THE EFFECT OF THE CEMENT TYPE AND OF CURING ON THE MASS AND DEFORMATIONS OF HARDENED CEMENT PASTE

Erika CSÁNYI*, György BALÁZS*[1] and Zoltán József OLASZ**

*Department of Building Materials and Engineering Geology
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
**HÍDÉPÍTŐ Co.
Budapest
[1]Corresponding author
Tel. +36-1-463-4068
Fax. +36-1-463-3450

Abstract

We have prepared test cylinders out of three cements significantly different in composition (clean portland cement, cement with 40% blast furnace slag content and cement with 20% fly ash content) changing the water/cement ratio (0.10, 0.15, 0.20) and the stamping force (5, 15, 50, 100 N/mm^2). The cylinders were cured under different conditions (air of 50–60% or 95% relative humidity or in lime saturated water), examined the change in length and the mass of them by time and determined their strength at the age of 90 days.

Out of the three cement types – stamped under the same conditions – the cylinders with fly ash content had the biggest porosity.

The curing method has significantly influenced the change of porosity, mass and deformation of the cylinders by time.

The effect of cement type has shown on one hand in porosity and on the other hand especially in the initial deformations of the cylinders the physical and chemical processes during setting (e.g. formation of ettringite).

Keywords: cements, porosity, climatic effects, specific deformations.

1. Introduction

The properties of concrete are determined by the cement paste, the aggregate and the adhesion between the two of them. In the following hardened cement paste will be termed in this article as cement stone; its properties depend on the type of cement and the pore structure of the cement stone. The main properties of clean portland cement are determined by the four clinker minerals ($3\text{CaO}\cdot\text{SiO}_2$, denoted by C_3S; $2\text{CaO}\cdot\text{SiO}_2$, denoted by $\beta\text{C}_2\text{S}$; $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, denoted by C_3A; and $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ denoted by C_4AF). The strength of cement stone is developing by the formation of the calcium-silicate-hydrates (CSH) during the hardening process of C_3S and $\beta\text{C}_2\text{S}$.

4–5% gypsum ($Cs = CaSO_4 \cdot 2H_2O$) is always present in cement. Directly after mixing within a few minutes during an expansion, uniformly shaped hexagonal structured crystals of ettringite (trisulphate) and monosulphate are forming which can be seen also in small magnification. The ettringite is not a stable hydrate, most of it recrystallises to monosulphate.

The most of the cements used in the construction industry, however, are blended cements in which apart from the clinkers and gypsum hydraulic additives are also present; namely blast furnace slag, trass and fly ash. These change the mechanism of hydration.

We summarised the mechanism of cement hardening taking into consideration different cases in [1].

From the point of the properties of concrete the pore structure and porosity of cement stone bears a great significance. WESCHE [2] has divided the pores into gel pores (diameter 1–10 nm), capillary pores (diameter 20 nm–10 μm) and air pores. SETZER [3] has further divided the capillary pore system and made six groups. He has given the freezing point of water and water permeability as the function of the pore diameter. According to POWERS [4] (which has been proved by experiments carried out by other researchers) the strength of cement stone depends on the strength of the assumed poreless cement stone and the porosity of cement stone (capillary and air pores). Apart from this there is a significance of the type of cement and the circumstances of curing (natural hardening, steam curing, autoclaving) in such an extent as much porosity depend on these. The non hydrated cement particles do not decrease strength because the strength of them is equal to that of basalt.

According to all previous researches, every factor which decreases the porosity of cement stone increases its strength.

Cement stone shrinks on air and expands in water. In order to explain this process let us examine the position of water in cement stone.

The position of water in cement stone can be as follows:

a) structurally or chemically bounded water
b) water on surface or between layers, physically bounded, so called adsorption water
c) capillary water.

While the capillary water is easily lost by the cement stone during drying and its loss hardly makes any change in size, the loss of the water bounded physically by the calcium-silicate hydrate (absorption and interlayer water) may cause significant size changes. While the capillary water can leave fast, a long time is needed for the loss of physically bounded water. ARONI and MEHTA [5] showed that this water has a multiple of the viscosity more than that of ordinary water. According to our experiments [6] the shrinkage of C_3S was about half as that of βC_2S.

The shrinkage of the C_4AF pastes increased by fineness, and also increased by the decrease of gypsum content, the smallest was in the case of total lack of gypsum. The extent of the region was about double of that of the βC_2S pastes. The shrinkage region of the C_3A pastes was even double of the C_4AF pastes.

Summarising: the shrinkage of cements depend on their chemical and mineral composition, specific surface, the relative humidity and ambient temperature of the air, the thickness of test specimen and the age of cement stone.

2. Description of the Experiment

2.1. Plan of the Experiment

Taking into consideration the bibliographical data and our earlier experimental results we set up our task to examine the properties, size and mass changes, strength of cement stone for different cement types, changing initial porosity and curing.

The research program is shown in *Table 1*.

Table 1. Paste research program

Sign of experiment	Cement type	Water/cement ratio	Stamping pressure, N/mm^2
1		0.20	5
2		0.20	15
3	Bélapátfalva (B)	0.15	15
4		0.15	50
5	450 pc	0.15	100
6		0.10	50
7		0.10	100
8		0.20	5
9	Vác (V)	0.20	15
10		0.15	50
11	350 kspc 40	0.15	100
12		0.10	100
13		0.20	5
14	Bélapátfalva (B)	0.20	15
15		0.15	50
16	350 ppc 20	0.15	100
17		0.10	100

The used three cements significantly differed from each other. We show their name both according to the valid standard and their earlier names.

1. According to Hungarian Standard MSZ ENV 197-1/1994: CEM I 42.5 = Bélapátfalva 450 pc (clean pc)
2. According to Hungarian Standard MSZ ENV 197-1/1994: CEM II/A-V 32.5 = Bélapátfalva 350 ppc 20 (cement, containing 20% fly ash)

Table 2. Chemical composition of cements

Examined component [m%]	Bélapátfalva 450 pc	Bélapátfalva 350 ppc 20	Vác 350 kspc 40
Ignition loss	1.25	1.75	1.81
SiO_2	21.13	25.67	24.87
CaO	63.77	55.96	55.15
MgO	1.91	1.33	3.43
Al_2O_3	5.25	8.07	5.85
Fe_2O_3	3.20	4.25	2.34
SO_3	2.18	2.31	3.50
Free CaO	0.70	0.52	0.69
Mineral composition			
C_3S	57.23		
βC_2S	22.29		
C_3A	8.62		
C_4AF	9.86		

3. According to Hungarian Standard MSZ ENV 197-1/1994: CEM III/A 32.5 = Vác 350 kspc 40 (cement, containing 40% blast furnace slag)

During the research we used the earlier names of cement (giving the origin by abbreviating with the first letter of origin), because this gives information about the type and quantity of hydraulic additive.

