

Effect of AlF_3 Production Waste on the Properties of Hardened Cement Paste

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The possibility to use by-product $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (often called AlF_3 production waste) in cement casting has been attracting the interest of researchers for many years, although high content of fluorine makes the use of amorphous SiO_2 problematic. Finding the way of utilizing waste products is a very important research topic at the moment. In this study AlF_3 production waste was investigated as the basic ingredient of a new pozzolanic material. The goal of this study is to investigate the possibilities of using AlF_3 production waste, washed in ammonia solution, in cement stone specimens. Chemically treated silica gel additive was proved to reduce the amount of $\text{Ca}(\text{OH})_2$ and CaCO_3 in hardened cement paste samples. Experimental research has revealed that the density in hydrated samples reduces from 2220 kg/m^3 to 2030 kg/m^3 with the increase of silica gel content from 0 % to 35 %. The compressive strength of samples containing 10 % of silica gel additive increased by 8.04 % compared to the samples without the additive. SiO_2 additive used at 10 % and 20 % increased the maximum hydration temperature. In this case, the additive modifies the hydration kinetics.

Keywords: silica gel, concrete, AlF_3 production waste.

INTRODUCTION

Mineral additions are used as a replacement to cement based materials since they enable to change the hardened state and to obtain materials with higher resistance. Rice husk is one of the by-products of rice. The synthesis of nanosilica powder from rice husk and characterization of obtained pure silica is documented in research papers [1, 2]. The nanosilica powder was introduced into cement paste and the specimens were investigated. The experimental results have revealed that the cement paste incorporating nanosilica has higher compressive strength compared to the ordinary portland cement paste.

Silica sols synthesized via different routes, e.g. inorganic, organic and ion-exchange, have been incorporated in low cement alumina casting compositions in various proportions. It is observed that silica sol synthesized through cation exchange route has a significant positive effect on the properties of cast samples with 3% addition [3]. A. Roy et al. [4] observed that amorphous silica replacing up to 10 % of portland cement by mass in concrete behaved partly as traditional pozzolan, partly crystallized to quartz and the rest underwent some crystal structural reorganization without morphological changes.

Mortars and cement paste with additions of nanosilica, silica fume and nanosilica and silica fume were studied using factorial design approach [5]. The optimum amount of nanosilica and silica fume for each w/c ratio between 0.35 and 0.47 was determined by compressive strength at 28 days. In general, the addition of nanosilica affects the properties of mortars more significantly, than silica fume. The experimental results [6] showed, that the compressive strengths of mortars with nano- SiO_2 particles were all

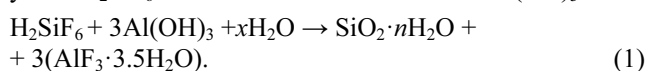
higher, than those of mortars containing silica fume at 7 and 28 days. The results of these examinations indicate that nano-scale SiO_2 behaves not only as a filler to improve microstructure, but also as an activator to promote pozzolanic reaction.

Previous studies [7] have shown that early strength and durability of sludge ash/cement mortar are improved by adding nanosilicon dioxide to the mortar. The cement was replaced by 0, 10, 20, and 30 % of sludge ash, and 0 % and 2 % of nano- SiO_2 additive was added to sludge ash paste or mortar specimens. The test results show that nano- SiO_2 additives not only effectively increase the hydration product (calcium silicate hydrate [C-S-H] gel), but also make the crystal structure denser.

Hydration and hardening of cement-based materials containing nano- SiO_2 were studied [8, 9]. The results show that nano- SiO_2 can consume large amounts of $\text{Ca}(\text{OH})_2$ because of its high pozzolanic activity, so that hydration can be accelerated and microstructure can be improved.

The investigation of SiO_2 and microsilica effect on cement stone has revealed that SiO_2 has a bigger effect [10]. For this reason solutions based on ammonium hydroxide and water could be one of the possible routes of producing SiO_2 . Therefore anisotropic etching of monocrystalline silicon was investigated. In 2.65 M NH_3 solutions at 80°C the addition of H_2O in concentration between $0.65 \times 10^{-2} \text{ M}$ and $1.84 \times 10^{-2} \text{ M}$ increases the silicon etch rate in the (100) direction to $75 \mu\text{m/h}$, which is a factor of about 2.5 higher compared to pure etchants. The temperature dependence of etch rates as well as the influence of post-treatments on the etching behaviour is discussed [11].

