THE INFLUENCE OF POLYMER LATEX AND SILICA FUME ADDITIVES ON THE PROPERTIES OF CEMENT MORTAR AND CONCRETE

Bronius Vektaris, Edita Smetonaitė, Vytis Vilkas

Laboratory of Modification Building Materials of Institute of Architecture and Construction, Tunelio g. 60, LT-3035 Kaunas, Lithuania. E-mail: asi@asi.lt

Received 08 Jan 2003; accepted 13 May 2003

Abstract. The article maintains that while mixing acryliated latex, cement, fillings, and relaxing additives, flexible, resilient and well sticking to concrete mortars are obtained. Their properties - the lengthening of a mortar layer, tensile strength and strength of adhesion to concrete - may be regulated while changing the quantities of cement and plasticisers. 10–30 % silica fume and Stoniškiai carbonate opoca additives grant to usual Portland cement mortar or concrete the resistance to sulfate corrosion. When the quantity of cement in concrete exceeds 400 kg/m³, an increased quantity of hydraulic additive is necessary 20–30 %. Opoca additive ensures a better Portland cement resistance to sulfate action than the same quantity of CaCO₃ and Norwegian silica fume mixture. This fact is explained by a larger activity of opoca. However silica fume activity may be increased by reducing silica fume to smaller units, for example by mixing it with coarse aggregate. In hardening, concrete silica fume and other hydraulic additives react with Ca(OH)₂ deriving from cement, that's why in hardened concrete free lime diminishes and less secondary expansion units are created. There are vivid peaks of CaSO₄·2H₂O and Ca(OH)₂ in XRD patterns of decayed samples. This research shows that gypsum formation is the main reason of concrete decay in Na₂SO₄ solution.

Keywords: repair mortar, tensile strength, protection, plasticity, concrete, hydraulic additives, sulfate resistant.

1. Introduction

Traditional cement mortars and concretes are brittle; they demonstrate poor adhesion to the foundation and poor resistance to sulfate corrosion. The above-mentioned properties are eliminated or improved with the use of polymeric and very small mineral concrete additives [1–6]. Cement mortars and concretes with polymeric additives are used for protecting of concrete and reinforced concrete constructions, as well as for repairing works and other purposes. Several series of European standards have been prepared that are also adopted in Lithuania [7, 8]. Research work with polymercement materials carried out at the Institute of Architecture and Construction during which local raw materials, polymeric dispersions, and other additives are used [9]. Some materials have already been produced and utilised in Lithuania.

A number of authors determined that polymeric additives influence hydration and hardening of Portland cement, since the interaction with their component is fluctuating, especially with Ca(OH)₂. During water elimination from the hardening product they either form or do not form films; the additives may stick separate concrete components and additionally strengthen the concrete [10, 11]. The mechanism of the interaction of Portland cement and the polymere has not been yet fully discovered, especially in the case of silica fume that also reacts with Ca(OH)₂.

Silica fume is a highly active hydraulic additive [12]. The activity of the hydraulic additives, ie their ability to tie free lime (Ca(OH)₂) deriving from the solution, is an essential factor in the increase of the traditional cement resistance to sulfate waters. When the reinforced concrete equipment in water – purification and in ports includes Portland cement of an ordinary composition with a great amount of C₃S and C₃A, the sulfate ions of the environmental water in the concrete pores react with free lime thus forming the gypsum less soluble than Na₂SO₄. During its crystallisation in the concrete pores the volume of the hard phase increases 2,3 times. If Na₂SO₄ reacts with tricalcium aluminium hydrate (C₃AH₆) and as a result ettringite (C₃A₃CaSO₄·32H₂O) is formed, the volume of the hard phase increases 4,8 times [13]. Interior tensions occure in the concrete as well as micro-gaps, which may result in the concrete decay. However the secondary ettringite is also formed in the free lime presence. Therefore the additives that tie Ca(OH)₂ may be useful for the increase of cement sulfate resistance.

The work aims at the analysis of the mortar deformative properties its tensile strength, the degree of ad-
hen we talk about the influence of the improving additives on the properties of the cement mortar and concrete, when the ordinary Portland cement is used.

