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DURABILITY OF STABILISED GALVANIC SEWAGE SLUDGE AGAINST THE IMPACT OF SEA WATER AND SULFATE SOLUTIONS

Solidification of industrial sludge in concrete matrices has been examined. The concrete mixes in which galvanic sewage sludge was immobilised were prepared with the use of two binder types: Portland-fly ash cement CEM II/B-V, and a binder composed of Portland cement (60%) and fly ash obtained from fluidized bed combustion of fuels (40%). Leaching of heavy metals (Cr, Cd, Zn, Ni, Cu, Pb, V) was observed from solidification matrices which had been exposed to various aqueous media (distilled water, sea water, sulfate solution) over a long period of time. Features of concrete were also studied which could directly influence the release of heavy metals, i.e. their microstructures and microporosity. Moreover, the effect of sewage sludge addition was shown on physical and mechanical properties of concrete, i.e. compression strength, water absorbability and water penetration depth were analysed. The research programme covered the periods of 1 year and 2 years, during which the concrete samples were stored in various aqueous environments. The stability parameters of the matrix which contained fly-ash from fluidized bed combustion of fuels were found not to be much different from the parameters for the matrix which was based on the Portland-fly ash cement. Leachability of heavy metals was demonstrated to increase in the aggressive aqueous medium as compared to the level obtained when the samples were stored in distilled water.

1. INTRODUCTION

One of the methods applicable in neutralization of a hazardous waste is its solidification/stabilization in concrete based on Portland cement and other cement grades with high contents of mineral additions such as fly ash or granulated blast furnace slag. The matrices used for solidification of hazardous wastes should demonstrate appropriate physical and mechanical properties which in the long run affect the service life of the resulting composites. The stability of the concrete mixes used for solidifica-

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tion of wastes is also very important in the context of leaching of heavy metals into the aqueous and/or soil environment which is in direct contact with the solidification matrices (since it is assumed that the resulting composites can find practical application).

The concrete mixes and/or mortars containing heavy metals, if then landfilled or utilised as aggregate or granulated material in civil engineering, are exposed to numerous and disadvantageous environmental conditions. Damage to concrete may result, e.g. from the impact of sulfate solutions or sea water [1].

The presence of sodium, potassium, magnesium and/or calcium sulfates may be faced everywhere in soil and in ground water. Sulfates in groundwater are in general naturally occurring compounds, but they may also come from fertilisers or industrial sewage. The soil in post-industrial land (close to gas-works in particular) may contain sulfates as well as other aggressive substance. Moreover, sulfates may be produced from sulfides which undergo oxidation, e.g. when they contact compressed air which is used in excavation work.

The reaction of sodium sulfate with calcium hydroxide which is present in the cement paste after its hardening follows the scheme [2]:

$$Ca(OH)_2 + Na_2SO_4 \cdot 10H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH + 8H_2O$$

The sulfate aggression against concrete may end up with [2]:

- expansion of cement paste which causes its cracking and failure,
- decline in concrete strength, as a result of decreasing cohesion forces in the hydrated cement paste and lower adhesion between the paste and aggregate.

Destruction of concrete due to attack of sulfate environment begins at the edges of a concrete element, which is followed by progressive cracking and chipping of the material, and that reduces the concrete structure to the brittle condition or even to the soft condition. The effect of the sulfate environment on concrete may be reduced by the use of a suitable kind of cement, e.g. the one which contains granulated blast furnace slag [2].

A concrete structure which is in contact with sea water may suffer from various impacts, like chemical attack (presence of chlorides), freezing-thawing cycles, salt erosion, and abrasive wear by the sand-water suspension. Whether those factors are more or less damaging to a concrete structure, it is much dependent on whether the structure is permanently immersed under the water surface, or it is exposed to sea water periodically [2].

