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The Utilization of Biomass Bottom Ashes in Cement System

Danutė Vaičiukynienė*, Vitoldas Vaitkevičius, Jūratė Krulikauskaitė

Kaunas University of Technology, Faculty of Civil Engineering and Architecture
Studentu st. 48, LT-51367 Kaunas, Lithuania

Aras Kantautas

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

Vilimantas Vaičiukynas

Aleksandras Stulginskis University, Faculty of Water and Land Management
Universiteto g.10, LT- 53361 Akademija, Kaunas District Municipality, Lithuania

Valdas Rudelis

Joint-stock company "LIFOSA", Juodkiškio st. 50, LT-57502 Kėdainiai, Lithuania

*Corresponding author: danute.palubinskaite@ktu.lt

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By producing 1 ton of Portland cement clinker in environment releasing about 0.85 tons of CO₂: 70% of limestone decarbonation and 30% of electricity and thermal consumption. High specific CO₂ emissions results take the responsibility of Portland cement industry for about 5% of global CO₂ emissions. One of the ways to reduce CO₂ emissions is the use of Portland cement substituting materials. Properly treated ashes could become not a waste of biofuel but a valuable raw material for new construction materials. This paper presents results about the characterization of the biomass bottom ash sourced from the combustion of plant biomass located in Lithuania, and the study of new cement formulations incorporated with the biomass bottom ash. The study includes a comparative analysis of the phase formation and the setting of cement with bottom ash composite. Techniques such as X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), measurement of hydration temperature were used to determine the structure and composition of the formulations.

KEYWORDS: biomass bottom ash, hardened cement paste, zeolite.

Introduction



Biomass is a renewable energy source that is increasingly being used worldwide. However, because of recent increases in production, waste products from biomass combustion are becoming a relevant environmental and economic problem. Currently biomass bottom ash from biomass combustion is waste with no practical applications and generally deposited in landfills.

Because of the pozzolanic contribution of conventional concrete, biomass bottom ash can also be used as a partial substitute for cement. Biomass fly/bottom ashes have been used to produce mortars in addition to commercial cement. The presence of ash modifies the pastes rheological behavior. Materials display fair compression strength after 28 d of ageing in water. Materials aged 180 d in water suffer of high potassium elution (Maschio et. al., 2011). In the research (da Luz

Garcia et al., 2013) suggest bottom-ash, a waste material to ground and to test for use as a partial cement replacement material. Mortar with ground bottom-ash showed marginal durability loss but improved strength at later ages. Ground bottom-ash, non-glassy, may be used as a filler, contributing to sustainable construction.

There are some results have been published on the use of biomass bottom ash as filler in concretes or in road embankments. The results prove the feasible application of biomass bottom ashes as filler in road embankments. Furthermore, its use as cement-treated materials or non-structural concrete, depending on the replacement percentage (Hinojosa et al., 2014). In the research (Beltrán et al., 2014), concrete consisting of recycled aggregate substitutions was manufactured by applying different replacement rates of natural sand with biomass bottom ash. The results showed a worse behavior in mechanical properties and durability properties, however these reductions were inferior to it can be expected, due to the appropriate manufacture of the concrete applied. In another work (Cabrera et al., 2014) it was determined that biomass bottom ash possesses acceptable properties to be used as a filler material in the core of road embankments over 5 m in height without additional precautionary measures, such as the construction of road shoulders. In the research (Beltrán et al., 2014) three series with different amount of biomass bottom ashes manufacture. Mechanical properties were negatively with the addition of recycled aggregates. Durability properties declined with increasing recycled aggregates. In another work (Modolo et al., 2013) determined that bottom ash from biomass burning can be used as aggregate in mortars. Incorporation does not induce negative impacts. Mortar producers due to the replacement of treated and calibrated sand may achieve economic savings. In the research (Beltrán et al., 2016) analyzed samples of biomass bottom ashes from wood and olive trees. Low density, high absorption and high organic matter content were observed. Biomass bottom ashes were classified as subsidiary material feasible as construction material. The use of the ashes as a filler material in road embankments was proved.