2. Materials and methods

Portland cements produced by the joint-stock company "Akmenės Cementas" CEM I 42.5 R and CEM II A-M/42.5, sand from the Rizgoniai sand-pit, 4/10 mm broken stone, polymeric dispersions, silica fume of two varieties – Norwegian granulated “Holla Metal” microsilica, further marked as NMS and the Ukrainian untreated silica fume further marked as UMS were used in the research work. For comparison the local hydraulic additive – the Stoniskiai carbonate opoca powder – was used. Taking into consideration that there are about 50 % CaCO₃ in carbonate opoca, another Karpenai limestone powder additive was used to determine its effect. Organic polymeric plasticisers and additives (methylcellulose, etc) were introduced, too.

Portland cement CEM II A-M/42.5 included 9–10 % CaO and 4 % gypsum. The clinker of this cement contained 55.8 % C₂S and 9.7 % C₃A, while the CEM I 42.5 R – 50.7 % C₂S and 9 % C₃A.

The activity of various kinds of silica fume and opoca depends on their fineness. However, there is a difficulty in determining the quality of fineness, since when fined the light powder aggregates and forms small clods and lumps. Therefore an attempt was made at pulverizing silica fume together with the filling to determine its activity according to the special fastened method invented by the authors of the article. It is founded in the following procedure: 1 g of the examined material is poured into 1 l plastic large-necked cylindric bottle together with some amount of the filling and 500 ml of substantial Ca(OH)₂ solution. The mixture is warmed up to 45±5 °C temperature, and after some time it is possible to determine how many milligrams of CaO were joined to 1 g of the investigated material [14].

The extension and tensile strength of the mortar were determined during the production and testing of 2 mm thick plates of which, after hardening, the samples of the necessary shape and size were cut. Adhesion to concrete was analysed by tearing the stuck concrete plates off.

The bending and compressive strength as well as resistance to sulfate corrosion was determined by testing 4x4x16 cm size prisms produced according LST 1413.8 and LST 1356 (in some cases 2x2x2 cm cubes). The fastened method of determining the resistance to aggressive solutions [15], was employed when the samples (4x4x16) were immersed in Na₂SO₄ = 3M NaOH solution. The samples were parallelly analysed regarding their frost resistance according to the LST 1428.17 fastened method.

3. Results and discussion

Differently prepared and modified latexes that included different additives did not show positive results. The mortar layers with these latexes were hard and unelastic. The acrylated vinyl acetate based on copolymeric latex (abridge – acrylated latex) may also serve the purpose. Acrylated latex of various lots acrylic latex with amount of total solids 48–51 % was employed. When mixed with cement and fillings, this latex acquired different properties. If various amounts of latex are added to the cement and sand mixture (1:1 according to mass), the hardening of cement slows down, but the compressive strength increases (Fig 1).

![Fig 1. The effect of the amount of added acrylated latex on the compressive strength. 1 – plain latex; 2 – plasticised latex. W/C = (L+W)/C = 0.4](image-url)

When 15 % of latex from the mass of cement is added, the compressive strength increases nearly twice. The plasticised latex (15 % plasticiser from the latex mass) additives considerably decrease the compressive strength (Fig 1). When in the mixture the amount of latex (especially plasticised) is increased up to 25–30 %, the elastic and flexible mortars (0,5–2 mm thick) were investigated when regarded as the protective cover of the cracking concrete.

These mortars well adhere to the concrete surface and thus cover the microcracks. When such a cover is flexible and elastic, new cracked constructions do not form in the concrete.

The properties of the mortar elasticity and flexibility depend on numerous factors. Fig 2 demonstrates how the tensile strength as well as adhesion to the concrete of the mortar layer varies with the change of the amount of the cement in the mixture.

The mortar including 25 % cement demonstrates the greatest tensile strength and adhesion to concrete. Although when stretched such a mortar shows the smallest extension, yet the extension is too big, resulting in 180 % and more [16].

During stretching, the extension of the layer samples when depends on the amount of cement, the alteration have been observed within the range of 20 %. However,
the extension mostly depends on the amount of plasticiser in the latex (Fig 3).

The samples of the mortar layer without a plasticiser extend about 50%. With the increase of the amount of the plasticiser (up to 25%) the extension increases about four times. Moreover, the value of the extension depends on the period of the sample hardening (Fig 3).

However, with the increase of the amount of the plasticiser in mortar, the mortar tensile strength and the adhesion to concrete decrease (Fig 4). When the latex without a plasticiser is used, the tensile strength is 2,4 MPa. When the amount of plasticiser reaches 25%, the tensile strength decreases up to 0,2 MPa (twelve times). The strength of adhesion, in its turn, changes from 1 MPa to 0,18 MPa (about 5,5 times). Therefore, with the alteration of the plasticiser amount in the mixture, the change of the properties of the hardened product is possible in a rather wide range.

