Research paper

Impact of acid aggressiveness on the filtration resistance of hardening slurries with an addition of fluidized-bed fly-ash

P. Falaciński[1] Z. Kledyński[2]

Abstract: The subject matter of the article comprises cement-bentonite-water hardening slurries with an addition of fluidized-bed fly-ash resulting from the combustion of hard and brown coal. The main objective of the study was to determine the filtration resistance of hardening slurries in the context of long-term exposure to the filtration of an aggressive substance in relation to a cement binder. A nitric acid aqueous solution with a concentration of 0.5 M was used, which modelled acid aggressiveness. The authors studied the hydraulic conductivity of the slurries as a function of time (18 months) for the exposure to a 0.5 M solution of nitric acid. Changes in the phase composition and hardening slurry surface structures were analysed in terms of their filtration resistance to the action of acid aggressiveness. The comparative base were samples subjected to filtration in tap water (neutral environment). The article reviews a methodology for studying hydraulic conductivity (k10) of hardening slurries. It also presents a study involving the phase composition using the X-ray diffraction analysis (XRD) method, infrared (IR) spectroscopy and showing an image of the hardening slurry surface structure. The findings of other researchers that the application of fluidized-bed fly-ash additives positively impacted improving the resistance of the cement matrix to acid aggressiveness were confirmed. The hydrated colloidal compounds, identified within the subsurface zone of the slurry, which has been in contact with an acidic environment, provide extra sealing of the material structure, thus significantly limiting the access of aggressive substance to the interior of the slurry.

Keywords: hardening slurries, cut-off walls, acid aggressiveness, fluidized-bed fly-ash, circular economy

[1] DSc., PhD., Eng., Warsaw University of Technology, Faculty of Building Services, Hydro and Environmental Engineering, Nowowiejska 20, 00-652 Warsaw, Poland, e-mail: pawel.falacinski@pw.edu.pl, ORCID: https://orcid.org/0000-0001-7090-5233

[2] Prof., DSc., PhD., Eng., Warsaw University of Technology, Faculty of Building Services, Hydro and Environmental Engineering, Nowowiejska 20, 00-652 Warsaw, Poland, e-mail: zbigniew.kledynski@pw.edu.pl, ORCID: https://orcid.org/0000-0002-8387-3119

1. Introduction

The growing awareness of the deteriorating natural environment results in great emphasis on developing eco-friendly technologies and expectations that economic and civilization growth will be sustainable. Strategies of complex legal, economic and educational nature are being developed, apart from technical tools. Their objective is to shape a responsible approach of the societies towards environmental protection and natural resources. One of such concepts is Circular Economy, which involves striving for repeated re-use of products, including by-products. It requires not only changing habits, legal standards and appropriate economic tools prioritizing recycled materials, but primarily the development of appropriate technologies, since only they can make recycled products as good as original.

One of the key issues in certain EU countries are the millions of tons of coal combustion by-products (CPBs) generated each year [2] and further millions of tons already accumulated at landfills. Utilizing CPBs in line with the ideas of Circular Economy, in economy branches such as civil engineering, hydrotechnical construction, road construction, agriculture or the plastics industry is not always possible due to the particular properties of such waste. According to the data [2], only 25% of the CPBs are re-used, satisfying the principles of Circular Economy. Ashes from coal combustion in fluidized-bed boilers are particularly difficult in terms of reusing. A different crystallographic structure, increased (relative to conventional ash) content of calcium compounds and unburned coal components, as well as high water demand, significantly restrict the application-related potential of this waste.

In searching for new methods of utilizing fluidized ashes, studies were undertaken regarding the possibility of adding them to hardening slurries [3, 4]. According to the definition [5], a hardening slurry is a suspension, which contains cement or another binder and additional materials such as clay (bentonite), ground granulated blast furnace slag (GGBFS) or pulverized fuel ash (PFA), fillers, sand and admixtures.

The waterproofing membranes made of hardening slurries are crucial elements in hydrotechnical facilities. Their task is, e.g., the protection of levees against long-term freshets or the protection of landfill embankments against the migration of polluted eluates to groundwater. In such a context, a hardening slurry must maintain durability in contact with a chemically aggressive aqueous environment. In the case of chemically aggressive waters flowing through a cut-off wall, a hardening slurry must exhibit permanent filtration resistance. Filtration resistance, understood as a measure of

hardening slurry tightness, is determined through hydraulic conductivity (hydraulic permeability coefficient, filtration coefficient).

