

The Influence of Aluminum Hydroxide ($\text{Al}(\text{OH})_3$) Additive on the Physical and Mechanical Properties of Alkali-Activated Slag

Danutė Vaičiukynienė*, Eugenijus Janavičius, Andrius Kielė, Siddeshwaran Parthiban

Department of Building Materials, Kaunas University of Technology
Studentu str. 48, LT- 51367 Kaunas, Lithuania

Aras Kantautas

Department of Chemical Technology, Kaunas University of Technology
Radvilenu st. 19, LT-50254 Kaunas, Lithuania

*Corresponding author: danute.palubinskaite@ktu.lt

 <http://dx.doi.org/10.5755/j01.sace.17.4.16731>

Alkali activation is a highly active and rapidly developing field of activity in the global research. Alkali-activated cements have found a variety of applications: transportation, industrial, agricultural, residential, mining and so on. Alkali activated binders are made by mixing industrial aluminosilicate waste materials such as one of them is slag. This study aims to evaluate the influence of incorporating aluminum hydroxide on the physical and mechanical properties of alkali-activated slag. Mineralogy of composites were studied using X-ray diffraction analyze. The results showed that the molar ratio of raw materials strongly affects the kinetics of reaction and the structural evolution of the solid phases forming in alkali silicate activated binders. The role of $\text{Al}(\text{OH})_3$ in the mixtures in activated binders is closely related to the availability of Al in the system, because it controls the concentrations of secondary products such as zeolites. Based on the experimental results, it can be concluded that by reducing Al_2O_3 from 1.30 mol till 0.75 mol (in the mixtures of raw materials) the compressive strength of samples increases from 27 - 42 MPa till 39 - 54 MPa.

KEYWORDS: alkali-activation, slag, $\text{Al}(\text{OH})_3$ addition.

The development and assessment of alkali-activated materials has become increasingly widespread over the past few years. Alkali activation is a rapidly developing field of activity in the research society. Such a great interest of alkali activated materials resulted in a large amount of waste recycling. Provis et al. (2015) identify important needs for future research and development to support the optimal and appropriate utilization of alkali activated materials as a component of a sustainable future construction materials industry.

Many studies have described the reaction products, physical-mechanical properties, micro-structure of alkali-activated binders. Some researchers mixed slags with different another waste materials such as fly ash and then activated with NaOH solutions. At 28 days of reaction, the mixture 50% fly ash /50% slag activated with 10 M NaOH and cured at 25°C, develop com-

JSACE 4/17

The Influence of Aluminum Hydroxide ($\text{Al}(\text{OH})_3$) Additive on the Physical and Mechanical Properties of Alkali-Activated Slag

Received
2016/11/08

Accepted after
revision
2016/12/22

Introduction



Journal of Sustainable
Architecture and Civil Engineering
Vol. 4 / No. 17 / 2016
pp. 77-83
DOI 10.5755/j01.sace.17.4.16731
© Kaunas University of Technology

pressive mechanical strengths of about 50 MPa. The main reaction product in these pastes is a hydrated calcium silicate, like CSH gel, with high amounts of tetra coordinated Al in its structure, as well as Na ions in the interlayer spaces (Puertas et al. 2000). In the study (Lee and Lee 2015), the microstructure, reaction products, and reactivity of alkali-activated, fly ash/slag binders synthesized at various mixture ratios of two raw materials were examined. It was found that the amount of added slag primarily affected the amount of reaction product and its silicate structure. In this case when the amount of added slag increased, the amount of C-S-H gel increased and the amount of aluminosilicate gel decreased. Marjanović et al. (2015) investigated physical-mechanical properties of alkali-activated binders based on blends of fly ash (FA) and blast furnace slag (BFS). It was found that the compressive strength mostly depended on the composition of the FA-BFS blends and the water/binder ratio. The setting time highly depended on the activator concentration, while the drying shrinkage was mostly affected by the curing temperature.

In the previous research (Gebregziabihher et al. 2015) the early age reaction kinetics and microstructural development in alkali-activated slag binder are discussed. Microstructure and strength development were monitored to correlate the heat evolution with the property development. In-situ isothermal calorimetric data for sodium hydroxide-activated systems exhibited only one major heat evolution peak with no dormant period. Sodium silicate-activated pastes exhibited multiple peaks and extended dormant periods.

