KAUNAS UNIVERSITY OF TECHNOLOGY

CIVIL ENGINEERING AND ARCHITECTURE FACULTY

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THE USE OF BIOMASS BOTTOM ASHES IN THE CEMENT SYSTEMS

Master's Degree Final Project

Supervisor
Prof. dr. Danutė Vaičiukynienė

KAUNAS, 2017

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Structural and Building Products Engineering (code 621H20001)

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"The use of biomass bottom ashes in the cement systems"

DECLARATION OF ACADEMIC INTEGRITY

09 January 20 18
Kaunas

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Elene, Bokuchava. The use of biomass bottom ashes in the cement systems. Master's Final Project / supervisor assoc. prof. dr. prof. dr. Danutė Vaičiukynienė; Faculty of civil engineering and architecture, Kaunas University of Technology.

Study field and area: civil engineering, building products engineering

Keywords: biomass, bottom, ash, cement, calcium, chloride.

Kaunas, 2018. 47 p.

SUMMARY

Concrete is the most often used building material. Several materials can be used to create its commonly used binder – cement. In this work, we investigate the use of biomass bottom ashes in cement systems. The above-mentioned ashes are being collected from the three different plants located in Lithuania. The thesis is divided into three parts: introduction, project study and the conclusion.

Bokuchava, Elene. Biomases pakuros pelenu naudojimas cementinese sistemose. Magistro baigiamasis projektas / vadovas doc. dr. Danutė Vaičiukynienė; Kauno technologijos universitetas, statybos inžinerijos ir architektūros fakultetas.

Studijų kryptis ir sritis: statybos inžinerijos

Reikšminiai žodžiai: biomasė; pakura; pelenai; cementas; kalcis.

Kaunas, 2018. 47 p.

SANTRAUKA

Viena populiariausių statybinių medžiagų yra betonas. Betone rišiklis, tai yra cementas, yra viena brangiausių sudedamųjų dalių. Šiame darbe biomasės pakuros pelenai naudojami cemento sistemoje. Minėti pelenai buvo gauti iš trijų skirtingų Lietuvos katilinių. Darbą sudaro trys dalys: įvadas, eksperimentinis tyrimas ir duomenų analizė bei išvados.

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ACKNOWLEDGEMENTS

A very special gratitude goes out to my project supervisor to Professor Dr. Danutė Vaičiukynienė who did her best to give me the thoughtful insights into the field of ecological and green building materials and who has also provided me through moral support.

I am also grateful to the department of civil engineering faculty and whole KTU stuff, especially my coordinator - Laura Jankauskaitė-Jurevičienė who was helping me in the hardest moments.

Finally, great thanks to my family and friends who have supported me during the whole time.

1. Introduction

The use of biomass, one of the important renewable energy sources, it is being increased day by day. For now, biomass bottom ash has no popular approved use that causes its transformation into the ecological waste with no practical applications. After biomass combustion, the biomass bottom ash is usually being deposited in the landfills.

There is a wide range of biomass bottom ash potential use. Due to its pozzolanic properties, one of the methods is its use as an additive for cement. Biomass bottom ash is responsible for the modification of the cement's rheological behaviour.

Aim and tasks of the work

The aim of the research is to explore the possibility of using biomass bottom ash as a cement substitute material in cement systems.

To achieve this aim, the following work tasks are shown:

- To determine the influence of biomass bottom ash on the cement paste hydration processes and the main properties of cement stone;
- To carry out the chemical modification of biomass bottom ash and to analyse the obtained products;
- To determine the effect of modified biomass bottom ashes on cement systems.

Scientific novelty

The scientific novelty of this work is the study of the effect of modified biomass bottom ashes on cement systems. Chemical modification was carried out using a hydrofluoric acid. After chemical modification, instead of dangerous CaO and MgO compounds we got $CaCl_2$ and $MgCl_2$ forms.

1.1. Fields of BFA and BBA uses

One of the most important steps that ensure a high-quality life and bright ecological situation of the future is to use the renewable resources with the help of environmentally “green” technologies.

The rising price of fossil fuels, the uncertain safety of the nuclear energy and the necessity of CO_2 emission reduction – let us assume that in future years, biomass will have a great perspective to be used as a natural resource for renewable energy [1].

The European Parliament are promoting the renewable energy use [2]. According to the European Directive 2009/28/EC, biomass represents a recyclable waste, and remains from the biological source of farming, forestry, and correlated industries. According to Martín Mateo [3] “biomass energy may be described as the solar energy transformed into chemical energy through photosynthesis being stored in a plant material.”

Biomass ashes (BA) are dense by-products that represent a result of the complete or partial combustion of the organic material. Biomass bottom ash (BBA) or slag and biomass fly ash (BFA) are the components of the industrial BA that is being created commonly under 800 – 1600°C [4].

BBA and BFA have been broadly studied concentrating on several different uses. Due to its mineral nutrient composition that includes calcium, potassium, and phosphorus, BFA is typically being used in agriculture [5]. BFA has been explored for its use in construction materials because of its increased production. The most studied fly ash (FA) so far is fly ash from coal combustion as an additive to traditional concrete. Effective management [6] and application of bottom ash have been infrequent compared to the extensive exploration of fly ashes. Generally, BBA is being disposed to landfills. There are two possible ways of biomass waste treatment: [7] one is to refine the fluidized bed boilers for a better combustion process to reduce BBA’s amount, and the other is to create an effective and efficient way of its use. The corresponding mass of 5, 10, 20 and 30 wt.% BFA or BBA has been used as a mortar paste by replacing commercial cement [8][9].

