Technical Sciences 17(4), 2014, 361–370

ANALYSE OF THE DURABILITY OF ASH-CEMENT COMPOSITES WITH FLY ASHES FROM THE HEAP MICHELIN POLAND SA SUBJECTED TO CORROSION

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Received 21 August 2014, accepted 20 November 2014, available on line 24 November 2014.

Key words: fly ashes from the heap, hydrates lime, corrosion.

Abstract

Useless waste materials are often stored in urban areas taking valuable land and polluting the environment. There has been undertaken research which aim was to test the applicability of the ashes from multi-year heaps as a partial substitute for sand. In the ash-cement composites 10%, 20% and 30% weight of sand was replaced by an ash. Composites sand-ash-cement was modified by an addition of hydrated lime. Introduction of new materials environmentally friendly, using industrial waste is desirable when by using waste materials there is a possibility to obtain materials with desired, assumed technical characteristics and durability. The 30-day trials were subjected to corrosion in 6% solution of sodium chloride and magnesium sulfate. After the corrosion designated the compressive strength of each series, which compared with strengths of series in the same age and not subjected to corrosion. Generally, all composites with the ashes scored higher compressive strength in the control series – without ash. The presence of ash in composites significantly reduced the effects of corrosion. These results suggest the possibility of using these composites in road construction.

Introduction

Power engineering in Poland is mainly based on coal combustion. In 2012 Poland prepared 135,209,000 tons of waste materials including combustion by-products (ash and slag) accounted for approximately 10%. In the Warmia-Mazury made at this time 815 300 tonnes of waste materials, including fly ash accounted for 5.10% of all waste materials (*Environment protection* 2013).

At the turn of the twentieth and twenty-first centuries a result of efforts to sustainable development great importance is attached to the disposal of industrial waste. The result of these trends, a large percentage of by-products

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of combustion is regularly used in various sectors of the economy especially in the building engineering. By-products of combustion (BC) are a valuable component of cement. This applies, unfortunately, only the ashes collected from the electrostatic precipitators. For decades, the ashes – by-products of coal combustion were collected in heaps, often in areas or near cities and were troublesome waste. Development of ash rising. However, people should look for new uses of ash, which involves the study of this group of waste (KRUGER 2005, SVOBODA et al. 2007). Fly ashes that remain for many years in landfills still represent a big problem for local residents and local governments. This problem did not pass Olsztyn – the city of a typical tourist.

Rational utilization of the combustion by-products, the development and dissemination of new technologies to produce goods will always be up to date.

There is thus justified by the need for greater use of ashes, among other things, as an addition to the fine-grained composites made with sand, cement and ashes. Increasingly becoming too noticeable deficit irreproducible coarse-grained mineral aggregates, which leads to greater use of sands, which are still widely available raw material.

In the present study performed a series of tests with a limited amount of mortar cement, in which the ash from a heap replaced a part of sand. Mortars modified with hydrated lime in an amount of 4 to 6% by weight of ash added.

The aim of this study was to optimize the composition and determine the durability of composite sand-ash-cement with fly ash from long-term heap local origin subjected to corrosion. In this work were used as the corrosives solution of 6% of sodium chloride and magnesium sulfate. The introduction of new technologies environmentally friendly with the use of industrial waste is expedient if there is possible to get the materials with expected technical properties and durability.

Materials and methods

The following materials were used for tests:

– natural sand with a particle size 0–2 containing 81.5% quartz, chalcedony and opals, 12% of the igneous and metamorphic rocks, 5.3% sedimentary rocks with the alkaline reactivity of 0;

– fly ash heap of long-term loss on ignition approximately 15%, with about 60% of a fraction 0,063–0,5 mm with CaO containing about 2%;

– Portland cement CEM I – 32.5R;

– hydrated lime;

– 6% solutions of NaCl and $MgSO_4$;

– distilled water.

With these ingredients made a series of sand and ash and cement mixtures. As the series 0 adopted the qualitative composition similar to mortar Standardization (by determining the class of cement), but the plot frame sand was replaced with natural sand and were reduced by 80% weight of the cement (from 450 g to 90 g). Natural sand by the composite with addition of ash equal to 10%, 20%, and 30% by weight of sand was replaced.. The composites with the addition of fly ash modified with the addition of hydrated lime at 4 and 6% by weight of added ash (series 1.4, 1.6, 2.4, 2.6, 3.4 and 3.6). Calcium hydroxide was distributed in the make-up water. Volume of water in each series of tests were experimentally selected to obtain a constant consistency of composites.