The production of phosphoric fertilizers from apatites yields H_2SiF_6 acid which is neutralized with $\text{Al}(\text{OH})_3$:



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The possibility to use reaction (1) by-product $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (often called AlF_3 production waste) in cement casting has been attracting the interest of researchers for many years, although high content of fluorine (up to 33 %) makes the use of amorphous SiO_2 problematic [12].

Pyrolysis is one of the possible ways to remove fluorides from AlF_3 waste [13]. Silica gel was found to be a suitable additive in hardened cement paste only when thermally activated for 1 hour at 800 °C. Amorphous SiO_2 present in this additive reacts with Ca(OH)_2 formed during cement hydration and produces hydrosilicates of $(1.5-2.0)\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ type that add additional strength to the specimens. With the optimal additive content being 10 % the compressive strength of hardened cement paste increases by 5 MPa–7 MPa compared to the specimens without the additive.

Finding the way of utilizing waste products is a very important research topic at the moment. In this study AlF_3 production waste was investigated as a basic ingredient of a new pozzolanic material.

The goal of this study is to investigate the possibilities of using AlF_3 production waste, washed in ammonia solution, in cement specimens.

MATERIALS AND TESTING METHODS

Portland cement CEM I 52 R (specific surface area at 370 kg/m², the paste of normal thickness at 27.3 %, initial setting time at 130 min, final set at 215 min.) mineral composition $\text{C}_3\text{S} = 50.7\%$; $\text{C}_2\text{S} = 18.5\%$; $\text{C}_4\text{AF} = 14.2\%$; $\text{C}_3\text{A} = 9.7\%$ was used in this study.

X-ray diffraction analysis was conducted using DRON-6 diffractometer. The investigation was carried out with a 2θ angle range 4°–70° with Ni-filtered $\text{CuK}\alpha$ radiation.

Thermal imaging was done on a differential scanning calorimeter “STA 409 PC” from Netzsch. The maximum temperature was 1500 °C, temperature increase rate was 10 °C/min.

Particle size distribution and specific surface area were determined by “Mastersizer 2000” instrument from Malvern. Red light was produced by helium-neon laser and blue light was obtained from a solid phase source. The measuring principle was used Mie scattering analysis.

Cement paste calorimetry tests were done with 8-Channel USB K Type Thermocouple Data Acquisition Module (measured temperature range from 0 to 1000 °C).

For the analysis of the effect of silica gel addition (5, 10, 15 % of mass) on the properties of concrete, the series of hardened cement paste mixtures were chosen and mixed in laboratory setting. Samples were formed, i.e. prisms of (4×4×16) cm in size, and left to harden for 28 days under the conditions defined in EN 12390-2 standard. The compressive strength of hardened cement paste was evaluated according to EN 196-1 standard. A ToniTechnik 2020 press was used to evaluate the compressive strength of hardened cement paste.

RESULTS AND DISCUSSION

AlF_3 production waste is one of the raw materials rich in silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O} = 53.20\%$; $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O} = 32.05\%$;

$\text{AlO(OH)} = 2.62\%$; $\text{H}_2\text{O} = 12.13\%$). When this by-product is treated with ammonia solution at room temperature (Fig. 1, curve 1) the change in its mineral composition occurs.

Reaction with NH_4OH water solution produces soluble ammonia salts that are washed from silica gel with water. This waste contains about 72.3 % of silica after chemical modification.