The previously conducted studies on hardening slurries with an admixture of fluidized combustion ashes indicated an improved resistance of the slurries to corrosion in the case of certain aggressiveness of an aqueous environment and a capillary-diffusive transport of aggressive substances [6, 7].

The presence of acid-corrosive compounds in groundwaters or leachates, e.g. nitric acid, is particularly dangerous in terms of material durability. The process of acid corrosion involving cement-based binders results primarily from their reactivity with acid solutions [8, 9, 10, 11, 12]. Reducing the pH changes the hydrate distribution dynamics. Acidic solutions dissolve the paste already at a pH of approximately 5.0 [9]. Cement binders can corrode when exposed to an acidic liquid, the pH of which is below 6.5, with a pH under 5.5 indicating strong aggressiveness, and below 4.5 – very strong aggressiveness, whereas the corrosion progress is impacted not only by an aggressive liquid pH, but also the transport conditions of aggressive ions. The ingredient of a set cement binder most susceptible to acids is $Ca(OH)_2$, but also the C-S-H phase, calcium hydro-aluminates and calcium carbonate can also be attacked [10].

The resistance of Portland clinker-based materials to aggressive acidic waters can be achieved by the application of hydraulic and pozzolanic additives [13]. The impact of pozzolanic additives involves decreasing the $Ca(OH)_2$ value and increasing the share of the C-S-H phase in the paste, which significantly lowers the content of large capillary pores (mesopores) [14, 15].

Increased corrosion resistance of cement mortars and pastes with an addition of fluidized-bed brown coal fly-ash was noticed also by other researchers [11, 16]. This process can be explained by the fact that gypsum, gibbsite (aluminium hydroxide), iron (III) hydroxide and amorphous hydrated silica gel are formed in the conditions of long-term exposure to an aggressive chemical solution (which models acidic corrosion). The development of similar colloidal systems, including silica sol and gelous aluminium hydroxide was presented also by Szperliński [17], relative to the coagulation process.

The article reviews the results of filtration resistance tests involving hardening slurries with fluidized-bed hard and brown coal fly-ash, subjected to long-term (18 months) exposure to the filtration of an 0.5 M nitric acid solution, which modelled acid aggressiveness. Corrosion-related changes were compared with samples of a slurry subjected to tap water filtration. The paper also presents the methodology and results of hydraulic permeability tests involving hardening slurries.

In order to identify the corrosion changes, the authors presented the results of infrared (IR) spectroscopy, X-ray diffraction analysis (XRD) and the photographs of hardening slurry surfaces after long-term (18 months) exposure to the filtration of a nitric acid solution and only tap water.

Characteristic compounds responsible for increased corrosion resistance of slurries in acid aggressiveness conditions were identified based on the analysis of the obtained test results.

2. Hardening slurry preparation and preliminary tests

The slurries used for the research were prepared based on the following components, mixed in the appropriate order: water and sodium bentonite (3 minutes) plus Portland cement CEM I 32.5R (1 minute), plus fluidized-bed hard coal fly-ash and / or fluidized-bed brown coal fly-ash (1 minute). In order to obtain the appropriate values (according to [5]) of the properties in the liquid state (Table 2), the compositions of the FPK and FPB hardening slurries slightly differ (Table 1).

Table 1 shows the composition of investigated hardening slurries with hard coal - FPK and brown coal - FPB fluidized-bed fly ash.

Table 1. Compositions of hardening slurries

No.	Component	FPK	FPB
1	2	3	4
1	Tap water [dm^3]	1000	1000
2	Bentonite Dywonit S [kg]	40	30
3	Fluidized-bed hard coal fly ash	323	0
4	Fluidized-bed brown coal fly ash	0	326
5	CEM I 32.5R cement [kg]	163	170

Hardening slurry were prepared according to the compositions in Table 1, and their basic properties in liquid state were tested (Table 2).

Tests were conducted to determine the density (ρ) of liquid slurries, their conventional viscosity ratio (L), and 24h water bleed (O_d) – [4]. The volumetric density (ρ) of the slurries was tested using Baroid balance, and their conventional viscosity – using a viscometer (Marsh's funnel). The 24 h water bleed 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 holding it in a measuring cylinder.

Table 2. Properties of liquid slurries.

