

Influence of Fly Ashes on Hardening Slurries Resistance to Sulphate Attack

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Abstract

Rapid development of slurry wall technology in the underground constructions caused a noticeable increase in interest, cut-off walls well known in the past. Introduction of hardening slurry to this technology makes their construction easier and creates new possibilities for their application. Current challenge lies in subsoil insulation in order to avoid contamination spread into the ground waters. Thus, besides the already well known problems, new ones appeared, in that the issue of corrosion, especially of a chemical nature, to which the cut-off walls are exposed in the environment of aggressive groundwater. The paper focuses on the assessment of the hardening slurries to sulphate attack. The results of own investigations of cement-bentonite hardening slurry and cement-bentonite-ash hardening slurry prepared with the addition of aggressive liquid, as well as, with tap water and kept in a sulphate ion medium for 1 year are presented. Contamination spreading in non-filtration conditions was modelled. Tests of samples made with tap water and stored in tap water are considered as controls. The paper presents results of tests of liquid slurries properties and results of assessments of hardened slurries. Changes in mass of slurries, compressive and tensile strength and changes in sample storage environment chemistry were measured. Thermographic investigations of slurries were also conducted. The results of investigations and review of literature data on hardening slurries corrosion resistance to sulphate attack are presented. Practical suggestions in relation to the application of cut-off walls made of hardening slurries are made.

Key words: groundwater protection, sulphate attack, cut-off walls, hardening slurries

1. Introduction

Rapid development of slurry walls technology in the underground constructions caused a noticeable interest increase in cut-off walls well known in the past. Introduction of hardening slurry to this technology makes their construction easier and creates new possibilities for their application. The current challenge lies in

subsoil insulation in order to avoid contamination spreading into the groundwater. Thus, besides the already well-known problems, new ones appeared, in that a issue of corrosion, especially of a chemical nature, to which the cut-off walls are exposed in the environment of aggressive groundwater. The paper focuses on the assessment of the hardening slurries to sulphate attack.

The term hardening slurry describes a tixotropic liquid supporting the stability of the narrow excavation or the bore-hole in the soil, subsequently hardening and changing into solid state. From the point of view of their content they can be defined as a liquid mixture of bentonite, water and binding substance (most often cement) and optionally: additional binding substances, filling substances and chemical additives.

The individual characteristics of the slurry include: the major content of water, presence of the substance giving the tixotropic properties (bentonite), ability of conversion from liquid to solid state due to the presence of binding substance and special technical requirements in the liquid state important in their application.

Among hydrotechnical applications of the hardening slurries the cut-off walls dominate (Jawański et al 1996, Kledyński, Kozyra 1997, Kłosiński, Rafalski 1985, Lewandowski 1998, Rafalski 1995). They are of special importance in environment protection – protection of groundwater from contamination (Khera, Tirumala 1992, Kledyński 2000, Pisarczyk 1997).

The construction of the cut-off walls from the hardening slurries in the trenches excavated in the non-rocky ground can be achieved in the following three ways:

1. the excavation of the trench is carried out under the protection of hardening slurry, then left to bind and harden into the proper cut-off wall (single-phase method).
2. the excavation of the trench is carried out under the protection of the bentonite-water slurry (phase 1), which is then expelled from the trench by the hardening slurry (phase II) constituting the final material of the cut-off wall (double phase technology).
3. the excavation of the trench is carried out under the protection of the bentonite-water slurry, then this slurry is used to form the hardening slurry through the addition of cement mixture (a variant of the double phase technology).

The conditions for the hardening slurries used in the protection of the groundwater from contamination, i.e. in cut-off walls separating unpolluted water from the contaminated one are different from those found in the cut-off walls used in the basement of the dams. The differences arise from the chemical aggressiveness of the water environment; the hydraulic gradients on the thickness of the cut-off walls are also reduced (Kledyński 2000).

In such case, the diffusion of the pollutants through the cut-off wall is possible, as is observed in the loam sealants (Grube 1992).

The ways the aggressive water environment influences the construction material of the cut-off wall depends not only on the chemical composition of the water-subsoil environment, but also on the material used in the construction of the cut-off wall.

In the single-phase method (pt. 1) and modified double phase technology (pt. 3) the contact of the slurry with groundwater is relatively the longest and it is possible to introduce the pollutants present in the ground into the content of the hardening slurry.