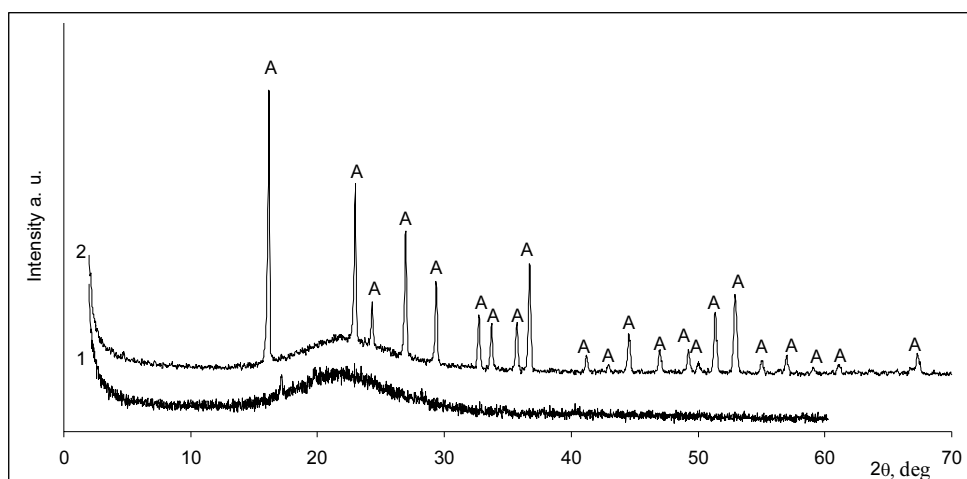
The strength of cement stone specimens depends on the granular composition of the aggregates. The particle size and size distribution analysis has revealed that the diameter of modified silica gel particles in modified SiO_2 waste changed from 60.3 μm to 79.4 μm (Fig. 1, b) and the specific surface area was $S = 0.53 \text{ m}^2/\text{cm}^3$, corresponding to an average particle size.

After 28 days of hydration non hydrated alite $\text{Ca}_{54}\text{MgAl}_2\text{Si}_{16}\text{O}_{90}$ ($d = 0.304, 0.279, 0.275, 0.261 \text{ nm}$) was found in hardened cement stone samples (Fig. 2); reaction products were portlandite Ca(OH)_2 ($d = 0.491, 0.262, 0.193, 0.179 \text{ nm}$) and calcium hydrosilicate C-S-H ($d = 0.303, 0.279 \text{ nm}$), CaCO_3 ($d = 0.303, 0.228 \text{ nm}$), β-belite $2\text{CaO} \cdot \text{SiO}_2$ ($d = 0.73, 0.59, 0.218 \text{ nm}$), ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$ ($d = 0.967, 0.560 \text{ nm}$). Portlandite peaks in samples without the additive were found to be sharper and more intensive compared to the samples containing 10 % and 20 % of the additive. (Fig. 2, curves 2 and 3). The X-ray diffraction pattern (Fig. 2, curve 1) of the specimens containing 35 % of the additive shows that diffraction peaks of portlandite are again more intensive compared to Ca(OH)_2 peaks in control sample. However, this intensity of peaks is related not to the higher content but to improved crystallization of portlandite because the results of thermographic analysis have shown that the content of portlandite in cement stone reduces with the increase of additive content in the cement paste. To summarize the results of both analyses we may state that the presence of chemically treated silica gel reduces the amount of free Ca(OH)_2 in cement stone specimens.

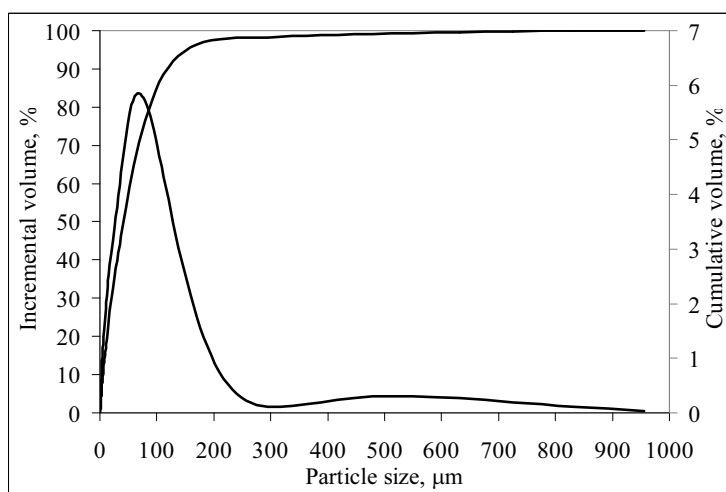
Thermal analysis is an important experimental procedure used to measure cement hydration. Endothermic peaks in the temperature range from 102 °C to 108 °C of thermal analysis curves shows partial dehydration of C-S-H and aluminates phases. The second type of intensive endothermic peaks in the temperature range from 446 °C to 452 °C in all DSC curves shows the disintegration of Ca(OH)_2 . Endothermic peaks at 642 °C to 665 °C show disintegration of CaCO_3 . The most intensive CaCO_3 peak is observed when no additive is used. It become less intensive when 10 % or 20 % of additive is used.

