CONSTRUCTION AND MATERIALS

PROPERTIES AND COMPOSITION OF CONCRETE CONTAINING DIVERSE POZZOLANIC ADMIXTURES

Genady Shakhmenko[*] Asist Prof. Dr.sc.ing., **Diana Bajare**[*], Assoc Prof. Dr.sc.ing.**, Inna Juhnevica**[**], Leading researcher. Dr.sc.ing, **Nikolajs Toropovs*,** PhD student, **Janis Justs**[*]**,** PhD student, **Aljona Gabrene**[**]**,** PhD student
[*] Riga Technical University, Faculty of Civil Engineering, Institute of Materials and Structures
[**] Riga Technical University, Faculty of Material Science and Applied Chemistry, Institute of Silicate Materials
Address: Kalku Street 1, Postal index LV–1658, Riga, Latvia
Phone: 371+29160832, e-mail: genadijs.sahmenko@rtu.lv

ABSTRACT

Micro-sized particles are used in modern concrete technology as a part of multi-component cementitious systems. Adding of micro-filler admixtures improves the properties of both fresh and hardened concrete. Local and commercially available micro-fillers were used in this research: dolomite powder, microsilica, calcined local (illite) clay and calcined kaolinite clay. Firstly, the basic micro-filler properties were studied, such as particle size distribution, particle morphology, specific surface and content of reactive components. The second experimental part covered production of fine-grained mixes, sample curing and testing. Compressive strength and water absorption were tested. Mineral formation processes were investigated using X-Ray analysis and IR spectroscopy.

As a result, it is concluded that the main factors, which determine the effectiveness of admixture, are pozzolanic reactivity, particle grading and morphology. The most effective fillers in this research were silica fume and calcinated kaolinite clay. Results for dolomite fillers were the same as for the inert fillers. Addition of local calcined illite clay improved tested concrete properties; consequently other locally available clay materials should be investigated more specifically as potential pozzolanic materials in future.

Keywords: Calcined clay, pozzolanic admixture, High performance concrete.

INTRODUCTION

The task of modern concrete industry is producing durable and sustainable concrete. It means: a highly workable concrete mix, stable and predictable properties of hardened concrete, high durability and other high performance characteristics. Traditional concrete consists of cement and macroscopic aggregates - sand and coarse aggregate. Modern concrete is a multi-component composite material, its structure can be regarded in 3 levels: macro (sand and coarse aggregate), micro (cement, micro-fillers) and nano-sized modificators. Micro and nano elements compose cementitious system or cement paste. The current trend in concrete production worldwide is to use multi-component cementitious systems, which allows obtaining of high performance concrete with high durability (Presuel-Moreno, 2012). At the same time it contributes to the following ecological and economic benefits:

- to reduce clinker content (clinker is the most energy consuming component which is responsible for the majority of carbon dioxide emissions);
- to utilise industrial waste and by-products as mineral admixture;
- to minimize concrete price and transport charge.

Most often multi-component cementitious systems are obtained by combining cement with supplementary fine-graded materials (powders) having pozzolanic activity (Cook, 1980). The most popular pozzolanic admixtures are silica fume and fly ash. Pozzolanic reaction is a simple acid-based reaction between calcium hydroxide $Ca(OH)_2$ or CH and silicium acid H_4SiO_4 (Cook, 1986). As a result the calcium silicate hydrate (CSH) gel is formed that fills in pores and strengthens the cement matrix.

Authors (Sabir et al, 2001) emphasize that nowadays the term pozzolans has been extended to cover all siliceous/aluminious materials which react with calcium hydroxide (CH). Clay is among the natural hydrous siliceous/aluminious raw materials. Pozzolanic admixture can be obtained from clay with thermal treatment at 600-900^oC. Metakaoline is an aluminium silicate mineral ($Al_2O_3x2SiO_2$, or AS_2), it is considered as the most effective pozzolanic admixture obtained from clay after thermal treatment. Pozzolanic reaction between clay aluminium silicate AS_2 and CH forms additional aluminium containing CSH gel (Sabir et al, 2001). Some industrial wastes, for exapmle, fluid cracking

