

LEAK TIGHTNESS OF HARDENING SLURRIES WITH FLUIDAL
ASHES IN CHEMICALLY AGGRESSIVE ENVIRONMENTS

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Abstract: This article presents test results for hydraulic conductivity and porosity structure of hardening slurries prepared of Portland cement, betonite, water and fluidal ashes from the combustion of hard and brown coal. The slurries were exposed to persistent filtering action (180 days) of liquids chemically aggressive to cement binders, i.e. distilled water, 0.5% solution of nitric acid, 1% solution of sodium sulphate, 1% solution of magnesium nitrate and 1% solution of ammonium nitrate. Samples exposed to filtration of tap water constituted the reference base. The research was into relations between hydraulic conductivity and pore structure parameters in slurries, as well as into the influence of the type of aggressive medium on leak tightness of slurries (their porosity and hydraulic conductivity).

INTRODUCTION

Nearly the whole power industry in Poland is based on the combustion of solid fuels. Combustion of hard or brown coal generates yearly millions of tones of combustion by-products. Some of them get industrially utilized but large amounts have to be disposed to overloaded waste dumps.

In recent years, a method of solid fuel combustion in furnaces with a circular fluidal layer, usually associated with sulphur removal from combustion gases, has been under development. The new combustion technology provides inter alia for a lower emission of noxious substances to the environment. Thus the amount of waste created in Poland as a result of fluidal combustion has considerably increased.

Due to a lower combustion temperature and a sorbent addition, ashes produced from fluidal boilers are significantly different from those created in conventional furnaces fired by pulverized fuel [8]. The special characteristics of fluidal fly ashes are: a higher content of calcium and sulphur compounds (as compared to conventional ashes), a higher content of unburnt coal elements, and a dissimilar crystallographic structure. These features limit possible applications of ashes in the construction industry [5, 13].

In the search for new ways of utilisation of fluidal ashes, research was undertaken to examine the possibilities of adding them to hardening slurries [3].

A hardening slurry is a mixture of water (the major constituent by volume), betonite and cement, which in the liquid state has tixotropic characteristics (important in the case of liquids expanding trenches during excavation), and, after binding, characteristics of a construction material adequately durable and waterproof to be used, for instance, in cut-off walls. Since various additives and admixtures can be added to hardening slurries and thus modify their technological or functional properties, it is possible to design various formulae depending on the destination of the material.

Combustion wastes, including fluidal ashes, are rather special additives used in hardening slurries. They are mineral materials with binding characteristics [5, 18, 20]. Therefore, they can act not only as fillers but also as additional binders [4].

Favorable anticorrosive characteristic of the addition of ashes from conventional coal combustion to cement concrete are well-known [7, 14]. Moreover, research on hardening slurries with addition of ashes from conventional combustion has shown an improvement in the slurries' resistance to corrosion with some water environment aggressiveness, and in the conditions of diffusive capillary transport of aggressive substances [3, 9]. This is particularly significant where cut-off walls are used to separate underground waters from pollution sources.

In the light of the above, the response of slurries with fluidal fly ashes in conditions corrosive for cement binders was also tested, where contact with aggressive liquids was ensured by forcing their filtration through the porous structure of the material [4].

The complicated nature of the chemical changes occurring in mineral binding materials and the characteristics of fluidal ashes call for a deeper insight into their application in hardening slurries. A special challenge is to recognize the properties of hardening slurries with the addition of fluidal ashes functioning in a chemically aggressive water-ground environment, which takes place in cut-off walls in hydraulic structures used for environment protection (waste dumps or facilities protecting against pollution of underground water intakes, etc.).

The measure of leak tightness of hardening slurries is their hydraulic conductivity. The latter is primarily conditioned by the porosity structure and the characteristics of the filtering medium. Apart from the temperature and the physical features of the liquid (viscosity and density), its chemical characteristics are equally important, and in particular its capacity to react with slurry ingredients (corrosive processes). These processes can significantly change the structure of the material and its characteristics, including hydraulic conductivity.

This article presents a testing methodology and results for the basic – for application in cut-off walls – characteristic of hardening slurries, i.e. their hydraulic conductivity after persistent filtration over several months with tap water and liquids chemically aggressive to cement binders. Also, results of porosity tests of slurries after long-time exposure to filtering action of different liquids are discussed, as well as correlations between parameters characterizing the porosity of slurries, and hydraulic conductivity.

In addition, microstructure images of hardening slurries made with a scanning microscope are included here.

FORMULAE OF SLURRIES COMPOSED OF CEMENT, ASH, BETONITE AND WATER

The slurries used for the research were prepared from the following ingredients:

- sodium bentonite DYWONIT S;
- portland cement CEM I 32,5R;
- fluidal fly ash from hard coal – PK (Żerań Thermal-electric Power Station);
- fluidal fly ash from brown coal – PB (Turów Power Plant).

Table 1. shows the composition of the investigated hardening slurries.

Table 1. Formulae of hardening slurries

No.	Component	PK	PB
1	2	3	4
1	Tap water [dm ³]	1000	1000
2	Bentonite Dywonit S [kg]	40	30
3	Fluidal fly ash from hard coal [kg]	323	0
4	Fluidal fly ash from brown coal [kg]	0	326
5	Cement CEM I 32,5R [kg]	163	170

TESTS OF LIQUID SLURRIES

Batches of slurries were prepared according to the formulae in Table 1, and their basic properties in liquid state were tested (Table 2).

Table 2. Properties of liquid slurries

No.	Parameter	PK	PB
1	2	3	4
1	Volume density [g/cm ³]	1.29	1.30
2	Conventional viscosity ratio [s]	45	39
3	24h water setting [%]	3.0	5.0

Tests were performed to determine density (ρ) of the liquid slurries, their conventional viscosity ratio (L), and 24h water setting (O_d). Volumetric density (ρ) of the slurries was tested with Barroid's balance, and the conventional viscosity – using a viscometer (Marsh's funnel). The 24h water setting test can be described as determining the percentage share of the volume of spontaneously separating water in 1 dm³ of liquid slurry after one day of it standing in a measuring cylinder.

PREPARATION OF SAMPLES FOR TESTING AFTER HARDENING

Hardening slurry test cylinders were prepared in PVC moulds of 8 cm in diameter and 8 cm in height. Before the slurry set, the samples were kept under a foil covering in the laboratory. After 3–4 days the samples were submerged into water. The water temperature was $+18^{\circ}\text{C} \pm 2^{\circ}\text{C}$. The samples were left under water until the moment of measurement.

Leak tightness of the contact of the sample and the mould was assured by crimping of the internal wall of the mould and an additional silicon seal.

Testing of hardened slurries was limited to hydraulic conductivity and porosity measurements, and in addition, photographs were taken with a scanning microscope.