We examined the cements according to the standards MSZ EN 196, MSZ 523 and MSZ 525. The chemical and mineral compositions of the cements are given in *Table 2*, and the physical properties in *Table 3*.

The different initial porosities were achieved by applying different stamping pressure (5, 15, 50, 100 N/mm^2).

We chose the water/cement ratios to be 0.10, 0.15, 0.20. We decided for such a small ratio because the stamping pressure has pressed the water out in case of 0.20. We changed stamping pressure of the specimens prepared with the same W/C ratio.

2.2. Preparation of Test Specimens

We show the drawing of stamping device in *Fig. 1*. The 3 parts of the steel stamping device are precisely polished to each other. On the stamping plunger and the support plunger small grooves ease air discharge.

Preparation of test specimens:

- *Preparation of mixture*. We determined the necessary amount of cement and

Table 3. Physical and strength properties of cements

Examined property	Bélapátfalva 450 pc	Vác 350 kspc 40	Bélapátfalva 350 ppc 20
Specific gravity [g/cm^3]	3.16	3.08	3.07
Specific surface [m^2/kg]	332	302	282
Particle size > 0.09 mm [m%]	0.9	2.22	5.82
Water demand	0.26	0.28	0.28
Setting start	2 hour 00 sec	3 hour 20 sec	1 hour 20 sec
Setting end	3 hour 55 sec	4 hour 35 sec	3 hour 15 sec
Bending strength, N/mm^2			
3 days	3.66	2.70	2.80
7 days	6.10	6.41	5.41
28 days	7.50	8.12	6.41
Compressive strength, N/mm^2			
3 days	14.5	9.9	10.9
7 days	27.0	20.7	19.8
28 days	47.7	36.8	36.1
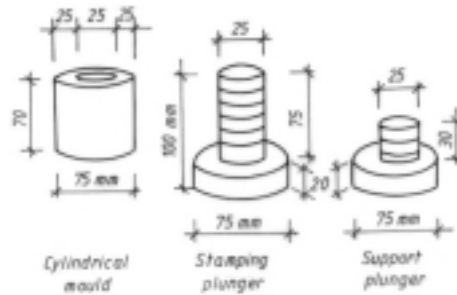
Fig. 1. Stamping device

water by pre-experiment. The (always same) batched quantities were care-
fully mixed taking big care to obtain a mixture as homogeneous as possible.
- *Filling the mixture into the mould and stamping*. Hereupon the mixture was
poured into the mould and stamped with the force of 2.5; 7.5; 25; 50 kN.
(The cross sectional area of the cylinders was about 5.0 cm^2, so the stamping
pressure was 5, 15, 50 and 100 N/mm^2.
- *De-moulding of test specimens*. By pushing out from the cylindrical mould
the so obtained test specimens, having different initial porosities we obtained
the specimens with a diameter of 25 mm and about 50 mm height.

The process of stamping and de-moulding is shown in *Fig. 2*. Before prepar-

ing each cylinder we cleaned thoroughly by a dry rug the stamping device, the mixing bowl and the stamping plunger.
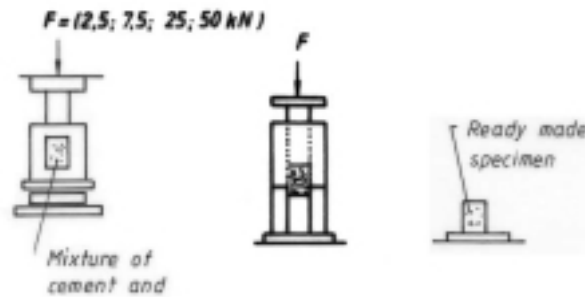

Fig. 2. Preparation of test specimens

2.3. Curing of Test Specimens

On one group of the test specimens we only determined the strength and porosity, and carried out DTA and TG examinations in different ages. These specimens were kept in room ambient temperature and relative humidity of about 95% until the time of the experiment.

Those specimens on which we made measurements regarding mass and size changes were kept in three ways:

a. One hour after the specimen preparation we put the specimens into moist air of about 95% relative humidity and 20–24 °C temperature.
b. One hour after the specimen preparation we placed the specimens into climatic chamber the temperature of which was set to about 14–18 °C and the relative moisture content to 50–60%.
c. Until the age of 24 hours of the specimens they were kept in moist air then put into lime saturated water at the temperature of 20–24 °C. The 24 hour grace period was necessary because otherwise the specimens would have fallen apart in the water.

2.4. The Method of Investigations and Results

2.4.1. Density along the Height of the Test Specimens

We could count with a change in the density along the height since we could only stamp the specimens from one end. As a first step we wanted to split the specimens

to 1cm thick layers but could not. We then succeeded to split the specimens to three pieces which were finally enough to determine inhomogeneity.

This investigation was carried out on specimens without admixtures, series prepared out of three different types of cement, 1–1 piece of big, medium and small porosity specimens at the age of 90 days. Since the third parts of the specimens were non uniform bodies we carried out our examination using the principle of liquid displacement.

The tendency was the same independently from the initial porosity and the type of cement. In all cases the top part of the paste cylinders had the highest density.

The density values in function of the cement type, the W/C ratio and the stamping strength are summarized in *Table 4*.

The effect of this inhomogeneity of the test specimens – arising from the stamping technology – we eliminated by using always the whole specimen for our investigations.

2.4.2. Change in Mass

On 3–3 specimens in case of all three kinds of curing methods we registered the mass change of the cylinders in time. The values were taken daily for one week, following which we recorded the masses less frequently for about 40–50 days.

We summarized the specific mass change in function of time for the differently cured cylinders in *Figs. 3–11*. In *Figs. 12* and *13* we summarized two extreme cases, the specific mass change of the cylinders of the 1st and 5th specimen series.

2.4.3. Size of Change

Following the preparation of each specimen cylinder immediately we measured its length, diameter and mass. In order to be able to measure the changes by time we had to place a spherical object at one end plane of the specimens in the center, to be able to define the basic length properly. To solve this problem we prepared several pre-experiments.

In order to place a spherical object on one end surface of the cylinder in the middle (measuring point) by using a hand drill of 4 mm diameter made a 2–3 mm deep hole.

As a spherical surface first we used steel ball of 5mm diameter, and for fixing gel instant glue. This solution did not prove to be good because the instant glue did not stick properly to the wet surface of the mixture and in wet environment, in the lime water the steel ball started to rust. Further we used glass ball glued by a two component resin based adhesive the name of which is ARALDIT.