Qualitative and quantitative composition of respondents series of tests are presented in Table 1. In all series of tests was performed to study the compressive strength after 30 and 90 days of setting and hardening (Tab. 2). There are also shown changes in the compressive strength of 90 days in relation to the strength 30 days old samples (Fig. 1).

Table 1

Qualitative and quantitative composition of composites

Series	Sand	Ash	Water	Hydrated lime	
				4% by weight of ash	6% by weight of ash
	g		cm^3	g	
0	1350	–	142	–	–
1.4	1215	135	167	5,4	–
1.6	1215	135	167	–	8,1
2.4	1080	270	167	10,8	–
2.6	1080	270	167	–	16,2
3.4	945	405	191	16,2	–
3.6	945	405	191	–	24,3

The weight of cement in all series of tests has become 90 g
Source: own research

Corrosion resistance test was conducted of all series of tests of composites.

As corrosive media were used:

– 6% sodium chloride solution;

– 6% magnesium sulfate solution.

Capacity of the above solutions, in which the samples were immersed equal to 1.5 volumes of tested samples. During the test solutions were not exchanged, and in the case of evaporation it was supplemented with distilled water to a constant volume. Changes in the concentration of the solutions had to be only the result of reaction with components of the composite. Operation of corrosive

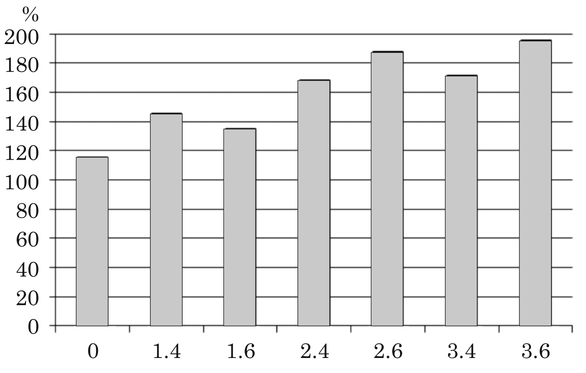

Fig. 1. Change of the compressive strength 90-day old samples in relation to the strength of the trial 30-day old samples

Source: own research.

solutions was carried out in a static system. Effects of 60-day interaction of NaCl and $MgSO_4$ solutions for cement-fly ash composite was determined by measuring the compressive strength f_{cm}.

The obtained values of the compressive strength after corrosion of the samples were compared to corresponding values of the tested samples at the same age not subjected to corrosion.

Discussion of the results

The results (Tab. 2) confirm the fact that the processes of hydration of fly ash-cement mixtures are slower than made of pure cement (BENTZ, FERRARIS 2010). With a very limited amount of cement in the hydration reaction is formed a small amount of calcium hydroxide. The ash content in all series of tests significantly exceeded cement content. There was added calcium hydroxide in an amount of 4 to 6% by weight of cement to enable the reaction of pozzolanic of ash, with about 2% of CaO, which may be insufficient to each series of tests, (GARCIA-LODEIRO et al. 2013). Significant increases in the compressive strength of composites of ash and sand-cement samples were obtained for the 90 day tests compared to 30 days. Changes in the compressive strength series 1.490/1.430 are almost 45% while the strength of the reference mortar without ash after the same period of time has increased by less than 15%.

The highest changes in the strength of 90-day trials in relation to the 30-day trials were obtained for a series 2.6 and 3.6 of 187 and 195% (Fig. 1).

In recent years, great attention is paid to testing the durability of materials, especially those made of cement (KURDOWSKI 2010, NEVILLE 2012). The reason for interest in sustainability is big air and water pollution. Associated with that the aggressiveness of the environment increases the rate of corrosion reaction. The presence of fly ash in building material should not result in corrosive solutions for greater destruction than is the case in the material made of conventional materials. Applied in research NaCl and $MgSO_4$ solutions are typical corrosive media, which are exposed construction materials.

Chloride salts are harmful to the cement matrix. Chloride aggression is mainly connected with the action on materials commonly used de-icing agents. The most commonly temperature lowering compound is a low-grade (2% and 3%) solution of sodium chloride. To obtain the effect of corrosion at higher concentrations in a shorter time applied in the study 6% sodium chloride solution in which were immersed tested series for a period of 60 days. The corrosion of the composite cement and fly ash requires the transport of reactive ions to the reaction space, it means to the inside of the composites.

This may take place generated by two mechanisms:

– migration, flow to the inside of the composite as a result of capillary (SPIESZ, BROUWERS 2013);

– diffusion of ions as a result of a concentration gradient in different areas (AMARNATH et al. 2011).