catalyst (FCC), may also be used as siliceous/aluminious pozzolanic admixture (Žvironaitė et al, 2011).
Kaoline clay is not among the natural resources available in the Baltic States. However, according to the experience of other countries, other types of local clay can be used as pozzolanic admixture of concrete after thermal treatment as well. It has been proved that carefully calcined marl (calcareous clay) can be transformed to a very effective pozzolan that can replace cement in mortar (Ostnot et al, 2011).
It must be noted that mainly one-component cement is used nowadays in the Baltic States for concrete production. The main reasons for this situation are lack of experience and absence of available local high quality pozzolans. The price of imported pozzolans, such is fly ash, is much higher than the price of cement.
This paper discusses the possibilities of using diverse locally available pozzolanic admixtures, including the ones obtained from local clay.
The basic properties of micro filler are its pozzolanic activity, grading and morphology of particles. Particles with high pozzolanic activity are more effective as they react with cement, but inactive micro fillers can improve particle packing and rheological properties of concrete mix (for example, dolomite powder; micro-filler obtained from crushed concrete waste (Finoženok, 2011)).
Micro fillers can be divided in three groups: based on natural materials, derived from industrial by-products and commercial products. The suggested scheme of classification is shown in Figure 1.

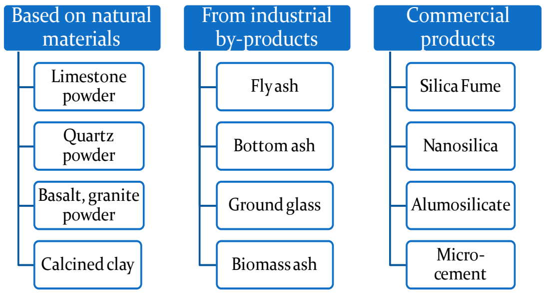


Figure 1. Classification of micro/pozzolanic admixtures

In this research the use of diverse pozzolanic admixtures, such as silica fume, dolomite powder (local material), calcined kaoline clay and local (illite) clay as part of two-component cementitious system, has been discussed.

METHODS

Investigation methods of micro admixtures

When preparing micro-filler admixtures it is important to examine them in detail as it allows one to assess the effectiveness of micro fillers and to eliminate possible consequences if micro fillers contain substances having a negative impact on the cement hydration process.
The basic properties and their assessment methods in this research are the following:
Grading (particle size distribution) was determined by Dynamic Light Scattering (DLS) method;
Specific surface was determined by BET method using nitrogen absorption;
Pozzolanic reactivity was estimated taking into account the content of active SiO_2/R_2O_3. The principle of this method is determination of content of amorphous oxide reacting with calcium hydroxide (product of cement hydration);
SEM (Scanning Electron Microscope) micro-scopy (Mira\LMU "Tescan") was used to determine real size and morphology of micro-particles.

Concrete preparation and testing methods

The effect of admixtures was estimated by testing specially prepared fine-graded concrete samples based on cement and quartz sand. The sample producing procedure included mix preparation, sample moulding and curing.
Raw materials were dosed by mass and mixed in the laboratory high shear mixer at a speed of 150 rotations per minute, total mixing time 4 minutes.
Standard samples (prisms) with the dimensions of 40x40x160 mm were produced from the concrete mix. After 2 days the samples were demoulded, then measured and weighted. Samples were cured in normal hardening conditions, ensuring the temperature at +20^{o}C and relative humidity not falling below 95%.
The testing program of hardened concrete samples included mechanical testing, water absorption testing and the physical study of hydrated products.
Mechanical properties were determined according to LVS EN 12390-3 Testing hardened concrete - Part 3: **Compressive strength** of test samples.
Density was determined according to LVS EN 12390-7 Testing hardened concrete - Part 7: Density of hardened concrete.
Water absorption was calculated taking into account: the mass of water saturated samples and the mass of oven-dried samples (105^{o}C during 48 hours).
Mineralogical composition of hardened specimens was investigated using X-Ray analyse equipment with Rigaku Optima Plus diffractometer and CuKα.
Hardening processes of cement paste was investigated using Fourier Transmission Infrared Spectroscopy (FTIS). The method is based on activating the molecules by means of infrared ray energy and recording the intensity curve after energy transmission through material. The character of absorbed energy curve depends on the nature of chemical bonds in the material. The method allows one to control the forming of functional groups and new chemical bonds. Average infrared wave range

2.5 – 25 μm (4000 – 400 cm^{-1}) was applied in this research.

MATERIALS USED

In the frame of this work the following micro powdered materials were applied as concrete admixture: dolomite powder (Saulkalne, commercially available), Silica fume (Elkem microsilica 971U, commercially available), Illite type local Latvian clay (deposit Liepa) and kaoline clay (commercially available). Chemical compositions of raw materials are summarised in Table 1. Clay materials were specially prepared (dried, calcined and ground) prior to use as a concrete admixture. The basic properties of used fillers were determined.