The chosen glue had to satisfy two important requirements: that is to ensure long term adhesion between the glass ball and the wet surface of the test specimen

Table 4. Change of density along the height of test cylinders

Sign of series	Layers	Cement type	Water/cement ratio	Stamping force kN	Density g/cm^3
1	bottom middle top	B 450 pc	0.20	2.5	1.73 1.88 1.98
4	bottom middle top		0.15	25.0	1.96 2.07 2.17
7	bottom middle top		0.10	50.0	1.99 2.13 2.25
8	bottom middle top	V 350 kspc 40	0.20	2.5	1.64 1.70 1.82
10	bottom middle top		0.15	25.0	1.86 2.00 2.10
12	bottom middle top		0.10	50.0	1.90 2.09 2.20
13	bottom middle top	B 350 ppc 20	0.20	2.5	1.48 1.66 1.75
15	bottom middle top		0.15	25.0	1.71 1.84 1.95
17	bottom middle top		0.10	50.0	1.80 1.88 2.13

and also had to be able to resist the different curing conditions. The glued glass ball is shown in *Fig. 14*.

The appropriateness of both the glass ball and the adhesive was checked experimentally. Before using the adhesive we measured its shrinkage as follows. A trial ball was glued with the mixed adhesive on a steel test specimen and the base length measured with the length change measuring device (introduced later). Following this we experienced that after taking readings at first in every minute then in every five minutes after the passing of the 35th minute the adhesive totally hardened and the value of shrinkage was not bigger than one thousandth of a millimeter. This can practically be neglected.
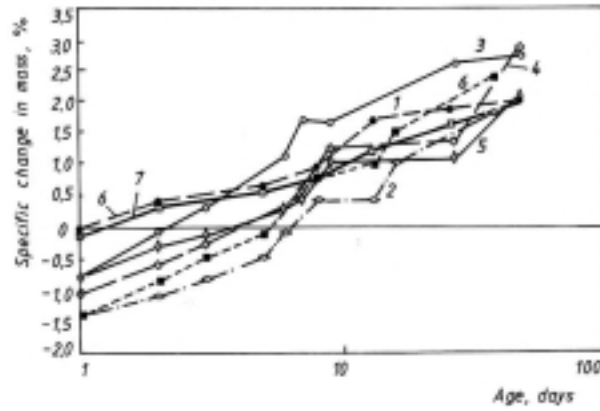
Fig. 3. Specific change in mass in the function of time of paste cylinders prepared out of B 450 cement and cured under moist circumstances (1–7 Sign of series)
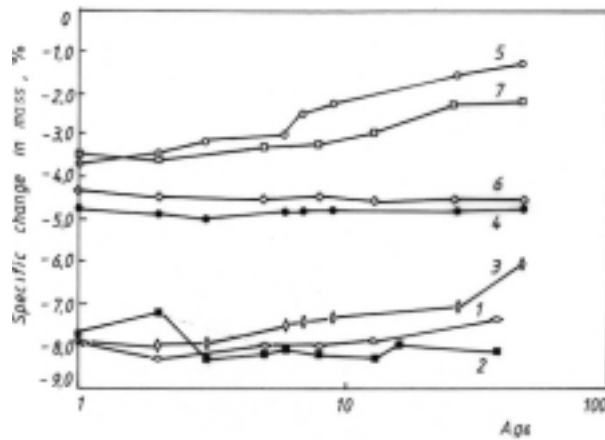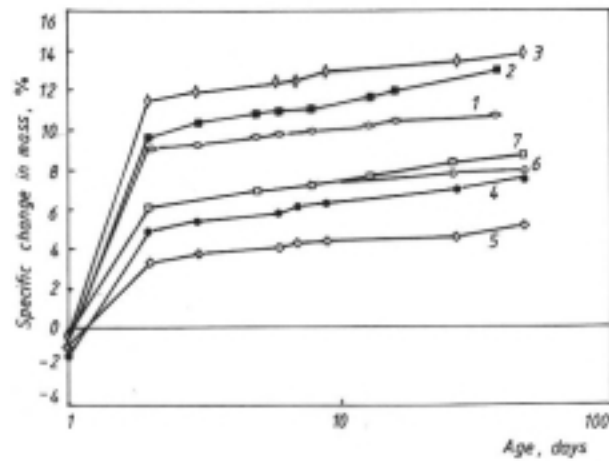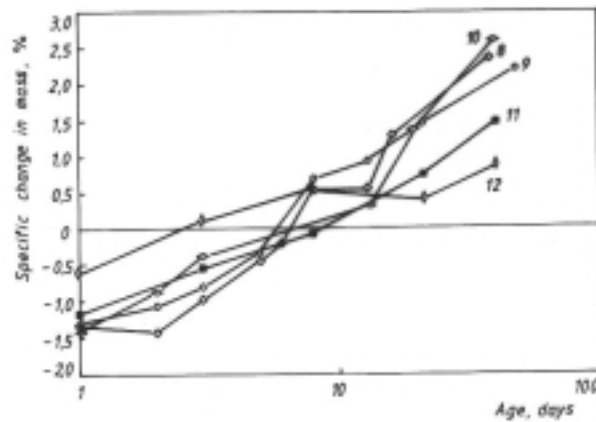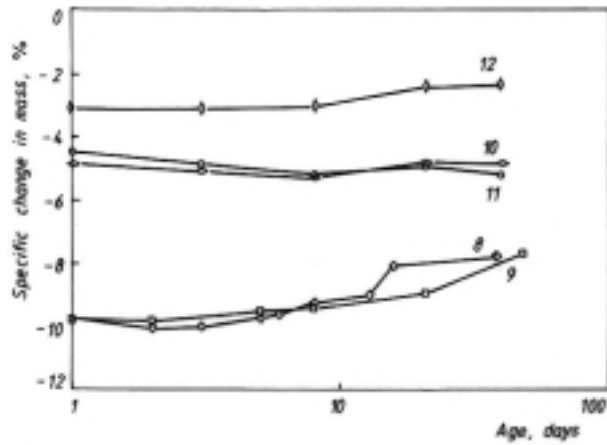

Fig. 4. Specific change in mass in the function of time of paste cylinders prepared out of B 450 cement and cured in climatic chamber (1–7 Sign of series)

The alkaline environment standing capability of the glass balls was checked by keeping them in lime saturated water for 74 hours and examining their surface under magnification. Following the treatment the surface of the glass balls was absolutely intact and later, during the experiments we also did not observe any change on them.

