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Concrete Based on Fly Ash Alumosilicate Polymers

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Abstract: Concretes on the basis of the alumosilicate polymer can be prepared by alkali activation (NaOH, sodium water glass) of waste brown coal fly ash. The preparation is possible: (1) by using a short-term heating of the concrete mix (to 80 ℃); or (2) by allowing the mix to harden spontaneously at a temperature of 20 ℃. The concretes prepared by short-time heating attain high strength values after their preparation; the values are comparable to those characterizing concretes obtained on the basis of Portland cement. The strength development of concretes hardening at 20 ℃ is substantially less steep but, nevertheless, the strength attained after about 60 days is practically identical with that of the concretes exposed to a short-time heating. The shrinkage of concretes prepared by short-time heating is very small as compared with the concretes allowed to harden spontaneously; the shrinkage of latter concretes is larger than that of the concretes on the basis of Portland cement. The concretes on the basis of alumosilicate polymer exhibit much better resistance to the corrosive action of the environment as compared with those prepared on the basis of Portland cement.

Key words: Alumosilicate polymer, geopolymer, concrete, fly ash.

1. Introduction

The exposure of aluminosilicate bodies of the type cement clinker, slag, fly ash or thermally activated substances to very alkaline environments (hydroxides, silicates) gives rise to the formation of new materials-alumosilicate polymers characterized by a two- to three-dimensional Si-O-Al structure. Substantial attention has been given to these new materials, for instance, at symposia [1-7]. Such contributions deal not only with the results obtained during the investigation into the synthesis of alumosilicate polymers and their microstructure but also with their possible applications particularly in conjunction with the valorization of inorganic rejects (first of all, fly ashes). Our previous work [8] in the field of alumosilicate polymers on the basis of Czech brown coal fly ash focused on the microstructure and properties of slurries and mortars.

There are only few published data dealing with the properties of concretes on the basis of alumosilicate polymers [9-11]. Therefore, the present paper deals with the investigation into the properties of the concretes on the basis of alumosilicate polymers [12, 13].

2. Materials and Methods

Waste brown coal fly ashes from Czech power plants were used for investigation. Their specific surface area ranged from 210 to 300 m^2/kg (Blaine). The chemical composition of the fly ashes is given in the Table 1.

The differences in the compositions of individual fly

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Table 1 The chemical composition of the used Czech brown coal fly ash (wt.%).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2
53.7	32.9	5.5	1.84	0.92	0.46	1.76	0.37	2.1

ashes fluctuated by ± 5% (relative). The concrete was prepared by mixing fine-grained and coarse-grained crushed quarry aggregate with the grain size ranging from 0 to 16 mm, fly ash and other ingredients with the solution of an alkaline activating agent (Fig. 1).

The SiO_2-to-Na_2O ratio (M_S modulus) in the alkaline activating agent was adjusted by adding NaOH to soluble glass in order to obtain M_S values ranging from 1 to 1.6. The overall concentration of the alkaline activating agent varied in the range of 6 to 10% Na_2O (expressed as percentage of the fly ash weight). The experiments were carried out by using concretes characterized by the water coefficient (the H_2O-to-fly ash ratio) w = 0.30-0.40.

The aggregate was composed of three fractions; the main goal was to approach - as much as possible - the exemplary spline cumulative grain size curve recommended in the standard DIN/ISO 3310-1 (Fig. 2). The curve was modified partially to suit the alumosilicate polymer concretes. Concrete mixtures were prepared with different fly ash quantity within the range of 200-700 kg/m^3 of concrete mixture. Water ratio (weight ratio of water to fly ash) was chosen so that the workability of mixtures was approximately the same (Fig. 3). This workability corresponded to the slump test level S3 (ČSN EN 12350-2).

The mix prepared by mixing lasting about 2 to 5 minutes and poured into molds having the dimensions of 100 × 100 × 100 mm and 100 × 100 × 500 mm was subjected to vibrations for 2 to 4 minutes.