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

3. Preparation of hardening slurry samples for further research

Hardening slurry samples were acquired for the tests in PVC cylinders, with a height and diameter equal to 80 mm. Until the curing of the binder, the slurry samples remained in a laboratory room, covered with foil. After approximately 3-4 days, the samples were placed in water and remained there until the test was conducted. Water temperature was $+18°C \pm 2°C$.

4. Hydraulic conductivity tests

4.1. Instruments

The hardening slurries were exposed to the filtration action of a 0.5 M nitric acid solution and tap water for a period of 18 months. The tests were conducted in specially designed, chemically-resistant instruments made of plastic (plexiglass and PVC) [4]. The samples were 28 days old on the day of commencing the tests. The observation period involved measuring the hydraulic conductivity, and tracking its change trends.

4.2. 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 with a cross-sectional area a, over established times t_1, t_2 etc. during the liquid's flow through the sample with a length (height) L and cross-sectional area A. In this case the hydraulic conductivity is calculated with the following formula Eq. (5.1):

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

(5.1.)

where:

k_T – hydraulic conductivity at temperature T, [m/s]; a – cross-sectional area of the supplying tube, [m²]; L – length (height) of the sample, [m]; A – cross-sectional 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 to measure small water flows and forcing high water pressures. The action of the filtering media, tap water and aggressive water solution, on the tested sample was of gravitational nature. The measurements were conducted with a decreasing initial hydraulic gradient. The sample was placed in the apparatus and had liquid poured over it, up to a level, which induced a 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 taken. 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. Hydraulic conductivity calculated with formula no. 1 does not take into account the influence of filtering liquid temperature. The k_T values obtained during the tests (at temperature T) were recalculated into k_{10} values corresponding to a temperature +10 °C. The following formula Eq. (5.2) was used:

$$k_{10} = \frac{k_T}{0,7 + 0,03T}$$

(5.2.)

As a result of continuous filtration through a sample of the hardening slurry, the HNO_3 acid solution was replenished in the expansion tank so as to maintain a constant gradient of 45. After the hydraulic conductivity test (once a week), the apparatus and the supply tube were completely filled with 0.5 M nitric acid solution. The complete exchange of the HNO_3 solution in the measuring equipment took place once a week.

The low concentrations of the solutions HNO_3 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

4.3. Test results

The hydraulic conductivity results for hardening slurries exposed to the filtration transfer of an aggressive medium (0.5 M HNO_3) and tap water (reference samples) are presented as a time function (trend lines) in Figure 1.
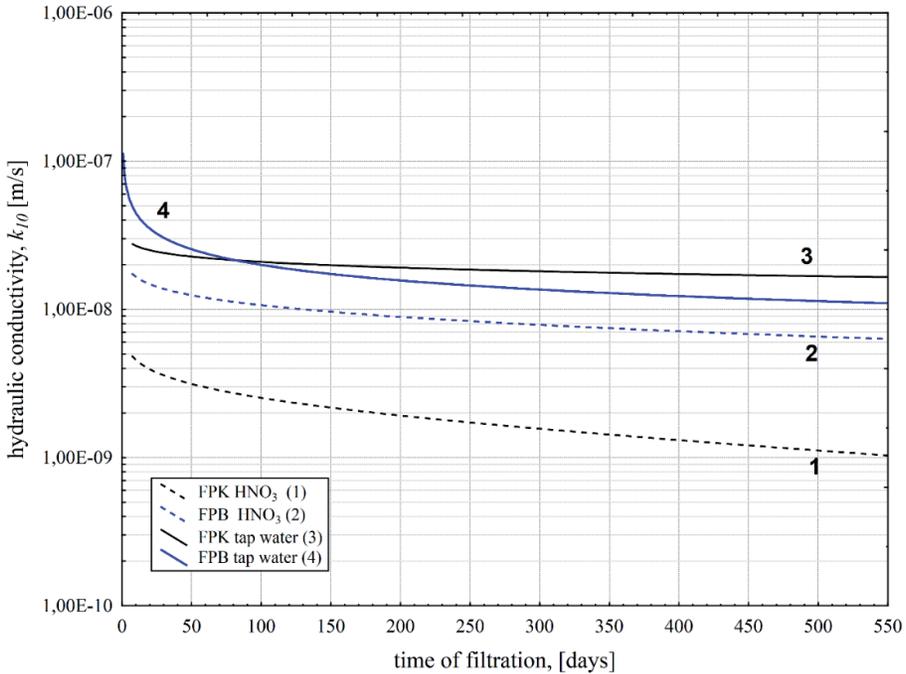
Fig. 1. Hydraulic conductivity of a hardening slurry with addition of hard coal fluidized-bed ash (FPK) and brown coal fluidized-bed ash (FPB) in the time function (trend lines).