To examine the length change we used MILITAST 1082 type equipment

Fig. 5. Specific change in mass in the function of time of paste cylinders prepared out of
B 450 cement and cured in lime saturated water (1–7 Sign of series)

Fig. 6. Specific change in mass in the function of time of paste cylinders prepared out of
V 350 cement and cured under moist circumstances (8–12 Sign of series)

with digital display and a sensitivity of 0.001 mm. During setting up the mea-
suring equipment we tried to eliminate all vibration effects. Since the measuring
equipment was fixed and we kept the test specimens in different places, before
starting the regular measurements it had to be cleared if the existing temperature
differences would cause inaccuracies. In the climatic chamber the temperature

Fig. 7. Specific change in mass in the function of time of paste cylinders prepared out of V 350 cement and cured in climatic chamber (8–12 Sign of series)
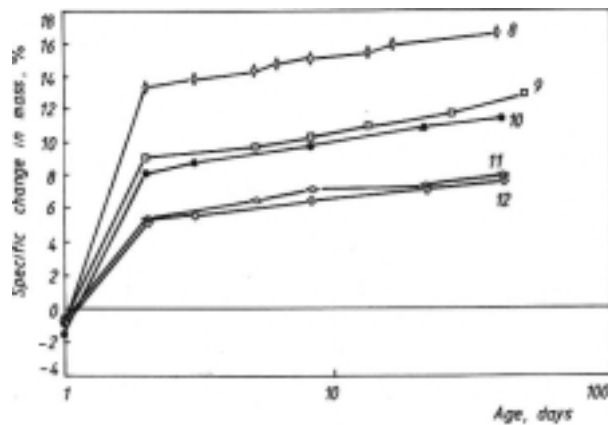

Fig. 8. Specific change in mass in the function of time of paste cylinders prepared out of V 350 cement and cured in lime saturated water (8–12 Sign of series)

was 14 °C while in the laboratory, where the measurements were carried out, it was 20–22 °C. The length measurements lasted for about two hours in every occasion. This possible source of inaccuracy we checked in case of all three cement types as follows. One of the specimens we took from the chamber and put it into the measuring device and made zero adjustment. Then we took readings from the display in every minute for 15 minutes then at 5, 10, 15, 30 and 60 minutes. This
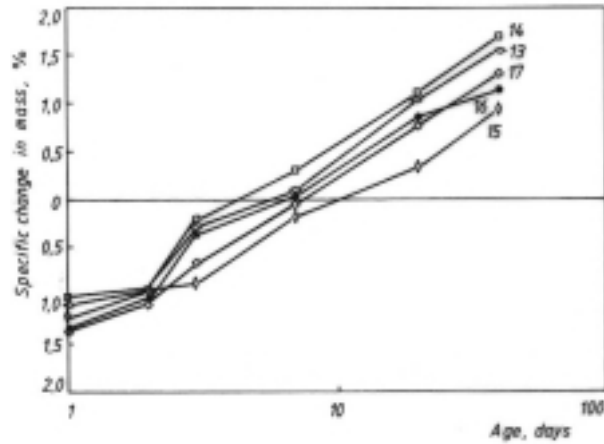
Fig. 9. Specific change in mass in the function of time of paste cylinders prepared out of
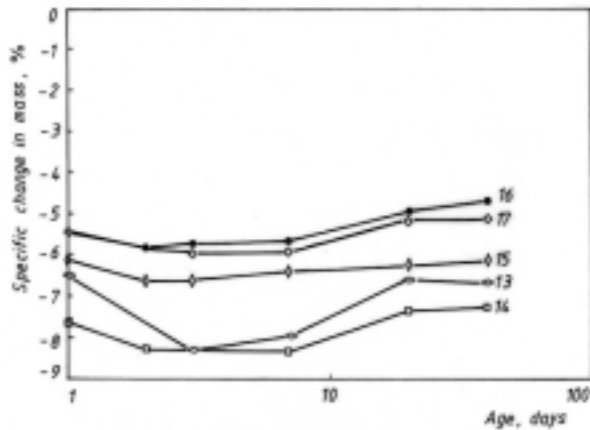B 350 cement and cured under moist circumstances (13–17 Sign of series)

Fig. 10. Specific change in mass in the function of time of paste cylinders prepared out of
B 350 cement and cured in climatic chamber (13–17 Sign of series)

measurement was carried out during four hours after which the average change in
length of 0.002 mm was negligible. We can surely say that the effect of the effec-
tive temperature change during the measurements practically did not influence the
length change of the test specimens.

During the pre-experiments we observed that the change of the measured
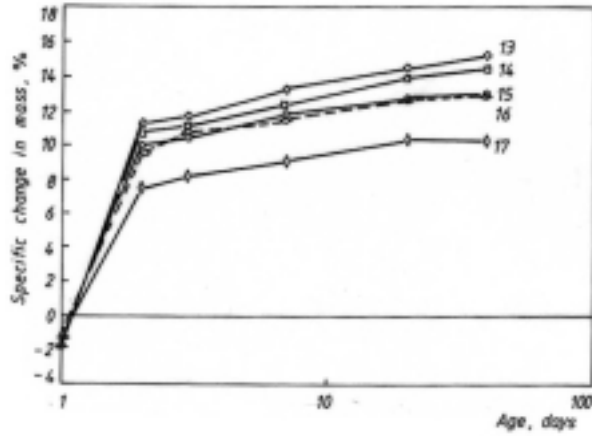
Fig. 11. Specific change in mass in the function of time of paste cylinders prepared out of
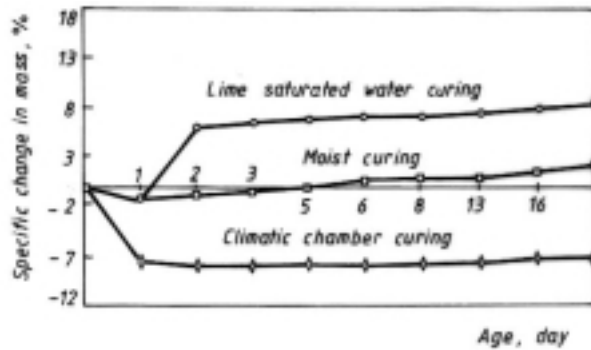   B 350 cement and cured in lime saturated water (13–17 Sign of series)

Fig. 12. Specific mass changes of the 1st series in different curing conditions

values was significant in the first four hours. After the sixth hour the until then ob-
served changes in the values have decreased to their tenth or even smaller. Due to
this reason in the comparison of the length changes of the test specimens prepared
out of different cements with different porosity we have scheduled the measure-
ments such that between the mass measurement and glass ball gluing the measure-
ment of length was made one hour from the preparation of the mixture. After this
we measured the length changes during the first four hours hourly then until the
age of one week daily and for further until the age of 90 days weekly.

We measured length changes on a set of 3–3 specimens which were prepared
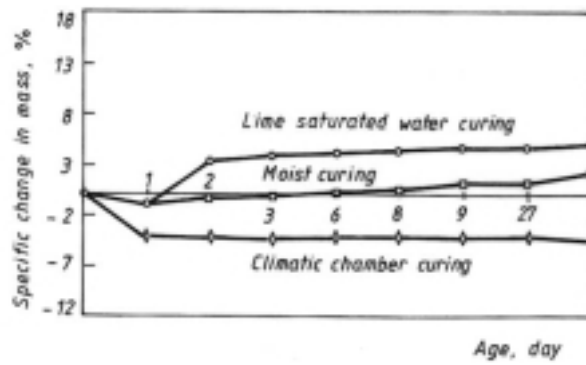out of different cements. From the values of the length changes obtained at dif-

Fig. 13. Specific mass changes of the 5th series in different curing conditions
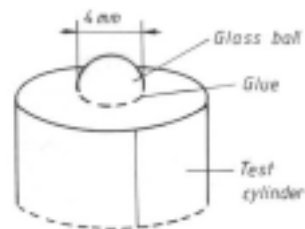

Fig. 14. Glass ball glued to the test specimens

ferent times and the height of the prisms after their preparation we calculated the average specific length changes which are plotted against time in *Figs. 15–23.*

2.4.4. Strength Measurements

At the end of the experiments we determined the strength of the cylinders. For the measurements we used a ball joint adjusted to the size of the specimens.