Acrylic latex contains about 50% of water. In fact, when a greater amount of water is added, the properties of the mortar improve [16].

It is obvious that in some components the mortar composition has a different effect on the properties of the product. The pouring of 15% from the latex mass of both water and plasticiser is welcome, since it increases the tensile strength. The adhesion strength also increases when up to 0,4% methylcellulose is added to mortar. The silica fume additive does not have a considerable effect on this type of mortar.

The role of silica fume as well as its effect on the properties of the mortar and concrete were also analysed, first of all, the ability of different varieties of this material to react with Ca(OH)₂.

Fig 5 shows the ability of the NMS, the UMS, and the opoca powder to join CaO from the solution after their keeping at 45 ± 5°C temperature for 3 days.

Silica fume mixed with sand joins the double amount of CaO when prepared to a fined silica fume. The activity of UMS even without additional fining is high enough.

The activity of opoca is smaller than that of silica fume. However taking into consideration the fact that the amount of opalic SiO₂ in opoca is only about 50%, it is important to recognise that carbonate opoca is an active hydraulic additive of cement and concrete.

It has been determined that when 1 g of the NMS is poured into a plastic bottle together with 40 g granite broken stone, and, by producing both rotatory and shaking movements during 4–5 minutes the NMS fractions get fined, and thus their additional fining is avoided.
Table 1. The effect of the NMS, limestone powder (CaCO₃) and opoca powder additives on the resistance of concrete samples (4x4x16 cm) to 5 % Na₂SO₄ solution. CEM I 42.5R and lignosulphonate plasticiser SBS were used. W/C = 0.5

| Amount of cement kg/m³ | Amount of additives, %, of cement mass | Samples density kg/m³ | Tensile/compressive strength after 28 days of hardening, MPa | Properties after 375 days immersion of additives, %, | Properties after 28 days of immersion, mm/m | changes of mass, % | condition of samples |
|------------------------|--------------------------------------|-----------------------|-------------------------------------------------|-------------------------------------------------|-----------------------------------------------|-------------------|---------------------|
| 440                    | –                                    | 2390                  | 7.6/61.4                                       | + 1.43                                          | +0.42                                         | broken            |                     |
| 440                    | 0.7 SBS                              | 2250                  | 6.8/48.4                                       | + 6.17                                          | +3.51                                         | broken            |                     |
| 440                    | 15 CaCO₃                            | 2330                  | 7.1/59.3                                       | + 1.67                                          | +2.00                                         | broken            |                     |
| 440                    | 15 NMS                               | 2310                  | 7.6/71.0                                       | +4.85                                           | +2.15                                         | broken            |                     |
| 440                    | 10 CaCO₃ 15 NMS                      | 2380                  | 8.7/57.6                                       | -0.09                                           | +0.79                                         | good              |                     |
| 350                    | 12.5 CaCO₃ 12.5 NMS                 | 2380                  | 8.3/62.8                                       | +0.76                                           | +2.19                                         | good              |                     |
| 440                    | 20 opoca 0.7 SBS                     | 2390                  | 7.3/76.4                                       | -0.91                                           | +0.73                                         | good              |                     |
| 440                    | 30 opoca 0.7 SBS                     | 2480                  | 8.1/79.2                                       | +0.33                                           | +0.39                                         | good              |                     |
| 395                    | 11 opoca 0.7 SBS                     | 2410                  | 7.3/58.0                                       | +0.3                                            | 0.92                                          | good              |                     |
| 350                    | 25 opoca 0.7 SBS                     | 2330                  | 6.8/58.8                                       | -0.20                                           | +0.35                                         | good              |                     |

Table 2. Resistance of fine concrete (cement:sand = 1:3) samples (4x4x16 cm) with additives of the NMS and the UMS to 5 % Na₂SO₄ solution. CEM I 42.5R was used