4.4. Test result analysis

When analysing the results of hydraulic conductivity tests involving slurries subjected to filtration of a nitric acid solution, it should be noted that the course of the process is slightly different relative to the case of exposure to tap water.

Studies involving the long-term filtration of an 0.5 M HNO_3 solution by hardening slurries show that in the case of both ash types, the value of the k_{10} coefficient decreases clearly and significantly (Figure 1). This is visible already at the beginning of the experiment, which indicates a rapid reaction

between an aggressive fluid and slurry components. After approximately 550 days, the hydraulic conductivity value is even lower, which indicates sealing of the slurry structure (for FPK and FPB) progressing over time. This is confirmed by the k_{10} values decreasing from approx. 6.0×10^{-8} m/s to approx. 1.0×10^{-9} m/s for FPK and from approx. 9.0×10^{-7} m/s to approx. $5,0 \times 10^{-8}$ m/s for FPB.

In the case of tap water filtration by the FPK slurry, the value of the hydraulic conductivity coefficient k_{10} was recorded at a practically constant level of approx. 9.0×10^{-7} m/s. For an FPB hardening slurry, which was exposed to tap water filtration, the authors recorded structural sealing during the experiment, confirmed by a reduction in the value of the k_{10} coefficient from ca. 1.0×10^{-7} m/s to ca. 1.0×10^{-8} m/s.

Hardening slurries containing bentonite and fluidized-bed fly-ash (from hard and brown coal combustion) are a multiphase material. As a result, under the influence of acid aggressiveness (HNO_3 solution), the hardening slurry exhibits a different hydraulic conductivity variability trend than concretes and mortars.

An explanation of this phenomenon can be found in the specificity of a hardening slurry internal system and the presence of bentonite and fluidized-bed ash therein. Under the impact of an 0.5 M HNO_3 solution, the pH of which is $1 - 2$, the structure of the system is loosened rather rapidly, following a formation of water-absorbing gel products. Hydrated products take up more volume, resulting in sealing of the structure, but following a different principle than in the case of densification. Furthermore, it should be assumed that further ion exchange processes occurred in bentonite in a system with a relaxed structure. Skalmowski [18] points out that a characteristic trait of montmorillonites (primary component of bentonite) is their high adsorption and cation exchange capacity. Cations can be ranked as follows, according to the bond durability: $Na^+ K^+ < Mg^{2+} < Ca^{2+} < H^+$ [18]. Cations located on the left side of the row are more easily exchanged with right-side cations. Although earlier, after preparing the slurry, Na^+ ions were exchanged with Ca^{2+} ions and the bentonite swelling capacity was reduced due to a more polarizing effect of bi-positive cations on water molecules, their re-exchange from Ca^{2+} to H^+ originating from the acidic solution, increases the bentonite water-binding properties. Therefore, the greater amount of bentonite in an FPK slurry may be responsible for their lower hydraulic conductivity, compared to an FPB slurry (Figure 1).

It should be stressed that nitric acid belongs to strong acids (strong electrolytes), which react already at quite a low concentration, practically with all ingredients of set paste [10]. In the case of 0.5 M HNO_3 solution filtration, we can expect a reaction with $Ca(OH)_2$ remaining in the system - including the formation of readily-soluble calcium nitrate, resulting in destabilization and hydrolysis

of calcium aluminates and silicates. The direct reaction of HNO_3 with hydrate phases, as well as its role as an oxidizing agent should also be considered. The result of direct reaction with hydrated calcium aluminates and silicates is the formation of calcium nitrate (V), hydrated silica gel and aluminium hydroxide [19].

In reference to the presented hypotheses, the slurry composition and the course of the study itself, we can make a thesis on the formation of colloidal silicic acid. The formed colloid, in combination with active clay minerals supplied from bentonite, seals the slurry microstructure (both FPK and FPB), contributing to a significant reduction in their hydraulic conductivity (Figure 1). Given the high alkalinity of the produced system, which, so to say, creates a buffer capacity, it can explain the resistance to acid aggressiveness.