The double phase technology (the variant of expulsion of the expanding slurry by hardening slurry – pt. 2) gives the greatest chance for maintaining the designed content of the slurry following its hardening.

2. The Slurry Analyses and Results

The assessment of the cement-bentonite-water slurry (A) and cement-bentonite-ash-water slurry (B) was carried out.

The first was mixed with aggressive water solution of sodium sulphate of 1% concentration (samples: AR), this can to a certain degree simulate unfavourable conditions of cut-off wall application in the environment of aggressive water using method 1 or 3, and subsequently placed in the aggressive solution (samples: AR/R).

Additionally, the series of samples of cement-bentonite-water slurry was prepared, mixed with tap water (samples: AW) and placed in the aggressive solution (samples: AW/R), simulating the exposition of the slurry formed without contact with aggressive environment, and then exposed to it. This corresponds to the application of cut-off walls using the double-phase method – method 2.

Taking into consideration the beneficial influence of ashes on the resistance to sulphate attack of the materials made with cement binding materials, the cement-bentonite-ash-water slurry (B) was also created, mixed with tap water (samples: BW), and the samples were stored in the 1% solution of the sodium sulphate (samples: BW/R) and water (samples: BW/W).

The code of studied samples identifying the sort of slurry, mixed liquid, environment of storage and position of studied material in the sample are shown in Table 1.

The compositions of the studied slurries are given in Table 2, and their properties in the liquid state in Table 3.

Until the taking out of forms, samples of slurries were kept in the laboratory under foil. After 7 days, samples were taken out of forms and dipped into the water or aggressive solution.

During the exposition of the samples of the slurries (blocks of $4 \times 4 \times 16$ cm) to the action of the aggressive solution of the sodium sulphate, deep cracks were observed on the surface of the cement-bentonite-water slurry in tap water

Table 1. The code of samples

Mixed liquid / Environment of storage		Type of slurries and code of samples	
		A – cement-bentonite-water slurry	B – cement-bentonite-ash-water slurry
Mixed with:	water (W)	AW	BW
	aggressive solution (R)	AR	–
Stored in:	water (W)	AW/W	BW/W
	aggressive solution (R)	AW/R and AR/R	BW/R
In the thermographic studies:	material from inside blocks	AW/R-W	BW/R-W
	material from subsurface layers	AW/R-Z	BW/R-Z

Table 2. The composition of the studied hardening slurries

Hardening slurry ingredient	Dosing [kg/m ³ of slurry] of the cement-bentonite-water slurry ingredients (A)	Dosing [kg/m ³ of slurry] of the cement-bentonite-ash-water slurry ingredients (B)
Tap water (Central Water Works – Warsaw – 9.02.1999)	871	776
Portland cement PN-B-19701-CEM I 32.5	250	116
Bentonite “Zębiec”	150	116
Fly ashes from HCPP Żerań in Warsaw	–	272

Table 3. Properties of the liquid slurries

Type of slurry (samples)	Solvent (liquid)	Density [g/cm ³]	Relative viscosity [s]	24h water separation [%]
cement-bentonite-water: (AR) (AW)	1% Na ₂ SO ₄	1.23	33.8	1.5
	tap water	1.25	37.8	2.6
cement-bentonite-ash-water (BW)	tap water	1.28	46.0	1.5

(AW/R) after 48 days storage. The samples of the slurry (at the age of 76 days) mixed with tap water (AW/R) after 69 days of storage in 1% solution of Na₂SO₄ are shown in Photo 1, and the samples of the slurry (at the age of 365 days) after 358 days of storage in 1% solution of Na₂SO₄ are shown in Photo 2. The samples stored in the solution of Na₂SO₄ and the samples with addition of ashes did not show any cracks.

The changes in the mean mass of the samples are shown in Figure 1.

After prescribed duration of storage in the aggressive solution the tensile and compressive strength tests were carried out. Applied testing methods were similar to methods of testing cement according to PN-EN 196-1 (1996). The results of these tests are given in Figures 2 and 3.