When sea water affects the concrete surface, the following chemical reaction takes place:

$$MgSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Mg(OH)_2$$

The reaction yields $Mg(OH)_2$ (brucite) which is deposited in pores close to the concrete surface and forms a protective coat which prevents further reactions. However, when the abrasive attack is able to remove the surface deposits of brucite, the reactions with the magnesium ions will continue to proceed. Permanent and complete immersion in sea water thus seems to improve the conditions of concrete exposition in that environment [2]. Proper selection of the binding materials to be employed in te production of concrete elements to be exposed to sea water, is also of particular importance, so that low permeability concrete be obtained.

The paper presents the leaching effect of sulfate containing environment and of sea water which elute heavy metals (Cr, Cd, Zn, Ni, Cu, Pb, V) from concrete in which galvanic sewage sludge has been solidified. Moreover, the experimental results were provided for stability of concrete matrices exposed to those aggressive media.

2. MATERIALS AND METHODS

Materials. Galvanic sewage sludge (GS), classified as 190813* (sludges containing dangerous substances from other than biological treatment of industrial waste water) pursuant to [3], were subjected to stabilisation. Chemical compositions and contents of heavy metals in the sewage sludge are specified in Table 1. The table also provides the heavy metal contents in the water extract from the sludge, compared to the permissible concentrations of heavy metals in wastes to be sent to the waste landfill facilities for “inert” wastes and for “non-hazardous wastes” [4].

Table 1

Chemical composition and heavy metals content in galvanic sewage sludge and water extracts from sludge

Main components [wt. %]		Heavy metals [mg/kg d.s.]			Permissible content in water extracts [4] [mg/kg d.s.]	
Loss on ignition	41.35	Heavy metal	Solid mass	Water extracts	Inert waste	Non-hazardous waste
SiO_2	3.01	Cr	270100.7	3.04	0.5	10.0
Al_2O_3	0.83	Zn	1441.1	4.44	4.0	50.0
Fe_2O_3	1.08	Ni	12789.6	8.86	0.4	10.0
CaO	0.11	Cu	38443.5	0.48	2.0	50.0
MgO	0.01	Cd	1133.5	0.71	0.04	1.0
SO_3	5.85	Pb	545.8	0.017	0.5	10.0
Na_2O	3.11	V	185.6	0.003	–	–
K_2O	0.18					

Concrete for stabilisation of sewage sludge were made of: Portland-fly ash cement CEM II/B-V 32,5R-HSR (FAC) which contained about 35% of fly ash, special binder – 60% CEM I 32,5R + 40% fly ash obtained from fluidized bed combustion of fuels (SBC). Chemical compositions for concrete constituents are given in Table 2.

Table 2

Chemical composition of ingredients used in researches [wt. %]

Component	CEM I 32,5R	CEM II/B-V 32,5R-HSR	Fluidal fly ash (AFBC)
Loss on ignition	3.46	3.71	3.20
CaO	64.60	48.11	18.70
SiO_2	19.20	27.10	33.90
Al_2O_3	4.69	10.84	17.90
Fe_2O_3	3.04	3.93	6.70
MgO	1.22	1.61	3.10
SO_3	2.65	1.95	9.00
Na2Oeqa	0.62	1.32	2.80

[a] $Na_2O_{eq} = Na_2O + 0.658\ K_2O$

Methods. Strength tests of concrete samples were performed in accordance with EN 206-1:2000 [5]. Determination of water penetration depth in concrete followed the procedure specified in EN 12390-8:2000 [6], while concrete absorbability was found according to PN-88/B-06250 [7].

The mercury porosimetry method was employed to conduct porosity measurements, and the Poremaster 60 instrument (Quantachrome, USA) was used to measure distribution of pore diameters within the range of from several hundred micrometers up to 3.5 nm.

Microstructural observations were based on the scanning electron microscopy (SEM) by the energy dispersion spectroscopy (EDS) method. That combination made it possible to analyse the chemical composition of samples in micro-zones.