Some scientists suggest biomass bottom ashes to utilize as component in building materials. For ashes that cannot be recycled it is possible to utilize as building material or as component in building products. The key factors for success in all forms of utilization are consistency of ash quality and availability of large quantities (Pels et al., 2005). In the present work (Wang et al., 2007) the use of biomass bottom ash significantly increased the porosity of mortars and it led to the decline of mechanical properties. According to the Carrasco et al., (2014) the addition of bottom ash increases the material's porosity, thereby decreases its thermal conductivity and compressive strength. The mixture with a 1:1 Si/Ca molar ratio shows the best mechanical characteristics (61.11 MPa) with acceptable thermal conductivity value (0.773 W/mK) and could potentially be used in products such as building blocks, since partially replacing the cement with ash produced samples based on criteria of the EN standards.

The aim of this work is to investigate possibilities of hydrothermal treated biomass bottom ashes in Portland cement mixtures.

XRD analysis data show that in the biomass bottom ashes (Fig. 1) silicon dioxide and calcium carbonate prevailed. There are small amount of calcium oxide, magnesium oxide, anorthoclase and gehlenite. In investigated biomass bottom ashes it is believed that calcium oxide should be left after firing of biomass. It is slowly hydrate and going carbonation.

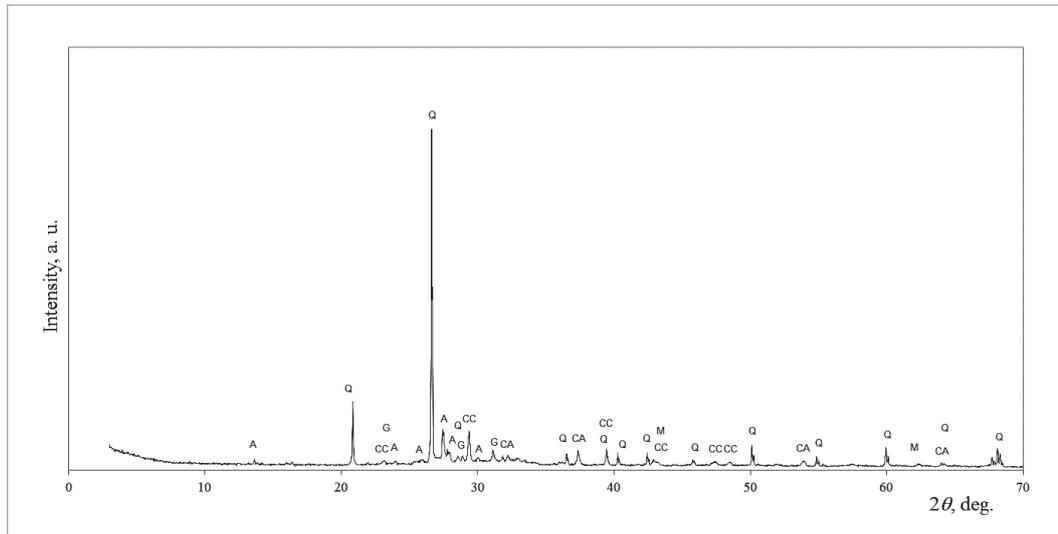
Amorphous SiO_2 waste are industrial by-product, i. e., amorphous $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (Lifosa, Lithuania). This amorphous SiO_2 is polluted with the impurities of fluoride compounds. Chemical composition of this waste is show in Tabale 1.

The commercial Portland cement of type CEM I 52.5R was used for the tests. Chemical composition of Portland cement and biomass bottom ashes was given in Table 1. After the XRF analysis it was determined that CaO (48.97 %), SiO_2 (22.39 %), MgO (8.29 %), and K_2O (8.69 %), contain the largest amount of oxides in the biomass bottom ashes (Table 1).

Materials and methods

Fig. 1

X-Ray diffraction pattern of biomass bottom ashes



NOTES: Q – silicon dioxide SiO₂, CA – calcium oxide CaO, M – magnesium oxide CC – calcium carbonate CaCO₃, A – anorthoclase (Na,K)(Si₃Al)O₈, G – gehlenite Ca₂Al(AlSiO₇).

