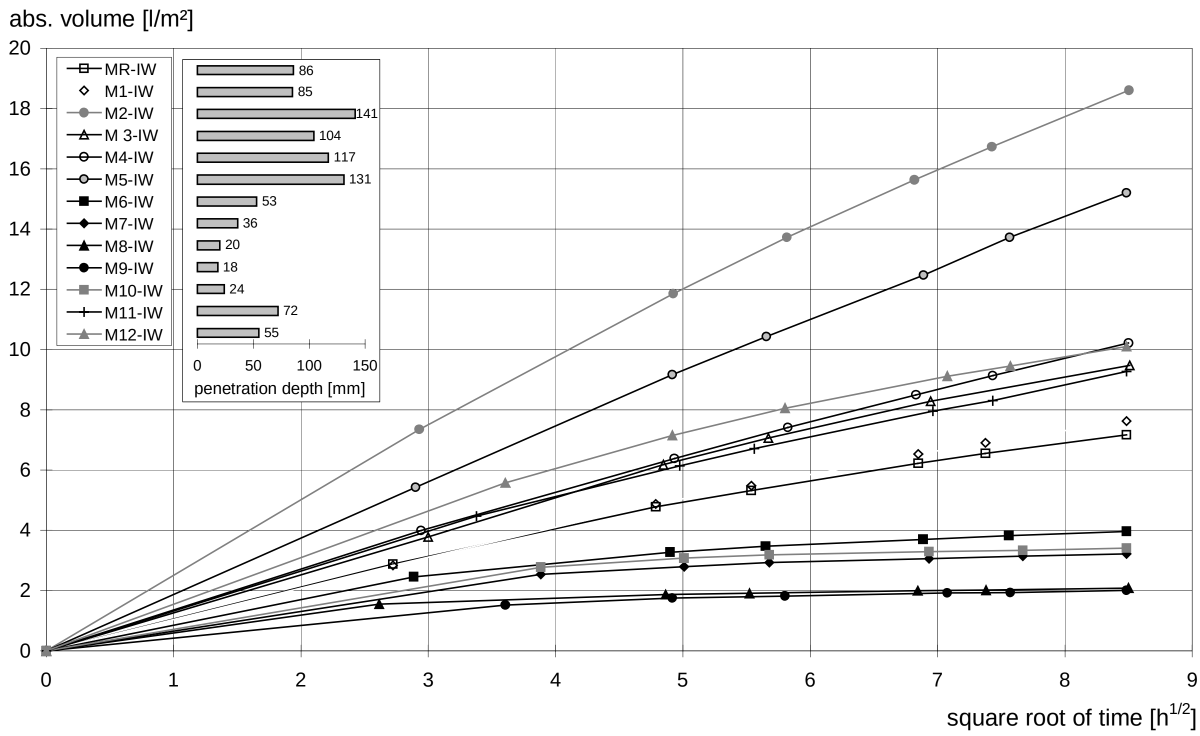

Fig. 5. *72-h-infiltration tests with water: progression of absorption, penetration depths*

3.2 Results of calculations

The pore parameters calculated from the results of penetration tests with n-decane are given in Table 5. r is the pore parameter of the cylinder capillary model with a single pore radius, PR, $\bar{r}$, and $\overline{r^2}$ are those of the model with distributed pore radii. 1 and 2/π therein limit the expected value for $\overline{\cos\theta}$.