The concrete samples (labeled "*tempered*') obtained in the above way were subjected to a heat treatment process under "dry conditions": the samples were kept in a dryer at a temperature ranging from 40 to 90 ℃ (in the open atmosphere) for 6 to 24 hours. The concrete samples after heating were kept in open atmosphere at temperature 20-25 ℃ and 50% relative humidity. The part of "tempered" concrete were after 24 hours put in water basin left in water until the strength tests.

In another procedure (labeled "*ambient*"), the concrete samples were kept free in ambient air at temperature 20-25 ℃ and 50% relative humidity. In these cases, the hardening accelerator of alumosilicate

Preparation of geopolymer concrete
Aggregate + Fly ash
+ Alkaline activator (NaOH + Na silicate, water glass, Ms = 1.0-1.6, Na_2O 6-10%, w = 0.30 – 0.40)
↓
Mixture 6-12 hours open atmosphere 60-80 ℃
"*tempered*" version
or
at 20-25 ℃ open atmosphere
"*ambient*" version
↓
Storage (20-25 ℃ open atmosphere)

Fig. 1 Procedure used for the preparation of alumosilicate polymer materials.

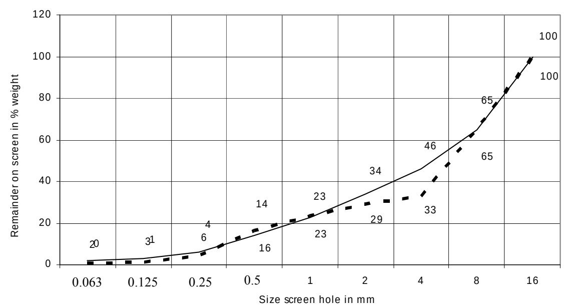

Fig. 2 Spline aggregate gradation 0/4, 4/8, 8/16 in comparing to exemplary spline.

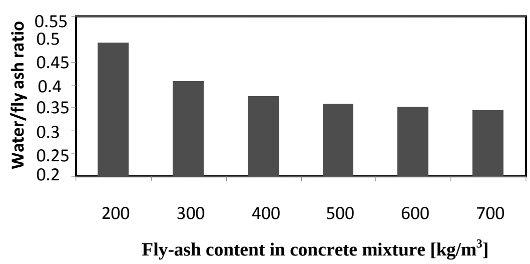

Fig. 3 Water to fly ash vs. fly ash content in concrete mixture at same workability (S3 slump test).

polymers was used (eg. $Ca(OH)_2$ and others). These samples of ambient air-cured concrete were after 28 days put in water basin and were left in water until the strength tests. All concrete samples were measured volume changes depending on the time. The samples dimensions were regularly measured before any strength test.

The test pieces were transferred to an environment kept at a temperature of –20 ℃; this happened immediately after their preparation described above. The specimens prepared in the above way were de-molded after 7 days and, once again, exposed to a temperature of –20 ℃.

The samples of concretes ("tempered") were then kept in the solutions of Na_2SO_4, $MgSO_4$ and NaCl in accordance with the instructions (CSN EN 206-1 standard) for the testing of concretes.

A scanning electron microscope was used for the investigation of the microstructure on the fracture surfaces of the fragments remaining after the destruction tests. Selected spots were analyzed with the aid of an ED spectrometer.

3. Results and Discussion

3.1 Rheological Properties

Rheological properties of the fresh fly-composition are dependent on the fly ash content in the mixture. In comparison with the fresh cement concretes, the mixtures containing higher percentages of fly ash exhibit a different rheological behavior (Fig. 4).

Viscosity of the alumosilicate polymer paste is substantially higher in comparison with Portland cement paste. Therefore, longer treatments by vibration or by other techniques are required in both cases and the aggregate setup (i.e. the solid components of the mixture) must be selected with great care (Fig. 5).