The filtering mediums in the conductivity tests were tap water and liquids aggressive towards cement binders.

From among typical aggressive environments, five were selected: a leaching one – distilled water, general acid solution – 0.5% of HNO_3 , sulphate solution – 1.0% of Na_2SO_4 , magnesium solution – 1.0% of $\text{Mg}(\text{NO}_3)_2$, and ammonium solution – 1.0% of NH_4NO_3 . The reference base was constituted by test results of slurries exposed to filtering action of tap water.

The slurries were exposed to filtration for 180 days. Prior to the start of the research program, the samples were matured for 65 days. Measurements of hydraulic conductivity were taken over the testing period to track trends in the changes of this quantity. After the exposure period was completed, material for porosity tests was taken from the slurry samples, and thus distribution of pore sizes and characteristics of the pores were obtained. Also, a number of microstructural photographs were taken using a scanning microscope.

LONG-TERM TESTS OF HYDRAULIC CONDUCTIVITY

Apparatus

Hydraulic conductivity tests of hardening slurries exposed to the action of tap water and selected chemically aggressive liquids were carried out in specially constructed chemically resistant plastic apparatus (plexiglass and PVC).

Figure 1 presents the apparatus at work.



Figure 1. Apparatus for testing hydraulic conductivity with a sample of hardening slurry as tests are performed

Measurement methodology

The hydraulic conductivity of hardening slurries is very low (similar to that of cohesive soils), and so the time needed to obtain the balance of supply and outflow of water from the sample is long. In such cases, conductivity tests are performed with a variable hydraulic gradient. This method consists of determining the values of water pressure h_1 , h_2 etc. in the supply tube of cross-section area a , in established times t_1 , t_2 etc. during the liquid's flow through the sample of length (height) L and cross-section area A . In this case the hydraulic conductivity is calculated with the following formula:

$$k_T = \frac{a \cdot L}{A \cdot \Delta t} \ln \frac{h_1}{h_2} \quad (1)$$

where:

k_T – hydraulic conductivity in temperature T , [m/s]; a – cross-section area of the supplying tube, [m²]; L – length (height) of the sample, [m]; A – cross-section area of the sample, [m²]; Δt – time between pressure measurements h_1 and h_2 , $\Delta t = t_2 - t_1$, [s]; $h_{1,2}$ – values of water pressures at times t_1 and t_2 , [m].

The main advantage of this testing method is the possibility it offers of measuring small water flows and forcing high water pressures.

The action of the filtering media (tap water, distilled water and aggressive water solutions) on the tested sample was of gravitational nature. The measurements were performed with a decreasing initial hydraulic gradient.

The sample was placed in the apparatus (Fig. 1) and liquid poured over it up to the level which forced the maximum hydraulic gradient equal to 45 (hydraulic gradient is the quotient of water pressure measured in m and height of investigated sample in m).

Once a week, a measurement of hydraulic conductivity was performed.

The range of hydraulic gradients acting on the samples was from 20 to 45, and gradients lower than 45 were only acting on the days of the hydraulic conductivity measurements (once a week) for no longer than 4 hours. The hydraulic conductivity calculated with the formula no. 1 does not take account of the influence of temperature of the filtering liquids. The k_T values obtained during the tests (at temperature T) were recalculated into k_{10} values corresponding to the temperature +10°C.

The following formula was used:

$$k_{10} = \frac{k_T}{0.7 + 0.03T} \quad (2)$$

The low concentrations of the solutions (0.5% HNO₃, 1.0% Na₂SO₄, 1.0% Mg(NO₃)₂ and 1.0% NH₄NO₃) entitle one to treat them as tap water, and thus ignore the influence of changes in their viscosity and density on the hydraulic conductivity of the slurries.

Test results

The results of hydraulic conductivity tests of hardening slurries in the conditions of filtering transport of aggressive media are presented in Figure 2 (slurries with ash from hard coal – PK) and Figure 3 (slurries with ash from brown coal – PB).

The diagrams show matching lines (trends) for the series of individual hardening slurries (formulae) exposed to the filtering action of tap water, and aggressive solutions (distilled water, HNO₃, Na₂SO₄, Mg(NO₃)₂, NH₄NO₃).

For each day of the hydraulic conductivity test, four repeated measurements were made with a gradually decreasing initial gradient (the first and the last measurement in the series were rejected). Earlier, the influence of hydraulic gradient on the result of conductivity measurements had been tested – in the applied range of gradients there was no relationship between these results. Table 3 shows the final values of hydraulic conductivity of hardening slurries exposed to persistent (180 days) filtration of aggressive solutions and tap water.

Table 3. Final values of hydraulic conductivity of hardening slurries exposed to persistent (180 days) filtration of aggressive solutions and tap water

No.	Type of slurry	Hydraulic conductivity – k_{10} [m/s]					Tap water
		Distilled water	0.5% solution of HNO_3	1.0% solution of Na_2SO_4	1.0% solution of NH_4NO_3	1.0% solution of $\text{Mg}(\text{NO}_3)_2$	
1	2	3	4	5	6	7	8
1	PK	$9.0 \cdot 10^{-8}$	$2.1 \cdot 10^{-9}$	$5.0 \cdot 10^{-9}$	$2.4 \cdot 10^{-7}$	$4.0 \cdot 10^{-8}$	$2.5 \cdot 10^{-8}$
2	PB	$5.5 \cdot 10^{-8}$	$1.0 \cdot 10^{-8}$	$9.0 \cdot 10^{-9}$	$3.5 \cdot 10^{-7}$	$1.6 \cdot 10^{-8}$	$2.8 \cdot 10^{-8}$

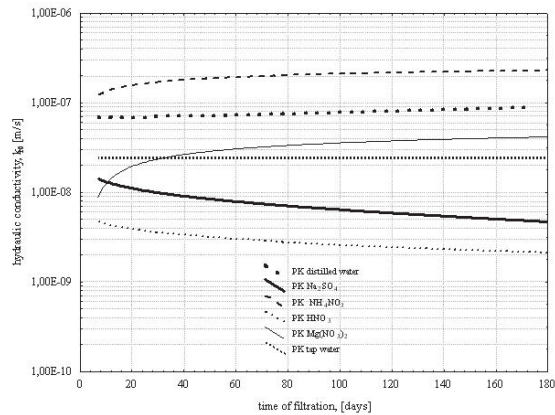


Figure 2. Hydraulic conductivity of hardening slurry with addition of fluidal ash from hard coal (PK) in time function (trend lines)

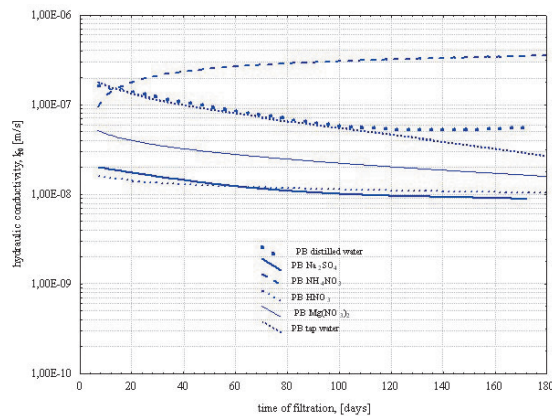


Figure 3. Hydraulic conductivity of hardening slurry with addition of fluidal ash from brown coal (PB) in time function (trend lines)

POROSITY TESTS OF SLURRIES

Hydraulic conductivity which is the most significant characteristic of the hardening slurry as a construction material for cut-off walls is influenced by many factors. However, it needs to be stressed that this characteristic primarily (directly) depends on the structure of the slurry [17]. Its structure, in turn, is inextricably related to porosity and the structure of pores [12].

