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A Study of Metal-Cement Composites with Additives

Victor Mironov[1], Ina Pundiene[2], Alexey Tatarinov[3], Janis Baroninsh[4],
[1,3,4]*Riga Technical University*, [2]*Vilnius Technical University*

Abstract – **The application of small-sized metal fillers (SMF) provides a combination of high bulk density, increased durability and ferromagnetic properties of composite materials on the cement basis. However, the total strength of the composite can be compromised by poor adhesion of metal particles with the cement matrix. The use of versatile additives like microsilica and metakaolin is able to improve the structural integrity and mechanical properties of heavy concretes. The paper considers the results of a study using specimens of heavy concretes with SMF aiming to estimate its strength, structural features and ultrasonic parameters. It was found that the contact of SMF particles with the cement was not perfect, since the voids appeared between them and the cement matrix during the cement hydration process (exothermal reaction). Due to the border porosity, the specimens with the metal fillers have lower compressive strength, lower ultrasound velocity and increased frequency slope of attenuation. Microsilica and metakaolin additives facilitate better contact zone between the cement matrix and metal fillers.**

Keywords **– Additives, metal fillers, metal-cement composites, strength, ultrasonic testing.**

I. INTRODUCTION

Heavy concretes (HC) with a density of 4 g/cm^3 and above [1] are used for the manufacture of ballasts and preloads in seaport construction, for floating oil and gas platforms, safety elements of subsea pipelines, soil stabilization, protection from electromagnetic exposure, etc. Metalworking waste products can be used as the metallic fillers in HC to provide high density and high wear resistance. High barrier properties against electromagnetic fields in HC are obtained by introduction of special fillers with high content of iron (35 % – 70 %), such as barite, ilmenite, magnetite and hematite [2]. Particularly heavy concretes with a density of more than 5.0 g/cm^3 intended for protection against radioactive and electromagnetic interference [3] contain metal slag with chromium and lead, as well as ferrochrome, ferrosilicon, ferro-phosphorus and boron containing materials.

Due to the high cost of HC products with natural aggregates, the use of metal waste is of increasing interest. The rational use of metal waste is also an important area of the environment protection. Research of new building materials with iron waste, in particular, perforated steel tape, percussion caps, dust waste from filters and metal powders [4–6] have shown the feasibility of its use in HC. Portland cement, pozzolan, slag and aluminate cements can be used as a binder [7]. Positive factors are low price, the possibility of effective utilization, as well as obtaining products with new properties. However, the use of waste results in deterioration of material quality in some cases. In this regard, it is necessary to develop the optimum compositions of HC and control the properties by versatile techniques.

Metal-cement composites with small-sized metal fillers (SMF) have a high wear resistance, high temperature resistance and low shrinkage. However, it is difficult to fully eliminate the shrinkage and cracking on the boundary of cement and metal fillers [7]. In addition, SMF presents work complications because of difficulties to mix and to lay, as well as due to the problems of lamination of the concrete mix. Different types of SMF were considered [8]. SMF partially replace sand and effectively increase density [8]. However the increase of SMF content in concrete reduces the concrete's strength and the sediment cone. Presumably, total strength of the composite may be reduced because of poor adhesion of metal with cement. To increase the strength by improving the quality of contact zone of fillers with cement matrix, special additives including those at nano-scale, such as superplasticizers, silica fume, metakaolin, microsilica should be used [6].

Mechanical properties of composite materials can be evaluated non-destructively [9]. In particular, ultrasonic measurements can be effective to assess presence of pores, accumulation of micro-defects and uniformity of volume. Recent studies showed that not only ultrasound velocity, but other ultrasonic parameters such as quality factor can be sensitive in revealing accumulation of micro-cracks in

TABLE I
COMPOSITION OF CONCRETE SPECIMENS

Type of concrete	Components given in weight parts (PC – Portland cement, G-gravel, SMF – small-sized metal fillers, W/C –water-to-cement ratio, MS, MK, SP, N – additives (see in text))							
	PC	G	Sand	MS	MK	SMF	SP	N	W/C
K	1.0	3.95	1.65				0.015		0.55
KMP	1.0	1.00	0.65			3.95	0.015		0.62
KS	1.0	1.00	0.47	0.185		3.95	0.015		0.54
KSMK	1.0		0.28	0.185	0.185	3.95	0.015		0.55
MN	1.0		1.65			3.95	0.015	0.00005	0.52

concretes [10]. Meanwhile, there is a lack of such data on HC with SMF.