Table 1

Chemical composition of Portland cement clinker and biomass bottom ashes and amorphous SiO₂ waste

Reagents NaOH (Delta Chem, Czech Republic), Al(OH)₃ (Lachema, Czech Republic) was used in this work as well.

The X-ray diffraction analysis of the materials was performed using the X-ray diffractometer Bruker D8 Advance. CuKα radiation and Ni filter were used. The powder 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.

The cement paste hydration temperature measurements were performed with 8-channel USB TC-08 Thermocouple Data Logger (temperature measurement range from -270 to +1820 °C).

The suspension of biomass bottom ash was treated in hydrothermal way. Zeolitization conducted in the kiln SNOL 200/200 for 1 hour at 100°C.

Chemical composition, %	Portland cement clinker	Biomass bottom ashes	Amorphous SiO ₂ waste
SiO ₂	20.61	22.39	71.64
Al ₂ O ₃	5.45	2.51	11.26
Fe ₂ O ₃	3.36	2.18	1.31
CaO	63.42	48.97	0.42
SO ₃	0.80	0.58	-
MgO	3.84	8.29	-
K ₂ O	1.31	8.69	-
Na ₂ O	0.94	0.28	-
P ₂ O ₅	-	5.05	-
MnO	-	0.35	-
TiO ₂	-	0.33	-
BaO	-	0.16	-
SrO	-	0.06	-
Rb ₂ O	-	0.02	-
ZrO ₂	-	0.04	-
ZnO	-	0.04	-
CuO	-	0.02	-
Cl	-	0.04	-
F	-	-	20.84

By replacing 10 % of Portland cement to biomass bottom ashes 4×4×16 cm samples from this cement paste were made. It was found that micro and macro cracks opened while these samples were hardened (Fig 1.). The reason of these defects should be calcium and magnesium oxides hydration reaction (1 and 2). It causes volume expansion, internal stresses and cracks appearance in the solid sample. Therefore, in cement systems biomass bottom ashes cannot be used without additional processing.

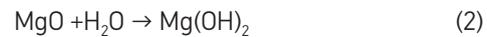
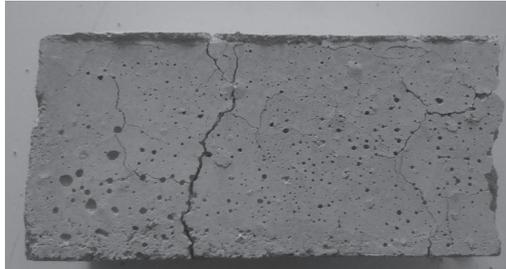
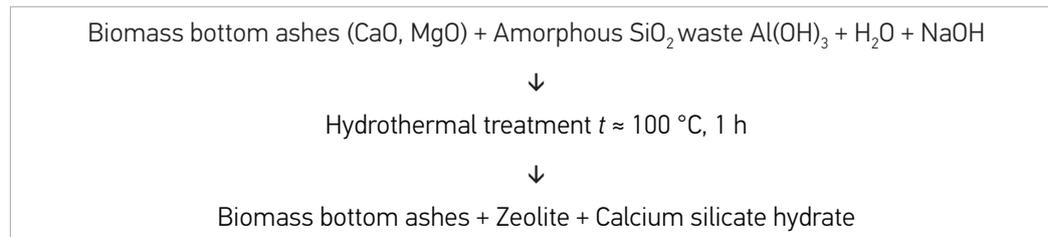


Fig. 1

Hardened cement paste sample with biomass bottom ashes (One half of sample 4×4×16cm)

There are many researches (Liu, 2016; Nagrockiene et al., 2016; Gerengi et al., 2015; Małolepszy et al., 2015), where zeolite as Portland cement substituting materials are widely used. Therefore, in this study the biomass bottom ashes were an attempt to zeolitize.

The zeolitization of biomass bottom ashes may be obtained by heating some aluminosilicate materials in the presence of alkaline solutions. The process of zeolitization took place according this scheme:



It was prepared five samples series (Table 2). In the mixtures No 1 and No 2 only biomass bottom ashes without amorphous SiO₂ waste addition was used. In the last three (No 3, No 4 and No 5) mixtures two-aluminosilicate materials was used.