Despite the higher viscosity and a rather pronounced adhesion ability of the fresh composition coarser and heavier grains of the aggregate start settling at higher values of the water coefficient; this process is accompanied by the displacement of the mortar and the paste towards the surface of the processed fresh concrete mix (Fig. 6). This situation occurs not only during an intense dynamic treatment by vibration but also during a simple free deposition of the cast composition of the fresh alumosilicate polymer concrete. Solid fine-grained additives, e.g. ground limestone, ground slag, milled silica powder, etc. yielded good results in this case.

The mixing process of all the components of the alumosilicate polymer concrete results in the absolutely perfect coating of even the smallest grains of the aggregate. However, a faster mixing of the

Fig. 4 Character of the fresh alumosilicate polymer concrete.

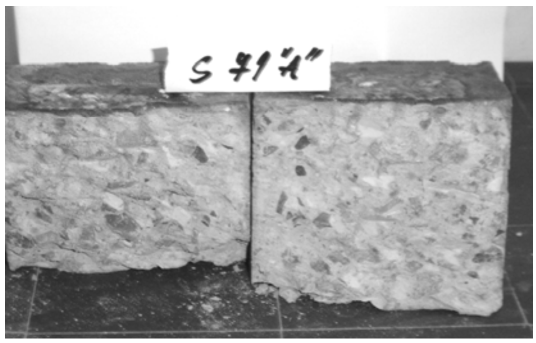

Fig. 5 Correctly composed mix, uniform distribution of the aggregate.

Fig. 6 Incorrect mix, aggregate segregation and the mortar displaced towards the surface.

alumosilicate polymer concrete is accompanied by the entrainment of a considerable amount of air into the fresh alumosilicate polymer concrete.

This air which is concentrated in small bubbles in the whole volume of the composition is not able to leave the composition within a reasonable period of time because of the low mobility of the binder component; hence, its substantial part remains enclosed in the processed mix. It is evident from the microscopic pictures the air occurs in the form of closed air pores that are not accessible to water; therefore, such pores are harmless from the viewpoint of the water absorption of the alumosilicate polymer concrete (Fig. 7).

3.2 Properties of Hardened Concrete

The strength values of concretes of the alumosilicate polymer on the basis of fly ashes show an increasing trend after 2-140 days from the moment of their preparation.

The difference in the strength development rates characterizing the two types of samples (“tempered” and “ambient”) is evident in Fig. 8. The concretes prepared following the “tempered” mode attain high strength values after their preparations; such values are comparable with those characterizing the concretes on the basis of Portland cement. The strength development typical for “ambient” mode concretes is substantially less steep but, nevertheless, the strength values achieved after about 60 days are practically identical with those observed with the “tempered” mode concretes. The slow strength development in the “ambient” mode concretes is due to the poor reaction ability of the Czech brown coal fly ash. The concretes representing both preparation modes exhibited an additional very slow growth in their strength, which is in agreement with the strength data published for slurries and mortars [11] as well as with the data showing the long-term strength of concretes [9-11] as shown in Figs. 9-11.

The strength of the concretes on the basis of alumosilicate polymers are dependent on the fly ash

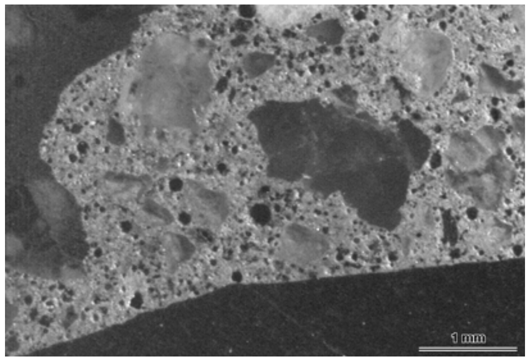

Fig. 7 Alumosilicate polymer concrete (polished section, optical microscope).