Pores in cement batch develop as a result of the adopted proportions of key components (mainly w/c), blending and condensing methods, and conditions of concrete maturation [6, 19].

The description of cement matrix as a porous body can also be used for analysis of porosity of hardening slurries. This description is substantiated by the production method of slurries (mixture of mineral components which binds owing to binder hydration, and their characteristics (coming in between those of weak cement mortars and firm cohesive soils).

In a hardened batch, air pores can be distinguished as the largest, with diameters of over 10 μm . These are created either unintentionally – as a result of incomplete condensation of the mixture – or deliberately, produced with special aeration measures. Air pores, easy to observe with simple optical appliances or even with the naked eye, are of spherical, oblong shape and are not directly connected to one another.

Another group of pores with a dominating effect on many characteristics of the material are capillary pores, also named mesopores or macropores [1, 17]. Their sizes in typical mature cement batches range mostly between 0.01 μm and 0.2 μm . They form a system of irregularly connected voids of diverse shapes, randomly arranged in the matter of hardened cement batch. A common feature of capillary pores is their capacity to transport gases and liquids, mainly water and substances dissolved in water. Some of the smallest capillary pores (0.01–0.05 μm) are practically always filled with water, while others (large capillary pores of 0.05–10 μm) can temporarily give out water (through evaporation) only to take it in later (adsorption, capillary pressure). The mesopores which determine the transport of liquids or gases in the hardening slurry structure have to be integral, with suitably large, unfilled sections. Their shape is as important as their diameter. Non-integral pores containing adsorbed water and with narrow inlets are insignificant as regards conductivity [15].

The group of pores of the smallest sizes are gel pores or micropores [1, 17]. The name of gel is given to the products of cement hydration, i.e. colloid solutions and hydrates of various degrees of crystallization with internal voids filled with chemically unbounded water. The sizes of gel pores range between 0.0015 μm and 0.004 μm . Water in gel pores is very strongly adsorbed, removable only by drying the material in high temperature of ca. 150°C. Gel pores take minimal part in liquid circulation but they do influence diffusion [11].

Integral capillary pores (mesopores) play the greatest role in the conduction of liquids through the structure of concrete (slurry). Research shows [10] that the formation of pore structure is particularly influenced by the water-binder ratio w/d (w/c) but also by duration and degree of cement hydration.

Measuring method. Measuring apparatus

Hardening slurries are porous materials. Pores with the same relative volume in the material can have totally different structures.

One of the methods of measuring open porosity is mercury porosimetry. Not only does this method determine the total volume of open pores but it provides information on the volume of pores of specific sizes (the so-called distribution of pore sizes). In conjunction with microscope examination of the structure and density measurements, porosimetry permits comprehensive determination of the structure of a porous material in terms of both quality and quantity.

Mercury porosimetry makes use of the capillarity phenomenon. If a capillary tube of radius r_k is immersed in a container with liquid, then the level of liquid in the capillary is conditional upon the surface tension of the liquid γ_i and the angle of wetting the capillary material Θ by the liquid in the container. If the wetting angle exceeds 90° , the level of liquid will settle below its level in the container. In order to equalize the levels of liquid, pressure P of the following value should be exerted on the liquid:

$$P = \frac{-2 \cdot \gamma_i \cdot \cos \Theta}{r_k} \quad (3)$$

where:

r_k – capillary radius [m];

γ_i – surface tension of liquid [N/m];

Θ – wetting angle of the material [$^\circ$].

This equation is known as Washburn equation, and was published in 1921 with a suggestion of using it for determining porosity distribution in materials. Mercury is used as a non-wetting liquid as its wetting angle with regard to most materials is much larger than 90° [1, 17].

A sample of porous material is placed in a container named penetrometer. The penetrometer is tipped with an open capillary of known diameter. After completely filling up the penetrometer with mercury, the former is placed in a chamber filled with liquid. A scheme of the penetrometer is presented in Figure 4. In this chamber, pressure can be increased with the use of a pressure generating system, and precise measurements of its value can be made. As pressure of liquid in the chamber rises, mercury will penetrate into pores of the sample (the capillary being open, mercury is ‘pushed’ into the pores by pressure identical to that in the chamber). The total measured porosity volume (i.e. the volume of mercury ‘pushed’ into pores) in relation to 1 gram of the sample is called intrusion I [ml/g]. Measuring the tip of the mercury column moving along the capillary of the penetrometer, one measures the volume of the pores penetrated with the increase of pressure from P_{ki-1} to P_{ki} . As radiuses of the penetrated pores can be assigned to pressure values on the basis of a simple transformation of equation 3:

$$r_i = \frac{-2 \cdot \gamma_i \cdot \cos \Theta}{P_{ki}} \quad (4)$$

thus the volumes of pores of radiuses from r_{ki-1} to r_{ki} (as corresponding to pressure values P_{ki-1} to P_{ki}) are measured. Therefore, by making a number of measurements for consecutively accruing pressure values, one can determine the volume of pores in function of their diameter, that is – measure porosity distribution in the investigated sample.