Water extracts from the waste were obtained according to EN 12457-1-4:2002 [8], while water extracts from concrete in which sewage sludge had been stabilised were prepared as described in EA NEN 7375:2004 [9]. The method, however, was modified in the course of experiments; the properties of the leaching liquid were changed. One series of test samples was exposed to artificial sea water (SW), and another series was subjected to treatment with a sulfate solution (SS). Those solutions were prepared with due observance of the recommendations provided in the standard [10]. In order to prepare artificial sea water (named sea water in this paper), the following of reagents in 1000 g of distilled water were dissolved:

- sodium chloride (NaCl) – 30.0 g,
- magnesium chloride $MgCl_2 \cdot 6\ H_2O$) – 6.0 g,
- magnesium sulfate ($MgSO_4 \cdot 7\ H_2O$) – 5.0 g,
- calcium sulfate ($CaSO_4 \cdot 2H_2O$) – 1.5 g,
- potassium bicarbonate ($KHCO_3$) – 0.2 g.

The sulfate solution of the concentration of (16.0 ± 0.5) g SO_4/dm^3 was obtained from reagent grade sodium sulfate (Na_2SO_4 or $Na_2SO_4 \cdot 10\ H_2O$).

3. RESULTS AND DISCUSSION

The concrete mixes based on the Portland cement CEM II/B-V 32,5R-HSR (FAC) and on the SBC binder made matrices for solidification of galvanic sewage sludge. The waste was added at the amount of 10 wt. % of dry matter on the cement content in the concrete mix. The concrete mix with the cement content of 300 kg/m^3, and water to cement ratio $w/c = 0.6$, was prepared as described in [11]. The concrete mixes with the addition of the sludge were then moulded as blocks of the dimensions as required by applicable standards. The test pieces which contained sewage sludge were designated with the additional letters GS.

Table 3

Compressive strength of concrete without and with addition of sewage sludge [MPa]

Concrete mixes	2 days	7 days	28 days	180 days	360 days	720 days
FAC	7.38	11.20	25.20	40.47	55.80	61.50
FAC GS	18.58	27.31	35.33	36.79	50.44	57.98
SBC	10.27	27.07	37.11	50.23	52.30	56.40
SBC GS	23.34	32.86	37.41	35.53	42.40	50.32

In addition to the most important feature which is expected for concrete mixes to be used for solidification of hazardous wastes, i.e. high fixation potential for heavy metals, those matrices should also offer high stability from the viewpoint of their physical and mechanical properties. Table 3 presents changes in compression strength for concrete samples with the addition of sewage sludge (FAC GS, SBC GS), and strength parameters for reference samples (FAC, SBC). The admixture of sewage sludge does not cause any decline in strength parameters which were investigated between day 2 and day 28 of hydration. The composites were also tested after 180, 360 and 720 days, and their strength declined in each case analysed. That may result, inter alia, from the fact that composites contained big amounts of heavy metals, like lead and cadmium, which are known to extend the cement setting time, and hence to lower the strength of concrete; that effect was already described in literature [12].

The impact on strength of composites was also assessed from their service in the sulfate solution and from sea water (after 1 and 2 years of hydration). The findings are presented in Fig. 1, and they were referred to strength of concrete which were stored under laboratory conditions. The sulfate solution and sea water were found to be responsible for a considerable decrease in strength parameters of concrete elements to which galvanic sewage sludge had been admixed, and that decline was noticed to take place between the first and second year of hydration. Declining strength of composites containing sewage sludge may be connected with destruction of concrete internal structures by sea water and/or sulfate solution penetrating inside test samples.