704 °C–716 °C temperature initiated exothermic peaks observed in thermal images indicate the conversion of calcium hydrosilicates, where $\text{CaO}/\text{SiO}_2 = 0.8-1.25$, into volastonite. The lower is this ratio the higher is the intensity of the peak. The test has shown that with the increase of silica gel additive up to 20 % (i.e. with lower CaO/SiO_2 ratio) the exothermic peak is initiated at lower temperature.

The comparison of samples without the additive and samples containing 10 % or 20 % of the additive has shown that the content of Ca(OH)_2 produced in the hydration of minerals present in the cement goes down



a



b

Fig. 1. X-ray diffraction patterns (a) and distribution of silica gel particles (b): 1 – is a test sample after modification with NH_4OH ; 2 – is a test sample before modification. Notes: A is $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$

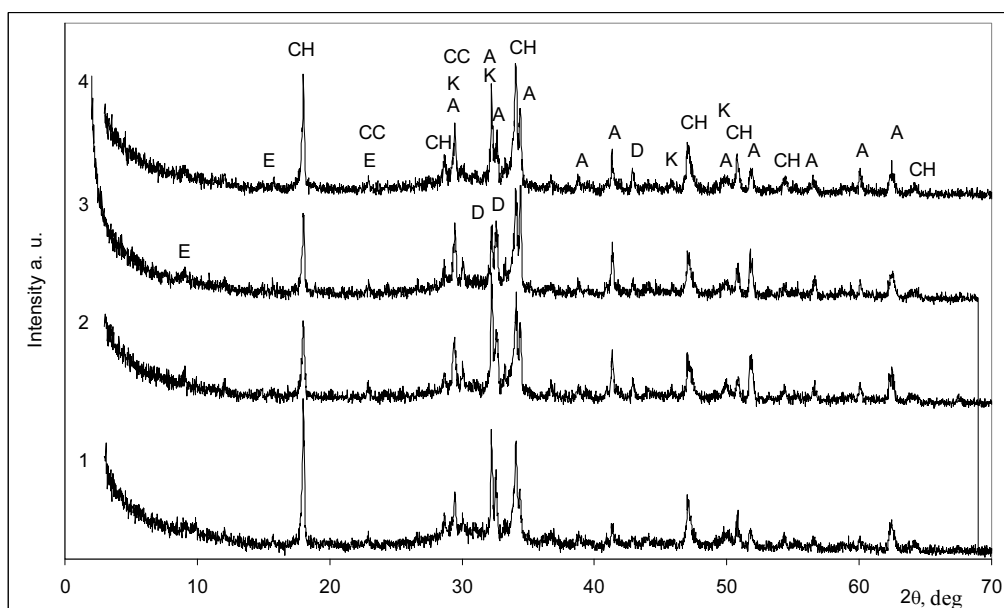


Fig. 2. X-ray diffraction patterns of hardened cement paste after 28 days containing: 1 – 35 %; 2 – 20 %; 3 – 10 %; 4 – 0 % of silica gel. Notes: CH is $\text{Ca}(\text{OH})_2$; A is $\text{Ca}_{54}\text{MgAl}_2\text{Si}_{16}\text{O}_{90}$; K is C-S-H; D is $2\text{CaO} \cdot \text{SiO}_2$; CC is CaCO_3 ; E – $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$