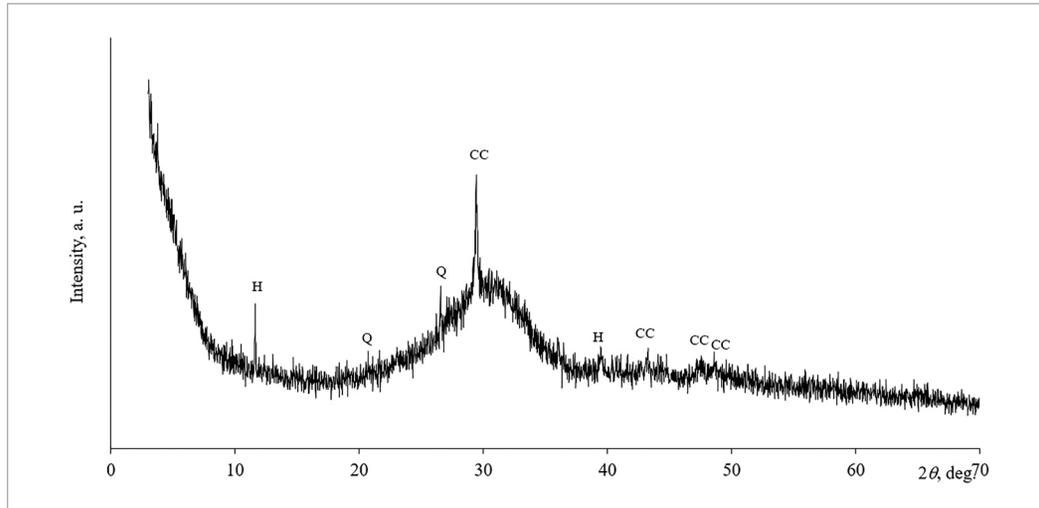
Gu et al. (2015) indicated that the impact of the curing temperature was much more significant on the setting time of AAS than on that of ordinary Portland cement (OPC). The shrinkage of AAS were slightly reduced or retarded by curing at below normal temperature.

The hydration and the microstructure of three alkali activated slags (AAS) with MgO contents between 8 and 13 wt.% are investigated. Higher MgO content of the slag resulted in a faster reaction and higher compressive strengths during the first days. The formation of C(-A)-S-H and of a hydrotalcite-like phase was observed in all samples. Increasing the MgO content of the slag from 8 to 13% increased the amount of hydrotalcite and lowered the Al uptake by C-S-H resulting in 9% higher volume of the hydrates (Haha et al. 2011).

It is very important to assess the necessary amounts of initial materials. Many papers have been published related with the choosing of initial materials including Al_2O_3 contents in alkali activated systems. Haha et al. (2012) studied the hydration of two slags with different Al_2O_3 contents. In all systems, C-S-H incorporating aluminum and a hydrotalcite-like phase with Mg/Al ratio ~2 are the main hydration products. The C-S-H gels present in NaOH activated pastes are semi-crystalline; a calcium silicate hydrate (C-S-H) and a sodium rich C-N-S-H with a similar Ca content are observed at longer hydration times. In another research the hydration and microstructural evolution of three alkali activated slags (AAS) with Al_2O_3 contents between 7 and 17% wt. % have been investigated. The formation of C(A)-S-H and hydrotalcite was observed in all samples. Higher Al_2O_3 content of the slag decreased the Mg/Al ratio of hydrotalcite, increased the Al incorporation in the C(A)-S-H and led to the formation of strätlingite. Increasing Al_2O_3 content of the slag slowed down the early hydration and a lower compressive strength during the first days was observed. At 28 days and longer, no significant effects of slag Al_2O_3 content on the degree of hydration, the volume of the hydrates, the coarse porosity or on the compressive strengths were observed (Haha et al. 2012).

The aim of this research was to evaluate the influence of aluminum hydroxide additive on the physical and mechanical properties of alkali-activated slag.

In this study slag was used as raw material. According to the X-ray diffraction curves (Fig. 1) this High calcium oxide and silicon oxide were obtained after the investigated slag analysis (Table 1).