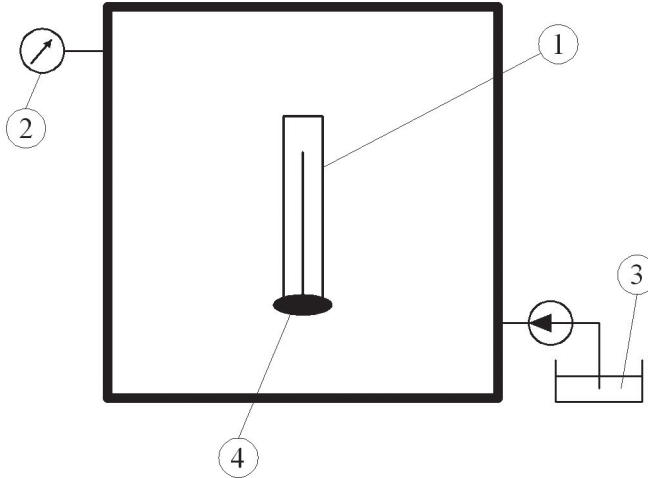


Figure 4. Scheme of porosimeter

Test results

Porosity structures of slurries were tested in a mercury porosimeter. The test was performed on the samples of hardening slurries with addition of fluidal ashes (PK and PB), after their long-term exposure (180 days) to filtering action of tap water and liquids chemically aggressive toward cement binders. The sample of slurry with addition of ash from brown coal, which was exposed to filtration of 1.0% solution of ammonium nitrate (NH_4NO_3), underwent a partial corrosive decomposition. The slurry structure was so corroded that it got damaged on the strength of the mercury pushed (under pressure) into it. Therefore, the results for this sample were not included in further analysis.

The results of the porosity tests are presented in the form of distributions of pore sizes (exemplified in Figure 5). On the basis of the diagrams, microstructure parameters of the tested samples were determined. These values are illustrated in Figure 5 and compiled in Table 4 where the following symbols are used:

A_p – total pore area, [m^2/g];

$v_p < 0.2$ – volume of pores of diameters smaller than $0.2 \mu\text{m}$;

$v_p > 0.2$ – volume of pores of diameters larger than $0.2 \mu\text{m}$;

P_c^p – total porosity of sample, [-];

d_{max} – maximum diameter of pores, [μm].

Table 4. Specification of microstructure parameters of investigated hardening slurries

No.	Type of solution	PK	PB	PK	PB	PK	PB	PK	PB	PK	PB
		A_p [m ² /g]		$v_p > 0.2 \mu\text{m}$		$v_p < 0.2 \mu\text{m}$		P_c [%]		d_{max} [μm]	
		3	4	5	6	7	8	9	10	11	12
1	Tap water	99.54	100.91	0.89	0.99	0.46	0.44	76.22	75.90	4.0	7.0
2	Distilled w.	102.02	114.29	1.00	1.15	0.46	0.44	77.21	74.51	4.5	10.0
3	HNO ₃	91.61	98.96	1.11	1.04	0.39	0.40	77.02	77.01	5.0	5.0
4	Na ₂ SO ₄	89.87	85.88	0.78	0.83	0.44	0.36	74.32	71.04	2.5	10.0
5	Mg(NO ₃) ₂	68.67	74.69	0.96	0.59	0.27	0.30	71.58	67.04	10.0	10.0
6	NH ₄ NO ₃	111.72	43.92*	1.29	0.77*	0.51	0.31*	78.72	71.48*	6.0	4.5*

* erroneous result, rejected in analysis

in Table 4 where the following symbols are used:

A_p – total pore area, [m²/g];

$v_p < 0.2$ – volume of pores of diameters smaller than 0.2 μm;

$v_p > 0.2$ – volume of pores of diameters larger than 0.2 μm;

P_c – total porosity of sample, [-];

d_{max} – maximum diameter of pores, [μm].

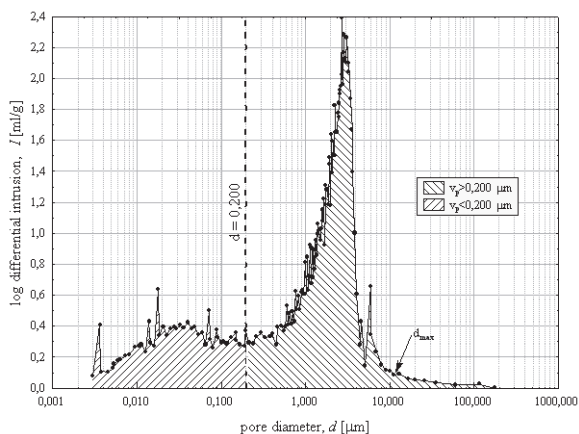


Figure 5. Distributions of pore sizes in hardening slurry with fly ash from hard coal (PK) after exposure to 180-day filtration with 1.0 % solution of NH₄NO₃

EXAMINATION OF MICROSTRUCTURES OF HARDENING SLURRIES WITH SCANNING MICROSCOPE (SEM)

The microstructures of slurries were examined using a scanning microscope (SEM). The examined slurry material was identical to that in porosity tests, i.e. hardening slurries with addition of fluidal ashes (PK and PB) after long-term exposure (180 days) to filtering action of tap water and liquids chemically aggressive towards cement binders.

The selected photographs are presented in Figures 10 ÷ 15.

ANALYSIS OF TEST RESULTS

Deepened analysis of the influence of persistent action of chemically aggressive solutions on hydraulic conductivity of slurries was conducted for the comparative slurries – those exposed to persistent action of tap water.

The results of hydraulic conductivity tests of hardening slurries in the conditions of filtering transport of aggressive media are shown in time function (trend lines) in Figure 2 (slurries with ash from hard coal – PK), and Figure 3 (slurries with ash from brown coal – PB).

The PK sample exposed to persistent filtering action of potable water demonstrates stable response – hydraulic conductivity values of ca. 2.5×10^{-8} m/s, while the action of sodium sulphate (sulphate aggressiveness) resulted in increased leak tightness of the slurry structure, which is confirmed by a drop of hydraulic conductivity value from ca. 1.5×10^{-8} m/s to ca. 5.0×10^{-9} m/s.

A different effect is observed in the case of magnesium aggressiveness (1.0% solution of $\text{Mg}(\text{NO}_3)_2$). Leak tightness of the slurry exposed to filtration of this solution was reduced, as confirmed by an increase of hydraulic conductivity value from ca. 8.0×10^{-9} m/s to ca. $4.0 \cdot 10^{-8}$ m/s.

Another analyzed solution is nitric acid (acid aggressiveness). Interesting and worth demonstrating are the completely different ranges of hydraulic conductivity values in the two liquids. The acid corrosion action, of strongly softening properties, brought about definitely lower hydraulic conductivity values in comparison to those of the reference base (tap water). These values ranged between ca. 5.0×10^{-9} m/s and ca. $2.0 \cdot 10^{-9}$ m/s. Such a reaction of a material with cement binder to this type of corrosion is different than the phenomena described in the relevant bibliography (e.g. regarding concretes). This process has not been fully examined yet. In passages below, these results will be collated with parameters characterizing porosity of the slurry material.

A typical phenomenon (dealt with in the reference literature) of de-sealing of the slurry structure is observed in the action of ammonium aggressiveness. An increase of hydraulic conductivity was registered, from ca. 1.2×10^{-8} m/s to ca. $2.4 \cdot 10^{-8}$ m/s.