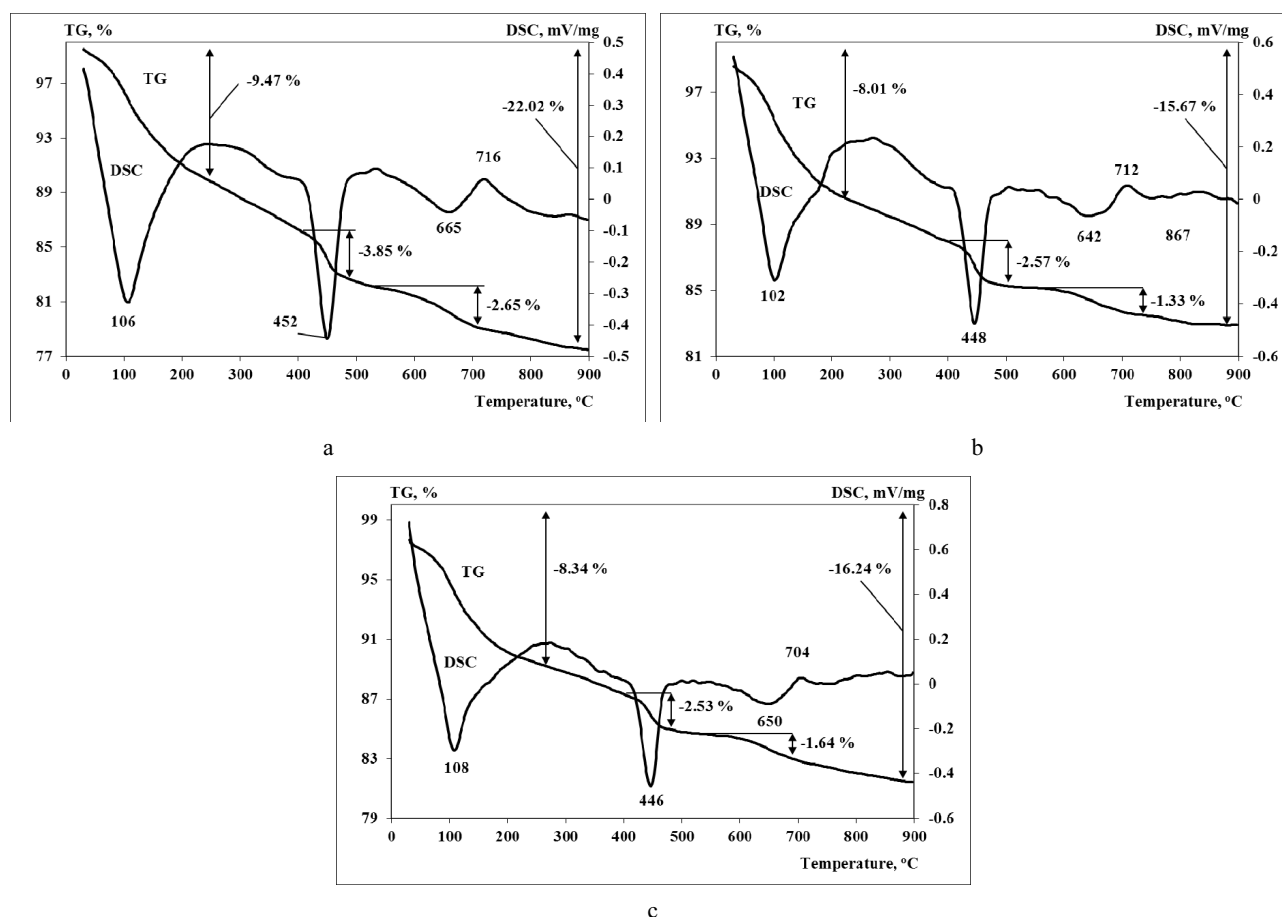


Fig. 3. The results of thermal analyses of hardened cement paste after 28 days containing: a – 0 %; b – 10 %; c – 20 % of silica gel

after 28 days of hardening: $\text{Ca}(\text{OH})_2$ content in hardened cement paste without the additive was 15.8 %, whereas $\text{Ca}(\text{OH})_2$ content in hardened cement paste containing 10 % and 20 % of the additive was 10.6 % and 10.4 % respectively. Silica gel used in the testing also reduces CaCO_3 content in the cement stone: CaCO_3 content in samples without the additive was higher (6.0 %) than in the samples containing 10 % and 20 % of the additive, where CaCO_3 content was 3.0 % and 3.7 % respectively.

With the addition of silica gel the density of the samples goes down from 2220 kg/m^3 to 2030 kg/m^3 (Fig. 4, a) because the used silica – AlF_3 by-product – is in the form of fine particle powder. This additive of amorphous structure can also improve the strength of hardened cement paste. In contrast to density, the compressive strength of the samples containing 10 % of

silica gel increased by 8.04 %, however the strength went down with the increase in the additive content up to 20 % or 35 % compared to the control sample (Fig. 4, b).