| Amount of additives, % | Tensile/compressive strength, MPa, after 28 days of hardening | 18 months of immersion in water | 18 months of immersion in 5 % Na₂SO₄ solution | Properties after immersion them in 5 % Na₂SO₄ solution for 24 days | Properties after 28 days of immersion, mm/m | change of mass, % | condition of samples |
|------------------------|---------------------------------------------------------------|--------------------------------|-----------------------------------------------|---------------------------------------------------------------|-----------------------------------------------|-------------------|---------------------|
| –                      | 8.1/66.5                                                      | 10.5/87.5                     | 8.2/58.0                                      | +1.59                                                        | +1.98                                         | broken            |                     |
| 5 NMS                  | 8.1/58.5                                                      | 10.4/74.0                     | 10.0/68.0                                     | +1.38                                                        | +1.89                                         | broken            |                     |
| 10 °°                  | 8.7/66.0                                                      | 10.4/74.0                     | 11.5/77.0                                     | +0.44                                                        | +1.49                                         | small changes     |                     |
| 30 °°                  | 7.4/52.0                                                      | 7.4/63.0                      | 11.4/57.0                                     | +0.18                                                        | +1.65                                         | good              |                     |
| 5 UMS                  | 8.9/66.0                                                      | 9.6/72.0                      | 9.6/72.0                                      | -0.78                                                        | +0.85                                         | small changes     |                     |
| 10 °°                  | 9.0/60.8                                                      | 10.4/67.0                     | 10.0/70.0                                     | -1.2                                                         | +0.75                                         | good              |                     |
| 20 °°                  | 8.0/56.6                                                      | 10.4/67.0                     | 8.7/60.0                                      | +0.18                                                        | +1.01                                         | good              |                     |
| 30 °°                  | 7.4/43.2                                                      | 8.1/55.0                      | 7.9/60.0                                      | 0.00                                                         | +0.73                                         | good              |                     |

The data presented in Table 1 shows what effect the NMS, the opoca and limestone additives have on concrete when the samples (4x4x16 cm) are kept in 5 % Na₂SO₄ solution.

The Portland cement CEM I 42.5 R was used during the experiments. In fact it is not sulfate-resisting cement. Therefore the samples without other additives than lignosulphonate plasticiser SBS and 15 % limestone in 375 days got decayed in the mentioned solution. When hardening they have extended and their mass has increased. The same happened with samples including 15 % NMS additive because this additive was not fined and therefore demonstrated inconsiderable activity.

When the NMS were used together with 10 % limestone, the samples did not decay. When the amount of cement in the concrete decreased up to 350 kg/m³, the concrete is resistant with 12.5 % NMS + 12.5 % CaCO₃. It proves the positive effect of CaCO₃ which has already been mentioned in scientific literature [17–19]. The opoca additive also increases the concrete resistance to sulfate corrosion (Table 1). When the amount of cement does not exceed 400 kg/m³, 11 % of opoca is sufficient. When it is 440 kg/m³, the amount of opoca should make 20–30 % of the cement mass. Similar results of sulfate resistance were achieved with the samples (4x4x16 cm) produced of the fine concrete (1:3) with the use of the CEM II A-M/42.5 cement which included 9 % CaCO₃ (Table 2).

Strength of the samples either without additives or with UMS additive after having been kept in Na₂SO₄ solution for a year started decreasing, but with the 20–30 % NMS it has no changed (it is not demonstrated in Table 2). After a year and a half of being kept in an aggressive environment the strength of the samples without additives decreased by 12.8 %. In two years there appeared cracks on the edges of the samples, however, the strength of the samples with additives increased. It is important to mention that the mass of all the samples
kept in 5 % Na₂SO₄ solution increased, especially during the first twelve months – up to 0.73–1.65 %. Later it altered less, and reached 0.75–1.99 %. The greatest mass alteration was noticed in the samples either without additives or with 5 % NMS additive. The smallest changes up to 0.73–1.01 % observed when the UMS additive was used. The greatest and smallest deformations of samples correspond to the mass alterations. The greatest deformations up to 1.59 mm/m take place either in the samples without additives or with 5 % NMS. The sample deformations in the case of the UMS additive are the smallest. It has also been determined that these samples were not deformed by corrosion (Table 2).

The dilution of Portland cement with CaCO₃ as well as the mechanical decrease of the amounts of C₃S and C₃A in a certain percentage do not protect against long-term aggressive impact of Na₂SO₄ solution. However, at the beginning of the hardening process CaCO₃ additive stimulates C₃A₄H₆ and C₃A·CaCO₃·H₁₁ formation and suppresses the formation of C₃A₄H₆ [13], that is why this additive is harmless and welcome. Its action is complemented by the active SiO₂. The increase of sample mass in Na₂SO₄ solution (Tables 1, 2) occurred because of the formation the reaction products of low solubility when Na₂SO₄ reacted with Ca(OH)₂ and other cement minerals. With the increase of the samples mass and the volume of some components, the samples extended. The mass of the samples with the UMS increased considerably less (2–2.3 times) than the mass of the samples without additives. The samples extended significantly, or, in other cases, they contracted and showed no signs of decay. The suitable amount of silica fume in the concrete makes 10 to 20 % of the cement mass and this corresponds to the ratio 2 to 1 of free lime derived from cement and the added active SiO₂.