2.5. Examination of Porosity

We calculated the porosity of the paste cylinders using the following formula:
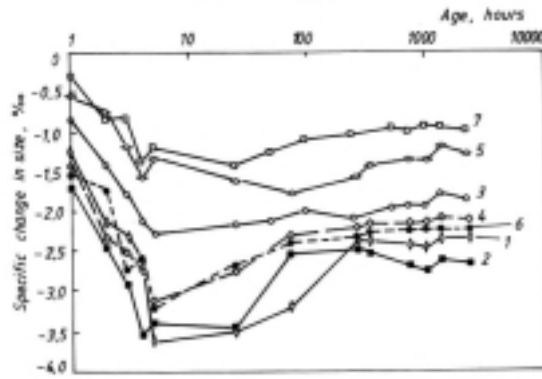
$$p_K = 1 - \frac{\rho_{t,K}}{\rho_K},$$

Fig. 15. Specific change in size in the function of time of paste cylinders prepared out of
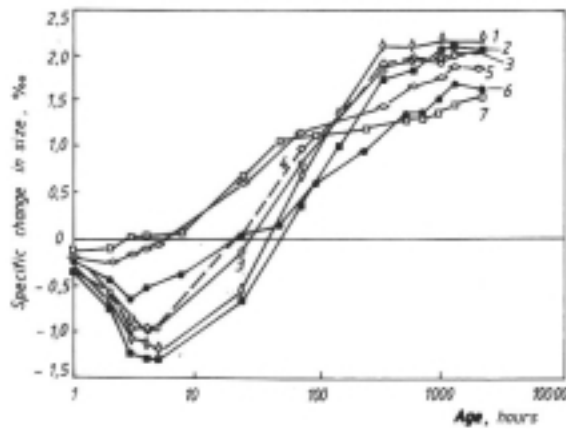B 450 cement and cured under moist circumstances (1–7 Sign of series)

Fig. 16. Specific change in size in the function of time of paste cylinders prepared out of
B 450 cement and cured in climatic chamber (1–7 Sign of series)

where:

p_K porosity,
$\rho_{t,K}$ density,
ρ_K specific gravity,
K time of testing.

During the initial (just after preparation) density calculation we assumed that the
water used for the preparation of the specimen has not yet got built in (hydration
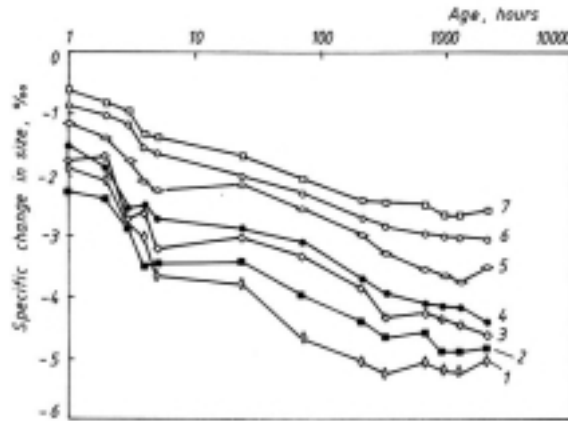
Fig. 17. Specific change in size in the function of time of paste cylinders prepared out of B 450 cement and cured in lime saturated water (1–7 Sign of series)
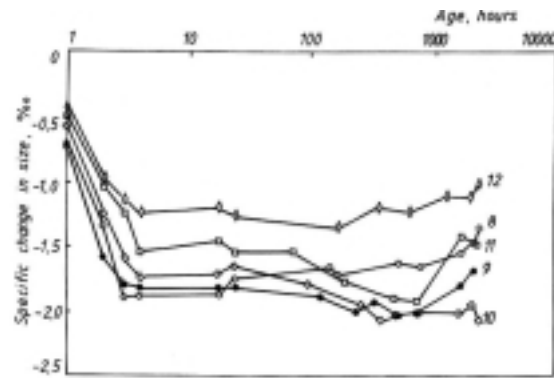

Fig. 18. Specific change in size in the function of time of paste cylinders prepared out of V 350 cement and cured under moist circumstances (8–12 Sign of series)

has not started yet), that is it could be eliminated by drying on the temperature of 105 °C. Thus knowing the quantity of cement used for the preparation of the specimens and the sizes of the specimens the initial 'dry' density can be calculated, and using the specific gravity of the cements the initial porosity of the specimens can be determined.

For the determination of the 90 days old density we used the specimens prepared for strength examinations, and for the density measurements we used the fractions following the examination of the strength. The specimens were pow-
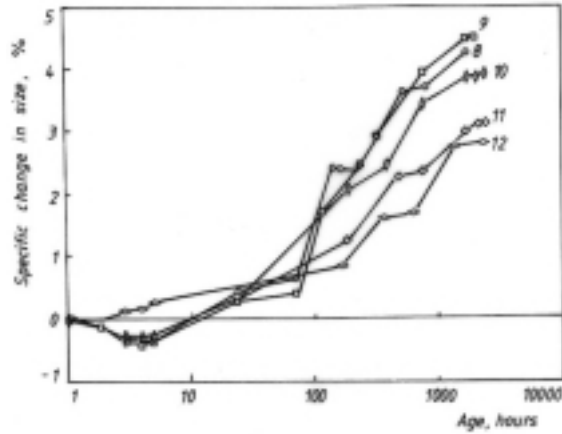
Fig. 19. Specific change in size in the function of time of paste cylinders prepared out of V 350 cement and cured in climatic chamber (8–12 Sign of series)
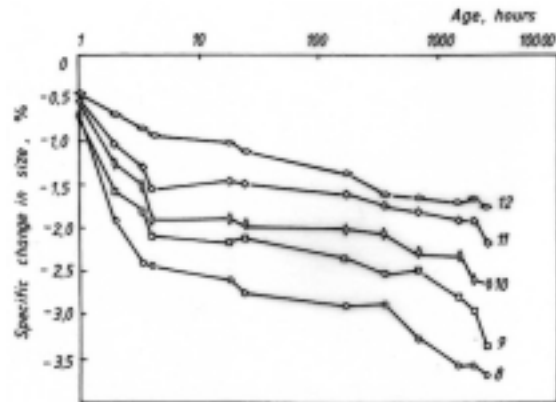
Fig. 20. Specific change in size in the function of time of paste cylinders prepared out of V 350 cement and cured in lime saturated water (8–12 Sign of series)

dered until the total quantity has passed the sieve 0.063 mm following which we determined the specific gravity by pycnometric method using alcohol as immersion liquid.