Table 5. *Pore parameters calculated from test results with n-decane*

concrete	r		sorptivity S_{SD}	S_{ID}	penetr. coeff. B_{SD}	B_{ID}	gross+pure densities ρ_{65}	ρ_{105}	ρ_R	P_R	μ_{SD}	μ_{ID}	$\overline{r_B}$		$\overline{r_B^2}$	
	[µm]		[l/(m².h^1/2)]		[mm/h^1/2]		[g/cm³]			[%]	[-]		[µm]		[m²]	
MR	0,79	0,50	0,750	0,931	10,5	12,1	2,271	2,257	2,595	11,6	0,613	0,660	0,49	0,61	3,858E-13	3,858E-13
M1	1,10	0,70	1,054	1,342	12,2	14,7	2,272	2,263	2,583	11,4	0,758	0,798	0,68	0,85	7,490E-13	7,490E-13
M2	1,16	0,74	1,491	1,971	14,1	17,2	2,066	2,049	2,533	17,4	0,606	0,657	0,32	0,40	3,767E-13	3,767E-13
M3	0,47	0,30	1,001	1,111	12,5	13,7	2,271	2,266	2,584	11,8	0,681	0,691	0,67	0,84	3,178E-13	3,178E-13
M4	0,71	0,45	1,006	1,162	13,3	15,2	2,282	2,273	2,593	11,5	0,660	0,668	0,82	1,02	5,830E-13	5,830E-13
M5	0,58	0,37	1,378	1,567	13,7	15,2	2,107	2,096	2,570	17,3	0,582	0,595	0,31	0,38	1,767E-13	1,767E-13
M6	0,38	0,24	0,661	0,757	10,3	11,0	2,321	2,306	2,616	10,4	0,622	0,661	0,62	0,77	2,379E-13	2,379E-13
M7	0,44	0,28	0,552	0,626	9,2	10,0	2,278	2,311	2,588	14,0	0,428	0,446	0,23	0,29	1,036E-13	1,036E-13
M8	0,56	0,36	0,422	0,471	7,2	8,0	2,294	2,284	2,561	9,8	0,596	0,599	0,35	0,43	1,958E-13	1,958E-13
M9	1,09	0,69	0,378	0,474	7,4	9,0	2,273	2,260	2,515	8,9	0,573	0,595	0,48	0,59	5,197E-13	5,197E-13
M10	0,47	0,30	0,659	0,756	8,1	8,9	2,121	2,104	2,511	14,5	0,560	0,587	0,17	0,21	7,971E-14	7,971E-14
M11	0,63	0,40	1,169	1,366	13,5	15,2	2,265	2,214	2,544	7,9	1,098	1,141	2,15	2,68	1,351E-12	1,351E-12
M12	3,37	2,15	1,307	2,245	11,9	18,5	2,087	2,074	2,484	15,1	0,725	0,802	0,32	0,40	1,094E-12	1,094E-12
cos θ=	*1*	*2/π*									*cos θ=*		*1*	*2/π*	*1*	*2/π*

index: SD: suction test with n-decane; ID: Infiltration test with n-decane; B: calculated from the penetration coefficient B

4 DISCUSSION OF RESULTS

From the curves for n-decane and water it follows that:

- n-decane penetrates in all examined concretes according to the $t^{1/2}$ law;
- the penetration behaviour of water deviates from the $t^{1/2}$ law;
- the deviations from the $t^{1/2}$ law increase with the pore fineness of concrete (see Table 5).

The deviation from the $t^{1/2}$ law is mainly due to the dissolution of calcium hydroxide from pore walls by penetrating water [Sosoro, 1995, 1998]. The dependence of deviation on the fineness of pore structure can be explained by the fact that the ratio of the part of the pore cross section in which chemical reactions occur and the entire pore cross section increases with decreasing pore radii. The undisturbed part of the pore cross section decreases accordingly. Further, the degree of hydration of high strength concrete is lower because of the low water/binder ratio of 0,32. Rehydration and wetting expansion processes are therefore far more extensive than in normal concrete and superimpose the solution processes [Sosoro, 1998].

A prediction of the penetration behaviour of liquids which don't react with concrete can be made with the parameters of pore structure (r or P_R, $\bar{r}$ and $\overline{r^2}$) determined experimentally from suction and infiltration tests performed with n-decane (or another liquid also not reacting with hardened cement paste) by placing the values for surface tension σ and dynamic viscosity η in equation (1) or equations (3) and (4). This is confirmed by suction tests with cyclohexane on MR, M1, M8 and M11. As the $\sqrt{\sigma/\eta}$-values of n-decane and cyclohexane differ only slightly (Tab.3), equations (1), (3) and (4) predict an almost identical penetration process. The experimental results confirm this forecast: the dashed curves for cyclohexane in Fig. 3 are almost congruent with the corresponding curves for n-decane.

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