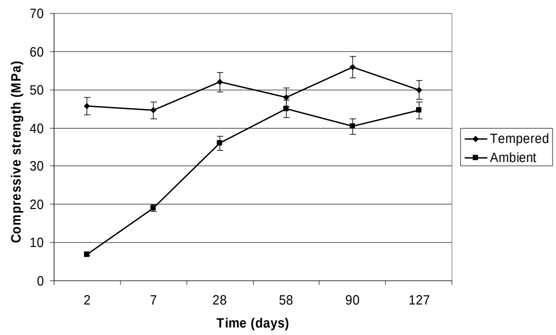

Fig. 8 Compressive strength of “tempered” and “ambient” concrete vs. time (fly ash content in the mixture 400 kg/m^3).

content. The content of 300 kg of fly ash per 1 m^3 is sufficient for achieving optimum results.

The density concretes on the basis of alumo-silicate polymers is smaller than that of the concretes on the basis of Portland cement (Figs. 12 and 13). The ratio of the compressive strength to the tensile strength under bending varies in the range of 10:5.5 (the ratio for cement-based concrete ranges from 10.0:1.0 to 10.0:1.5) which means that a higher tensile strength of the alumosilicate polymer concrete gives the possibility to reduce the quantity of the reinforcement in the structural elements.

In contrast to the concretes made from Portland cement the concrete on the basis of alumosilicate polymers possesses the ability to harden at low temperatures (Fig. 14) even if the achieved values of its strength are rather low.

The shrinkage of concretes prepared by short-time heating is very small as compared with the concretes

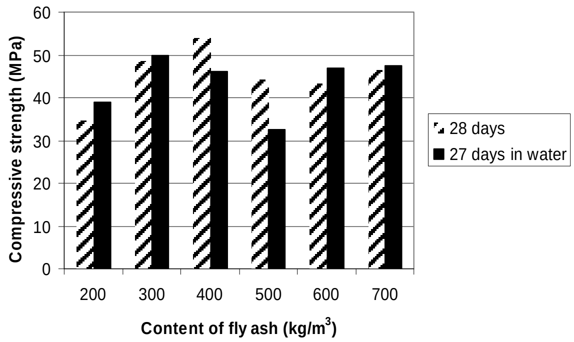

Fig. 9 Compressive strength of "tempered" concrete.

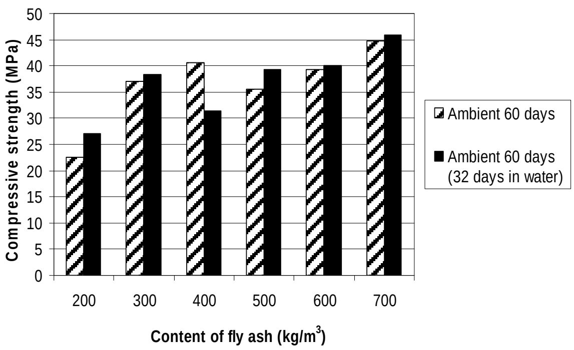

Fig. 10 Compressive strength of "ambient" concrete.

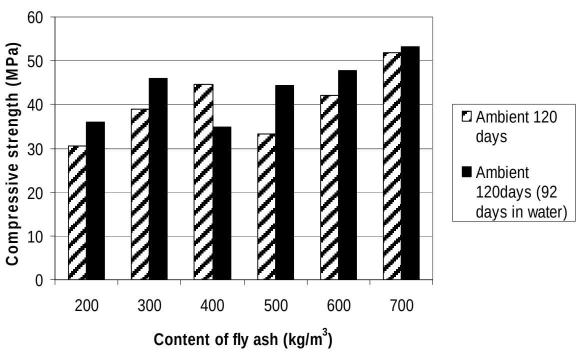

Fig. 11 Compressive strength of "ambient" concrete.