The first mechanism has a much higher speed of transport, which entails a rapid progress of corrosion. The role of large capillary pores in the acceleration of corrosion is evident. The diffusion coefficient D decreases and salt concentration increasing in time, which is caused by the progressive hydration of the cement (HA-WON et al. 2008). Assessing the migration process in the hardened cement paste, and probably also in the ash-cement composites should be aware that this is not a pure diffusion. Diffusing ions react with the grout phases and are adsorbed on the amorphous surface of the phase C-S-H. Chloride ions also react with hydrated calcium aluminates giving Friedel's salt ($C_3A \cdot CaCl_2 \cdot 10H_2O$). This compound does not cause expansion, on the contrary reduces the amount of generated expansive compounds (CHALEE et al. 2007, KURDOWSKI 2010, AMARNATH et al. 2011).

Chloride corrosion in the present study examined composites sand and ash-cement decreased their compressive strength. The highest decreases in strength was observed in the control sample (without ash) – 27%. The increase of ash and calcium hydroxide in the composites affected favorably on the corrosion resistance. In the series of tests with the6% addition of lime, and increasing amounts of ash 10, 20, 30% after the corrosion reported lowest declines of endurance equal 11.5%, 11.1% and 7.0% (Fig. 2). Increasing amount of ash with the addition of lime proofed composites to chloride corrosion.

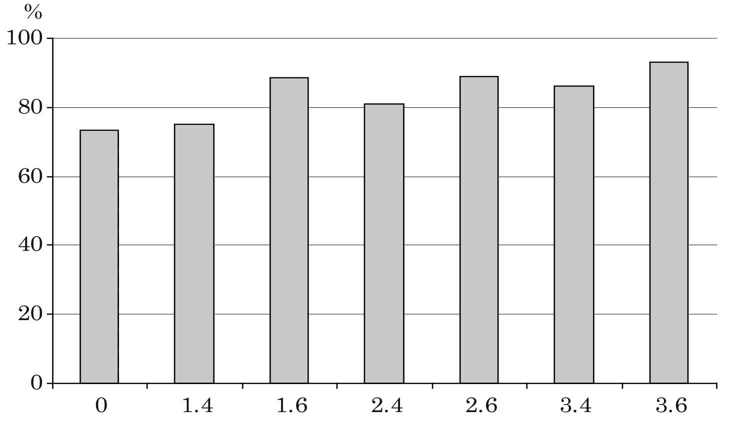

Fig. 2. Change of compressive strength of samples after 60 days of corrosion at 6% NaCl solution in relation to the samples of the same age not subject to corrosion
Source: own research.

$MgSO_4$ corrosive action causes not only sulfate corrosion, but also magnesium. Hydration products of ash-cement composites contain significantly less calcium hydroxide. During penetration of composites with ash by solutions containing sulfate ions an important role played pore size, the content of aluminum oxide and calcium oxide included in ashes. They may participate in the reaction with sulphates, especially when Al_2O_3 and CaO are present in the enamel of fly ash, thus providing a source of material which reacts with sulphates. The high ratio of silica to aluminium oxide reduces the sensitivity of the binder with ash on sulfate aggression but it is not completely proven (NEVILLE 2012).The reaction products of magnesium sulfate with calcium hydroxide, which is formed by binding the alite and belite, are sequentially calcium sulfate, calcium sulfate, dehydrate calcium sulfate, which in the presence of C_3A passes to ettringite. In addition there also arises brucite. Brucite can settle in the pores thereby forming at the surface of composite protective layer, which prevents further penetration of sulphate and magnesium ions to the interior. Generally concretes made with cement containing the ashes are characterized by increased resistance to aggressive agents. These properties intensify with increasing ash content in the composite. In the case of sulfate corrosion intensity decreases with decrease of C_3A (KURDOWSKI 2010). Large water and air pollution by sulfur oxides, from which arises sulfuric acid and its salts, causes the sulphate corrosion of building materials from many years has been a subject of many scientific studies (MARCHAND et al. 2002, SANTHANAM et al. 2006, SAHMARAN et al. 2007, BASSIST, WĘGLEWSKI 2009, TKACZEWSKA, MAŁOLEPSZY 2009, LOTHENBACH et al. 2010, LORENTE et al. 2011, SCHMIDT et al. 2012, RUDZIŃSKI 2013). The authors of mentioned works as

Table 2
Compressive strength of composite sand-ash-cement before and after corrosion

Series	Compressive strength				Absorbability [%]
	before corrosion		after corrosion		
	30-day trials	90-day trials	6% NaCl	6% $MgSO_4$	
0	1.3	1.5	1.1	1.2	12.6
1.4	2.2	3.2	2.4	2.5	13.3
1.6	2.6	3.5	3.1	3.0	13.2
2.4	2.5	4.2	3.4	3.8	16.5
2.6	2.4	4.5	4.0	4.1	16.8
3.4	2.1	3.6	3.1	3.7	21.1
3.6	2.2	4.3	4.0	4.3	21.4

Source: own research.