The aim of this study was to evaluate the effect of SMF and several additives on the strength of HC specimens, as well as to evaluate the usefulness of ultrasonic measurements to control HC properties by a non-destructive way. The images obtained by optical microscopy should show the specific fracture surfaces of specimens of different composition and adhesion of SMF with the cement matrix.

II. Materials and Methods

SMF in HC specimens were steel waste from stamping driving chains in the company JSC “DITTON Driving Chain Factory” (Latvia). SMF had the shape of a disk with a diameter of 3.0 mm – 5.8 mm, a height of 1.03 mm – 2.3 mm and a density of 7.8 g/cm^3. Portland cement CEM I 42.5 N (PC) was used to make the mixture. The additives were microsilica (MS), metakaolin (MK), nano-microsilica (N), the additive MS (RW-Fuller, RW-Silicium) comprising SiO2 (98 %) and Fe2O3 (up to 0.05 %), the additive MK (Centrilit NC, Bauchemie), where SiO$_2$ content was not less than 50 % and Al2O$_3$ – not more than 45 %, the additive N with SiO$_2$ not less than 99.9 % with a mean particle diameter of 12 nm. For the preparation of concrete mix, large filler (gravel fraction 4/8) and small filler (sand fraction 0/4) and superplasticizer (SP) (Glenium 440, BASF) were used. The composition of the HC specimens is shown in Table I.

Concrete mixtures were prepared in a planetary mixer and kept for 1 day in molds at a temperature of 20 °C ± 2 °C and a humidity 95 % ± 5 %, and further under ambient conditions at a temperature 20 °C ± 2 °C and a humidity 65 % ± 5 % in order to avoid corrosion of SMF. The composition of K group (concrete without SMF) was prepared for comparison with the compositions KMP, KS, KSMK, and MN, where gravel and sand have been partially replaced by SMF, S, MK and N.

Specimens were sized 40 mm x 40 mm x 40 mm. This relatively small size of specimens was caused by deficiency of additives amounts for all specimens, on the one hand, and permissible ratio of the greatest filler equal to 45.8 mm to the overall size of the specimen to be ~1:7. Tests were conducted at the age of 7 days, 28 days and 6 months. Number of specimens in each group was 4 for final ultrasonic and strength examination and 12 accounting intermediate tests on the 7th and 28th days.

Ultrasonic (US) testing of samples was carried out in 6 months after manufacture. US measurements were performed by through transmission with coaxial positioning of the emitting and receiving transducers (Fig. 1). The data acquisition unit comprised a waveform generation unit (140 V p-t-p) and a receiving amplifier/digitizer (30 MHz sampling rate, 10-bit). The measurements were made in 3 locations by the height of the specimens, where the top and bottom of the specimens were determined by the position during the hardening and in two 2 planes as shown in Fig. 1. Two ultrasonic characteristics were determined: velocity of propagation of bulk longitudinal waves and frequency attenuation coefficient.

Ultrasound velocity was measured by means of a pair of transducers with piezoelectric elements of the plate type at a frequency of 300 kHz, emitting and receiving ultrasound by the edges of the plates with the contact surface of 18 mm x 1 mm, oriented horizontally. The excitation pulse contained 2 periods of sine, enclosed in the envelope of the Gaussian function. US velocity was calculated by the formula: $C = L / (t - dt)$, where L is the width of the specimen at the measurement place, t is the time-of-flight of US pulse, dt is the transducer’s constant sensors, defined on the zero base.