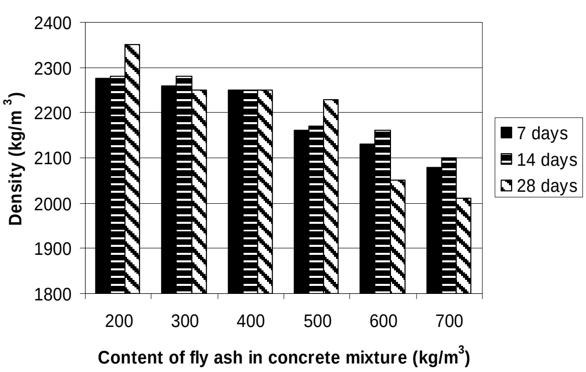

Fig. 12 Density of concrete ("ambient").

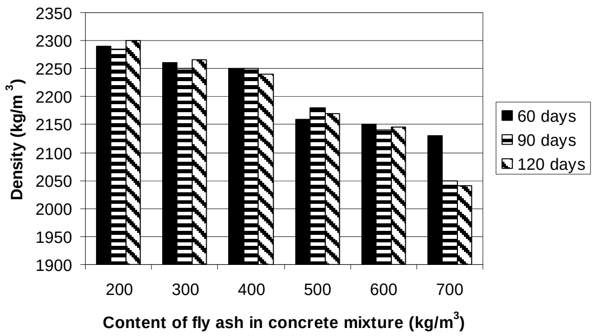

Fig. 13 Density of concrete ("tempered").

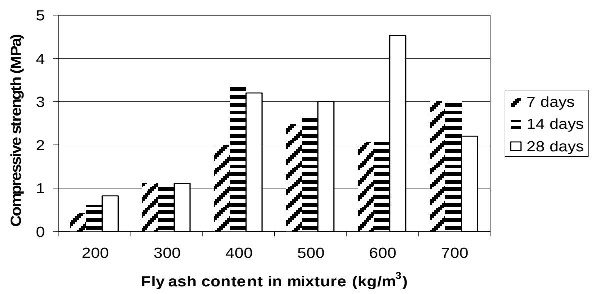

Fig. 14 Compressive strength of concrete, at -20 ℃.

allowed to harden spontaneously; the shrinkage of latter concretes is larger than that of the concretes on the basis of Portland cement (Fig. 15).

An ordinary cement-based concrete that prepared by using the cement belonging to the 52.5 R class, exhibits more or less constant values of the modulus of elasticity at an age of 7 to 130 days elapsed from the production day. On the contrary, the concrete on the basis of an alumosilicate polymer is characterized by a slow increase in its strength and, hence, by a slow growth of its modulus of elasticity (Fig. 16). The values of the static modulus of elasticity at an age of 130 days amounted to about 66 percent of the values of the modulus of elasticity of an ordinary concrete [12].

3.3 Alumosilicate Polymer-aggregate Interface

There is a transition layer between the aggregate grain and hardened cement in the ordinary concrete on the basis of the standard Portland cement. The thickness of the layer ranges from 20 to 100 μm; the layer microstructure and composition differ from that of hardened cement. The contents of $Ca(OH)_2$ and

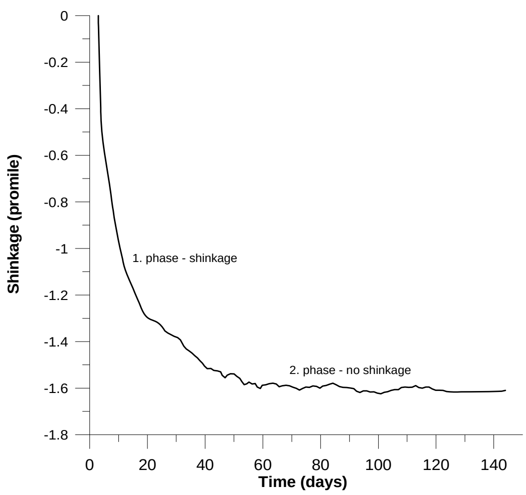

Fig. 15 Shrinkage of concrete "ambient".