The influence of the additionally pulverised NMS additives on the concrete resistance to the aggressive solutions and frost has also been investigated throughout the research. Granulated silica fume was fined while intensively mixing it in turn with the broken stone, sand, cement, and the humid concrete mixture of which 4x4x16 cm samples were formed. After 28 days they were immersed in 8 % Na₂SO₄ + 3M NaOH solution, as it is presented in [15], and the deformations were measured. Analogical actions were carried with the concrete without additives and the concrete with an opoca additive. Another series of hardened samples was cooled up to ≥ -16 °C and warmed up to 18 ± 2 °C in 5 % NaCl solution. The samples without additives extended intensively for about 60 days (Fig 6), but in 10–20 days the positive effect of the NMS and opoca was discovered.

The samples without additives extended about 3.5 mm/m. The higher extension of the samples [14] may be explained by the secondary extension or by formation of the 4CaO·0.9Al₂O₃·1.1SO₃·0.5Na₂O·16H₂O (the so-called the fourth phase).

However, during the samples cooling the negative effect of NMS was discovered. After 40 fastened cooling cycles (about 120 ordinary freeze-thaw cycles) the samples with NMS additive started cracking (Fig 7). The samples without NMS and the ones with the opoca additive did not crack. The samples immersed in an aggressive solution after keeping them for about 360 days did not crack either. Therefore it is important to improve the frost resistance of the concrete, which included silica fume.

The decreased concrete resistance to frost, when the silica fume additives are employed, is most probably depends on “fresh pumilation” phenomenon that requires additional investigation.
dried in 110 °C temperature). Other X-ray diffraction patterns did not show it (Fig 8).

The Portland cement samples with 30–50 % opoca additives remained in the best state. In their X-ray diffraction patterns the gypsum peaks has not been discovered. However, the samples with 10 % CaCO₃ and 5 % NMS got decayed. The same happened with the samples having no CaCO₃, but including 15 % NMS. Their XRD patterns showed the peaks of both Ca(OH)₂ and CaSO₄·2H₂O (Fig 8).

The samples with 10 % CaCO₃ and 15 % NMS did not decay. Thus the results of the XRD research allow the conclusion that the main destructive factor of the concrete in Na₂SO₄ solution is the formation of the secondary gypsum:

\[ \text{Ca(OH)}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} + 2\text{NaOH}. \]

Gypsum may form when the solution includes free Ca(OH)₂, because Ca(OH)₂ in solution Na₂SO₄ increase and soluble gypsum decrease. Obviously, free Ca(OH)₂

![Fig 8. XRD patterns of cement stone samples exposed for 3 years in 5 % Na₂SO₄ solution.](image)

1 – 85 % CEM I 42.5 + 10 % CaCO₃ + 5 % NMS; 2 – 75 % CEM I 42.5 + 10 % CaCO₃ + 15 % NMS; 3 – 70 % CEM I 42.5 + 25 % NMS. G – bassanite, C – Ca(OH)₂, K – calcite, Q – quartz.
is tied by active amorphic SiO$_2$ that is found both in opoca and silica fume.

4. Conclusions

1. When mixing acrylic latex, cement, fillings, and the relaxing additives in respective raiusious, elastic, flexible, and well adhering to the concrete mortars are produced. They may be used for the repairing and protection of the concrete and reinforced concrete constructions. The extension of the mortar layers as well as their tensile strength and the strength of adhesion to the concrete can be controlled with the change of the amounts cement and plasticiser.

2. Silica fume and the Stoniškių carbonate opoca additives increase the resistance of ordinary Portland cement concrete to sulfate corrosion. The effectiveness of anti-corrosive additives depends on their origin, activity, and amount of the additives. When the amount of cement exceeds 400 kg/m$^3$, greater amount of hydraulic additive (20–30 %) is required.

3. The opoca additive guarantees a stronger sulfate-resistance of Portland cement concrete than a certain amount of the CaCO$_3$ and silica fume mixture. This fact could be explained by the greater activity of opoca. The activity of silica fume may be increased by fining, ie mixing it with a coarse filling.