A similar phenomenon occurs in the case of leaching aggressiveness (distilled water). Lower resistance of the material to the action of corrosion of this type (different value range and de-sealing of the slurry structure) is confirmed by hydraulic conductivity values growing from 6.0×10^{-8} m/s to ca. $9.0 \cdot 10^{-8}$ m/s.

The next stage is the analysis of resistance of hardening slurries with addition of fly ashes from brown coal to corrosion by the action of aggressive solutions (towards cement binders) – the trend lines in Figure 3.

The first comparison is that of reactions to tap water and sodium sulphate solution. It shows clearly that tap water causes increased leak tightness of the slurry structure. This is confirmed by a drop of hydraulic conductivity values from ca. 1.7×10^{-7} m/s to ca. $2.8 \cdot 10^{-8}$ m/s.

The action of sodium sulphate also increased leak tightness of the slurry structure – its hydraulic conductivity decreased from ca. 2.1×10^{-8} m/s to ca. $9.0 \cdot 10^{-9}$ m/s.

The action of magnesium nitrate (magnesian corrosion) on the slurry material results in its increased leak tightness, proven by hydraulic conductivity reduced from ca. 5.0×10^{-8} m/s to ca. $1.6 \cdot 10^{-8}$ m/s.

As was the case of hardening slurry with addition of ash from hard coal, the slurry with addition of ash from brown coal retains a differing resistance to the action of acid aggressiveness (as compared to that described in the reference literature). A distinct range of hydraulic conductivity values has to be noted (in relation to tap water), as well as their drop from ca. 1.7×10^{-8} m/s to ca. $1.0 \cdot 10^{-8}$ m/s.

A quite dissimilar effect has the action of ammonium nitrate solution (ammonium corrosion) on the slurry material. Decreased leak tightness is clearly visible, and confirmed by hydraulic conductivity values growing from ca. 1.0×10^{-7} m/s to ca. $3.5 \cdot 10^{-7}$ m/s.

The action of distilled water (leaching corrosion) was bringing about identical hydraulic conductivity values (in relation to tap water) over quite a long filtration time. However, after the completion of the exposure period, these values were somewhat different from each other. Filtration of distilled water resulted in slightly higher hydraulic conductivity values than that of tap water, which testifies to greater desealing of the slurry material. The final value of hydraulic conductivity in relation to distilled water reached $5.5 \cdot 10^{-8}$ m/s (and that of tap water – $2.8 \cdot 10^{-8}$ m/s). Distilled water caused desealing of the slurries with ashes both from hard (PK) and brown coal (PB), as well as leaching of some of their components (calcium compounds, most probably) [4, 21]. This resulted in an increase of hydraulic conductivity k_{10} .

It is worth noting that the values of hydraulic conductivity of the slurries exposed to acid and sulphate aggressiveness are similar and change over the testing period in a similar way (especially in the case of the slurry with non-activated ash). This is in spite of differences between the chemical processes of sealing of the structure of the materials. With the sulphate aggressiveness, complex hydrated sulphate salts are formed [2, 9, 16] and in the case of acid aggressiveness it is possible to reseal the material with amorphous products (gel) of C-S-H phase decomposition in acid environment [4, 16].

Nearly identical resistance to corrosion by ammonium nitrate solution was demonstrated by PK and PB slurries. In both cases the slurry material de-sealed.

A different phenomenon occurs with the action of magnesium nitrate solution. There was a marked de-sealing of the structure of PK slurry – Figure 2, while PB slurry sealed up, as shown in Figure 3.

Another step in the analysis was to look for a relation between hydraulic conductivity and the quantities characterizing the microstructures of hardening slurries, as obtained after 180 days of exposure. Such correlations could explain the observed changes of hydraulic conductivity of slurries over the period of persistent filtration with the liquids in question.

Correlation analysis of the tested quantities characterizing the microstructures of slurries (given in Table 4) and hydraulic conductivity (values specified in Table 3) was conducted. Apart from obvious correlations resulting from mutual – often mathematical – links between some of the quantities, the following can be considered statistically significant (at 95% reliance level): the correlation of hydraulic conductivity k_{10} and the total pore surface A_p (correlation coefficients 0.62 for PK samples and 0.74 for PB samples), and the correlation of hydraulic conductivity k_{10} and the volume of pores of diameters larger than $0.2 \mu\text{m}$ (mesopores) – $v_p > 0.2 \mu\text{m}$ (correlation coefficient 0.77 for PK samples and 0.58 for PB samples).

Moreover, correlations of quantities A_p and $v_p > 0.2 \mu\text{m}$ (correlation coefficient 0.97), as well as A_p and $v_p < 0.2 \mu\text{m}$ (correlation coefficient 0.94) were noted. However,

these interrelations are strongly linked to one another in consequence of the constitution and structure of the materials, and thus can be considered as dependent variables. The quantities A_p and $v_p > 0.2 \mu\text{m}$ are representative and strongly influencing hydraulic conductivity k_{10} . Therefore, the further analysis below is limited to these correlations – k_{10} (A_p) and k_{10} ($v_p > 0.2 \mu\text{m}$).

Figures 6 and 8 present experimental points (k_{10}, A_p), and Figures 7 and 9 present experimental points ($k_{10}, v_p > 0.2 \mu\text{m}$), the location of which confirms the positive correlation of the tested quantities.

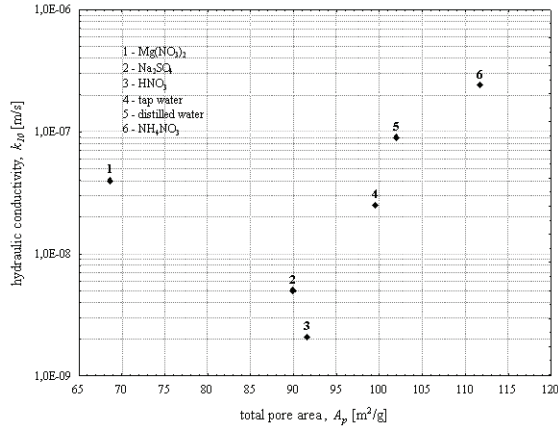


Figure 6. Test results for PK slurry exposed to filtration of tap water and aggressive media; experimental points (k_{10}, A_p) are shown

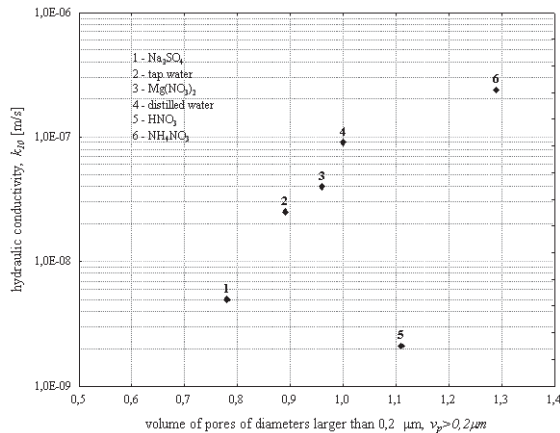


Figure 7. Test results for PK slurry exposed to filtration of tap water and aggressive media; experimental points ($k_{10}, v_p > 0.2 \mu\text{m}$) are shown