Frequency attenuation coefficient (α) was determined by the results of the spectral processing of frequency sweeping signals in a range from 100 kHz to 600 kHz (total length of sweep was 0.5 ms) as the ratio of ultrasonic attenuation at low and high frequencies. The sweep signals were received by a pair of broadband transducers having multiple operating frequencies expressed in the mentioned range. Processing of sweep signals and determining α included the following steps: a) construction of the frequency spectra of the sweep signals using the fast Fourier transform; b) normalization of the spectra by the amplitude-frequency characteristic of the transducers in a reference liquid with low attenuation (distilled water); c) measurement of the amplitude of normalized spectrum at 6 selected frequencies from 100 kHz to 600 kHz with a 100 kHz step; g) calculation the coefficient α as the ratio of the amplitudes sum at low frequencies (100 kHz – 300 kHz) to the same at high frequencies) (400 kHz – 600 kHz): $\alpha = A_{N(1,2,3)} / A_{N(4,5,6)}$, wherein $A_{N(1,2,3)}$ and $A_{N(4,5,6)}$ are the amplitudes sums at 100 kHz, 200 kHz, 300 kHz and

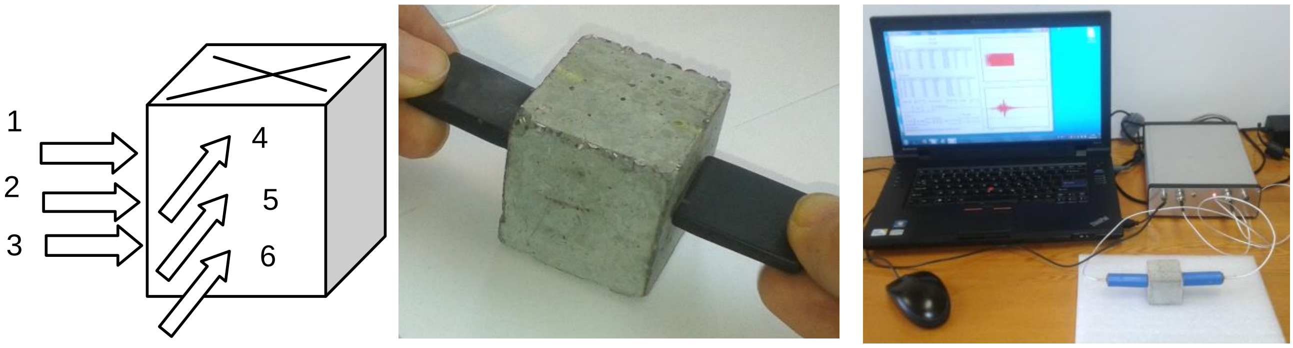

Fig. 1. Illustrations of US testing: directions of through transmission (left); application of transducers (middle) and acquisition setup (right).

400 kHz, 500 kHz, 600 kHz, correspondingly. Thus, the higher is α, the stronger is ultrasound attenuation at high frequencies in relation to attenuation at low frequencies. In our case, coefficient α is a dimensionless value.

Reproducibility of US measurements was within ±30 m/s – 40 m/s for ultrasound velocity and within ±1.2 – 0.7 for α as measured by the standard deviation in repeated measurements ($n = 12$) in the same point during removal and restoration of acoustic contact.

The compression strength was defined according to the requirements of the standard LVS EN 12390-3:2009 using press testing machine “Controls” 50-C56G2. The specimens were loaded with a constant speed within the range from 0.2 MPa/s to 1.0 MPa/s until the maximum force was achieved before the specimen’s failure. The compression strength was calculated as the ratio of the maximum force to the specimen’s cross-sectional area multiplied by a scaling coefficient.

To evaluate the quality of SMF adhesion with cement in fracture surfaces of specimens of different composition an optical microscope Keyence VHX 2000 was used. This computer controlled microscope is equipped with a camera with a resolution of 54 megapixels and moved in *x*, *y*, *z* axes. The specimens were first tested for compressive strength and then fracture surface characteristics were studied at 500-fold magnification. The surface topography and the size of voids were assessed using two-dimensional (2D) images, and the relief of the fracture surfaces was quantified by three-dimensional (3D) images, in which different heights were coded by color.

III. RESULTS AND DISCUSSION

The results of compression tests at the specimens’ age of 7 days (Fig. 2) revealed lower compressive strength to 20 %–30 % in concretes with SMF additives (KMP, MN, KS) comparing to control group K. Meanwhile, the combined use of additives MS and MK allowed achieving higher strength of 40 MPa that 7 MPa exceeds the strength of the specimens of K group. At the age of 28 days, HC specimens of compositions. KS and KSMK with MS additive reached the highest compressive strength, 46 MPa and 50 MPa. Meanwhile, these specimens of KS and KSMS groups with microsilica also showed the highest deviation within the group data (Table II) that was probably caused by their increased structural heterogeneity.