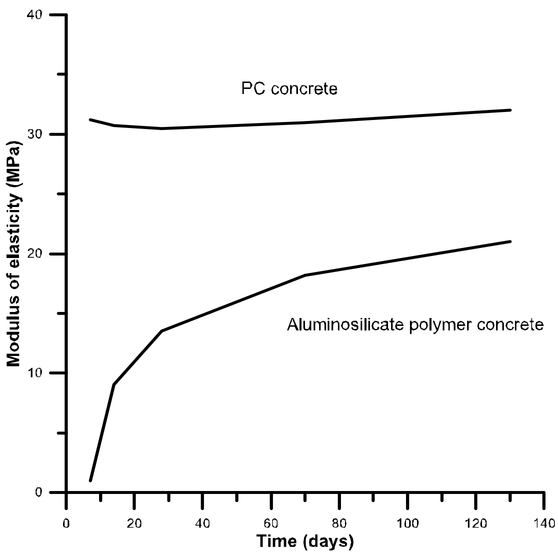

Fig. 16 Modulus of elasticity vs. time.

ettringite are higher. There are often $Ca(OH)_2$ particles oriented along the aggregate particles. The porosity of the transition layer is larger than that of the hardened cement and a porosity gradient with the decreasing character in the direction away from the aggregate particles could be observed [14, 15].

The character of the alumosilicate polymer–aggregate boundary is quite different. No transition zone could be detected either morphologically or by a direct measurement of the alumosilicate polymer compositions in the proximity of the aggregate itself

The Al_2O_3-to-SiO_2 ratios (point analyses) are shown in Fig. 17 in dependence on the distance from the aggregate particle. We can say that-within the range of experimental error (heterogeneous character of alumosilicate polymer)-no important changes in the alumosilicate polymer compositions take place in the close proximity of the aggregate as this is usually the case of Portland cement.

3.4 Durability of the Alumosilicate Polymer Concrete

The mass of the sample bodies did not change practically during the freezing and defrosting cycles taking place in the aqueous environment (no disintegration of the samples took place). No visible defects or deformation could be observed after 25-150 cycles. It is obvious from the results obtained that the alumosilicate polymer materials on the basis of the fly ash possess the good frost resistance.

The exposure of concrete on the basis of aluminosilicate polymer to the solutions of sulfates and NaCl did not result in the formation of new crystalline phases (Fig. 18). The RTG diffraction analysis only confirmed the occurrence of original crystalline phases present in the fly ash. The absence of expansive products as, for instance, the ettringite ($C_6AS_3H_{32}$) or Friedel salt (C_4AClH_{11}) in the samples after the two-year exposure to the salt solution is an important finding.

The resistance of aluminosilicate polymer concretes

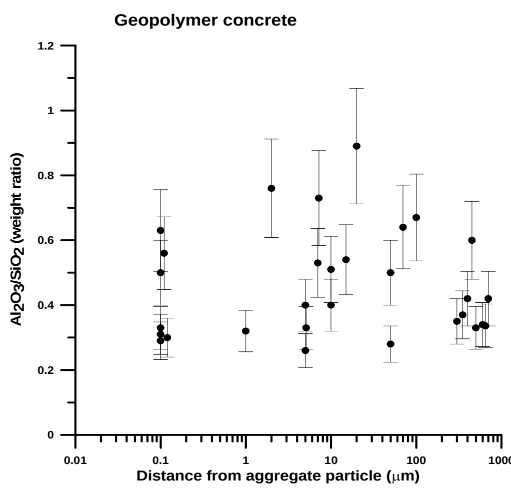

Fig. 17 Dependence of the Al_2O_3-to-SiO_2 ratio on the distance from the aggregate grain in a alumosilicate polymer concrete.

(A)

(B)

Fig. 18 Alumosilicate polymer concrete after the 1.5-year exposure to the solutions of NaCl (A) and $MgSO_4$ (B) salts.

to the action of salt solutions is better than that of the cement-based concrete in which the crystalline ettringite or the Friedel salt are formed; eventually, the body disintegrates in result of the crystallization stress.