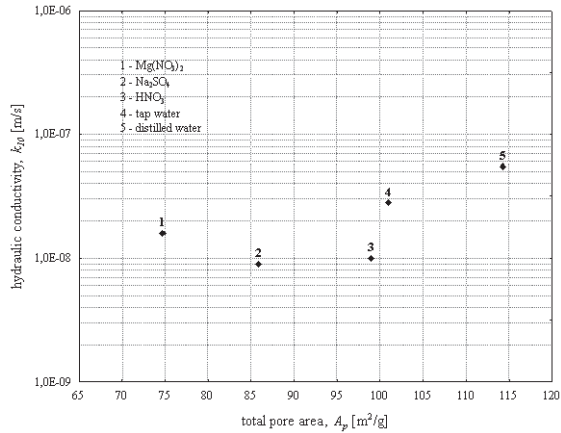


Figure 8. Test results for PB slurry exposed to filtration of tap water and aggressive media; experimental points (k_{10} ; A_p) are shown

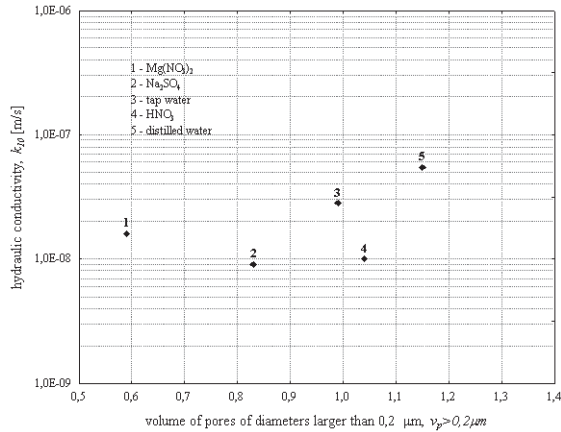


Figure 9. Test results for PB slurry exposed to filtration of tap water and aggressive media; experimental points (k_{10} ; $v_p > 0.2 \mu m$) are shown

The distribution of points in Figure 6 (the samples of slurry with addition of ash from hard coal – PK) indicated that the larger the total pore surface, the higher the value of hydraulic conductivity. Only the sample exposed to filtration of magnesium nitrate solution slightly departs from this rule showing intermediate values – a low A_p value and a medium (in relation to others) value of hydraulic conductivity. A quite interesting response is demonstrated by the sample of slurry exposed to the action of nitric acid, i.e. the lowest value of hydraulic conductivity with one of the lowest values of total pore surface. The low A_p value explains the k_{10} value being that low. It is, however, an unusual phenomenon, at least in concretes where this type of aggressiveness makes a cement matrix effectively decompose. A microstructure photograph taken with a scanning microscope is presented in Figure 10. The Figure illustrates filling mass in the form of hydrated calcium

silicates of C-S-H type shaped as so-called crumpled foil – typical for a hardening slurry matrix. Also, numerous voids representing micropores are observed.

The highest values of the analyzed quantities were registered in the sample of slurry exposed to filtration of ammonium nitrate solution. This sample is presented in the scanning microscope photograph in Figure 11. One can see a clear matrix in the form of hydrated calcium silicates of C-S-H type shaped as so-called crumpled foil, and numerous voids – mesopores, produced as a result of leaching of easily soluble calcium nitrate compounds (products of ammonium nitrate reacting with calcium hydroxide). Intermediate values are observed in the samples exposed to tap and distilled water.

Further analysis concerns k_{10} and $v_p > 0.2 \mu\text{m}$ quantities. Pores with diameters larger than $0.2 \mu\text{m}$ are responsible for the scale of filtration through a porous body so correlations of this kind may facilitate the explication of such processes.

Figure 7 illustrates the distribution of the analyzed points. The lowest values were observed in the sample exposed to filtration of sodium sulphate (sulphate aggressiveness). A microscopic image of this sample is presented in Figure 12. The slurry sample shows filling mass in the form of hydrated calcium silicates of C-S-H type, in which there are crystal clusters in the form of needles characteristic for ettringite and shaped as tubes arranged spokewise towards one another. Moreover, there are numerous micropores in the filling mass.

Low k_{10} values were also registered in the sample exposed to HNO_3 solution but it had somewhat higher values of mesopore volumes. This result is a slight departure from the raising trend line based on the other samples. It is a rather interesting phenomenon attesting to unusual transformations of the internal structure of the slurry as a response to this kind of aggressiveness.

The highest values of the analyzed correlation were again observed in the sample exposed to filtration of ammonium nitrate solution.

The analyses to follow also concern the above-described correlations but in the samples with addition of ash from brown coal – PB.

The relation of the analyzed points k_{10} and A_p is illustrated in Figure 8. As A_p values increase, so do k_{10} values. The sample exposed to filtration of magnesium nitrate fairly departs from this rule. The lowest values were observed in the sample filtered with sodium sulphate solution, and the highest – in the case of distilled water filtration. A scanning microscope image for this sample is presented in Figure 13. Again, one can see filling mass in the form of hydrated calcium silicates of C-S-H type shaped as so-called crumpled foil, in which numerous mesopores are located.

Low values (and at the same time departing from the concrete theory) were observed in the sample exposed to filtration of nitric acid solution. A microscope image for this sample is presented in Figure 14. One can see filling mass in the form of hydrated calcium silicates of C-S-H type, in which there are crystal clusters in the form of needles arranged spokewise towards one another. These formations have not been fully identified yet. This phenomenon may be identified in further specialist microstructural research. The matrix is rather leak tight, with no visible pores.

A very similar case is presented in Figure 9, which shows the relations of quantities k_{10} and $v_p > 0.2 \mu\text{m}$. Again, the lowest values were observed in the sample filtered with sodium sulphate solution, and the highest – in the case of distilled water filtration. An analogous response was also observed in the sample filtered with nitric acid solution – a

low k_{10} value and a higher value (in relation to the other analyzed samples) of mesopores volume.

Figure 15 presents a scanning microscope image for the sample exposed to filtration of tap water. One can clearly see filling mass in the form of hydrated calcium silicates of C-S-H type shaped as so-called crumpled foil, in which mesopores are located.