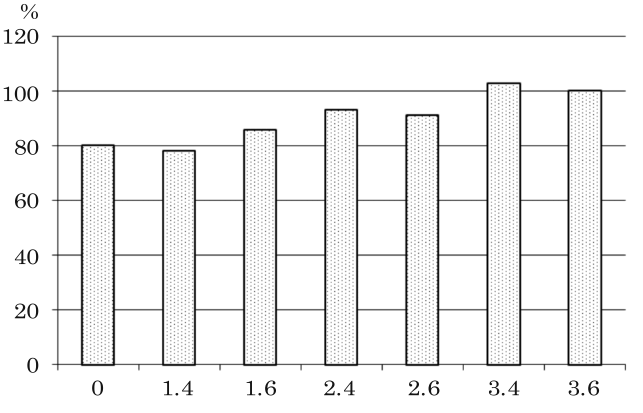

Fig. 3. The change of compressive strength of samples after 60 days corrosion in the 6% solution of $MgSO_4$ relative to the samples of the same age not subjected to corrosion
Source: own research.

corrosive solutions have used sulfate salt shaving different concentrations, wherein the concretes and mortars were subjected to corrosion for different periods of time (from several days to several years).In the present work sand-ash-cement composites were subjected by 60 days of action 6% magnesium sulfate solution. As in the case of chloride corrosion the lowest compressive strength was obtained after corrosion for a control series without ash and for a series with the lowest addition of ash and lime (Tab. 2, Fig. 3). Strength of test control series after sulfate-magnesium corrosion fell by 20%. Strength of the composites with 20% exchange sand by ashes fell by only a few percent. Strength of the 30% share of the ashes instead of sand after the corrosion practically did not change resistance, both from 4 and 6% with addition of lime (Tab. 2, Fig. 3).The composites with 30% conversion of the sand by ash from both the 4 and 6% with addition of lime – a series of 3.4 and 3.6, practically after the sulfate-magnesium corrosion did not change their strength.

Conclusions

The obtained results allow to conclude that:

– generally much higher compressive strength values obtained for a series of 90-dayssamples of sand-ash-cement composites as compared to strengths of 30-day samples;

– ash-sand-cement composites in which the ash from the heap was used as a partial replacement for sand have much higher strength than the ash-free composites with the same amount of cement;

– the effects of corrosion processes samples treated with 6% NaCl solution are significantly lower in composites with fly ash than in the control series of „0" – with no ash;

– corrosive action of 6% $MgSO_4$ solution that exposes concrete and mortar to magnesium and sulphate corrosion is weaker than in during of chloride corrosion – in the composite in which 30% of the sand was replaced with ash from the heap did not noted any negative effects of sulfate-magnesium corrosion.

Conclusions

Generally much higher compressive strength values obtained for a series of 90-days samples of sand-ash-cement composites as compared to strengths of 30-days samples, which amounts to a series of attempts – 1.4 – 45%, for 2.6 and 3.6 – 187% and 195%, and for the series without ash – only 15%.

Ash-sand-cement composites in which the ash from the heap was used as a partial replacement for sand have much higher strength than the ash-free composites with the same amount of cement. In a series of 90-days samples strength of the series 0 is only 1.5 MPa and in series with ashes from 3.2 to 4.5 MPa.

The effects of corrosion processes samples treated with 6% NaCl solution are significantly lower in composites with fly ash than in the control series of „0" – with no ash. Minimal reduction in the compressive strength after corrosion – 11.1% and 6.8% were obtained for a series of tests with 20 and 30% conversion of the sand to ash, while the strength of the control series dropped by 27%.

Corrosive action of 6% $MgSO_4$ solution that exposes concrete and mortar to magnesium and sulphate corrosion is weaker than in during of chloride corrosion. In the composite in which 30% of the sand was replaced with ash from the heap did not noted any negative effects of sulfate-magnesium corrosion. In the series of the control sample and 10% content of the ash compressive strength decreased by about 20%.

Conversion of 20% and 30% sand to ash in the ash-cement-sand composites with a very limited amount of the cement significantly reduces the effects of corrosion in the test.

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