No	SiO ₂ , mol	Al ₂ O ₃ , mol	Na ₂ O, mol	H ₂ O, mol	The source of SiO ₂ and Al ₂ O ₃	
					Biomass bottom ashes, %	Amorphous SiO ₂ waste, %
1	2	1	2	15	100	-
2	2	1	1	15	100	-
3	2	1	2	15	50	50
4	2	1	2	15	70	30
5	2	1	2	15	80	20

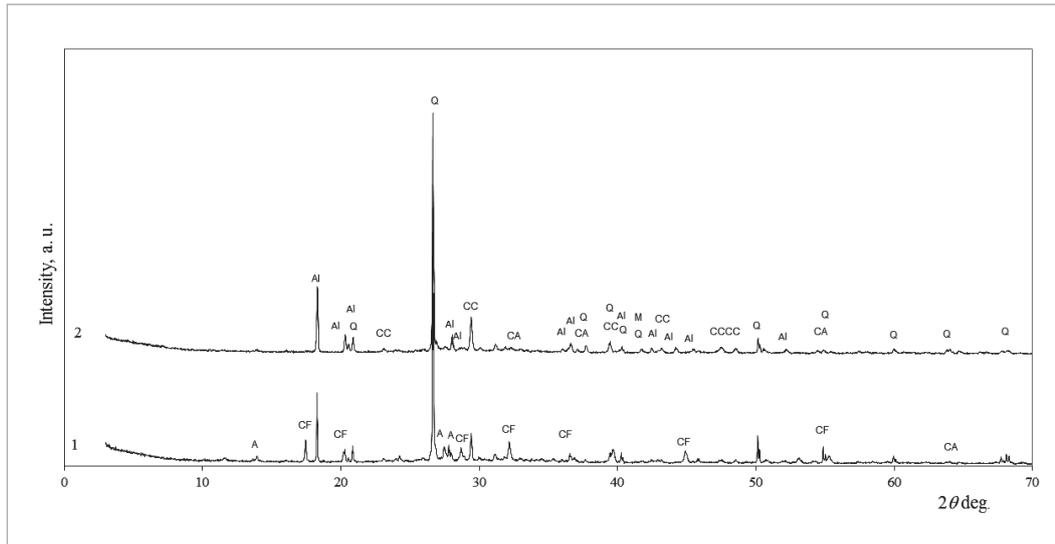
Table 2

The quantities of primary materials for zeolitization

After zeolitization of investigated mixture the mineral composition of it was found (Fig. 2). Based on the XRD investigation in mixtures products silicon dioxide, aluminum hydroxide, calcium aluminum iron silicate hydroxide, calcium carbonate predominates and harmful, not hydrated calcium and magnesium oxides there are. Thus, by using hydrothermal treatment of investigated mixture No1 and No2 the harmful calcium and magnesium oxides was not bonded to compounds.