4. The fastening method of determining the potential activity of silica fume and other hydraulic additives has been prepared.

5. On the basis of experiments, the conclusion can be made that in the hardening concrete silica fume and the other hydraulic additives react with Ca(OH)$_2$ derived from the cement. As a result, in the hardening concrete the amount of free lime decreases and less secondary compounds are formed. The XRD patterns of the decayed samples demonstrate the peaks of gypsum, and Ca(OH)$_2$. The formation of gypsum makes the chief reason of the concrete decay.

6. The NMS additive may become the reason of the decrease of the concrete resistance to frost. The frost resistance of the concrete that hardens for a longer time period (the testing encompassed a full year) increases.

References

1. The possibility of polymer resins for concrete and reinforced concrete structures (Приложение полимерных смол в бетонных и железобетонных конструкциях). Contribution to the USSR conference. Vilnius, 1971. 168 p. (in Russian).

2. Chandra, S.; Fladin, P. Interaction of polymers and organic admixtures on Portland cement hydration. *Concrete and Concrete Research*, 1987, Vol 17, p. 875–890.

3. Curbuzgen, R.; Diligres, P. Dispersion polymeric powder – peculiarity of behaviour in dry constructional mixture. *Building Materials* (Строительные материалы), 1999, No 3, p. 10–12 (in Russian).

4. Evdokimov, A. Dry water diluting latexes for constructional materials and paints. *Building Materials* (Строительные материалы), 1999, No 11, p. 20–21 (in Russian).

5. Ganesh Babu, E.; Surya Prakash, P. V. Efficiency of silica fume in concrete. *Concrete and Concrete Research*, 1995, Vol 25, No 6, p. 1273–1283.

6. Durekovic, A. Cement pastes of low water to solid ratio: an investigation of the porosity characteristic under the influence of a superplasticiser and silica fume. *Concrete and Concrete Research*, 1995, Vol 25, No 2, p. 365–375.

7. EN 1504 Parts 1–10. Products and systems for the protection and repair concrete structures.

8. EN 1542, 1543, 1766, 1767, 17799, 12188, 12189, 12190. Products and systems for the protection and repair concrete structures – Test methods.

9. Smetonaitė, E. Investigation of repair of mortar concrete constructions. *Materials Science* (Материалы), 2000, Vol 6, No 6, p. 72–75.

10. Cherkinsky, E. Polymer-cement concrete (Полимерно-цементный бетон). Moscow, 1984, 213 p. (in Russian).

11. Ramachandran, V. S. Concrete admixtures (Добавки в бетон). Moscow: Strojizdat, 1988, p. 298–381.

12. Vektoris, B.; Vilkas, V. The influence of silica fume on Portland cement hardening and concrete properties. *Chemical Technology* (Химичное технологии), 1999, No 2 (11), p. 60–64 (in Lithuanian).

13. Alekseev, S.; Ivanov, F.; Modry, S.; Shissl, P. Durability of reinforced concrete in aggressive media (Долговечность железобетона в агрессивных средах). Moscow, 1990. 93 p. (in Russian).

14. Vektoris, B.; Vilkas, V. Investigation of silica fume activity. *Materials Science* (Материалы), 2001, Vol 7, No 2, p. 123–126.

15. Li, G.; Le Bescop, P.; Morranville, M. Expansion mechanism associated with the secondary formation of the U phase in cement-based systems containing high amount of Na$_2$SO$_4$. *Cement and Concrete Research*, 1996, Vol 25, No 2, p. 195–201.

16. Smetonaitė, E. The influence of modified coatings for repair concrete constructions. *Materials Science* (Материалы), 2002, Vol 8, No 1, p. 109–111.

17. Zelić, J.; Krstulović, R.; Tkalečec, E.; Krolo, P. The properties of Portland cement – limestone-silica fume mortars. *Concrete and Concrete Research*, 2000, Vol 30, p. 145–152.

18. Kaminskas, R.; Vektoris, B. The influence of carbonate opoca on Portland cement hardening and properties. *Chemical Technology* (Химичное технологии), 1999, No 2 (11), p. 65–74 (in Lithuanian).

19. Kakali, S.; Tsivilis, E.; Aggeli M. Bati. Hydration Products of C$_3$A, C$_3$S and Portland Cement in the Presence of CaCO$_3$. *Cement and Concrete Research*, 2000, Vol 30, No 7, p. 1073–1077.