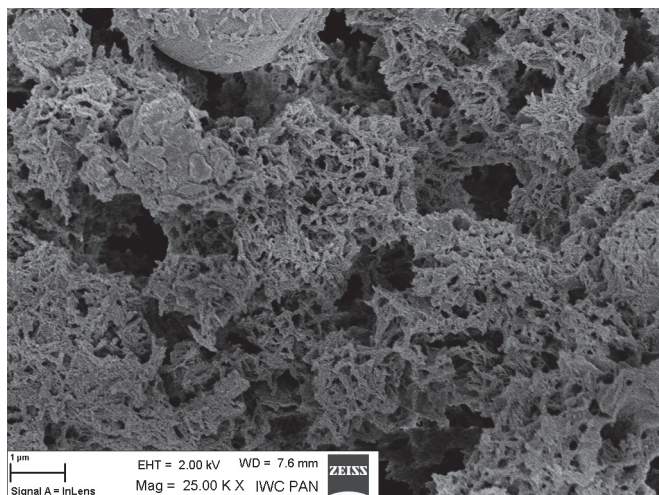


Figure 10. Microstructure of PK sample after 180-day exposure to 0.5% solution of HNO₃

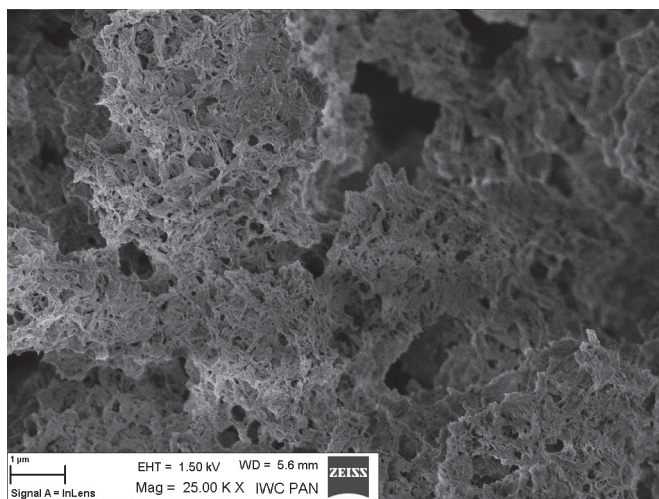


Figure 11. Microstructure of PK sample after 180-day exposure to 1.0% solution of NH₄NO₃

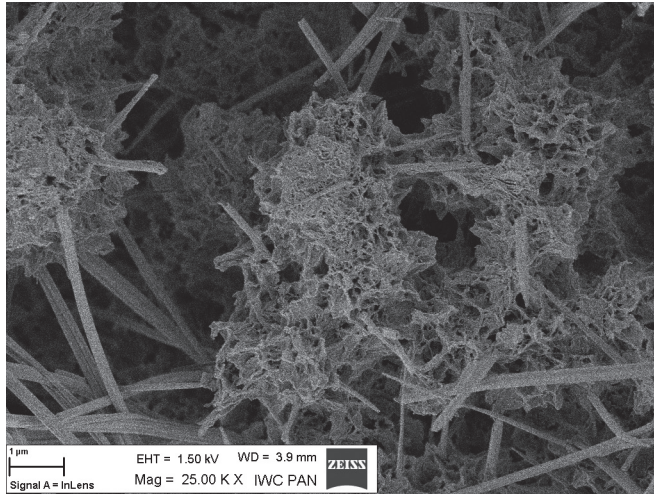


Figure 12. Microstructure of PK sample after 180-day exposure to 1.0% solution of Na_2SO_4

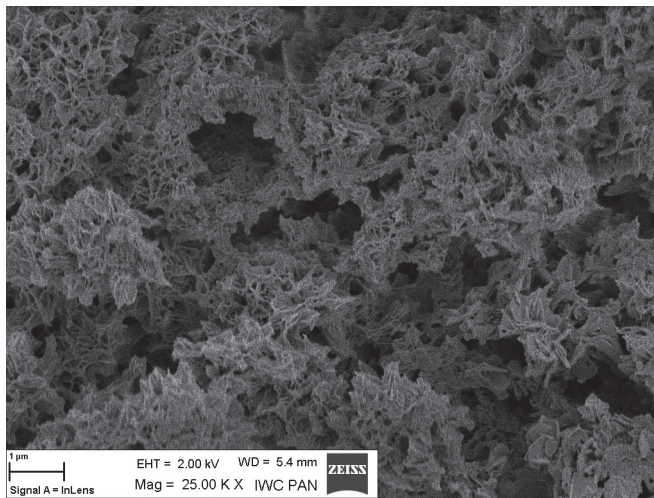


Figure 13. Microstructure of PB sample after 180-day exposure to distilled water

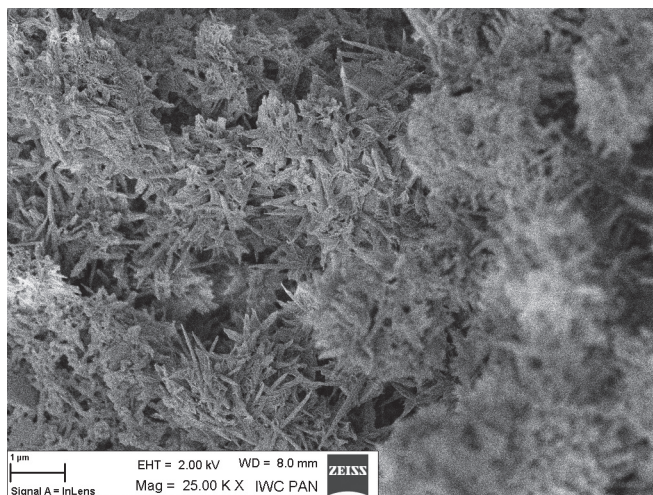


Figure 14. Microstructure of PB sample after 180-day exposure to 0.5% solution of HNO_3

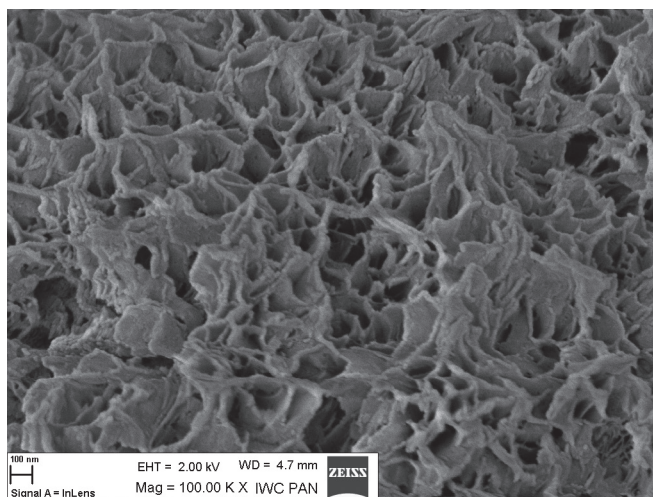


Figure 15. Microstructure of PB sample after 180-day exposure to tap water

CONCLUSIONS

Analysis of results of the hydraulic conductivity and porosity tests of hardening slurries with the addition of fluidal fly-ashes allows to draw the following conclusions:

The slurries exposed to filtration of ammonium nitrate solution and distilled water de-sealed in comparison to the slurries tested using tap water.