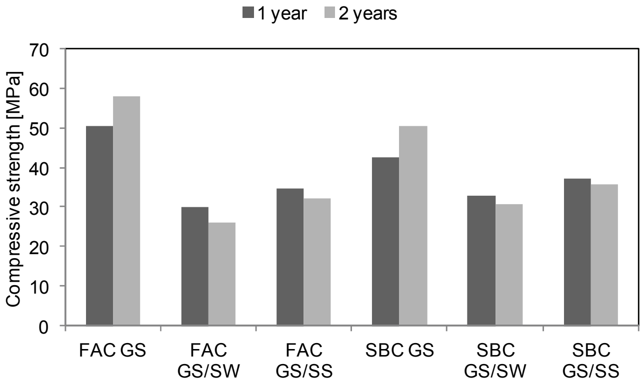


Fig. 1. Compressive strength of concrete with addition of the sewage sludge in various environmental conditions: SW – sea water, SS – sulfate solution

Concrete absorbability is increased by the addition of galvanic sewage sludge, with simultaneous increase in water penetration depth, e.g. in the case of concrete SBC GS (Table 4). The penetration depth of water makes also that feature of concrete which is utilised to evaluate concretes qualitatively. If penetration is lower than 30 mm, the concrete may be classified, according to Neville [2], as *impermeable under corrosive conditions, i.e. under aggressive attack*. Still, the penetration zone, which was used to solidify sewage sludge, is severely exposed to the attack of aggressive environments being the zone where destruction of concrete and drop in concrete strength may take place.

Table 4

Depth of water penetration and absorbability of concretes with sewage sludge

Concrete mixes	Depth of water penetration [mm]	Absorbability [%]
FAC	23.0	6.86
FAC GS	22.5	8.55
SBC	17.0	7.39
SBC GS	27.5	9.77

Numerous mechanical properties of set pastes and concretes are dependent not only on chemical composition of the hydrated binding material but also on microstructure of hydration products. Hence, it is important to know much about microstructure of set composites [2]. The highest importance in the process of permanent fixation of heavy metals (coming from waste to be stabilised) in the materials which are based on mineral binders is attributed to the phase C-S-H (calcium silicate hydrates). That can be found in calcium silicate hydrates with low level of structural orientation and changing chemical composition [13]. Microstructural investigation of composites, both with and without admixture of sewage sludge, revealed the presence of gel-type phase C-S-H, composed of fine nodules, in the hydrated paste. The phase C-S-H seems to be relatively compact. In both cases as mentioned above, lamellar products are formed (the hexagonal section of numerous lamellae suggests the presence of portlandite). The exemplary microstructural image, together with the chemical analysis for area 1 which confirms incorporation of chromium ions, is presented in Fig. 2.