5. X-Ray diffraction analysis of hardening slurries

5.1. Instruments

X-ray measurements were taken using a Bruker D8 Advance device equipped with a position-sensitive LYNXEYE detector operating over the Bragga-Brentano geometry, using CuKα ($\lambda = 0.15418$ nm) radiation with a nickel filter. The measurements were recorded over an angular range 2θ from 8 to 75° with an increment of 0.03° and a recording time of 960 s/increment.

5.2. Test results

Fig. 2 shows diffraction images of samples subjected to long-term (18 months) filtration of a solution aggressive to cement binders and tap water.

5.3. Test result analysis

The analysis of the diffraction patterns clearly shows greater reflections originating from quartz in the samples of FPK and FPB slurry after exposure to tap water, compared to FPK and FPB samples after exposure to the HNO_3 solution. This is confirmed by the occurrence of corrosion and decomposition of hydration products – including silicates. The presence of calcite was also confirmed in all samples, besides the FPK samples after exposure to the acidic solution. The presence of ettringite is confirmed by the reflections in the FPK sample after its exposure to tap water and the FPB samples after its exposure to a nitric acid solution.
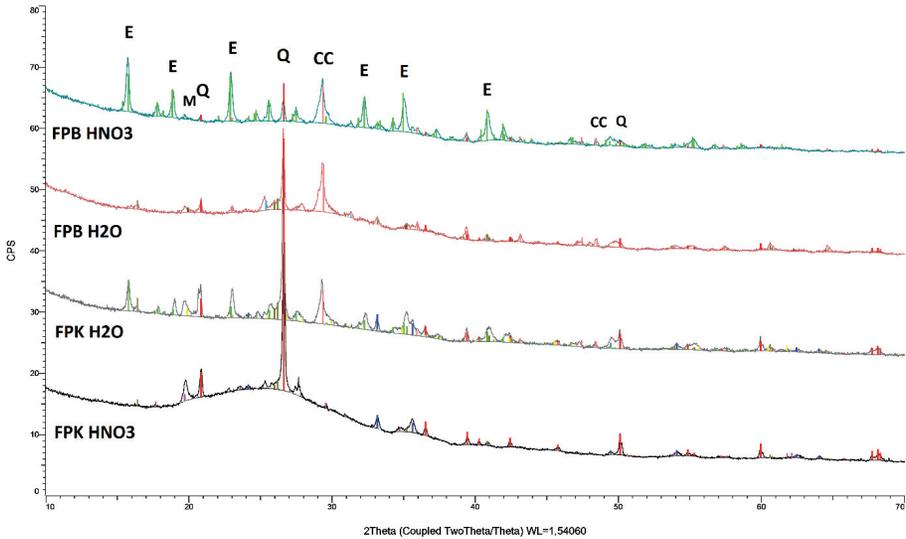
Fig. 2. X-ray diffraction pattern of samples of hardening slurries.

CC – calcite (calcium carbonate), E – ettringite, Q – quartz, M – montmorillonite.

6. Infrared (IR) spectroscopy analysis of hardening slurries

6.1. Instruments

IR spectra were recorded through a Genesis II FTIR spectrometer by Mattson, with the use of KBr preparations (200 mg KBr with spectral purity and 2 mg of sample), for wave number range of 4000 – 400 cm^{-1}. The test conducted using the infrared spectroscopy method are of qualitative analysis nature.

6.2. Test results

IR spectra for hardening slurry samples after prolonged (18 months) exposure to the filtration action of a 0.5 M solution of HNO_3 and tap water are shown in Figure 3.

6.3. Test result analysis

The obtained results indicate the following observations:

- the spectra of all samples are dominated by bands originating from antisymmetric Si-O silicate stretching vibrations (990-1040 cm^{-1}) and bands characteristic for water ~3250 cm^{-1} (stretching OH) and 1635 cm^{-1} (deformation OH),

- all samples were fairly homogeneous; band shifting from 954 cm^{-1} (FPB H$_2$O) through 960 cm-1 (FPK H$_2$O) to 1039 and 1042 cm^{-1} (FPB HNO$_3$ and FPK HNO$_3$) proves the increasing bentonite hydration degree,

- maximum band position ~1040 cm^{-1} and the presence of a weaker, broad band ~1160-1200 cm^{-1} prove the presence of amorphous silicates,