The initial and 90 days old measured and calculated mass distribution properties we summarised in *Table 5*.

Fig. 21. Specific change in size in the function of time of paste cylinders prepared out of B 350 cement and cured under moist circumstances (13–17 Sign of series)

Fig. 22. Specific change in size in the function of time of paste cylinders prepared out of B 350 cement and cured in climatic chamber (13–17 Sign of series)

3. Evaluation of Examination Results

3.1. Mass Distribution Properties

Out of three types of cement (PC, clean portland cement, BFSPC, portland cement containing 40% blast furnace slag, and FAPC, portland cement containig 20% fly ash) using 3 different water–cement ratios (0.10, 0.15 and 0.20) we prepared mix-
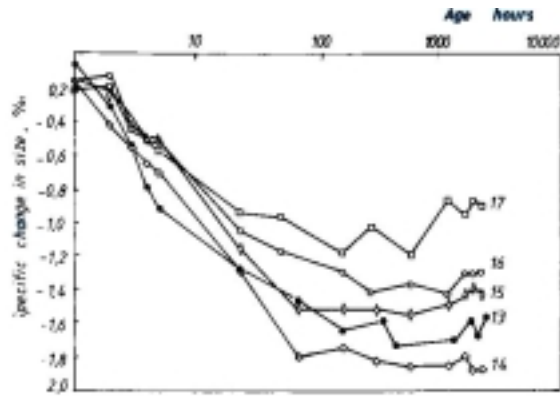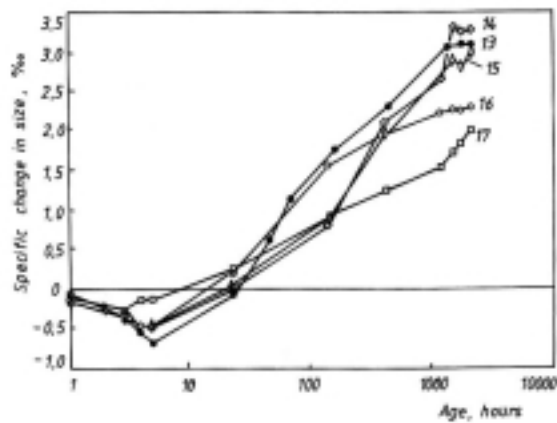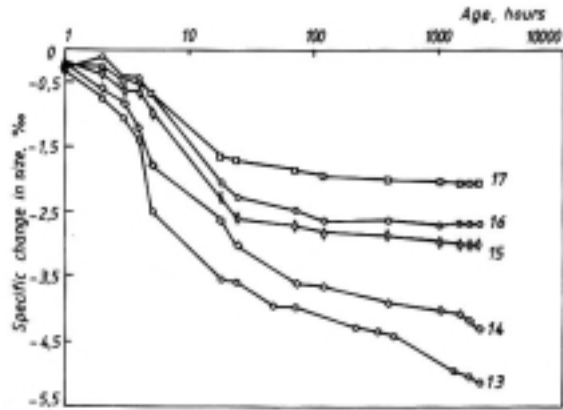
Fig. 23. Specific change in size in the function of time of paste cylinders prepared out of B 350 cement and cured in lime saturated water (13–17 Sign of series)

tures and by changing the pressure (5, 15, 50 and 100 N/mm^2) obtained the same size (diameter 25 mm, 48–52 mm height) paste cylinders. Using the available steel mould a series of tests was prepared according to *Table 1*.

Due to the stamping technology the test cylinders on the stamping plunger end have compacted more and so the density of the lower part of the test cylinders prepared out of PC (B 450) and BFSPC (V 350) was 86–90% that of the top while the lower part of the test cylinders prepared out of FAPC (B 350) was 85–88% that of the top. This difference naturally influenced the porosity values also which we could not take into consideration during further measurements. However, taking into consideration that the measurements were taken actually either for the whole test cylinders or on the parts which were powdered and homogenised, the density difference along the height did not influence the measurements or the evaluation of the results. We have also observed that applying the same pressure and using the same W/C ratio to prepare cylinders with the same geometry out of the mixture made out of FAPC we could work in smaller quantity, thus – due to the less compactibility of the cement type – these cylinders had the least initial density and the highest porosity. The initial (just after stamping) and at the age of 90 days the mass distribution properties of the cylinders are in *Table 5*. Based on the data in the table we calculated the decrease of initial porosity in % until the age of 90 days under different curing (storing) conditions. These values were summarised in *Table 6*.

Table 5. Initial and 90 days measured and calculated mass distribution properties of paste cylinders

Serial No	Initial		At the age of 90 days								
	dry density, kg/m^3	poro-sity	dry density kg/m^3	spec. gravity g/cm^3	poro-sity	dry density kg/m^3	spec. gravity g/cm^3	poro-sity	dry density kg/m^3	spec. gravity g/cm^3	poro-sity
			moist conditions			climatic chamber			lime saturated water		
1	1678	0.47	1909	2.52	0.24	1872	2.86	0.35	1837	2.50	0.26
2	1805	0.40	1928	2.52	0.23	1933	2.83	0.32	1964	2.45	0.20
3	1707	0.45	1905	2.52	0.24	1891	2.86	0.34	1941	2.45	0.21
4	1913	0.39	2040	2.59	0.21	2028	2.79	0.27	2100	2.45	0.14
5	2040	0.35	2157	2.63	0.19	2111	2.85	0.26	2193	2.54	0.14
6	1911	0.40	2036	2.66	0.23	2004	2.88	0.30	2092	2.50	0.16
7	2010	0.36	2117	2.68	0.21	2078	2.89	0.28	2152	2.52	0.15
8	1588	0.49	1730	2.56	0.33	1738	2.87	0.39	1629	2.47	0.34
9	1685	0.45	1806	2.53	0.29	1766	2.85	0.38	1926	2.41	0.30
10	1816	0.41	1919	2.62	0.27	1905	2.80	0.32	1934	2.48	0.22
11	1949	0.37	2076	2.58	0.19	1991	2.78	0.28	2060	2.49	0.17
12	1940	0.37	2032	2.65	0.23	1989	2.86	0.30	2047	2.53	0.19
13	1407	0.53	1432	2.63	0.45	1541	2.74	0.44	1605	2.52	0.35
14	1657	0.49	1613	2.66	0.39	1622	2.74	0.41	1640	2.52	0.35
15	1758	0.43	1818	2.79	0.35	1781	2.74	0.35	1771	2.55	0.31
16	1794	0.42	1832	2.78	0.34	1863	2.81	0.34	1844	2.62	0.30
17	1788	0.42	1838	2.61	0.34	1838	2.78	0.34	1868	2.59	0.28

In case of the same W/C ratio and stamping force the cylinders having the biggest density (from 1678 to 2040 kg/m^3) are the ones prepared out of PC and the smallest (from 1407 to 1788 kg/m^3) are the ones prepared out of FAPC. The initial porosity is also accordingly: the smallest is that of the cylinders prepared from PC ($47 \rightarrow 36$ volume %) and the biggest is that of the cylinders prepared from FAPC ($53 \rightarrow 42$ volume %).