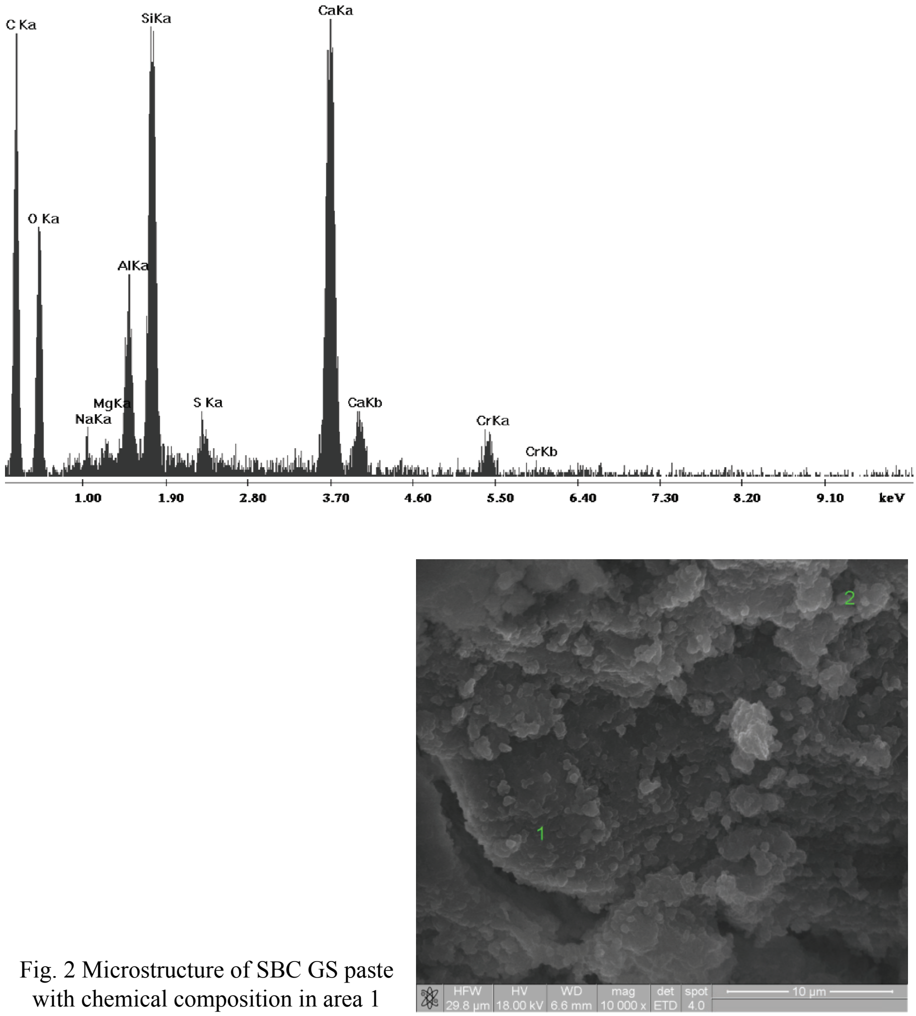
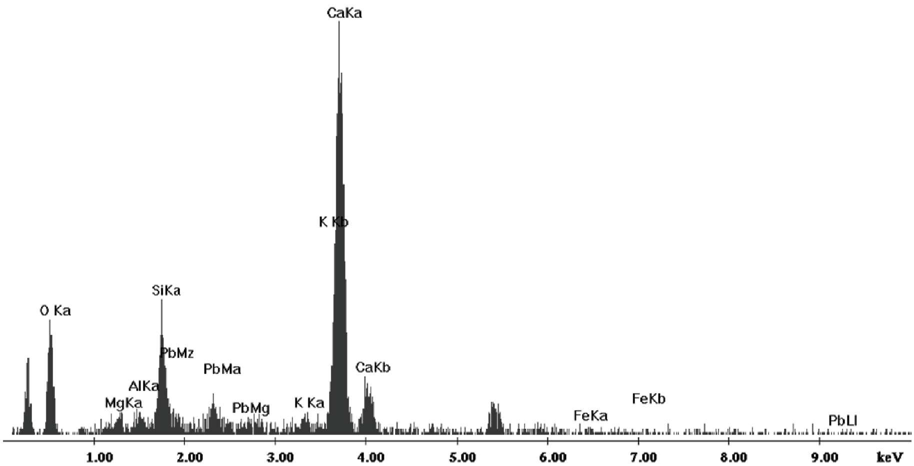


Fig. 2 Microstructure of SBC GS paste with chemical composition in area 1

When sludge is added to composites, new areas appear which represent formation of new phases in the presence of heavy metals. An exemplary microstructural image, together with the chemical analysis for area 4 which confirms incorporation of lead ions and formation of new structures, are presented in Fig. 3.



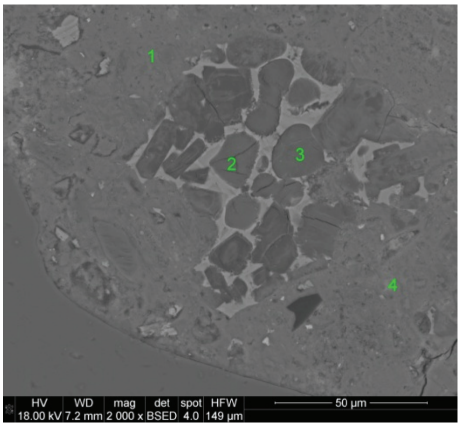


Fig. 3. Microstructure of FAC GS paste with chemical composition in area 4

Strength of binder matrices is also determined by porosity of paste as well as shapes and distribution of pores. Moreover, the effect of the amount and quality of mineral admixture, i.e. fly ash will have to be considered, too [14, 15]. Porosity of pastes is thus critically important in the context of producing stable composites which are used to solidify hazardous wastes. Porosity of pastes is a controlling factor for entry of liquids into the concrete, and for conveyance of liquids inside that matrix, while movements of liquids are directly related to higher or lower leaching of heavy metals from the structures of composites which immobilise hazardous wastes. Transport of water – together with aggressive substances – will be controlled by the following factors [16]:

- capillary pressure (water is “pulled up” in capillaries),
- crystallisation pressure of hydration products (e.g. ettringite),
- composition of liquid in pores,
- degree of interconnections.

The paste designated as FAC GS features much higher porosity after 6 months than the reference paste FAC. The difference can be illustrated by the following figures: 15.9% porosity for reference paste and 24.5% porosity for sludge-admixed paste. However, much smaller pores (with the diameters of several tens and several hundred micrometers) can be found in the paste FAC GS than in the reference material. The pastes SBC and SBC GS offer similar porosity parameters. The difference itself in porosity figures for the reference paste SBC (30.0%) and the sludge-paste mix SBC GS (26.3%) is small, and distributions in pore sizes are much similar to each other. And which is worth stressing, that was the only pair among the studied paste pairs in which porosity after 6 months was lower for the sludge-containing sample than for the reference sample. That could make evidence for the “sealing” effect of the galvanic sewage sludge on the paste structures.

Table 5 provides the parameters which characterise pore size distribution in reference pastes and in materials with additions of galvanic sewage sludge after 6 months and after 1 year of hydration. The median for that distribution as well as local peaks in the frequency curve, i.e. modal values (Mod), were presented. The obtained data pointed out that the admixture of galvanic sewage sludge increased the share of smaller sized pores in the mix which was based on the Portland cement (FAC GS and FAC pair of samples). The pore size distribution remained almost unaffected by the addition of galvanic sewage sludge to the paste which was based on the binder with fly ash obtained from fluidized bed combustion of fuels (pair SBC GS and SBC). The distribution medians, as presented in Table 5, suggest that the average pore size in the studied pastes oscillate close to the values which have been attributed to gel pores and it is similar for both research periods.

Table 5

Pore distribution in samples without and with the addition of sewage sludge

Sample	Hydration time	Median [μm]	Modal values [μm]
FAC	6 months	0.057	0.54–0.06–0.006
	1 year	0.062	0.59–0.07
FAC GS	6 months	0.042	0.58–0.04
	1 year	0.057	0.60–0.05
SBC	6 months	0.041	0.55–0.20–0.006
	1 year	0.054	0.61–0.06
SBC GS	6 months	0.061	0.52–0.07–0.005
	1 year	0.073	0.60–0.07

When evaluating persistence of stabilisation of hazardous wastes in concrete block matrices, one may not disregard the tests for leaching heavy metals out of those composites. Both concrete mixes: that based on Portland-fly ash cement (FAC GS) and that based on the binder which contained fly ash obtained from fluidized bed combustion of fuels (SBC GS), were subjected to the same evaluation procedure, pursuant to EA NEN 7375:2004 [9]. The combined heavy metal contents (after 1 and 2 years) in water extracts after distilled water immersion test (MDW) were presented in Table 6. The table also provides heavy metal concentration data for the concrete samples placed in sea water (MSW) and in sulfate solutions (MSS).