- weak bands at 1340-1380 cm^{-1} can be attributed to the presence of nitrates,

- the spectrum of the FPB HNO$_3$ sample has visible bands proving the presence of aliphatic organic compounds (2850-2950 cm^{-1}, stretching CH),

- the samples after tap water filtration (both FPK, as well as FPB), exhibit a clear band confirming the presence of carbonates; the case of samples exposed to tap water action, have a marked clear, mildly-intensive vibration band with an extreme at approximately 1420 cm^{-1}, which corresponds to the presence of CaCO$_3$ and an extreme at approximately 1385 cm^{-1}, which corresponds to the presence of alumina carbonates.

a. FPK – HNO$_3$

b. FPB – HNO$_3$

c. FPK – tap water

d. FPB – tap water
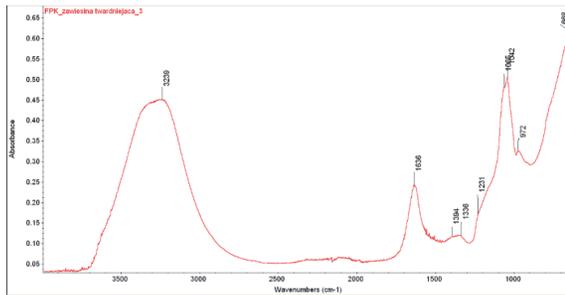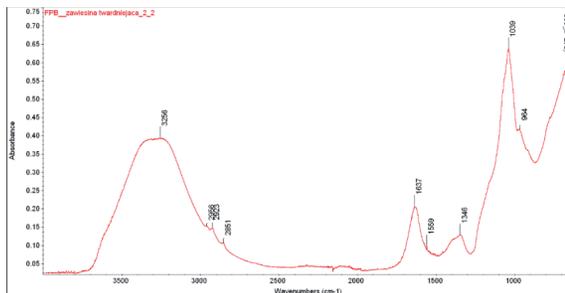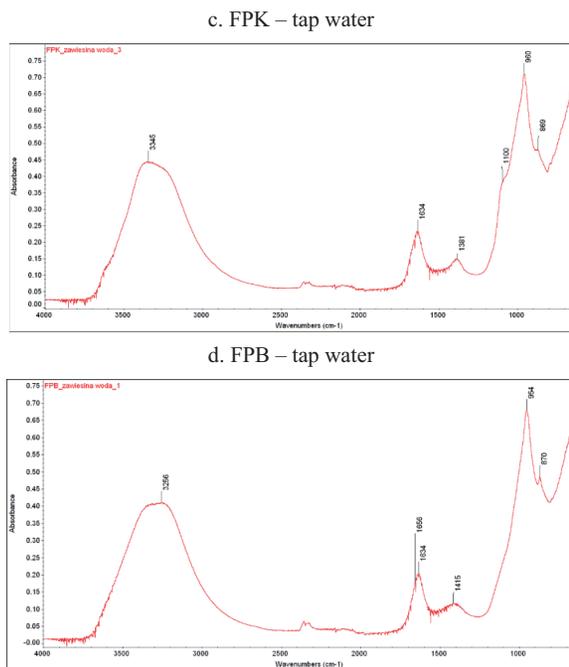
Fig. 3. IR spectra for samples of hardening slurries.

7. Hardening slurries surface photographs

7.1. Instruments

The photographs of the surfaces of studied slurries were taken using a USB Delta Optical Smart 5M PRO digital microscope with a magnification range of 20x–300x.

7.2. Photographs

Photographs (magnification of approx. 150x) showing the characteristic surface elements of FPK and FPB hardening slurry samples after long-term (18 months) exposure to the filtration of a 0.5 M HNO_3 solution are presented in Figure 4. The surfaces of samples in direct contact with the nitric acid solution were photographed.

a. FPK – HNO₃   b. FPB – HNO₃

Fig. 4. Hardening slurry surface photographs (magnification of ca. 150x).

7.3. Images analysis

When analysing the surfaces of FPK and FPB slurries shown in Figure 4, one can notice a yellow, jelly-like substance. It is undoubtedly a hydrated silica gel, which was formed as a consequence of an aggressive HNO_3 solution acting on hydrated calcium aluminates and silicates. The photographs confirm the findings from the IR study, on the presence of amorphous silicate forms.