In Fig. 5 the results of calorimetric measurement are shown as the rate of heat evolution curves and as the heat released. The results for pastes with 10; 20 and 35 % additive were compared with pastes without the additive. When SiO_2 additive was used at 10 % and 20 % the maximum hydration temperature rose, whereas with 35 % of the said additive the temperature went down (Fig. 5, curve 4). In this case the additive modifies hydration kinetics. The test results have proved that SiO_2 additive at 10 % and 20 % of the cement mass retarded the hydration from 593 min. (without the additive) to 703 min. and 759 min., but increased the maximum temperature of portland cement hydration by 10 °C and 4 °C respectively.

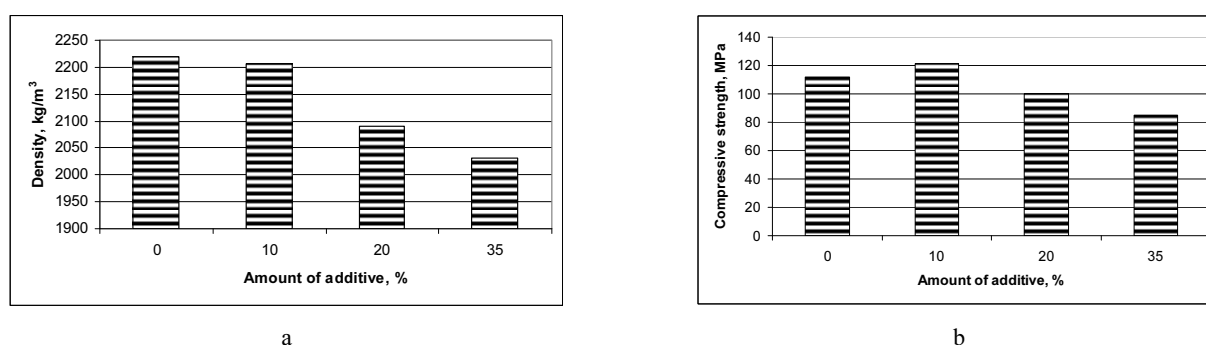


Fig. 4. Dependence of density (a) and a compressive strength (b) of hardened cement paste on the additive amount after 28 days

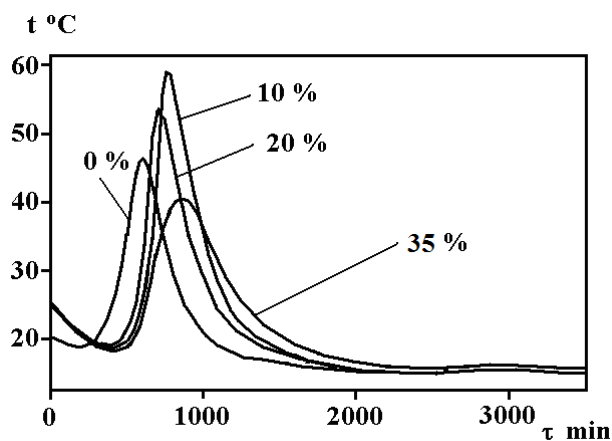


Fig. 5. Influence of additive amount on cement paste hydration temperature

The influence of AlF_3 production waste on properties of hardened cement paste as compared with silica fume and nano- SiO_2 [10] has been studied through measurement of compressive strengths of hardened cement paste, and by XRD analysis. Results indicated that the influence of AlF_3 production waste, nano- SiO_2 and silica fume on compressive strengths of hardened cement paste showed the same, all additions accelerated the cement hydration process. Compressive strengths of hardened cement paste incorporating all mentioned SiO_2 additions were obviously higher than those of control samples and all SiO_2 additions consume calcium hydroxide crystals, decrease the calcium hydroxide crystals.

So, all mentioned SiO_2 additive have similar character in cement hydration process. By utilizing AlF_3 production waste in Portland cement system, which is aggressive in the aspect of the environment, it will be solving ecological problem.