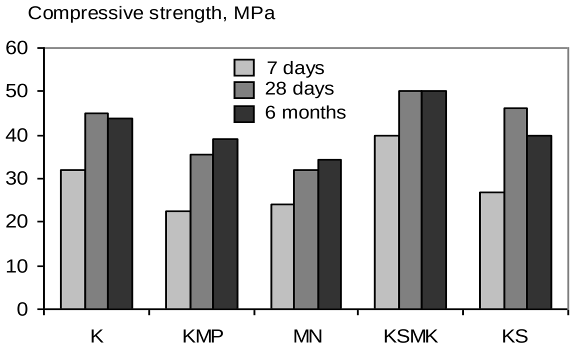

Fig. 2. Compressive strength of K, KMP, MN, KSMK and KS specimens at the age 7 days and 28 days and 6 months.

Averaged data for the density and ultrasonic parameters in the specimens groups at the age of 6 months are presented in Table II. Composites with cement and SMF conjunction having additives MS, MK, N possess sufficiently higher density (from 3.86 g/cm^3 to 4.18 g/cm^3) as compared to control group (2.30 g/cm^3). Introduction of MS and MK reduces the density, while addition of N increases the density of the specimens. That may be due to the use of additives of N allowing achievement of a lower W/C ratio (0.52) of the concrete mix.

The results showed weak expression of the dependence of ultrasound velocity on the density upon all the specimens and almost complete lack of correlation with compressive strength. The Pearson linear correlation coefficient was −0.73 and 0.10, respectively. Negative correlation with density is explained by the inverse relationship between the velocity and density at the similar elasticity modulus. Samples of K have a much higher US velocity than the samples with metal fillers, the density of which is almost two-fold higher than in group K. It is noteworthy that the content of metal − steel washers, US velocity in which is approximately 5,900 m/s, does not cause an increase in the US velocity in the composite samples on the additivity principle. This gives a reason to believe that the structure factor and, in particular, the quality of the cement bond with the metal and the possible presence of void spaces between cement and metal particles is the determining factor.

Coefficient α can serve to characterize the structural uniformity. As seen in Table II, coefficient α is the lowest in group K and substantially increases in composite specimens

TABLE II

AVERAGE DENSITY AND ULTRASONIC (US) PARAMETERS OVER GROUPS OF SPECIMENS

Type of concrete (specimen group)	Density, g/cm^3	Compressive strength, MPa	US parameters	
			Velocity C, м/c	Frequency attenuation coefficientα
K	2.30 ± 0.02	44.2 ± 5.3	4100 ± 79	2.6 ± 1.0
KMP	3.93 ± 0.07	39.3 ± 2.4	3104 ± 176	3.8 ± 2.5
MN	4.18 ± 0.06	34.0 ± 4.8	2969 ± 62	3.7 ± 2.5
KSMK	3.86 ± 0.03	50.4 ± 8.5	2741 ± 131	7.7 ± 2.4
KS	3.92 ± 0.04	40.9 ± 8.2	2652 ± 203	11.5 ± 8.0

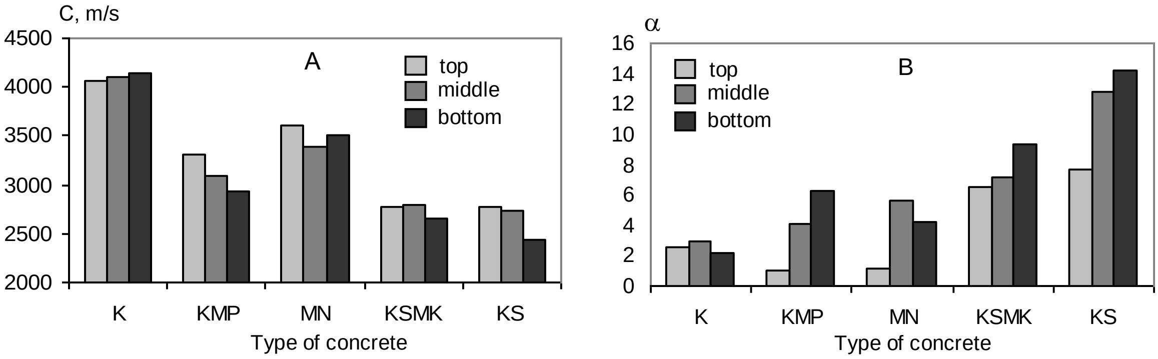

Fig. 3. Distribution of US velocity C (A) and frequency attenuation coefficient α (B) by specimens' height in different concretes.