The target of clay thermal treatment is dehydration and decarbonation of clay minerals and the transformation of SiO_2 and R_2O_3 into amorphous oxides. In the process of thermal treatment, water of crystallization is released from the structure of clay and chemical bonds disappear. As a result, the material becomes chemically active and capable of reacting with free calcium hydroxide. By analysing the literature sources it can be concluded that the optimum calcination temperatures for clay - ranges from 600-800 ^{o}C (Ambroise, 1986). Chemically bonded water from the kaoline clay is mainly released at a temperature of 600°C, but for montmorillonite clay, the temperature range is higher, namely, 600-780°C (Bain, 1974). Kuršs (1972) has performed research on mineralogical changes of the Latvian clay during the thermal treatment process and has concluded that the mineral structure remains without significant changes up to 400 – 500ºC. At a higher temperature the release of water can be observed. For the kaolinite it is most intense at the temperature between 450 and 650ºC. By fast thermal treatment hydroxyl groups are released at high temperature.

Vertical shaft kiln and rotary kiln are usually used for calcination of clay materials.

Table 1

Chemical composition of raw materials (mass percentage)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O+K_2O	SO_3	LOI	Other
C	25.0	2.1	3.0	66.0	0.7	0.2	2.3		0.7
K	52.1	41.0	4.32	0.07	0.19	0.89		0.6	0.8
M	54.83	19.05	6.0	9.39	1.77	3.65	2.9	1.48	0.9
SF	92.0	0.7	1.2	0.2	0.2	2.0		3.0	0.7

C- Cement; K- Kaoline clay; M- Illite clay; SF-Silica fume

Clay preparing procedure in laboratory was the following:

Clay was broken into smaller pieces and dried at a temperature of 100^{o}C to remove free water. Then the clay was additionally ground before calcination to obtain a particle size of <5 mm.

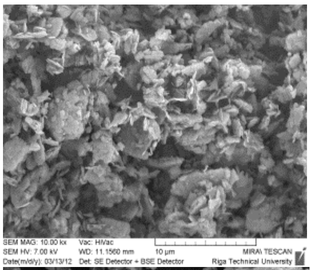
Clay calcination (burning) was done in a laboratory rotary kiln (diameter 70 mm, rotation speed 30 rpm) for about 15 minutes with designed temperature 700 ^{o}C.

After burning the material, it was ground in the laboratory planetary ball mill Retsch PM 400 for 15 minutes, providing a rotation speed of 300 rpms.

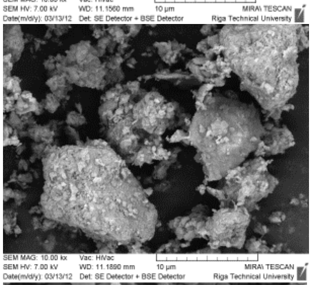
Estimating the environmental impact of using thermally treated clay, calcining energy consumption must be taken into account. It must be stressed that clay calcining requires much less energy (68 kJ/kg) than cement production (372 kJ/kg) (Cook, 1980). Additionally, this process is associated with significantly lower level of carbon dioxide emissions compared to cement production.

Grading and morphology

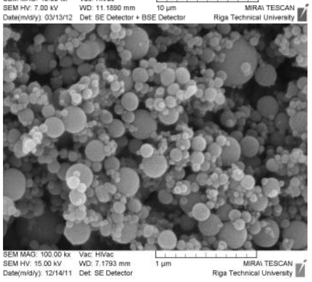
Particle size distribution and shape of particles are the basic parameters which determine rheological properties of mix and density of microstructural packing (Ulm and Acker, 2008). The shape of particles is an important parameter affecting the total specific surface and chemical reactivity.



Calcined Kaoline (metakaoline)
Shape of particles: irregular, flake-shaped, disperse packing



Calcined Illite llay
Shape of particles: irregular, flake-shaped, particle agglomerats (up to 1(μm)



Silica fume
Very fine material, shape of particles ideally rounded, wide range of sizes (20...450 nm)

Figure 2. SEM images and description of micro admixtures

Particle shape characteristics of used pozzolanic admixtures were investigated by means of a Scanning Electron Microscope, typical SEM pictures and particle characteristics are described in Figure 2. Basic characteristics of micro powdered admixtures and used cement are summarised in Table 2.