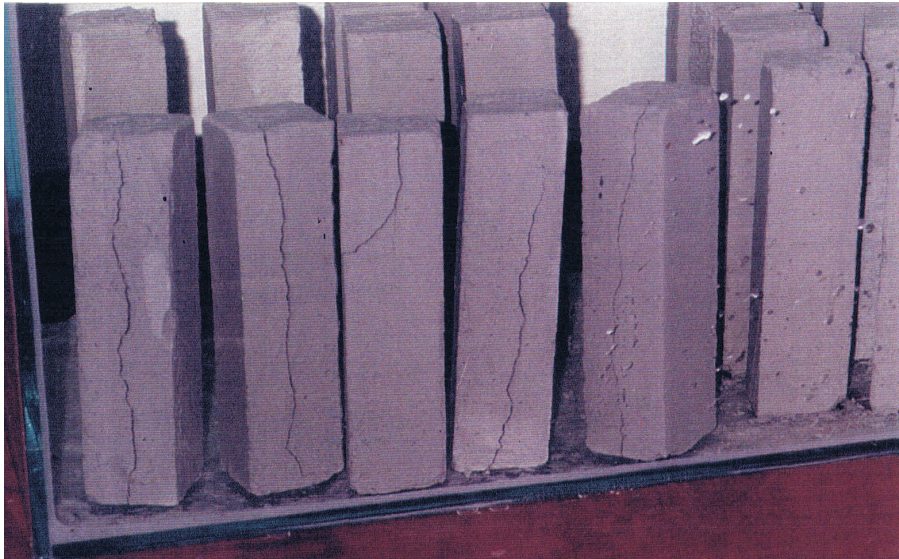


Photo 1. The samples of the slurry mixed with tap water (AW/R) after 69 days of storage in 1% solution of Na_2SO_4 , age of samples – 76 days



Photo 2. The samples of the slurry mixed with tap water (AW/R) after 358 days of storage in 1% solution of Na_2SO_4 , age of samples – 365 days

The thermographic analysis allows tracing of the thermal decomposition of the sample with simultaneous analysis of the mass loss (TG curve and its differential curve DTG) and concomitant thermal effects (DTA curve) in function of temperature (T curve).