with SMF and additives. Fig. 3 shows the distribution of US velocity C and coefficient α by the specimens' height in all examined groups. In the specimens containing metallic fillers, US velocity C is reduced in the lower third of the height (Fig. 3a), where metal filler concentration was increased due to sedimentation during hardening. The obtained spatial gradient of ultrasound velocity in specimens with SMF is much more pronounced that the same in common heavy and light cements, typically not exceeding 3 % [12]. The same effect with opposite trend was shown for coefficient α (Fig. 3b). Coefficient α increases sharply from the top to the bottom of the specimens with increasing concentration of the filler metal. In group K containing no SMF, this gradient does not exist. It is noteworthy that the absolute values of α is higher in groups KSMK and KS, where filler MS presents in addition to the metal filler and leads to an increased US attenuation at high frequencies. Meanwhile, the relative changes of α by the specimens' height are the largest in groups KMP and MN. It can be assumed that the drastic increase in these changes of α there is due to appearance of void spaces around the metallic fillers acting as additional effective scattering elements. This assumption is confirmed both by microscopy observations of fracture surfaces and reduced compression strength of these specimens as compared with others.

Microscopy images of the fracture surfaces in specimens of different compositions allow us to estimate quality and characteristic features of the SMF particle adhesion with cement, examples of which are shown in Fig. 4. On the surface of a specimen from K group, large pores with sizes ranging from 38.9 to 44.4 micrometers can be observed on the background of cement matrix. In a KMP specimen, smaller pores than in K (the largest size is 33.6 micrometers and a SMF particle positioned obliquely are observed). By means of computer software changing the direction of the virtual lighting, one can allocate voids formed between SMF particle and cement matrix. We assume that these voids are formed during hydration that is an exothermic reaction of cement, when the SMF particle initially heats and expands and then contracts with decreasing temperature. Perhaps, these voids can be a cause of the decreased compressive strength in the specimens with SMF. On the surface of a specimen from KSMK group, grain structure with a plurality of different void sizes (largest to 97.9 μm – 300 μm) was noted. The contact between the SMF particle and the cement matrix, in this case seems better than in that of KMP: the matrix adheres tightly to the SMF particle.

Traces of corrosion are present on the SMF particle surface, which indicates the presence of a reaction between the metal and MS. Then the highest mechanical strength in KSMK specimens can be explained by better interaction between the metal and cement components and by absence of void spaces between them, probably due to MS action.

IV. CONCLUSION

1. The use of small-sized metal particle as fillers reduced the compressive strength of heavy concrete specimens to 30 % as compared to control specimens without small-sized metal particle filler. Used in conjunction with small-sized metal particle, MS and N additives allow mitigation of this reduction to 20 %. The combined use of additives MS and MK increases the strength of specimens with small-sized metal particle to the value exceeding. These results indicate imperfect contact between the metal particle and the cement matrix in specimens with small-sized metal particle and possibility to improve it by using complex additives.