The relevant values of the blast furnace slag cement cylinders fall between the two (1588–1940 kg/m^3, and $49 \rightarrow 37$ volume %). The % values of *Table 6* show the decrease of porosity.

The tendencies are:

- Biggest is the clean portland cement, smaller is the blast furnace PC and the smallest is the fly ash PC.
- Biggest in case of stored in lime saturated water, slightly smaller in case of stored in moist surrounding and much smaller in case of climatic chamber storing. There is an exception for the case of FAPC: there is hardly any difference between the values from storing conditions of moist surrounding and climatic chamber.
- The mass loss of the pastes prepared out of the less initial porosity clean portland cements is a little bigger than the ones having bigger initial porosity. This, however, does not mean a higher degree of hydration because that would be indicated by the absolute value of the decrease.

3.2. Mass Change

Figs. 3–11 shows for the case of identical storing conditions but 1–1 cement types the behaviour of the paste cylinders prepared by different stamping pressure. Our conclusions are summarised below:

- From *Fig. 12* and *13* it can be seen that the three types of storing effects the mass change differently. In the climatic chamber within 1 day a big decrease in mass occurs due to drying, which hardly changes until the age of 90 days. In the lime saturated water following the starting of the storage a big mass increase happens which shows slight increase later. Finally, in case of moist surrounding following a small degree of mass decrease a small increase is observed.
- By plotting the specific mass change as the function of porosity (*Fig. 24*) it can be clearly seen that belonging to increase of porosity is an increase in mass increase (storing in lime saturated water) and increase in mass decrease (storing in climatic chamber). The type of cement is indicated by the porosity of cement stone. An exception is the storage in moist conditions, where the porosity has practically no effect.

Table 6. Change of porosity by different storing conditions at the age of 90 days of the
paste cylinders

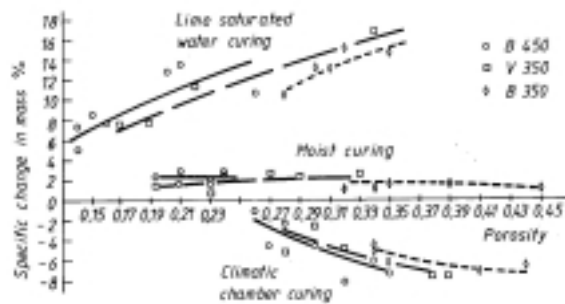| Serial No.	Initial porosity	Porosity decrease until the age of 90 days, %		
		moist conditions	climatic chamber	lime saturated water
1	0.47	49	26	45
2	0.40	43	20	50
3	0.45	47	24	53
4	0.39	46	31	64
5	0.35	44	26	60
6	0.40	43	25	60
7	0.36	42	22	58
8	0.49	33	20	31
9	0.45	36	16	33
10	0.41	34	22	46
11	0.37	47	24	54
12	0.37	38	19	49
13	0.53	15	17	33
14	0.49	20	16	29
15	0.43	19	19	28
16	0.42	19	19	29
17	0.42	19	19	33

Fig. 24. Change in mass of the paste cylinders until the age of 40–50 days as a function of
porosity

3.3. Deformation

By examining the curves (*Figs. 15–23*) showing the deformations by time of the cylinders prepared out of different types of cements and stored under different conditions the following tendencies can be observed:

- By placing the test cylinders into 95% relative moisture content conditions expansion takes place. This happens in case of PC and BFPC within 5 hours and in case of FAPC within 2–3 days. The extent of the expansion is the biggest in case of clean PC, 1.5–3.5 ‰ while in case of the other two cement types is smaller, about 1–2 ‰ and increases by the porosity. This expansion process actually happens during the setting of cement, which on one hand is during a heat evolution and on the other hand due to the formation of ettringite is together with an expansion. So can be explained why the biggest and fastest expansion occurs in case of cylinders made out of clean PC having big porosity. This is followed by the shrinkage, which will be the biggest in case of the cylinders having bigger porosity. Finally, the deformation process practically stops. The behaviour of the other two cements is similar but the expansion will be smaller and the shrinkage will be higher.

- In case of the test cylinders stored in lime saturated water unambiguously can be observed the expansion by time due to the absorption of water the value of which at the end of the examination time is 1.5–5.5 ‰ The rate of expansion in the first few hours is bigger, then later decreases but it can be observed during the total examination period (even between the age of 60–90 days). Naturally, when evaluating the test results we must take into consideration that the test cylinders were put into lime saturated water at the age of 1 day (due to the danger of crumbling), so the part of the processes described for the cylinders kept in moisture conditions have already taken place.

- In case when the tests were kept in the conditions of 50–60% relative moisture content it can also be observed the initial expansion of the specimens for a few hours (0.5–1.2 ‰), the magnitude of which – due to the reasons explained before – is the biggest in case of portland cement. Following this a drying shrinkage occurs the magnitude of which depends on the porosity and the type of cement. Until the age of 90 days the shrinkage of fly-ash portland cements is 2.8–4.5%, of portland cements 1.5–2.2, while the blast furnace portland cements fall in between.

- In *Fig. 25* we show the deformations of 90 days old cylinders as a function of porosity. By the increase of porosity the expansion of the tests stored in lime water and the shrinkage of the ones stored in climatic chamber is unambiguously increasing, while in the moist surrounding, similarly to what has been experienced for the case of change in mass, the deformation does not depend on porosity.

3.4. Strength

We summarised the strength of the paste cylinders kept under three types of storage conditions at the age of 90 days in *Figs. 26–28*. Conclusions:

- It is known that the strength of cement stone decreases by the increase of porosity. This law is valid for our case also for all cement types and storage conditions.
- The climatic chamber storage caused the biggest porosity and so the smallest strength (*Fig. 26*). The reason was that the samples dried soon and for the continuation of the hydration the water was not enough. The other two storage conditions (moist conditions, *Fig. 27* and lime water, *Fig. 28*) had similar effect both to the decrease of porosity and the strength. Both storage conditions resulted an undisturbed hydration.
- In *Fig. 29* we summarised all results. According to the figure porosity has a definite effect on strength. The effect of cement type and storage conditions is mainly shown on porosity.
- The initial and later porosity of B 350 type cement containing 20% fly ash was significantly bigger than that of the B 450 type clean portland cement prepared out of the same clinker. The specific surface of the first was 282, and the latter 332 m^2/kg. The cement containing fly ash was initially more roughly grained. The big difference in the strength is double:
  - On one hand due to the friction increasing effect of the fly ash the initial porosity under the same stamping pressure is bigger.
  - On the other hand the grain of the clinker is more rough than the one shown by the specific surface because when grinding fly ash together with the clinker the ash is grinded much more finely than the clinker.
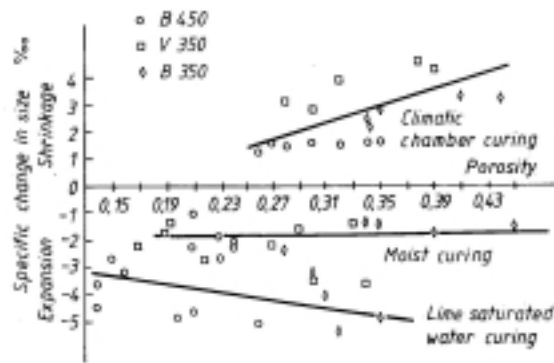