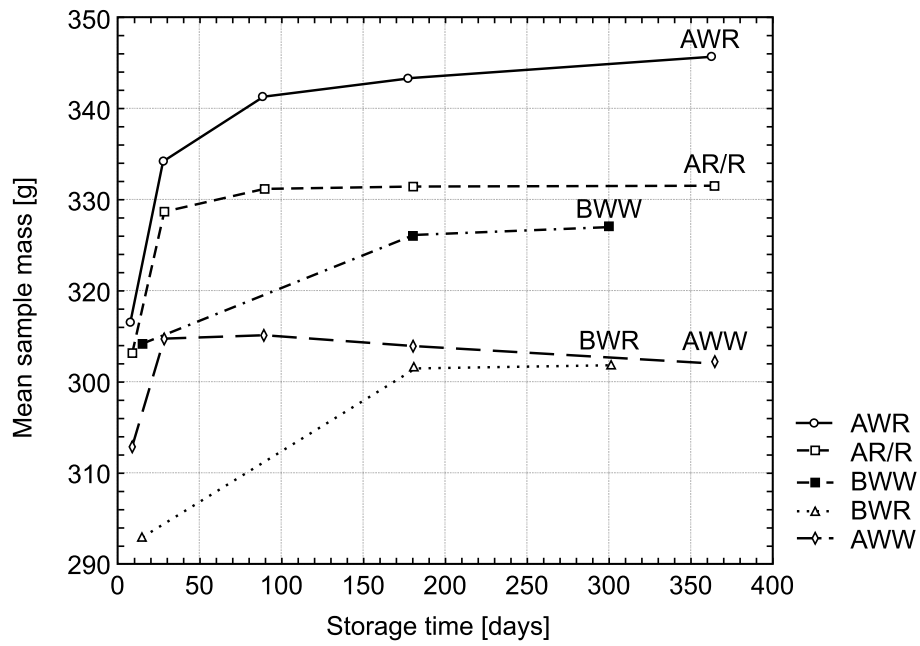


Fig. 1. Changes of the mean mass of samples in time

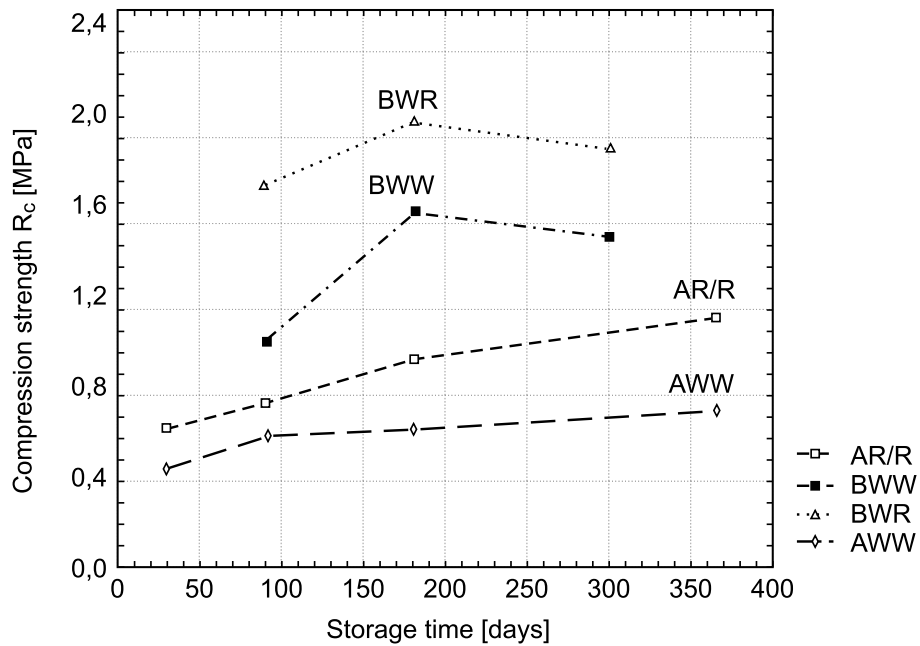


Fig. 2. Changes in compression strength in time

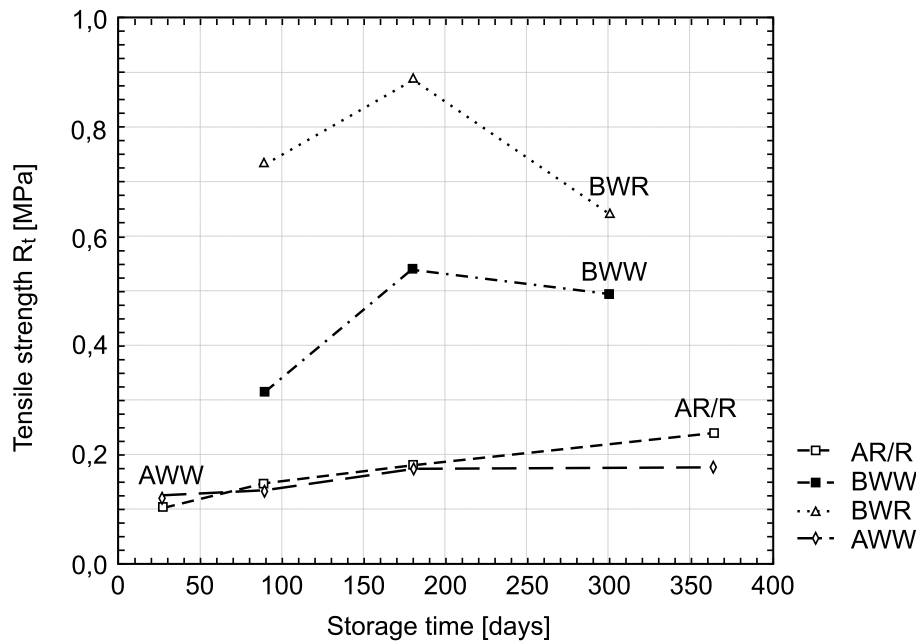


Fig. 3. Changes in tensile strength in time

Thermal decomposition of hardening slurry samples were tested with use of derivatiograph MOM 102, produced in Hungary. Derivatiograph tests were executed under the following conditions:

- sensitivity DTA: 1/1.5,
- sensitivity DTG: 1/1.5,
- mass of tested sample: 600 mg,
- atmosphere: air or nitrogen,
- temperature changing rate: 10°C/min,
- range of temperatures: 20–1000°C.

Thermograph's temperature estimation uncertainty is around $\pm 10^\circ\text{C}$.

The slurries samples mixed with tap water and stored in water (AW/W and BW/W) and in the solution of sodium sulphate (AW/R and BW/R) and the cement-bentonite-water slurry samples mixed with aggressive sodium sulphate solution and stored in it (AR/R) were studied.