The slurries exposed to filtration of aggressive solutions (nitric acid and sodium sulphate) sealed up – generally speaking – in comparison to the slurries exposed to filtration with tap water.

The slurries with addition of fluidal ashes from brown coal exposed to filtration of aggressive solutions demonstrate somewhat greater leak tightness of their structures than the slurries with addition of ashes from hard coal, regardless of the type of aggressive medium. This may result from an increased content of calcium compounds in these ashes.

A close relation exists between porosity structure and hydraulic conductivity of hardening slurries with addition of fluidal ashes. It is expressed by a strong correlation of conductivity and the total pore surface in the slurries, as well as the volume of mesopores.

With regard to the fundamental differences in the corrosion resistance of hardening slurries with fluidal ashes in relation to cement mortars and concretes in chemically aggressive environments, and in particular in contact with general acid aggressiveness, it would be expedient to continue specialist research aimed at a total explication of the corrosion processes occurring in hardening slurries.

REFERENCES

- [1] Aksielrud G.A., M.A. Altszuler: *Movement of mass in porous bodies* (in Polish). WNT, Warsaw, 1987.
- [2] Bassuoni M.T., M.L. Nehdi: *Durability of self-consolidating concrete to sulfate attack under combined cyclic environments and flexural loading*, Cement and Concrete Research, Vol. **39**, January 2009, pp. 206–226.
- [3] Falaciński P., K. Garbulewski, Z. Kledyński, Z. Skutnik, K. Ziarkowska: *Fluidised fly-ash cement-bentonite cut-off walls in flood protection*, Archives of Hydro-Engineering and Environmental Mechanics, vol. **52** (2005), No.1, pp. 7–20.
- [4] Falaciński P., Z. Kledyński: *Influence of aggressive liquids on hydraulic conductivity of hardening slurries with the addition of different fluidal fly ashes*, Environmental Engineering, Taylor&Francis Group, London 2007, s. 295–300.
- [5] Giergiczny Z.: *Properties of Cements Containing Fly Ash Together With Other Admixtures*, ACI Materials Journal, special publication, V. **132**, May 1992, pp. 439–456.
- [6] Glinicki M.A., M. Zieliński: *Air voids spacing in concrete with addition of fly ash from fluidized bed coal combustion*, CWB, 3/2007, pp. 133–138.
- [7] Gruener M.: *Corrosion and protection of concrete*. Arkady, Warsaw, 1983.
- [8] Havlica J., I. Oder, J. Brandstettr, R. Mikulikova, D. Walther: *Cementitious materials based on fluidised bed coal combustions ashes*, Advances in Cement Research, 2004, Vol. **16**, No. 2, pp. 61–67.
- [9] Kledyński Z.: *Influence of Fly Ashes on Hardening Slurries Resistance to Sulphate Attack*, Archives of Hydro – Engineering and Environmental Mechanics, 2004, Vol. **51**, No. 2, pp. 119–133.
- [10] Kurdowski W.: *Chemistry of cement*, Wydawnictwo Naukowe PWN, Warsaw, 1991.
- [11] Kurdowski W., A. Garbacik: *Efflorescence in concrete* (in Polish), Budownictwo, Technologie, Architektura magazine, special issue 2005, pp. 45–47.
- [12] Kurdowski W., B. Trybalska: *Phase composition of cement batch and properties of concrete* (in Polish), Conference materials from Concrete Days – Tradition and Modernity, pp. 65–78, Wisła, 11–13.10.2004.
- [13] Kūlaots I., A. Hsu, R.H. Hurt, E.M. Suuberg: *Adsorption of surfactants on unburned carbon in fly ash and development of a standardized foam index test*, Cement and Concrete Research, V. **33**, Issue 12, pp. 2091–2099, 2003.
- [14] Langan B. W., K. Weng, M.A. Ward: *Effect of silica fume and fly ash on heat of hydration of Portland cement*, Cement and Concrete Research, Vol. **32**, Issue 7, July 2002, pp. 1045–1051.
- [15] Neville A.: *Properties of concrete*, Polski Cement, Kraków 2000.
- [16] Neville A.: *The confused world of sulfate attack on concrete*, Cement and Concrete Research, Vol. **34**, April 2004, pp.1275–1296.
- [17] Nicos S. Martys, Chiara F. Ferraris: *Capillary transport in mortars and concrete*, Cement and Concrete Research, Vol. 27, No. 5, February 1997, pp. 747–760.
- [18] Papadakis V.G., S. Antiohos, S. Tsimas: *Supplementary cementing materials in concrete* Part I: efficiency and design Cement and Concrete Research, Vol. **32**, Issue 10, April 2002, pp. 1525–1532.
- [19] Rusin Z.: *Technology of freezeproof concretes*. Polski Cement Sp. z o.o., Kraków 2002.
- [20] Sakai E., S. Miyahara, S. Ohsawa, S. Lee, M. Diamon: *Hydration of fly ash cement*, Cement and Concrete Research, Vol. **35**, Issue 6, June 2005, pp. 1135–1140.

- [21] Zuquan J., S. Wei, Z. Yunsheng, J. Jinyang, L. Jianzhong: *Interaction between sulfate and chloride solution attack of concretes with and without fly ash*, Cement and Concrete Research, Vol. 37, February 2007, pp. 1223–1232.

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SZCZELNOŚĆ ZAWIESIN TWARDNIEJĄCYCH Z POPIOŁAMI FLUIDALNYMI W ŚRODOWISKU AGRESYWNYM CHEMICZNIE

Artykuł przedstawia wyniki badań przepuszczalności hydraulicznej oraz struktury porowatości zawiesin twardniejących sporządzonych z cementu portlandzkiego, bentonitu, wody oraz popiołów fluidalnych pochodzących ze spalania węgla kamiennego i brunatnego. Zawiesiny były poddane długotrwałej (180-dniowej) ekspozycji na filtracyjne działanie cieczy agresywnych chemicznie wobec spoiwa cementowego, tj.: wody destylowanej, 0,5% roztworu kwasu azotowego, 1% roztworu siarczany sodu, 1% roztworu azotanu magnezu oraz 1% roztworu azotanu amonu. Bazę porównawczą stanowiły próbki poddane filtracji wody wodociągowej. Badano związki przepuszczalności hydraulicznej z parametrami charakteryzującymi strukturę porów w zawiesinie oraz wpływ rodzaju agresywnego medium na szczelność zawiesiny (jej porowatość i przepuszczalność hydrauliczną).