Materials and methods

Fig. 1

X-ray diffraction pattern of slag were H is hydrotalcite - $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$ (14-191), Q is quartz SiO_2 (78-2315), CC is calcite $CaCO_3$ (72-1651)

| CaO | SiO ₂ | Na ₂ O | Al ₂ O ₃ | MnO | MgO | K ₂ O | Cl | Fe ₂ O ₃ | SrO | BaO | ZrO ₂ | SO ₃ | TiO ₂ |
|------|------------------|-------------------|--------------------------------|-------|------|------------------|-------|--------------------------------|-------|-------|------------------|-----------------|------------------|
| 45.2 | 37.1 | 1.02 | 6.44 | 0.194 | 5.76 | 0.517 | 0.053 | 0.793 | 0.069 | 0.068 | 0.02 | 1.85 | 0.285 |

Table 1

Chemical composition of slag

The slag was hydrated in the presence of NaOH like alkaline activator and the lacking amount of aluminum adjusted by adding of $Al(OH)_3$. The mixing procedure was as follows: the solid precursor (slag), NaOH and $Al(OH)_3$ were weighed, and the dry powders were mixed. The water was added and the paste were mixed externally till homogenous mass. Similar mixing procedure was used in the previous research (M. Ben Haha et al. 2012).

| Mixture No | SiO ₂ , mol | Al ₂ O ₃ , mol | Na ₂ O, mol | H ₂ O, mol | SiO ₂ /Na ₂ O molar ratio |
|------------|------------------------|--------------------------------------|------------------------|-----------------------|---|
| 1 | 5.0 | 0.75 | 1.4 | 11.1 | 3.5 |
| 2 | 5.6 | 0.75 | 1.4 | 11.7 | 4.0 |
| 3 | 6.3 | 0.75 | 1.4 | 11.5 | 4.6 |
| 4 | 6.9 | 0.75 | 1.4 | 11.1 | 5.1 |
| 5 | 7.5 | 0.75 | 1.4 | 11.1 | 5.7 |
| 6 | 5.0 | 1.3 | 1.4 | 11.1 | 3.5 |
| 7 | 5.6 | 1.3 | 1.4 | 11.7 | 4.0 |
| 8 | 6.3 | 1.3 | 1.4 | 11.5 | 4.6 |
| 9 | 6.9 | 1.3 | 1.4 | 11.1 | 5.1 |
| 10 | 7.5 | 1.3 | 1.4 | 11.1 | 5.7 |

Table 2

The quantities of primary materials for alkali activation

The X-ray diffraction analysis of the materials was performed using the X-ray diffractometer Bruker D8 Advance. CuK α radiation and Ni filter were used. The power X-ray diffraction patterns were identified with references available in PDF-2 data base (PDF – 2 International Centre for Diffraction Data, 12 Campus Boulevard Newtown Square, PA 19073-3273 USA).

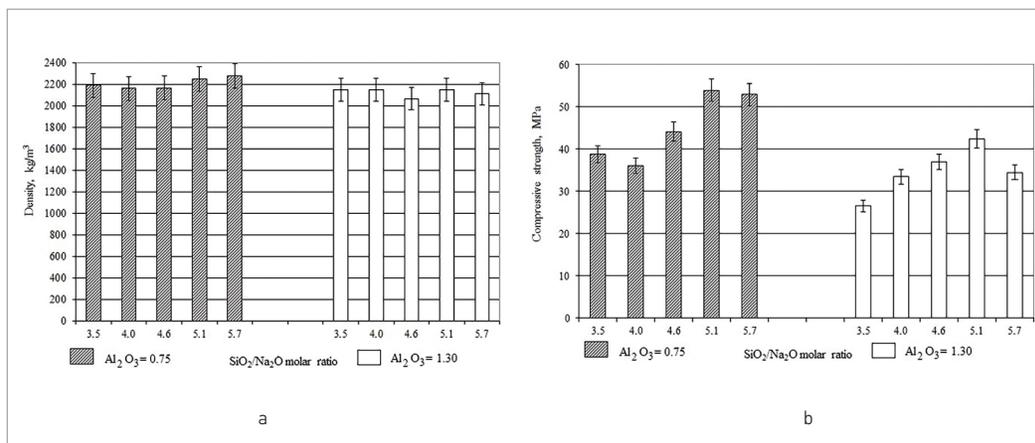
Chemical compositions of these materials were investigated by X-ray fluorescence spectrometer Bruker X-ray S8 Tiger WD, using rhodium (Rh) tube, anode voltage U_a up to 60 kV, electric current I up to 130 mA. The pressed samples were measured in helium atmosphere. Measurements were performed using SPECTRA Plus QUANT EXPRESS method.

All of the pastes were prepared with water to solid materials ratio of 0.3 (by mass). The formed test samples (2×2×2 cm size cubes) were hardened for 28 days. The compressive strength of hardened slag paste was measured by EN 196-1. An automated and computerized ToniTechnik 2020 press was used to evaluate the compression strength of hardened slag paste. It was used 6 probes for compressive strength. The density of hardened slag paste was obtained according to EN 12390-7 standard.