The described processes correspond to type II corrosion, so-called softening. New low-strength compounds, without binding properties, are formed as a result of nitric acid acting on the slurry surface [8, 11]. These products are amorphous and poorly soluble, hence, they are not leached out. This is of great utilitarian importance. Additional subsurface sealing of the material structure takes place in the subsurface sections of the hardening slurry composing the cut-off wall. Furthermore, corrosion products located on the surface weaken the further corrosion progress – softening (including resistance weakening) in deeper sections of the cut-off wall. This explains both the observed decrease in the hydraulic conductivity coefficient k_{10}, as well as the durability of this reduction – Figure 1, despite material destruction.

8. Conclusions

The analysis of the test results concerning hydraulic conductivity, phase composition and surface structure of hardening slurries with an addition of fluidized-bed fly-ash, subjected to long-term filtration of nitric acid and, for reference, tap water, enables to draw the following conclusions:

1. The slurries subjected to filtration of a nitric acid solution, which was aggressive to a cement binder, were additionally sealed, compared to slurries exposed to tap water filtration.

2. The slurry with an admixture of fluidized ash brown coal subjected to filtration by an aggressive solution and tap water exhibited a slightly higher structural tightness than a slurry with an admixture of hard coal ash.

3. The hardening slurries with an admixture of fluidized hard and brown coal ashes exposed to long-term filtration in strongly chemically aggressive environments (sodium sulphate solution) exhibited corrosion resistance. The pozzolanic properties of the applied fluidized-bed fly-ash and the high adsorption and cation exchange capacity of bentonite contributed to the weakening of the destructive effect of acid aggressiveness.

4. The formation of hydrated colloidal compounds in the subsurface slurry zone, in contact with an acidic environment, additionally seals the material structure, which not only improves the performance properties of the slurries in cut-off walls, but also significantly limits the access of aggressive substance to the interior of the cut-off wall.

5. Favourable filtration resistance of hardening slurries with an addition of fluidized-bed hard or brown coal fly-ash extends the application possibilities of CBPs in civil engineering, which contributes to the implementation of the Circular Economy concept.

References

[1] Z. Kledyński, A. Bogdan, W. Jackiewicz-Rek, K. Lelicińska-Serafin, A. Machowska, P. Manczarski, D. Masłowska, A. Rolewicz-Kalińska, J. Rucińska, T. Szczygielski, J. Walczak, M. Wojtkowska, and M. Żubrowska-Sudoł, "Condition of Circular Economy in Poland," Archives of Civil Engineering, vol. 66, no. 3, pp. 37–80, 2020, https://doi.org/10.24425/ace.2020.131820

[2] ECOBA, Production and Utilisation of CCPs in 2016 in Europe, www.ecoba.org, 2016.

[3] P. Falaciński, 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, pp 295-300, 2007.

[4] Falaciński P. Leak tightness of hardening slurries with fluidal fly ashes in chemically aggressive environments. Archives of Environmental Protection. Polish Academy of Sciences, vol. 37, no. 1, pp 115-134, 2011.

[5] PN-EN 1538. Execution of special geotechnical works – Diaphragm walls.

[6] Z. Kledyński, P. Falaciński, A. Machowska, J. Dyczek, Ł. Kotwica, Utilisation of CFBC fly ash in hardening slurries for flood-protection dikes. Archives of Civil Engineering, vol. LXII, Issue 3, pp 75-87, 2016.

[7] P. Falaciński, Possible applications of hardening slurries with fluidal fly ashes in environment protection structures. Archives of Environmental Protection. Polish Academy of Sciences, vol. 38, no. 3, pp 91-104, 2012, https://doi.org/10.1515/heem-2016-0004

[8] Gruener M. Corrosion and protection of concrete. Arkady, Warsaw 1983.