CONCLUSIONS

Experimental research has revealed that the density in hydrated samples reduces from 2220 kg/m^3 to 2030 kg/m^3 with the increase of silica gel content from 0 % to 35 %. The compressive strength of cement stone samples containing 10 % of silica gel additive increased by 8 % compared to the samples without the additive, whereas the compressive strength of samples containing 20 % or 35 % of silica gel additive reduced by 9.8 % and 25.9 % respectively. Chemically treated silica gel additive was proved to reduce the amount of free $\text{Ca}(\text{OH})_2$ cement samples. The comparison of samples without the additive and samples containing 10 % or 20 % of the additive has shown that the content of $\text{Ca}(\text{OH})_2$ goes down after 28 days of hardening: 15.8 % in hardened cement paste without the additive and 10.6 % and 10.4 % respectively in hardened cement paste containing 10 % and 20 % of the additive. The silica gel used in the testing also reduces CaCO_3 content in cement stone: CaCO_3 content in samples without the additive was twice as big (6 %) as in the samples with 10 % or 20 % of the additive (3 % and 3.7 % respectively).

Influence of the additive amount on a maximum hydration temperature was illustrated. Amorphous SiO_2

additive used at 10 % and 20 % increased the maximum hydration temperature, while higher content of the additive, i. e. 35 % decreased the temperature.

This experimental research data may be used in concrete technology as well.

REFERENCES

1. Thuadaij, N., Nuntiya, A. Synthesis and Characterization of Nanosilica from Rice Husk Ash Prepared by Precipitation Method CMU *Journal Natural Science* 7 2008: pp. 59–65.
2. Chandrasekhar, S., Satyanarayana, K. G., Pramada, P. N., Raghavan, P., Gupta, T. N. Review Processing, Properties and Applications of Reactive Silica from Rice Husk – an Overview *Journal of Materials Science* 38 2003: pp. 3159–3168.
3. Dasgoddar, D., Swapan, K. D., Dasgoddar, P. K. Effect of Silica Sol of Different Routes on the Properties of Low Cement Castables *Bulletin of Materials Science* 26 2003: pp. 227–231.
4. Roy, A., Moelders, N., Schilling, P. J., Seals, R. K. Role of an Amorphous Silica in Portland Cement Concrete *Journal of Materials in Civil Engineering* 18 2006: pp. 747–753.
5. Senff, L., Hotza, D., Repette, W. L., Ferreira, V. M., Labrincha, J. A. Influence of Added Nanosilica and/or Silica Fume on Fresh and Hardened Properties of Mortars and Cement Pastes *Advances in Applied Ceramics* 108 2009: pp. 418–428.
6. Jo, B. W., Kim, C. H., Tae, G. H., Park, J. B. Characteristics of Cement Mortar with Nano- SiO_2 Particles *Construction and Building Materials* 21 2007: pp. 1351–1355.
<http://dx.doi.org/10.1016/j.conbuildmat.2005.12.020>
7. Luo, H. L., Chang, W. C., Lin, D. F. The Effects of Different Types of Nano-Silicon Dioxide Additives on the Properties of Sludge Ash Mortar *Journal of the Air & Waste Management Association* 59 2009: pp. 440–446.
<http://dx.doi.org/10.3155/1047-3289.59.4.440>
8. Xu, X., Lu, Z. Y. Effect of Nano- SiO_2 on Hydration and Harden of Portland Cement 2006 *Xi'an International Conference of Architecture and Technology, Proceedings – Architecture in Harmony* 2006: pp. 609–613.
9. Jo, B. W., Kim, C. H., Lim, J. H. Characteristics of Cement Mortar with Nano- SiO_2 Particles *ACI Materials Journal* 104 2007: pp. 404–407.
10. Qing, Y., Zenan, Z., Deyu, K., Rongshen, Ch. Influence of nano- SiO_2 Addition on Properties of Hardened Cement Paste as Compared with Silica Fume *Construction and Building Materials* 21 2007: pp. 539–545.
11. Schnakenberg, U., Benecke, W., Löchel, B., Ullerich, S., Lange, P. NH_4OH -based Etchants for Silicon Micromachining: Influence of Additives and Stability of Passivation *Sensors and Actuators A: Physical* 25 1990: pp. 1–7.
12. Šiaučiušas, R., Sasnauskas, K., Balandis, A. Investigations of Synthesis Processes of Calcium Silicate Hydrates of Low Basicity with Participation of Aluminate. *Chemical Technology* 11 1999: pp. 31–38 (in Russian).
13. Vaičiukynienė, D., Kantautas, A., Vaitkevičius, V., Sasnauskas, V. Using of Modified AlF_3 Production Waste in Cement-Based Material *Materials Science (Medžiagotyra)* 15 2009: pp. 255–261.