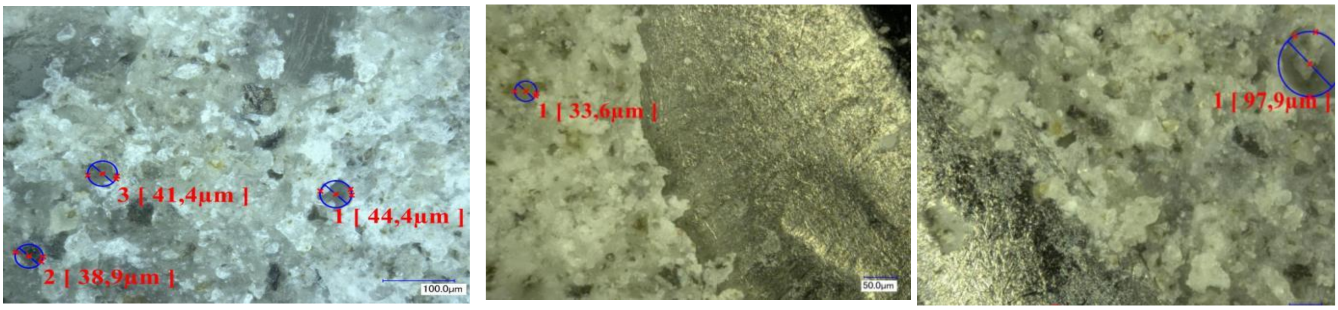

Fig. 4. Images of fragments of fracture surfaces in specimens from groups K (left), KMP (middle) and KSMK (right).

2. Small-sized metal particle fillers (steel washers and additives) affect parameters of ultrasound propagation in a sophisticated manner. US velocity in denser specimens with metallic filler is lower than in the control specimens without small-sized metal particle. US velocity and the compression strength of concrete with small-sized metal particle and additives do not correlate with each other, which is possibly due to complex interaction of metal, cement and additives, as well as by appearance of multiple microscopic voids between metal and cement during manufacturing of concretes with small-sized metal particle. It is found that the US method can be successfully used to assess the structural heterogeneity of heavy concretes, using gradients of US velocity and frequency attenuation coefficient by the specimen. Frequency attenuation coefficient can be an effective measure to check uniformity of the particle distribution in the volume of heavy concretes with small-sized metal particles. It is also potentially informative about the origin and amount of voids between the matrix and fillers.

3. Observation of the fracture surfaces by optical microscopy showed the presence of voids between small-sized metal particles and cement matrix. These voids are formed in the process of hydration of cement or exothermic reaction, causing gradual expansion and contraction of the metal at the sudden change of temperature. It is assumed that the voids may cause reduced strength of the specimens.

REFERENCES

[1] *DIN 1045-3 Tragwerke aus Beton, Stahlbeton und Spannbeton*. Teil 3: Bauausführung, Ausgabe 2001, pp. 7.

[2] I. B. Topçu. “Properties of heavyweight concrete produced with barite.” *Cement and Concrete Research*, vol. 33 (8), pp. 815–822, 2003. http://dx.doi.org/10.1016/S0008-8846(02)01063-3

[3] C. Basyigit. “The physical and mechanical properties of heavyweight concretes used in radiations.” *Journal of Applied Sciences*, vol. 6, pp. 762, 2006. http://dx.doi.org/10.3923/jas.2006.762.766

[4] V. Mironovs, J. Bronka, A. Korjakins, J. Kazjonovs. “Possibilities of application iron containing waste materials in manufacturing of heavy concrete,” in: *Proc. Civil Engineering '11: 3rd International Scientific Conference*, 2011, pp. 14–19.

[5] S. Puzirevskis, V. Mironovs. “Heavy weight concrete and its usage,” in: *Proc. 8th Int. Conference MET-2013: Materials, Environment, Technology*, 2013, pp. 108–110.

[6] I. Pundienė, V. Mironovs, A. Korjakins, E. Spudulis. “Investigation of hydration features of the special concrete with aggregates of various metal particles,” *Key Engineering Materials*, vol. 604, pp.297–300. 2014.

[7] P. K. Mehta, M. J. P. Monteiro. *Concrete Microstructure, Properties and Materials*. New York: McGraw-Hill, 2006. pp. 647.

[8] J. Kazjonovs, D. Bajare, A. Korjakins. “Designing of high density concrete by using steel treatment waste,” in: *The 10th International Conference Modern building materials, structures and techniques*, 2010, pp. 138–142.

[9] T. H. Panzera, A. L. Christoforo, F. P. Cota, P. H. R. Borges, C. R. Bowen. “Ultrasonic Pulse Velocity Evaluation of Cementitious Materials,” in: *Advances in Composite Materials – Analysis of Natural and Man-Made Materials*, INTECH Open Access Publisher, 2011. [Online]. Available: http://cdn.intechopen.com/pdfs-wm/18861.pdf [Accessed: Oct. 15, 2014].

[10] J. Rhazi S. Kodjo. “Non-destructive evaluation of concrete by the quality factor,” in: *Int J Phys Sc*, 2010, vol. 5(16), pp. 2458–2465.