Results and discussion

Higher content of Al₂O₃ changed the mineral composition of the samples and slightly decreased the density of the specimens (Fig. 2 a). The compressive strength development of alkali activated slag pastes by different amounts of Al₂O₃, Na₂O and Si₂O at the ages 28 curing days is shown in Fig. 2. Higher compressive strengths were observed in alkali activated slag samples by using smaller (0.75 mol) amount of Al₂O₃ compared to the samples with higher (1.3 mol) amount of Al₂O₃. The compressive strengths increased with an increasing Na₂O/Si₂O molar ratio till 5.1 but when molar ratio was 5.7 it lightly decreased (Fig. 2 b).

Fig. 2
Compressive strength (a) and density (b) of alkali-activated slag with different amount of raw materials



The high compressive strength of alkali-activated slag based-materials is attributed to the amorphous hydrated alkali-aluminosilicate produced for slag (Bernal et al. 2014) and the calcium silicate hydrate gel (C–S–H) formed for slag (Yip et al. 2005).

In the X-ray diffractograms of alkali activated samples cured for 28 d (Fig. 3), it is possible to identify the major X-ray crystalline phases previously observed in the unreacted slag: hydroxalite - Mg₆Al₂CO₃(OH)₁₆·4H₂O (14-191), calcite CaCO₃ (72-1651) and quartz SiO₂ (78-2315), along with three crystalline reaction products: a calcium silicate hydrate Ca_{1.5}SiO_{3.5}·xH₂O (33-306), and two aluminosilicate zeolite products sodium aluminum silicate hydrate 1.08Na₂O·Al₂O₃·1.68SiO₂·1.8H₂O (31-1271) and zeolite 5A (AlO(OH)₃)₆·2Ca₄₀Na₁₆Al₇₆Si₉₆O₃₈₄(CO)₄₀ (31-1271). The identification of C–S–H type phases is consistent in previous studies using slags and activated under different conditions (Bernal et al. 2014). The molar ratio of raw materials strongly affects the kinetics of reaction and the structural

evolution of the solid phases forming in alkali silicate activated binders. The role of Al_2O_3 in the mixtures in activated binders is closely related to the availability of Al in the system, because it controls the concentrations of secondary products such as zeolites.