Particle size distribution (grading curves) of calcined clay and silica fume are summarised in Figure 3. It must be noted that the calcined clay materials (both matakaoline and illite) are characterised by an extremely high specific surface (more than 15 m^2/g), 2-3 times exceeding the specific surface value of silica fume. Particle size distribution curves (Figure 3) are characterized by narrow range of sizes (low polydispersity) and very small particle size (<1 μm), placing clay between silica fume and cement. However, the dimensions of metakaolin particle sizes mentioned in different literature sources range from 1 to 10 μm, Possible reasons for these differences might be the following:

1. DLS analysing system outputs particle sizes, which are reduced to spheres of similar volume. If the particles are thin and flake-shaped, their real dimensions (length) could be considerably bigger.
2. Coarse particles can be observed in the SEM images, which can be agglomerated fine particles. Performing DLS test agglomerates dissolved in water, but rough particle sedimentation can take place in an environment of water suspension. However, in this case small dimensions of calcined clay particles from the DLS test confirm the high value of the specific surface from the BET analysis (Tab.2).

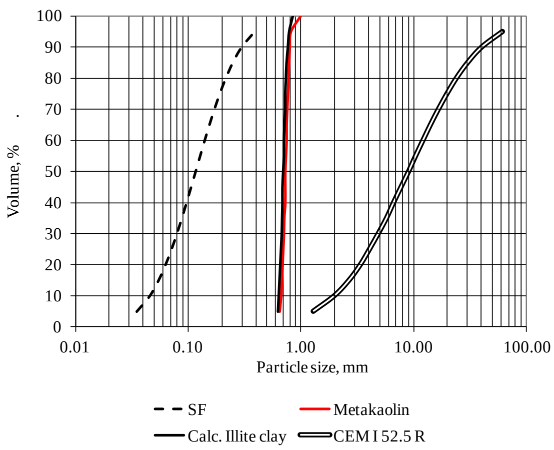


Figure 3. Particle size distribution

Table 2

Basic characteristics of used admixtures and cement

Powdered material	Effective particle size, □m	Specific surface (BET), m^2/g	Active SiO_2 and R_2O_3, %
Cement CEM I 52,5 R	40	0.45	
Dolomite powder	<...50	0.8	
Calcined illite clay	0.71	21.9	0.89 / 7.92
Calcined kaoline clay	0.74	16.5	1.10 / 32.76
Silica fume	0.3	7.92	>90/0

MIX DESIGN AND SAMPLE PREPARATION

White high-strength alite based cement CEM I 52.5R was used as a binding agent and pure quartz sand 0/1 mm was used as a filling agent. The experimental phase involved producing mix compositions replacing cement by different micro admixtures in the amount of 20% from the total amount of cement. The compositions of raw materials are summarised in Table 3.

All the mixes are characterised by homogenous and flowable consistence. Water content was provided constant for all mixes.

Table 3

Concrete mix composition

	K15	M15	D	SF	C
Cement CEM I 52,5 R	1	1	1	1	1.2
Sand 0/1 mm	2.64	2.64	2.64	2.64	2.64
Calcined kaoline clay	0.2				
Calcined illite clay		0.2			
Dolomite powder			0.2		
Silica fume				0.2	
Superplasticizer	0.01	0.01	0.01	0.01	0.01
Water	0.43	0.43	0.43	0.43	0.43

RESULTS AND DISCUSSION

Compressive strength and density

Concrete specimens were tested at the age of 7, 28 and 49 days of normal curing. The compressive strength results are summarised in Figure 4. Values of density of hardened specimens varied in range: 2140 – 2200 kg/m^3 for all mixes. Therefore it can be concluded that the deviation of density is insignificant and admixtures do not have a significant impact on density.

Summarizing compressive strength results: it may be said that the long-term hardening effect is related to composition based on calcined clay and silica fume. In addition, metakaoline (K15) composition results after 7 days of curing are similar to those of silica fume (SF) and cement without admixtures (CEM) composition, but at the age of 28 and 49 days, the compressive strength results of composition K15 are the highest, exceeding even the composition with silica fume. The lowest compressive strength results after 7 days are for composition D with dolomite powder, it increases and stabilises at the age of 28 and 49 days. Composition with calcined local metakaoline clay (M15) shows lower compressive strength results as composition CEM, but it increases after 28 days and continues to increase afterwards, becoming similar to the results of CEM, while 17% of the cement was replaced.