Fig. 2

X-Ray diffraction pattern
of zeolitized biomass
bottom ashes

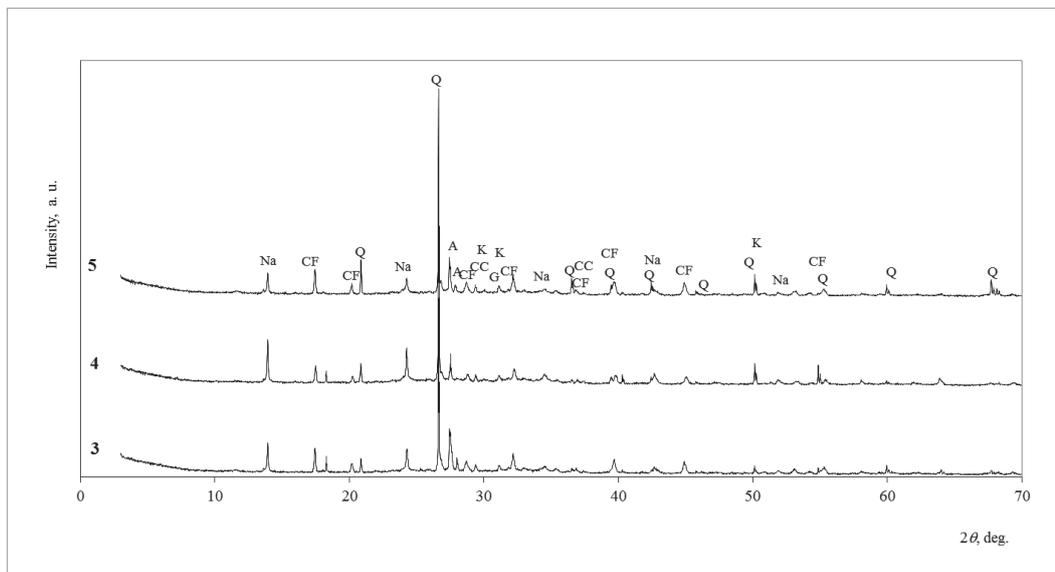


NOTES: Q – silicon dioxide SiO_2 , Al – aluminum hydroxide $\text{Al}(\text{OH})_3$, CC – calcium carbonate CaCO_3 , CA – calcium oxide CaO , CF – calcium aluminum iron silicate hydroxide $\text{Ca}_3\text{AlFe}(\text{SiO}_4)(\text{OH})_8$, A – anorthoclase $(\text{Na,K})(\text{Si}_3\text{Al})\text{O}_8$

Therefore, part of ash was mixed with amorphous SiO_2 waste in order to intensify the reaction of harmful calcium and magnesium oxides (Table 2, mixture 3-5). After the examination of zeolitized mixtures, it was found that in all three mixtures zeolite and calcium silicate hydrates were formed. It is important to emphasize that in this case, harmful calcium and magnesium oxides were fully bind into compounds that are harmless to cement hydration. It is likely that using zeolitized products of No 3 - No 5 mixtures as a Portland cement replacement material, it should not be caused problems for cement systems during hydration.

Fig. 3

X-Ray diffraction pattern
of zeolitized biomass
bottom ashes



NOTES: Q – silicon dioxide SiO_2 , CC – calcium carbonate CaCO_3 , Na – zeolite $\text{Na}_{20}\text{Al}_{20}\text{Si}_{31}\text{O}_{102}\cdot 1.8\text{H}_2\text{O}$, CF – calcium aluminum iron silicate hydroxide $\text{Ca}_3\text{AlFe}(\text{SiO}_4)(\text{OH})_8$, G – gehlenite $\text{Ca}_2\text{Al}(\text{AlSiO}_7)$, K – calcium silicate hydrate $\text{Ca}_{1.5}\text{SiO}_{3.5}\cdot x\text{H}_2\text{O}$

After the X-ray diffraction the hydration temperature of cement paste tests was measured (Fig. 4). It was determined that the main peaks of all investigated Portland cement pastes are higher in the specimens with 5% of zeolitized materials (mixtures 3 – 5). In all investigated cases, Portland cement paste hydration temperature increased compared with the reference specimen temperature. These temperature increases can be explained by filler effect. The physical presence of particles enhanced the hydration of the clinker phases. This effect is called the filler effect. This effect has been attributed to the increase of the number of nucleation sites provided by the extra surface from the particles (Berodier et al., 2012).