Table 6

Heavy metals leaching from monolithic forms of concretes solidifying galvanic sludge

Method of taking water extract	Sample	Time	Concentration in water extract [mg/dm^3]						
			Cr	Zn	Ni	Cu	Cd	Pb	V
MSW	FAC GS	1 year	1.233	0.444	0.046	0.054	0.007	0.095	0.096
		2 years	1.340	0.487	0.053	0.063	0.017	0.134	0.122
	SBC GS	1 year	1.674	0.578	0.145	0.177	0.022	0.222	0.211
		2 years	1.967	0.644	0.160	0.198	0.054	0.265	0.230
MSS	FAC GS	1 year	1.345	0.612	0.069	0.104	0.002	0.082	0.531
		2 years	1.369	0.713	0.078	0.109	0.004	0.099	0.546
	SBC GS	1 year	1.567	0.673	0.050	0.111	0.001	0.111	0.232
		2 years	1.842	0.804	0.071	0.115	0.001	0.117	0.247
MDW	FAC GS	1 year	0.098	0.101	0.004	0.069	0.0001	0.023	0.076
		2 years	0.106	0.111	0.005	0.073	0.0001	0.054	0.098
	SBC GS	1 year	0.124	0.002	0.008	0.007	0.0001	0.007	0.023
		2 years	0.158	0.002	0.009	0.008	0.0001	0.007	0.038
Permissible heavy metal concentration in waters with A1 category[a] [17], mg/dm^3			0. 05	3.0	0.05	0.05	0.005	0.05	1.0

[a]To A1 category belong surface waters requiring simple physical treatment, in particular filtering and disinfection [17].

The obtained results for leachability from concrete matrices, which were used to stabilise galvanic sewage sludge, of heavy metals in three aqueous environments clearly show that higher and higher amounts of heavy metals are released in time. That conclusion always results from summing up concentrations of heavy metals in water extracts which were obtained after 1 year and after 2 years. Hence, it is essential to note that considerable differences were observed in the increase of concentration for those two research periods (which were different for different samples, different metals and different aqueous environments).

It should be emphasised that both sea water and the sulfate solution enhance leachability of all tested heavy metals (Cr, Pb, Zn, Ni, Cu, Cd, V). Concentrations of most of them (Cr, Ni, Cu, Cd, Pb) in water extracts exceed the concentrations permissible for the highest class surface water quality (A1) [17]. Thus, the concrete with solidified waste, when contacted with water, may adversely influence water quality. That problem is most severe for leaching of chromium in particular.

4. CONCLUSIONS

The paper analyses selected durability features of concretes which were prepared with the use of Portland-fly ash cement and with the use of a binder which contained fly ash obtained from fluidized bed combustion of fuels; galvanic sewage sludge was solidified in those matrices to render it harmless. Durability of concrete was determined in three aquatic environments, i.e. the samples were stored in distilled water and in two aggressive media: sea water and sulfate solution.

The research on immobilisation of heavy metals (derived from galvanic sewage sludge) revealed that leachability of heavy metals is disadvantageously enhanced by both aggressive aqueous environments covered by study. The tests conducted 1 year and 2 years after placing the test samples in aqueous media showed that leachability of heavy metals (Cr, Cd, Zn, Ni, Cu, Pb, V) increased in aggressive environments in relation to leachability in distilled water. The eluate concentrations turned out especially high for chromium (see Table 6).

In order to evaluate durability of concrete to which sewage sludge was added, the following parameters were investigated: compression strength, water absorbability and water penetration depth. Increasing compression strength was observed after sewage sludge had been added, in relation to reference samples, at an early stage of the research programme – up to day 28 (see Table 3). However, that parameter declined under long-term storage conditions (between 180 and 720 days). Compression strength also dropped down when the concrete samples were exposed to the long-term impact of the aggressive aqueous environment, as referred to the equivalent impact of distilled water (Fig. 1). It is worth mentioning that the concrete mix prepared with the use of the binder (SBC) offers better strength parameters than the mix which was based on the Portland-fly ash cement (that refers to concretes which were cured in the aggressive environment).

In general, it was found out that the use of fly ash obtained from fluidized bed combustion of fuels as a component of matrices in which galvanic sewage sludge was solidified gave the similar durability results as those offered by the silica fly ash. That conclusion covers the study conducted in two environments aggressive towards concrete (sea water and sulfate solution). The research programme should verify efficient immobilisation of galvanic sewage sludge in solid matrices, with the use of fly ash obtained from fluidized bed combustion of fuels, under various environmental conditions.

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