From the samples mixed with water and stored in aggressive environment the material was sampled from both the near surface layers – from the depth of 0.1 cm to 0.7 cm (samples: AW/R-Z, BW/R-Z), as well as, from the centre of the block – from a depth greater than 1 cm (samples AW/R-W, BW/R-W). The material for the studies of the samples mixed with liquids, in which they were stored was averaged in the volume of the sample (samples AW/W, AR/R, BW/W).

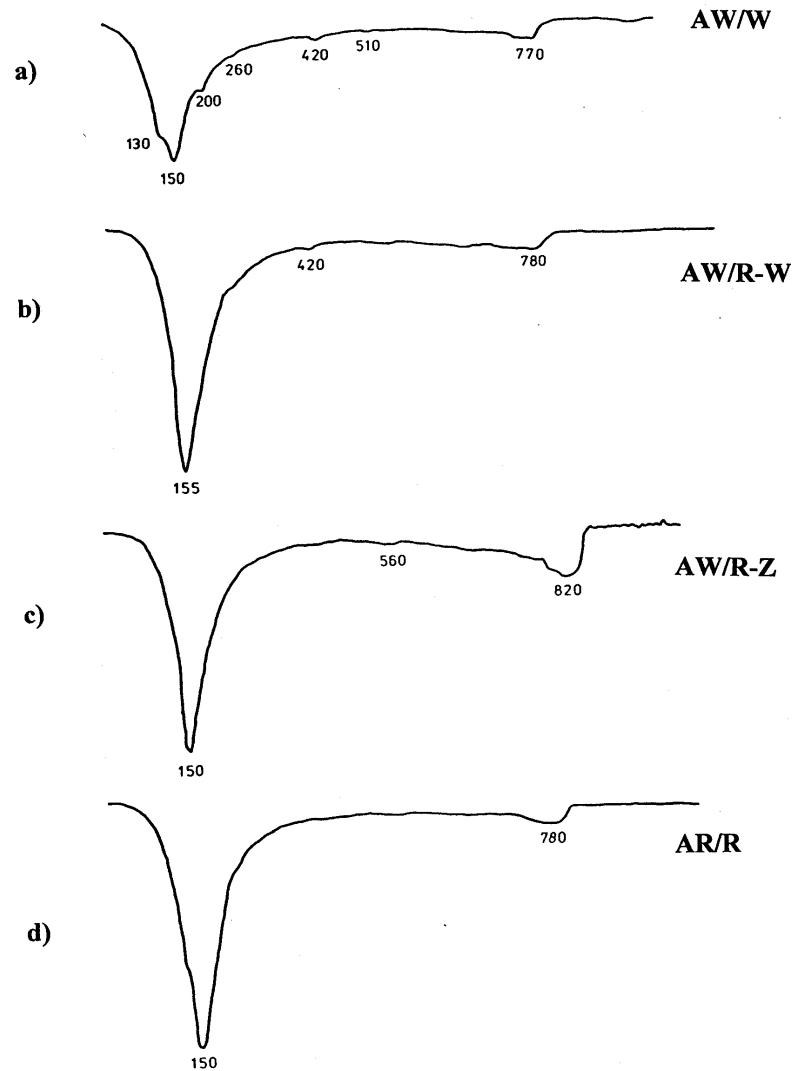


Fig. 4. Derivatiograms (DTA curves) of the hardening slurries: a) slurry with tap water and stored in tap water (sample AW/W), b) slurry with tap water stored in a solution of sodium sulphate – material from inside the block (sample AW/R-W), c) slurry with tap water stored in sodium sulphate solution – material from near surface layers (sample AW/R-Z), d) slurry mixed with sodium sulphate and stored in sodium sulphate (sample AR/R); studies carried out in air

The thermographic studies of the cement-bentonite-water slurry were carried out after a year of exposure to the aggressive environment and the studies of the cement-bentonite-ash-water after 110 days of storage in an aggressive solution. In that, due to the content of unburned particles of carbon in the furnace ashes and strong exothermic effects of its burning during thermic decomposition, the thermographic studies were carried out in a nitrogen atmosphere.

The results of the studies – in this paper only in the form of DTG curves – are given in Figures 4 and 5.