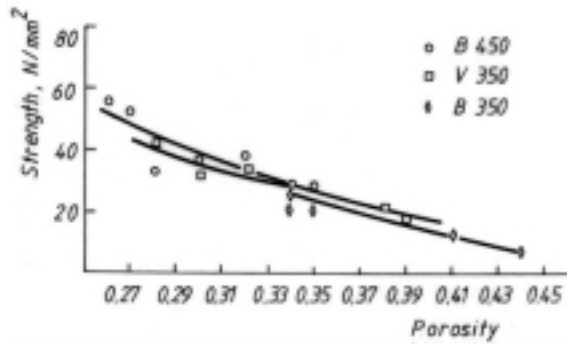*Fig. 25.* Specific change in size at the age of 90 days of the paste cylinders cured under different conditions

Fig. 26. Compressive strength as a function of porosity at the age of 90 days of paste cylinders cured in climatic chamber
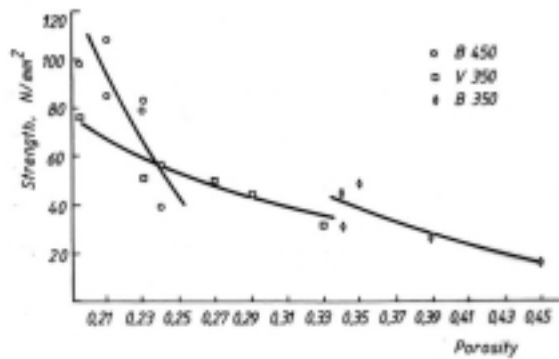

Fig. 27. Compressive strength as a function of porosity at the age of 90 days of paste cylinders cured in moist air

4. Conclusions

a) In case of paste cylinder specimens the initial porosity if prepared by the same stamping pressure and applying the same water/cement ratio out of clean portland cement and blast furnace portland cement was nearly the same (*Table 6*), while it was bigger when using fly ash portland cement due to the friction increasing effect of fly ash.

b) The initial porosity decrease during hydration significantly depended on the curing (storage). It was the biggest when curing in lime saturated water, and was a little smaller in moist air. The porosity of samples which were stored in climatic chamber decreased significantly less than in the other two cases
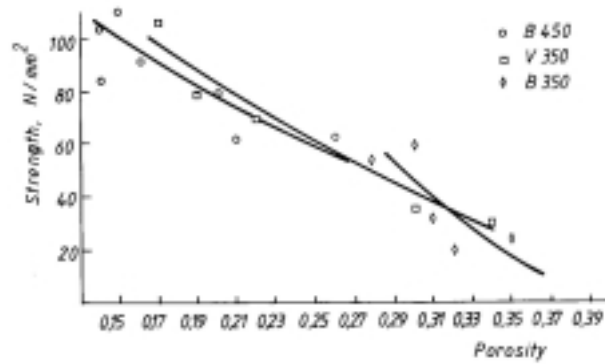
Fig. 28. Compressive strength as a function of porosity at the age of 90 days of paste cylinders cured in lime saturated water
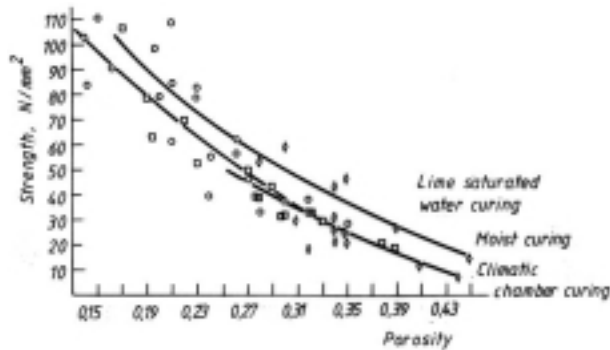

Fig. 29. The compressive strength of differently cured paste cylinders at the age of 90 days as a function of porosity

because for the hydration the water was not enough.

c) The change of mass by time significantly depended on the storing conditions (*Figs. 3–11*) and on the initial porosity. While the mass change of clean portland cement and the fly ash containing cement after about 60 days did not change, the one with blast furnace slag content did not tend to an asymptote. The mass change of the 90 days old cylinders is a function of the porosity (*Fig. 24*), the effect of cement type showed in porosity. The mass increased by porosity in case of storing in lime saturated water, decreased in the climatic chamber and was independent from it in case of curing in moist conditions, which shows a state of water content equilibrium through capillary porosity.

d) The change of deformation by time is effected by the initial chemical-physical processes (e.g. the formation of ettringite) but for the age of 90 days we experienced a similar tendency to the mass change (*Fig. 25*). With the increase of the porosity of the samples the shrinkage increased when cured in a climatic chamber, increased the expansion of those kept under water while the deformation was independent from porosity in case of moist curing conditions.

e) The compressive strength of 90 days old samples decreased by the increase of porosity. The effect of curing, type of cement and initial porosity has showed through porosity.

Acknowledgement

References

[1] BALÁZS, GY.: Energiatakarékos betonszilárdítás. Műszaki Könyvkiadó (1997).

[2] WESCHE, K. H.: Baustoffe für tragende Bauteile V.2. Bauverlag GmbH. Wiesbaden und Berlin (1974).

[3] SETZER, M. J.: Einwirkung von Kohlenoxid, Schwefeldioxid und Wasser auf Beton. *Langzeitverhalten und Instandsetzen von Ingenieurbauwerken aus Beton, Fachtagung 10/11.* März (1987) Bayerische Bauindustrieverband a. V. München und Baustoffinstitut der Technischen Universitat München.

[4] POWERS, T. C. – BROWNYARD, T. L.: Studies of the Physical Properties of Hardened Portland Cement Paste. *Journal of the American Concrete Institute.* Oct., Nov. and Dec. 1946, and Jan., Febr., March, Apr. 1947. Vol. 43.

[5] ARONI, S. – MEHTA, B. K.: Fundamentals Underlying Shrinkage in Concrete – a Rewiew. *The Indian Concrete Journal* (1965).

[6] BALÁZS, GY.: A betontulajdonságok a betonstruktúra függvényében. *BME Építőanyagok Tanszék Tudományos Közlemények* **36.** (1982).