The penetration of chloride and sulphate ions into the concrete (measured perpendicularly in the direction from the surface in contact with the chloride or sulphate solution) showed a decreasing tendency and the chloride or sulphate concentration in the body was low. The penetration of chloride ions was greater than that of sulfates; this fact is probably due to the smaller size of chloride ions (Figs. 19 and 20). Practically no corrosion products were observed on the surface of concrete kept in the NaCl solution (Fig. 18A).

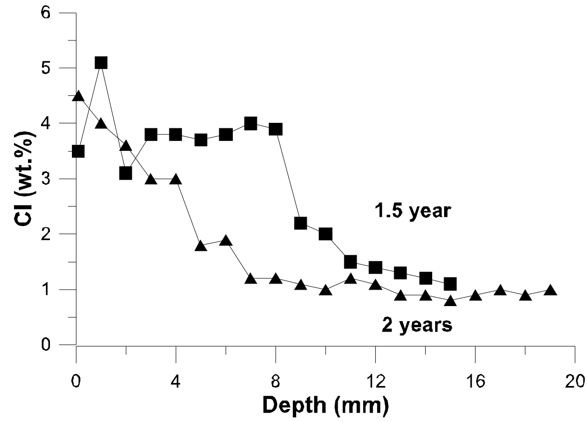

Fig. 19 Penetration of Cl^- (measured as Cl) in alumo silicate polymer concrete (1.5 years in NaCl solution), point analysis.

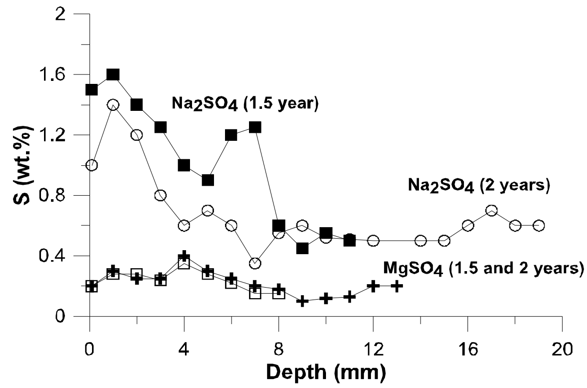

Fig. 20 Penetration of SO_4^{2-} (measured as S) in alumosilicate polymer concrete (1.5 years in Na_2SO_4, $MgSO_4$ solution), point analysis.

4. Conclusions

The concretes on the basis of the alumosilicate polymer can be prepared by alkali activation (NaOH, sodium water glass) of waste brown coal fly ash. The concretes can be prepared either by a short-term heating (80 ℃) of the concrete mix or by letting the mix harden spontaneously at a temperature of 20 ℃. The rheological properties of concretes on the basis of alumosilicate polymers are dependent on the content of the fly ash. The concretes obtained by a short-term heating attain high strength values after their preparation; such values are comparable with those characterizing the concretes on the basis of Portland cement. The strength development observed for concretes hardening at 20 ℃ is substantially less steep but, nevertheless, such concretes attain practically same strength values after about 60 days as those exposed to a short-term heating. A slow increase in the modulus of elasticity also takes place in the concretes allowed to harden spontaneously. A slow development in the strength values characterizing the concretes allowed to harden spontaneously is due to a poor reaction ability of the Czech brown coal fly ash used for the concrete preparation. An ulterior increase in the strength could be observed in concretes. The density concretes on the basis of alumosilicate polymers is smaller than that of the concretes on the basis of Portland cement. The rheological properties and the strength of the concretes on the basis of alumosilicate polymers are dependent on the fly ash content. The content of 300 kg of fly ash per 1 m^3 is sufficient for achieving optimum results. A concrete with a low content of water and a high content of fly ash can be prepared without impairing the required workability. The contraction of concretes prepared by short-term heating is very small whereas the shrinkage of the concretes allowed to harden spontaneously is larger than that characterizing the concretes on the basis of Portland cement. The concretes on the basis of alumosilicate polymers exhibit a substantially better resistance to the action of corrosive environments as compared with the behavior of the concretes on the basis of Portland cement. This regards particularly their resistance to the action of sulfate and chloride solutions. No transition phase with a different composition as this is typical for concretes on the basis of Portland cement could be found between the alumo-silicate polymer and the aggregate.