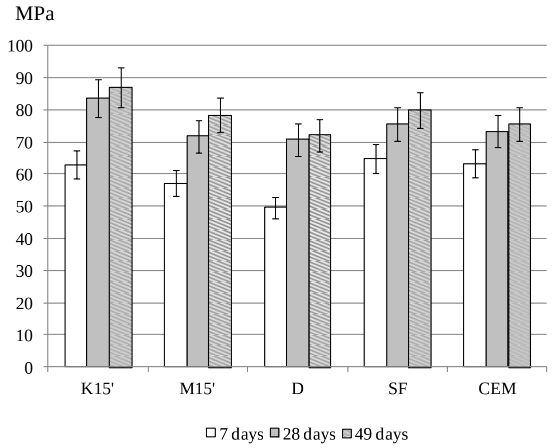


Figure 4. Compressive strength results: K15'- with metakaoline ground for 15 min., M15'- with calcined illite clay ground for 15 min, D – with dolomite powder, SF – with silica fume, CEM - cement without admixtures

Water absorption

Water absorption test provides information about open porosity of the material. Comparing water absorption results of different samples, the biggest water uptake values are indicated for mixes D (5.7%) and CEM (5.4%), which do not contain pozzolanic admixtures. The results are almost two times lower for the mixes containing silica fume and metakaoline (about 2%). Composition containing calcined illite clay also has quite a high value of absorption (4.9%), but the results are lower compared to compositions D and CEM. It indicates that the local clay have slight pozzolanic effect and microstructural packing capability of concrete. Water absorption data correlates with compressive strength results; the strongest compositions SF and K15 have the lowest values of water absorption.

X-ray diffraction analysis

X-Ray diffraction analysis was performed for concrete specimens after 28 days of curing. The results show the presence of mineral portlandite (Calcium hydroxide) in all samples. The biggest concentration of this mineral is indicated in samples CEM and D. Low content of portlandite is found in samples SF and K15 as well, this effect can be interpreted by the pozzolanic reactions (because silica fume and metakaoline are the most active pozzolans). Cement mineral hatrurite (alite) was found in samples CEM, D, K15, M15 and SF. The most typical X-ray diagrams (for mixes SF and D) are shown in Figures 6.

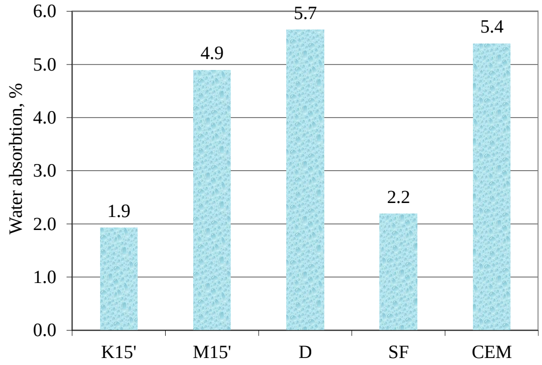


Figure 5. Water absorption results: : K15'- with metakaoline ground for 15 min., M15'- with calcined illite clay ground for 15 min, D – with dolomite powder, SF – with silica fume, CEM - cement without admixtures

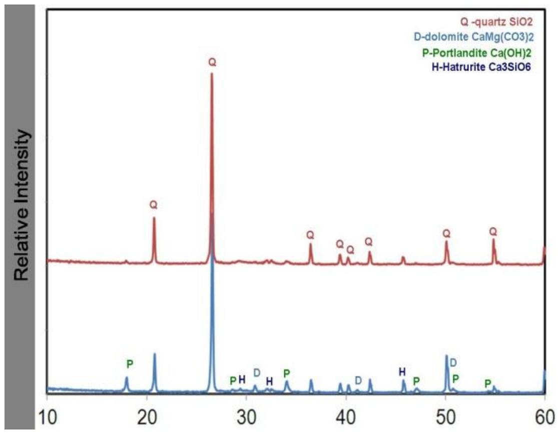


Figure 6. X-Ray diffraction results: mix D (below) with dolomite powder and mix SF (above) with silica fume

FTIS analysis

According to the results of the Fourier Transmission Infrared Spectroscopy (Fig. 7, 8) the following can be concluded:

- For samples with calcined clay (M15 un K15) infrared wave absorption is 671 cm^{-1} due to functional groups O-Al-O, which indicates the presence of aluminium containing CSH gel.
- Hydrated samples with dolomite (D) are characterised with infrared wave absorption in the range of 871 cm^{-1} and 1620 cm^{-1}, which corresponds

to fluctuations of C-O. It indicates a significant presence of CO_3^{2-} groups in sample