[11] *BS EN 12390-3:2009 Testing hardened concrete.* Compressive strength of test specimens, 2009.

[12] T. Ozturk, O. Kloggel, P. Grubl. *Propagation of ultrasound in concrete – Spatial distribution and development of the Young’s modulus*. BB 85-CD Intern. sympos. Non-Destructive Testing in Civil Engineer-ing. Berlin: 2003. Available: http://www.ndt.net/article/ndtce03/papers/v065/v065.htm [Accessed: Oct. 14, 2014].

Victor Mironov, *Dr. habil. sc. ing.*, Head of the Laboratory of Powder Materials, Professor in Dept. of Building Production of Riga Technical University, Institute of Building Production.
He graduated from Kalinin (Tver) Polytechnic Institute, Russia, with qualification of mechanical engineer (1965). Scientific degrees were obtained at Riga Technical University (Riga, Latvia) in Materials Engineering (1972), *Dr. sc. ing.*, and at the Institute of Fine Chemical (Moscow, Russia, 1986), *Dr. habil. sc. ing.* Scientific traineeship was done at Chalmers Technical University (Goteborg, Sweden), Technical High School (Zwickau, Germany), Dresden Technical University (Germany), Minsk Polytechnic Institute (Belorussia) and Linkoping Technical University (Sweden). Since 1972, he works at Riga Technical University as a senior researcher and a senior lecturer. Total number of scientific papers is more than 250, including 10 books. He is an Honored Inventor of Latvia since 1982 with 151 invention certificates and patents. Scientific interests include technology of powder metallurgy, materials processing in pulse magnetic fields, use of metal waste products in composite building materials.
Address: Azenes Street 16/20, LV-1048 Riga, Latvia.
E-mail: viktors.mironovs@rtu.lv

Ina Pundiene, PhD, a senior researcher at the Laboratory of Building Products Technology in Vilnius Gediminas Technical University, Scientific Institute of Thermal Insulation since 2000, graduated from Riga Technical University (Latvia) with engineering qualification in ceramics and chemical technology of refractory materials (1985) and obtained PhD degree in Technological Sciences in Materials Engineering (2000). Since 2009, she runs Technical Committee TC 58 (Refractory materials) in Lithuanian Standardization Department. Since 2012, she participates in the Lithuanian national project “Creation of energy-saving materials, research and application in building structures” (Project No. 07/2012 ATE). Current research interests are: refractory materials, composite materials, durability of building materials, binding materials.
Address: Linkmenu Street 28, LT–108217 Vilnius, Lithuania.
E-mail: ina.pundiene@vgtu.lt

Alexey Tatarinov, *Dr. sc. ing.*, a researcher at the Laboratory of Powder Materials, Riga Technical University, Institute of Building Production. He graduated from Riga Technical University with engineering qualification in civil and industrial engineering (1980) and obtained PhD degree in Latvian Traumatology and Orthopedics Institute (1989) in biomechanics. From 1996 to 2010 he worked as a researcher and invited scientist at Riga Technical University, Martin-Luther University Halle-Wittenberg (Germany), Artann Laboratories (NJ, USA). He participated in a series of research projects funded by NIH SBIR, DoD SBIR, NASA and ESA programs devoted to R&D in the areas of ultrasonic testing, bone and muscle research and biomedical engineering. Current research interests are: application of ultrasound in NDT and materials characterization, including biomaterials and biological tissues, use of ultrasonic surface and guided waves, assessment of porosity and structural integrity of materials.
Address: Azenes Street 16/20, LV-1048 Riga, Latvia.
E-mail: aleksejs.tatarinovs@rtu.lv

Janis Baroninsh, *M. sc. ing.*, post-graduate student at Riga Technical University (Latvia), graduated from RTU, Faculty of Materials Science and Applied Chemistry with engineering qualification in chemistry and MBA (2014).
In 2006–2013 he worked as a laboratory assistant in HC Betons and Riga Technical University and as a quality manager in Arcers Ltd. Currently he is working in a research project devoted to mineral-based self-adaptive tribology material in Tallinn University of Technology. His research interests are focused on new composite materials.
Address: Azenes Street 20, LV-1048 Riga, Latvia.
E-mail: janis.baronins@rtu.lv