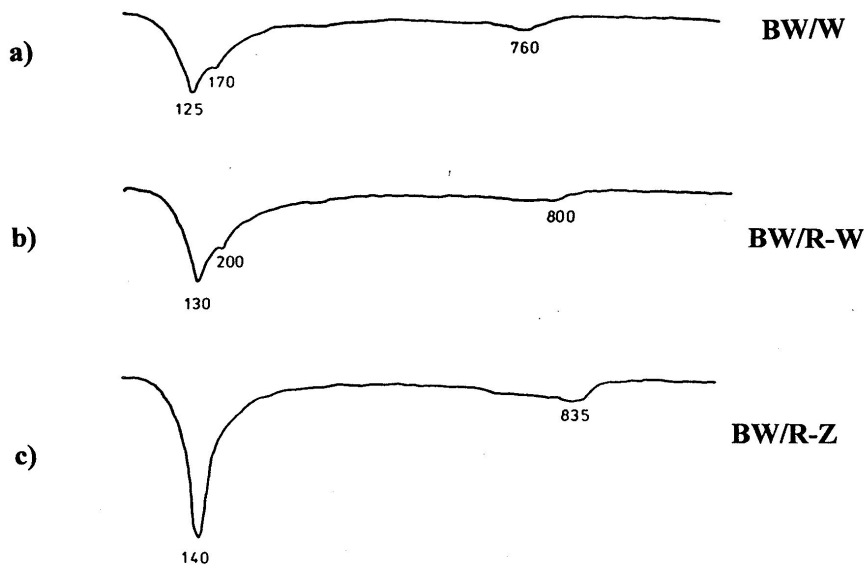


Fig. 5. Derivatograms (DTA curves) of the hardening cement-bentonite-ash-water slurries mixed with tap water and stored in: a) tap water (sample BW/W), b) 1% solution of sodium sulphate – material from inside of the block (sample BW/R-W), c) 1% solution of sodium sulphate – material from near surface layers (sample BW/R-Z); studies carried out in nitrogen atmosphere

3. Analysis of the Results

The most spectacular effect of the corrosive changes observed was cracking of the slurry samples mixed with water and stored in the solution of sodium sulphate (AW/R). The crack appeared after several days of exposure of the slurry to the aggressive environment of sulphate ions and were in the form of linear, deep cracks with sharp edges; with the course of time, those cracks became longer and wider.

After several days of storage of the samples mixed with water in the aggressive solution its composition changed: the content of sulphate ions was reduced and magnesium and calcium ions appeared. The electric conductivity of the solution also increased.

Results of chemical tests of storage environment of A type slurry are shown in Table 4.

Table 4. Results of chemical tests of liquid environment – initial state and state after several dozen storage of A type slurry

Lp.	Storage environment	Test	Initial state	State after storage	Time of storage [days]
1	2	3	4	5	6
1	tap water	– concentration of Ca^{+2}	[mg/dm ³] 92	240	50
			[mval/dm ³] 4.59	11.98	
		– concentration of Mg^{+2}	[mg/dm ³] 28	194	
			[mval/dm ³] 2.30	15.96	
		– conductivity	[mS] 0.126	1.5	
2	Na_2SO_4 solution	– concentration of SO_4^{-2}	[mg/dm ³] 7750	2637	37
			[mval/dm ³] 161.36	54.90	
		– concentration of Ca^{+2}	[mg/dm ³] 0	801	
			[mval/dm ³] 0	39.97	
		– concentration of Mg^{+2}	[mg/dm ³] 0	583	
	[mval/dm ³] 0	47.97			
		– conductivity	[mS] 6.7	14.5	

The slurries bind sulphate ions in sample structures, which results in increase in its weight. In the case of samples mixed with tap water and placed in sodium sulphate solution, also in uneven swelling of the slurry throughout the sample leading to its cracking.

The diagram of the changes in the compressive and tensile strength in the function of time of storage was given in Figures 2 and 3, respectively.

The cement-bentonite-water slurry mixed with tap water and stored in the solution of the sodium sulphate (AW/R) is not represented in the figures, as the samples underwent corrosive cracking and the strength tests were technically not possible. In this case, it can be assumed that full corrosive destruction was achieved, despite the fact that outside the cracks the slurry remained compacted and without any other obvious signs of damage.

The quantitative analysis of the individual effects of mass loss observed in the thermographic studies is extremely difficult and, thus, prone to error. The difficulties arise from superimposing of the effects of mass loss due to bentonite decomposition taking place in the wide range of temperatures and the effects of hydration of the cement decomposition products.