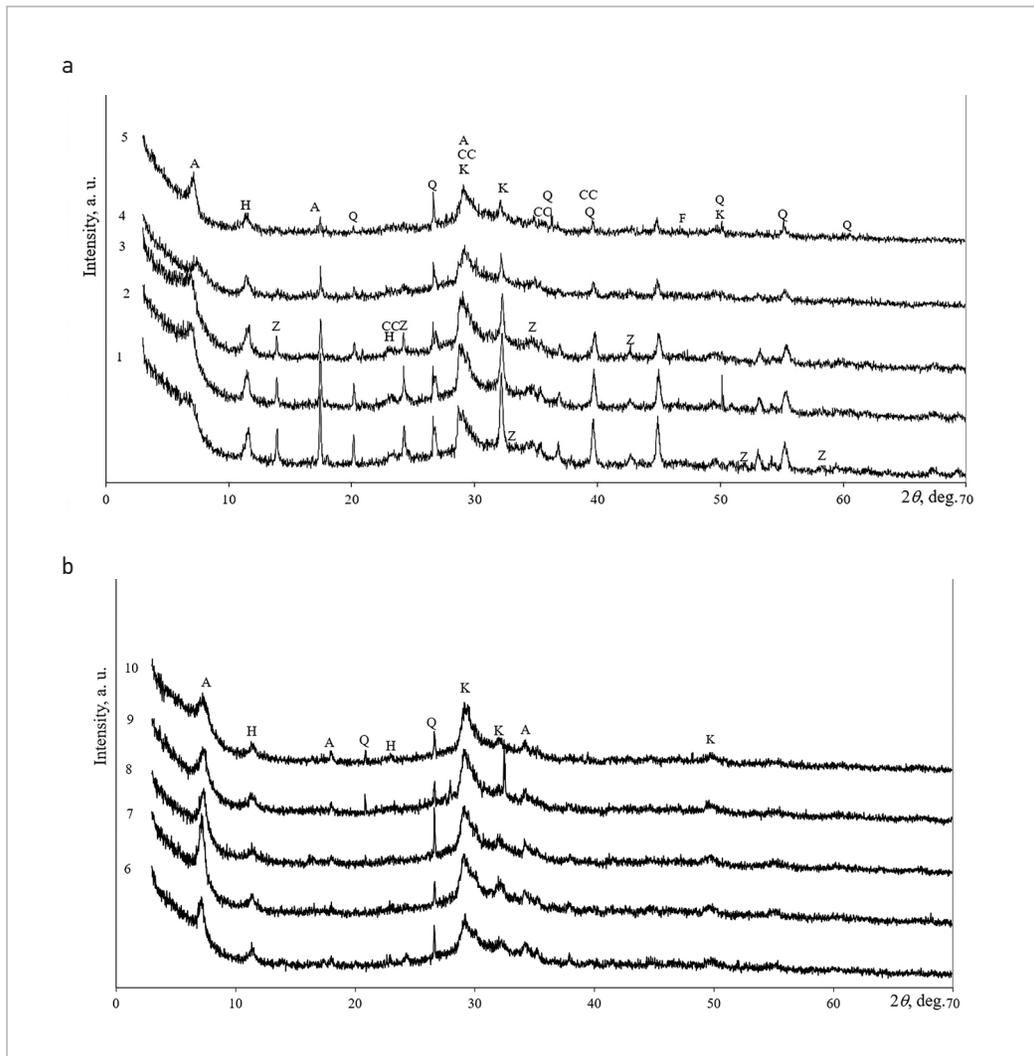


Fig. 3

X-Ray diffraction pattern of alkali-activated slag

Note: Q – quartz SiO_2 (78-2315), CC – calcite CaCO_3 (72-1651), K – calcium silicate hydrate $\text{Ca}_{1.5}\text{SiO}_{3.5}\cdot x\text{H}_2\text{O}$ (33-306), H – hydrotalcite $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ (14-191), Z – sodium aluminum silicate hydrate $1.08\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 1.68\text{SiO}_2\cdot 1.8\text{H}_2\text{O}$ (31-1271), A – zeolite 5A $(\text{AlO}(\text{OH})_3)_6\cdot 2\text{Ca}_{40}\text{Na}_{16}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}(\text{CO})_{40}$ (31-1271). Notes: a is 1 – 5 samples and b is 6 – 10 samples (Table 2).

This study presents the investigation of alkali-activated slag pastes. The dosage of Na_2O , Al_2O_3 and SiO_2 are significant factors influencing the binding mechanism and properties of alkali-activated slag samples. The main conclusions extracted from the present study are following:

- 1 The hydration products of alkali-activated slag pastes are mainly amorphous alkaline aluminosilicate and low-crystalline calcium silicate hydrate gel.
- 2 Formulating the mixture based on amorphous composition produced samples with a significantly higher compressive strength than those in which composition crystalline phase form.

Conclusions

3 In the mixtures of raw materials by reducing Al_2O_3 from 1.30 mol till 0.75 mol the compressive strength of samples increases from 27 - 42 MPa till 39 - 54 MPa. The highest compressive strength (54 MPa) has been observed in alkali-activated slag with $\text{Na}_2\text{O}/\text{Si}_2\text{O}$ molar ratio 5.1 and by using smaller amount (0.75 mol) of Al_2O_3 .