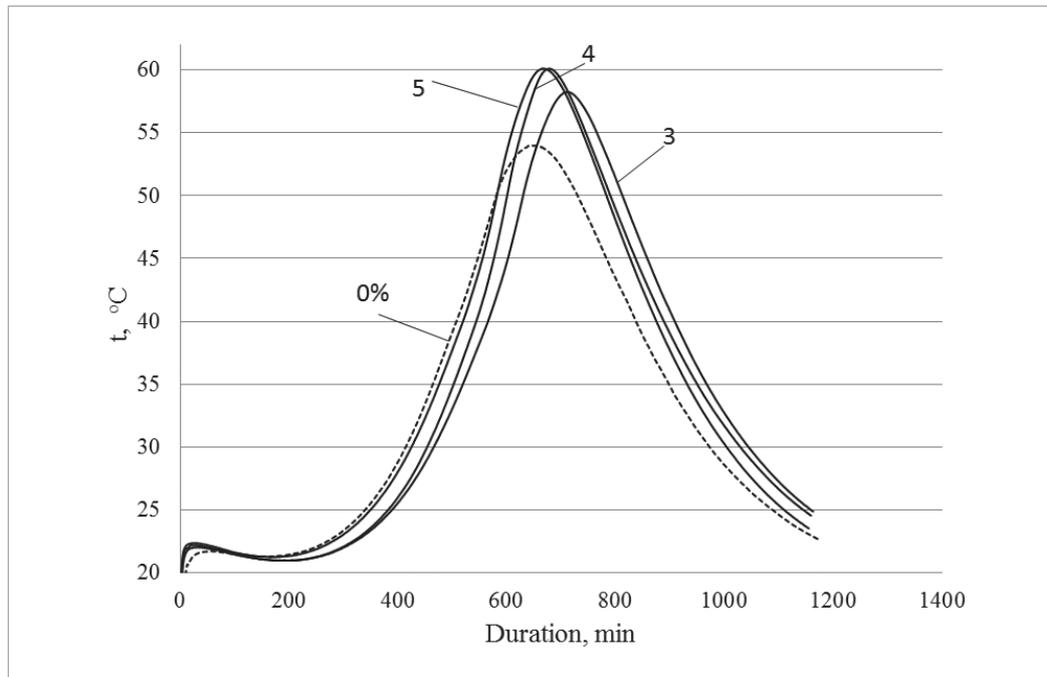


Fig. 4

The dependence of hydration temperature of Portland cement paste on the amount of biomass bottom ash

NOTES: 3, 4, 5 according Table 2.

Investigating specimens with No 4 and No 5 zeolitized material, hydration temperatures were very similar to the control specimen. By using zeolitized material No 3, the main reaction of hydration, it was with longer duration than control specimen (from 630 min until 702 min). This indicates that zeolitized material No 3 slightly delays the hydration of hardened cement paste.

- It was found that the biomass bottom ashes cannot be used directly as Portland cement substituting material due to calcium and magnesium oxides hydration reactions in already hardened samples. In these samples volume increases and cracks occur during hardening process.
- It has been found that in the zeolitization products of biomass bottom ashes with amorphous SiO_2 waste mixtures calcium and magnesium oxides are bind in complex compounds of zeolite and calcium silicates hydrates. For this reason, do not cause problems during Portland cement hydration.
- In all investigated cases, Portland cement paste hydration temperature increased compared with the reference specimen temperature. These temperature increases can be explained by filler effect.

Conclusions

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About the authors

DANUTE VAIČIUKUNIENĖ

Professor

Kaunas University of Technology,
Faculty of Civil Engineering and
Architecture

Main research area

Building materials

Address

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

VITOLDAS VAITKEVIČIUS

Professor

Kaunas University of Technology,
Faculty of Civil Engineering and
Architecture

Main research area

Building materials

Address

Studentu st. 48,
LT-51367 Kaunas,
Lithuania
Tel. +370 37 300465
E-mail: vitoldas.vaitkevicius@
ktu.lt

ARAS KANTAUTAS

Assoc. Professor

Kaunas University of
Technology, Faculty 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

VILIMANTAS VAIČIUKYNAS

Lector

Aleksandras Stulginskis
University, Faculty of Water and
Land Management

Main research area

Drainage construction materials

Address

Universiteto g.10, LT- 53361
Akademija,
Kaunas District Municipality,
Lithuania
Tel. +370 61434230
E-mail: vilimantas.vaiciukynas@
outlook.com

JŪRATĖ KRULIKAUSKAITĖ

Master student

Kaunas University of Technology,
Faculty of Civil Engineering and
Architecture

Main research area

Building materials

Address

Studentu st. 48,
LT-51367 Kaunas,
Lithuania
Tel. +370 37 300465
E-mail: j.krulikauskaite@gmail.
com

VALDAS RUDELIS

Engineer - technologist

Joint-stock company "LIFOSA"

Main research area

Building materials

Address

Juodkiškio st. 50, LT-57502
Kėdainiai,
Lithuania
Tel. +370 61282463
E-mail: v.rudelis@lifosa.com