The comparison of the DTA curves of the thermal decomposition of the cement-bentonite-water slurry (Figure 4) indicates significantly greater loss of

mass in the samples in contact with sulphates (samples AW/R-W, AW/R-Z, AR/R), than in samples mixed with water and stored in water (sample AW/W). This is especially evident in the range of temperatures of $100 \div 300^\circ\text{C}$ (with maximum reached in the temperature of around 150°) and can be the result of crystallization of the hydrated sodium sulphate.

As the one of the ingredients of the slurry is Portland cement, in that calcium trialuminate, it can be assumed that decomposition observed in the temperatures $100 \div 300^\circ\text{C}$ concerns highly hydrated complex salts, e.g. ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$). The presence of this compound can be the cause of advancing within a depth of the sample, in the course of sulphate ion penetration, ability of the material to expand. The differences in deformation of the internal and external layers cause linear cracks of the perpendicular blocks.

Unfortunately, the decomposition of the ettringite superimposes, in the DTA curves, the decomposition of other salts and it is difficult to identify without applying additional methods (e.g. XRD). Taking into consideration mainly the quantitative character of the analysis shown in the derivatiograms it can be assumed that hydrated sulphates managed to form within the whole volume of the perpendicular blocks of cement-bentonite-water slurry (blocks $4 \times 4 \times 16$ cm) mixed with water and stored for almost a year in the solution of sodium sulphate. This can be confirmed by the similar intensity of decomposition of the slurry from inside of the sample and from the near-surface layers of the blocks (samples AW/R-W and AW/R-Z) in the range of temperatures of $110 \div 300^\circ\text{C}$. This is even more probable as the deep corrosive cracks of the samples allowed for easier access of the aggressive solution deep into the sample.

Carbonates are found in all samples (the decomposition of carbonates takes place in temperature of $750 \div 900^\circ\text{C}$), however, in the near-surface layers of the samples placed in the sodium sulphate solution (sample AW/R-Z) there is evidence of very intense carbonization (the influence of the carbon dioxide from atmospheric air), which results in significant mass loss in the range of temperatures specific for decomposition of these salts. A shift of the maximal decomposition towards higher temperatures can be observed. It is probable, that carbonization is aided by the appearance of corrosive cracks caused by the expansion of sulphates.

The samples mixed with sodium sulphate solution and stored in this solution (AR/R) did not show corrosive cracks. It can be explained by even swelling of the material throughout the whole sample volume (the solution of sodium sulphate was mixed into the slurry), as the quantity of ettringite formed in the slurry seems to be similar to that observed when the slurry was mixed with water and stored in aggressive solution of the sodium sulphate (similar peaks of the samples AW/R-W, AW/R-Z and AR/R in the range of temperatures of $110 \div 300^\circ\text{C}$).

The explanation of the causes of the corrosive cracks appearing in the slurry samples mixed with tap water and stored in solution of the sodium sulphate through uneven expansion of the near-surface and internal parts of the slurry

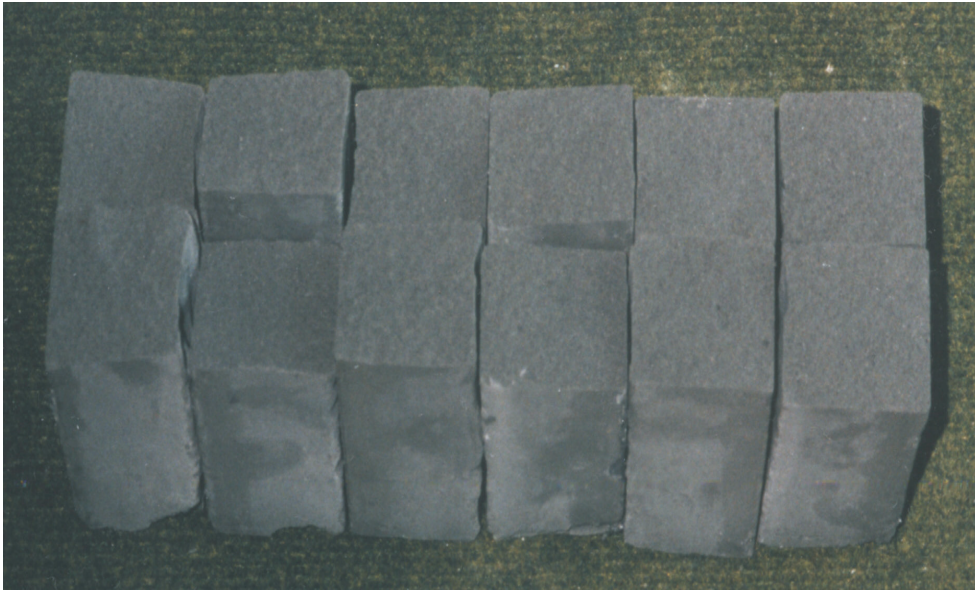


Photo 3. Fractures of slurry samples (BW/W) mixed with tap water and with the addition of ashes (after 90 days) stored for 76 days in tap water