In memoriam

The present paper is dedicated to the memory of Mr. Josef Doležal, a leading Czech specialist in the field of concrete technology, whose contribution to the research and development of concretes on the basis of alumosilicate polymers deserves the authors' long-lasting admiration and profound appreciation.

Acknowledgements

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References

[1] V.D. Gluchovskij, Ancient, modern and future concretes, in: Proceedings of the 1st Intern. Conference Alkaline Cements and Concrete, Kiew, 1994, pp. 1-9.

[2] J. Davidovits, Chemistry of geopolymeric systems terminology, in: Proceedings of the 2nd Intern. Conf. Alumosilicate Polymere "99" St. Quentin, 1999, pp. 9-40.

[3] J. Davidovits, Geopolymer chemistry and sustainable development, The Poly (sialate) terminology: A very useful and simple model for the promotion and understanding of green-chemistry, in: Proceedings of the World Congress Alumosilicate Polymer 2005 St. Quentin, 2005, pp. 9-17.

[4] W.M. Kriven, J. Bell, M. Gordon, G.G. Wen, Microstructure of geopolymers, CD GGC2005e, in: Proceedings of the GGC2005 Intern, Workshop on Alumosilicate Polymer and Alumosilicate Polymer Concrete, Perth, 2005.

[5] P. Krivenko, Status and prospects of research and application of alkali-activated materials, in: Proceedings of the 12th International Ceramics Congress, part H, Montecatini Terme, Italy, June 6-11, 2010.

[6] J.L. Provis, J.S.J. van Deventer, Introduction to Geopolymers in Geopolymers, Structure, Processing, Properties and Industrial applications, WP Ltd. Cambridge, 2009, pp. 1-7

[7] J. Davidovits, The synthesis of alumino-silicates mineral geopolymers, in: J. Davidovits: Geopolymers Chemistry and Applications, Institut Geopolymére, St. Quentin, 2008, pp. 59-192.

[8] F. Škvára , L. Kopecký, V. Šmilauer, Z. Bittnar, Material and structural characterization of alkali activated low-calcium brown coal fly ash, J. Haz. Mater. 168 (2009) 711-720.

[9] D. Hardjito, B.V. Rangan, Development and properties of low-calcium fly ash-based geopolymer concrete, Research Report GC 1, Faculty of Engineering, Curtin University of Technology, Perth, Australia, 2005.

[10] D. Hardjito, S.E. Wallah, D.M.J. Sumajouw, B.V. Rangan, On the development of fly ash-based geopolymer concrete, ACI Mater. J. 101 (2004) 67-72.

[11] S.E. Wallah, D. Hardjito, D.M.J. Sumajouw, B.V. Rangan, Geopolymer concrete: A key for better long-term performance and durability, in: Proc. ICFRC Inter. Conf. on Fiber Composites, High performance Concrete and Smart Materials, Chenni, India, 2004, pp. 527-539.

[12] T. Strnad, Properties of the materials on alkali activated fly ash, PhD Thesis, CTU Prague, 2010.

[13] R. Šulc, Concrete on the alkali activated fly ash, PhD Thesis, CTU Prague, 2011.

[14] S. Diamond, The microstructure of cement paste in concrete, in: Proc. 8th Int. Congr. Chem. Cement, Rio de Janeiro, 1986, pp. 122-147.

[15] J.C. Maso, The bond between aggregate and hydrated cement paste, in: Proc. 8th Int. Congr. Chem. Cement, Rio de Janeiro, 1986, pp. 378-380.