- Absorption in range 455 … 520 cm^{-1} corresponds to valence fluctuations of Si-O in the hydrated sample of cement paste (C-S-H gel).
- Intensity increase of the infrared wave absorption in the range of 3400…3500 $см^{-1}$, responsible for the valence fluctuations of O-H group, and absorption of 1620 $см^{-1}$ (deformation fluctuations of H-O-H) in infrared spectrum of silica fume (SF) and dolomite (D) can be explained by a high level of absorbed water in the admixtures compared to the spectrum of M15 and K15.
- Si-O fluctuations in the structure of C-S-H can be observed at 779 cm^{-1}. Fluctuations at 671 cm^{-1} correspond to the Si-O fluctuations in tetrahedron $[SiO_4]^{4-}$, which might indicate the presence of quartz.

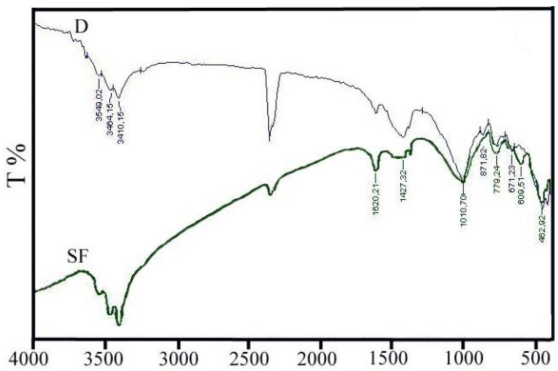


Figure 7. FTIS results: mix D with dolomite powder and SF with silica fume

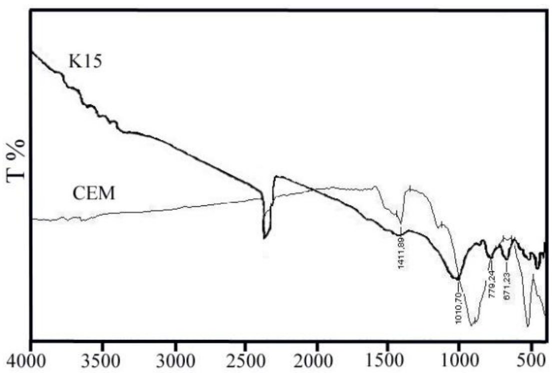


Figure 8. FTIS results: mix CEM - cement without admixtures and K15 with calcined illite clay ground for 15 min

- Absorption range 1010 cm^{-1} corresponds to asymmetric fluctuations of Si-O-Si, which indicates the presence of amorphous silica compounds (characteristic to all silicates), which are formed during the cement hydration process and which are impossible to detect with the X-ray test Wide range of infrared wave absorption 879….918 cm^{-1} for the specimen CEM compared to the narrow range of infrared wave absorbtion 1100 cm^{-1} for the specimens D, SF, K15 indicates a higher level of amorfisation.

It must be emphasised, that the method of the Fourier Transmission Infrared Spectroscopy can be used additionally to X-Ray difraction analysis to understand the mechanism of pozzolanic reactions.

CONCLUSIONS

Basic factors such as pozzolanic reactivity, particle grading and morphology determine the effectiveness of cement admixtures. Particle size distribution is the parameter, which may have an insufficient objectivity characterising a particular material, because the particles could be thin and flake-shaped. For this reason it is recommended to perform a BET analysis and particle morphology investigation as well.

Four admixtures have been compared in this research. It was tested and verified that the admixtures do not have a significant impact on the density of hardened concrete.

Mixes based of cement and cement combination with dolomite powder are non-effective binders, having a high water absorption rate and low compressive strength.

The most effective fillers in this case are calcined kaoline clay (metakaoline) and silica fume characterised by a high level of pozzolanic activity and specific surface. These mixes showed the highest mechanical strength results and low water absorption.

Calcined local illite clay demonstrated an insignificant effect comparing to metakaoline and silica fume, but some improvement in properties and long term curing effect took place. Red colour of calcinad illite clay may be used for creating an aesthetic concrete surface. Local Latvian clays are an unlimited natural resource, which successfully may be used as cement admixtures having some pozzolanic activity. Research in the future may be carried out, varying the clay type and conditions of production (temperature and grinding time).

The use of calcined locally available clay as a cement replacing admixture is an environmentally friendly way, because the calcining process requires 5 times less energy than cement production and is not associated with high level carbon dioxide emissions. Possibilities for the use of local calcined clay to improve concrete durability properties, must be investigated in the future.

ACKNOWLEDGEMENT

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