Photo 4. Fractures of slurry samples (BW/R) mixed with tap water and with the addition of ashes (after 90 days) stored for 76 days in 1% solution of Na_2SO_4

finds additional confirmation in the analysis of the cement-bentonite-ash-water slurry (Figure 5). The chemical changes in the slurry with addition of ashes are clearer, as the thermographic studies of this slurry were carried out during the process of sulphate penetration (after 110 days of storage in the solution), and not after nearly 360 days of storage, as it was in the case of cement-bentonite slurry, thus after practically complete penetration of sulphates inside the samples (aided by their earlier cracking).

The comparative analysis of the derivatiograms shown in Figure 5 indicates, that placing of the samples of the slurry mixed with tap water in the solution of the sodium sulphate causes migration of ions from the solution into the sample and material reconstruction. As the storage time in the aggressive environment was relatively short, the inside of the sample remained unchanged; the diagrams for samples BW/W and BW/R-W are very similar.

However, the samples BW/R-W and BW/R-Z differ significantly. In the near-surface layers changes took place, that could be seen in the curve BW/R-Z in the form of significant increase in the main peak with a temperature of 140°C and smoothing of secondary peaks onto the main peak.

This peak results from decomposition of hydrated sulphates, that were formed in the slurry mass as a result of the reaction with sulphate ions migrating towards the inside of the sample.

In the studied samples the effect of calcium hydroxide decomposition was not observed. This indicates its neutralization during mixing with tap water; the presence of ashes is the additional factor eliminating the calcium base, binding the calcium hydroxide created during hydration of cement in phase C-S-H (Bastian 1980, Kurdowski 1991).

Acknowledgement of described chemical changes proceeding in cement-ash-water slurry samples are the pictures of their fractures (Photos 3 and 4). The samples which were kept for 76 days in 1% solution of sodium sulphate are characterize with clearly marked fractures (Photo 4) – darker core and lighter periphery with more compact structure. The fractures of the samples stored in tap water (Photo 3) are homogeneous macroscopically.

4. Conclusions

1. The corrosive influence of the water environment containing sulphates on samples of hardening slurries indicates higher gain in weight of these samples than those stored in tap water. As arises from the thermographic studies of cement-bentonite-water slurries, cement-bentonite-ash-water slurries and appearance of fractures of samples with the addition of ashes, gain in weight is an effect of forming complex hydrated sulphate salts, including etringite.

2. The samples of hardening slurry made without addition of ashes, mixed with tap water and stored in aggressive solution of sodium sulphate, cracked under non-uniform expansion of material progressing from the surface to the inside of the samples, caused by complex hydrated sulphate salts.
3. Addition of ashes in the hardening slurries changes the process of sulphates influence so much that inequality of structural changes of slurry in studied samples does not cause their destruction.
4. If sulphate ions are introduced into the composition of the cement-bentonite-water slurry and the forming process of ettringite will appear uniformly in the whole material at the beginning of cement's binding, the corrosion cracks will probably not appear. This effect can be utilized when building cut-off-walls using methods without the exchange of the slurry (pt. 1 and 2) or introducing aggressive groundwater containing sulphates in the composition of the slurry.
5. Compression strength of cement-bentonite-water slurry mixed with a solution of sodium sulphate and stored in it, is higher than the strength of the control slurry mixed with tap water and stored in it. Tensile strength of both sorts of samples is almost the same.
6. The studies of cement-bentonite-ash-water slurry in sulphate ions environment indicate considerably higher resistance of the slurry mixed with tap water and with the addition of fly ashes than without it (cement-bentonite-water slurry). The slurry mixed with water and stored in a sodium sulphate solution for about one year does not reveal any corrosive damages and its strength is higher than that of the control slurry.

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