References

- Bernal S.A., San Nicolas R., Myers R.J., de Gutiérrez R.M., Puertas F., van Deventer J.S., Provis J.L. MgO content of slag controls phase evolution and structural changes induced by accelerated carbonation in alkali-activated binders. *Cement and Concrete Research*, 2014; 57: 33-43. <https://doi.org/10.1016/j.cemconres.2013.12.003>
- Gebregziabihier B.S., Thomas R., Peethamparan S. Very early-age reaction kinetics and microstructural development in alkali-activated slag. *Cement and Concrete Composites*, 2015; 55: 91-102. <https://doi.org/10.1016/j.cemconcomp.2014.09.001>
- Gu Y.M., Fang Y.H., You D., Gong Y.F., Zhu C.H. Properties and microstructure of alkali-activated slag cement cured at below-and about-normal temperature. *Construction and Building Materials*, 2015; 79: 1-8. <https://doi.org/10.1016/j.conbuildmat.2014.12.068>
- Haha M.B., Lothenbach B., Le Saout, G.L., Winnefeld F. Influence of slag chemistry on the hydration of alkali-activated blast-furnace slag—Part I: Effect of MgO. *Cement and Concrete Research*, 2011; 41(9): 955-963. <https://doi.org/10.1016/j.cemconres.2011.05.002>
- Haha M.B., Lothenbach B., Le Saout G., Winnefeld F. Influence of slag chemistry on the hydration of alkali-activated blast-furnace slag—Part II: Effect of Al_2O_3 . *Cement and Concrete Research*, 2012; 42(1): 74-83. <https://doi.org/10.1016/j.cemconres.2011.08.005>
- Haha M.B., Le Saout G., Winnefeld F., Lothenbach B. Influence of activator type on hydration kinetics, hydrate assemblage and microstructural development of alkali activated blast-furnace slags. *Cement and Concrete Research*, 2011; 41(3): 301-310. <https://doi.org/10.1016/j.cemconres.2010.11.016>
- Ismail I., Bernal S.A., Provis J.L., San Nicolas R., Hamdan S., van Deventer J.S. Modification of phase evolution in alkali-activated blast furnace slag by the incorporation of fly ash. *Cement and Concrete Composites*, 2014; 45: 125-135. <https://doi.org/10.1016/j.cemconcomp.2013.09.006>
- Yip C.K., Lukey G.C., Van Deventer J.S.J. The coexistence of geopolymeric gel and calcium silicate hydrate at the early stage of alkaline activation. *Cement and Concrete Research*, 2005; 35(9): 1688-1697. <https://doi.org/10.1016/j.cemconres.2004.10.042>
- Lee N.K., Lee H.K. Reactivity and reaction products of alkali-activated, fly ash/slag paste. *Construction and Building Materials*, 2015; 81: 303-312. <https://doi.org/10.1016/j.conbuildmat.2015.02.022>
- Marjanović N., Komljenović M., Baščarević Z., Nikolić V., Petrović R. Physical-mechanical and microstructural properties of alkali-activated fly ash-blast furnace slag blends. *Ceramics International*, 2015; 41(1): 1421-1435. <https://doi.org/10.1016/j.ceramint.2014.09.075>
- Provis J.L., Palomo A., Shi C. Advances in understanding alkali-activated materials. *Cement and Concrete Research*, 2015; 78: 110-125. <https://doi.org/10.1016/j.cemconres.2015.04.013>
- Puertas F., Martinez-Ramirez S., Alonso S., Vazquez T. Alkali-activated fly ash/slag cements: strength behaviour and hydration products. *Cement and Concrete Research*, 2000; 30(10): 1625-1632. [https://doi.org/10.1016/S0008-8846\(00\)00298-2](https://doi.org/10.1016/S0008-8846(00)00298-2)

DANUTĖ VAIČIUKYNIENĖ**Professor**

Kaunas University of Technology,
Faculty of Civil Engineering and
Architecture, Department of
Building Materials

Main research area

Synthesis of zeolites, zeolite
modification and their sorption
properties, use of zeolite in cement
and concrete systems, special-
purpose cement systems

Address

Studentu str. 48, LT-51367
Kaunas, Lithuania
Tel. +370 37 300465
E-mail: danute.palubinskaite@ktu.lt

ARAS KANTAUTAS**Assoc. Professor**

Kaunas University of Technology,
Department of Chemical
Technology

Main research area

Building materials

Address

Radvilenu st. 19, LT-50254
Kaunas, Lithuania
Tel. +370 37 300163
E-mail: aras.kantautas@ktu.lt

EUDENIJUS JANAVIČIUS**Assoc. Prof. Dr.**

Kaunas University of Technology,
Faculty of Civil Engineering and
Architecture, Department of
Building Materials

Main research area

Natural zeolites, cement
supplementary materials

Address

Studentu str. 48, LT-51367
Kaunas, Lithuania
Tel. +370 37 300465
E-mail: eudenijus.janavicius@ktu.lt

**About the
authors****ANDRIUS KIELĖ****PhD student**

Kaunas University of Technology,
Faculty of Civil Engineering and
Architecture, Department of
Building Materials

Main research area

Special-purpose cement concretes,
concrete additives

Address

Studentu str. 48, LT-51367
Kaunas, Lithuania
Tel. +370 37 300465
E-mail: andrius.kiele@ktu.lt

SIDDESHWARAN PARTHIBAN**Student**

Kaunas University of Technology,
Faculty of Civil Engineering and
Architecture, Department of
Building Materials

Main research area

Special-purpose cement concretes,
concrete additives

Address

Studentu str. 48, LT-51367
Kaunas, Lithuania
Tel. +370 37 300465
E-mail: siddeshwaran.parthiban@ktu.lt