[9]   Kurdowski W. Chemistry of cement and concrete. Polski Cement, PWN, Cracow 2010.
[10] Neville A. M. Properties of Concrete. Trans-Atlantic Publications, Inc. 5th edition, 2012.
[11] Słomka-Słupik B. The changes of phases composition of the paste from cement CEM III/A under the influence of NH4Cl water solution. CWB, 2, pp 61-66, 2009
[12] Stanaszek-Tomal E., Fiertak M. Biological and chemical corrosion of cement materials modified with polimer. Bulletin of the Polish Academy of Sciences, Technical Sciences, vol. 63, no. 3, 2015, https://doi.org/10.1515/bpasts-2015-0069
[13] Barbhuiya S., Kumala D. Behavior of Sustainable Concrete in Acidic Environmental. Sustainability, 9, pp. 1-13, 2017, https://doi.org/10.3390/su9091556
[14] T. Ramlochan , P. Zacarias, M.D.A. Thomas, R.D. Hooton, The Effect of Pozzolans and Slag on the Expansion of Mortars Cured at Elevated Temperature, Part 2, Microstructural and Microchemical Investigations, Cement and Concrete Research, vol. 34, pp 1341-1356, 2004.
[15] Glinicki M.A., Zieliński M.:Air voids spacing in concrete with addition of fly ash from fluidized bed coal combustion. Cement Lime Concrete no. 3, pp. 133-138, 2007.
[16] Stryczek S., Małolepszy J., Gonet A., Wiśniowski R., Kotwica Ł., Złotkowski A., Ziaja J. Ashes from fluidized combustion of brown coal as an additive to sealing slurries. AGH, Cracow 2013.
[17] Szperliński Z. Chemistry in environmental protection and engineering. OWPW, Warsaw 2002.
[18] Skalmowski W. Building minerals chemistry. Arkady, Warsaw 1971.
[19] Piasta J., Piasta W.G. Concrete: selection of aggregates and cements, concrete design, durability of concrete, chemical and thermal resistance, Arkady. Warsaw 1997.

Wpływ agresywności kwasowej na odporność filtracyjną zawiesin twardniejących z dodatkiem lotnych popiołów fluidalnych

Streszczenie:

Przesłony przeciwfiltracyjne wykonywane z zawiesin twardniejących mogą być realizowane w obiektach hydrotechnicznych oraz ochrony środowiska, gdzie pracują w warunkach filtracyjnego oddziaływania wód zanieczyszczonych. Tym samym kluczowa staje się kwestia odporności filtracyjnej i korozyjnej zawiesin w kontekście filtracyjnego oddziaływania różnorodnych środowisk agresywnych chemicznie.

Przedmiotem artykułu są zawiesiny twardniejące cementowo-bentonitowo-wodne z dodatkiem lotnych popiołów fluidalnych ze spalania węgla kamiennego i węgla brunatnego. Głównym celem pracy było określenie odporności filtracyjnej zawiesin twardniejących w świetle długotrwałej ekspozycji na filtracyjne oddziaływanie substancji agresywnej w stosunku do spoiwa cementowego. Zastosowano roztwór wodny kwasu azotowego o stężeniu 0,5 M, który modelował agresywność kwasową.

Badano zmiany przepuszczalności hydraulicznej zawiesin w funkcji czasu (18 miesięcy) oddziaływania roztworu 0,5 M kwasu azotowego. Analizowano zmiany w składzie fazowym oraz strukturze powierzchni zawiesin twardniejących w kontekście jej odporności filtracyjnej na działanie agresywności kwasowej. Bazę porównawczą stanowiły próbki poddane filtracji wody wodociągowej (środowisko obojętne).

W artykule przedstawiono metodykę badania przepuszczalności hydraulicznej (k_{10}) zawiesin twardniejących. Przedstawiono badanie składu fazowego metodą rentgenowskiej analizy dyfrakcyjnej (XRD), spektroskopii w podczerwieni (IR), a także obraz struktury powierzchni zawiesin twardniejących.

Analiza uzyskanych wyników badań zawiesin twardniejących poddanych filtracyjnemu oddziaływaniu roztworu kwasu azotowego pozwala stwierdzić, iż przebieg procesu korozji jest nieco inny niż materiałów budowlanych na bazie spoiwa cementowego.

Potwierdzono obserwacje innych badaczy, iż zastosowanie dodatku lotnych popiołów fluidalnych wpływa korzystnie na zwiększenie odporności matrycy cementowej eksponowanej na agresywność kwasową. Zidentyfikowane w przypowierzchniowej strefie zawiesiny, która miała kontakt ze środowiskiem kwaśnym, uwodnione związki koloidalne doszczelniają strukturę materiału, przez co znacząco ograniczają dostęp substancji agresywnych do wnętrza zawiesiny. Powstałe substancje bezpostaciowe, w formie żelu uwodnionej krzemionki, zwiększyły szczelność zawiesin, zidentyfikowaną obniżeniem wartości przepuszczalności hydraulicznej.