Lately, a wide study of BA was conducted by Vassilev et al., which classified BA into four types according to their mineral and chemical composition [4]. After the types were established, it was possible to evaluate their potential applications, ecological and technological pros and cons. Authors detected that after the enrichment of BA with the active, semi-active and pozzolanic phases that have cementitious behavior, it was appropriate to use this by-product as a construction material [10].

As far as biomass contains a big amount of ash, proportionally high volume of ash is being produced after the boiler combustion process. Moreover, it is to assume that the ash and its deposit amount will increase as far as the demand on the bioenergy products rises. Efficient management of this by-product is related to major challenges. The primary concerns are usage, disposal, and storage of ash and the unburned carbon. In case of the limited area for landfill extension, the nonstop increase of ash volume will result the reduced ash storing facilities, as well as augmented handling, transporting, and spreading prices.

Gomez-Barea et al. [11] proposed that fly ash can be utilized (a) in agriculture; (b) as fuel; (c) as a component of building materials.

Heavy metals and the extent that the ash is sintered to are having an influence on a potential use of ash [12]. Clean biomass comprises minerals and elements of significant importance that is the reason it can be recycled to the forest grounds; though these trace metals must be calculated, and their impacts should be examined in case they are applied to soils. To ensure that the ash disposal is not hazardous for the environment, environmental observation and protection must be carried out.

According to Demirbas [13], the fly ash that is produced by the biomass-fired grate boilers should not be used as soil additives because of the high number of carbon that it contains. The average amount of unburnt carbon in the fly ash produced by the grate boilers is around 50%. This data indicates ineffective fuel use and can decrease ash balance and meaningfully increases ash volume. To reduce the carbon contents, it is needed to re-burn the ash.

Ash utilization has been tested in building industry as well. According to Khan et al. [11], fly ash can replace cement in concrete, can be used for soil maintenance, as a road base, asphalt structural filler and asphalt base products, synthetic aggregate, and lightweight bricks.

While the utilization of fly ash is already well studied, the utilization of biomass bottom ash still stays undiscovered.

1.2. Ash from Biomass Combustion

There are two types of ashes after biomass combustion – fly and bottom ash. Bottom ash can be found on the grate in the boiler’s initial combustion chamber. This ash is often mixed with stones, sand, and dirt [14].

Fly ash is produced by getting ash from the bottom of the furnace. It gathers primarily in ceramic, electrostatic, or bag filter behind the furnace cyclones and directly in the multi-cyclones.

Ash contains much of the mineral segments of the biomass itself as far as it is an inorganic incombustible part of the fuel that is being left after the complete combustion [12]. Ash is an essential part of the plants and contains a variety of elements. Wood contains 2% of ash, while crop resources can produce from 5 to 10% of ash, milfoil and rice hull can produce around 30-40% of ash.

Relating to the type of biomass, soil and harvesting, the ash in the biomass fuels can be diverse. Overall, Ca, K, Na, Si, and P are the major ash-forming elements in biomass fuels, some of which act as significant nutrients for the biomass. Though some fuels from biomass, for example, rice husk, have high silicon content, others like wood, have high alkali metal content. The elemental composition of the biomass bottom ash is determined by the inorganic elements in the parent biomass, while the biomass combustion technique determines the mineralogy and crystallinity [15].

Fly ash derived from a wood combustion can contribute to sustainable and greener concrete. In fact, currently, most of the biomass ash that is produced in thermal power plants are being used to improve the alkali level of the soil or are being recycled to the forests [16]. Most of the time they are being disposed to the landfills without any control [17]. There is a risk that the air will get polluted with the fine particles of the wood ash, that might cause the respiratory health issues to the nearby residents, thus the landfills and the ash disposals must be properly designed [16].

If the plants are equipped with the efficient fluidized bed furnaces, it will produce mostly the fine fly ash that contains only a small fraction of coarse ash that is reserved within the combustion slot, but when the grate-fired furnaces are being used, the ash that is being produced is coarser and tend to stay inside the chamber as a bottom ash [17].

1.3. An Estimate of Potential Increase in Ash Production

The quantities of the wood biomass that may be or are used for producing ash define the estimated potential ash production, that needs a careful study. Wood by-products form significant energy related to gasification, combustion, pyrolysis, and others.

The European Parliament are promoting the renewable energy use [2]. In the directive 2009/28/EC, biomass is being defined as s recyclable section of products, waste, and remains from the biological source of farming (including animal and plant elements), forestry and correlated industries, along with the biodegradable section of urban and industrial waste. According to Martín Mateo [3] “biomass energy may be described as the solar energy transformed into chemical energy through photosynthesis being stored in plant material.”

The rising price of fossil fuels, the uncertain safety of the nuclear energy and the necessity of CO_2 emission reduction – let us assume that in future years, biomass will have a great perspective to be used as a natural resource for renewable energy [1] During the process of boiler combustion, we get big amount of ash. Similarly, the higher gets the request for bioenergy production, the higher the ash deposit volume will be. Efficient management of this by-product is related to major challenges.

In the USA for example, around 70% of the wood ash is being distributed to the landfills and around 25% of them are being used as a soil supplement. Still, the price of the landfilling is being increased that created the need for a new way of the waste use.

According to the Food and Agriculture Organization (FAO) [18], “approximately 10,507.4 m^3 of the wood residue was generated globally, as a yearly average from 1992 to 2010. For the sample period, the top five wood residue generating countries produced 1,637.1 m^3 from China, 1,498 m^3 from Brazil, 1,391 m^3 from the USA, 845.3 m^3 from the Russian Federation and 823.9 m^3 from France.”

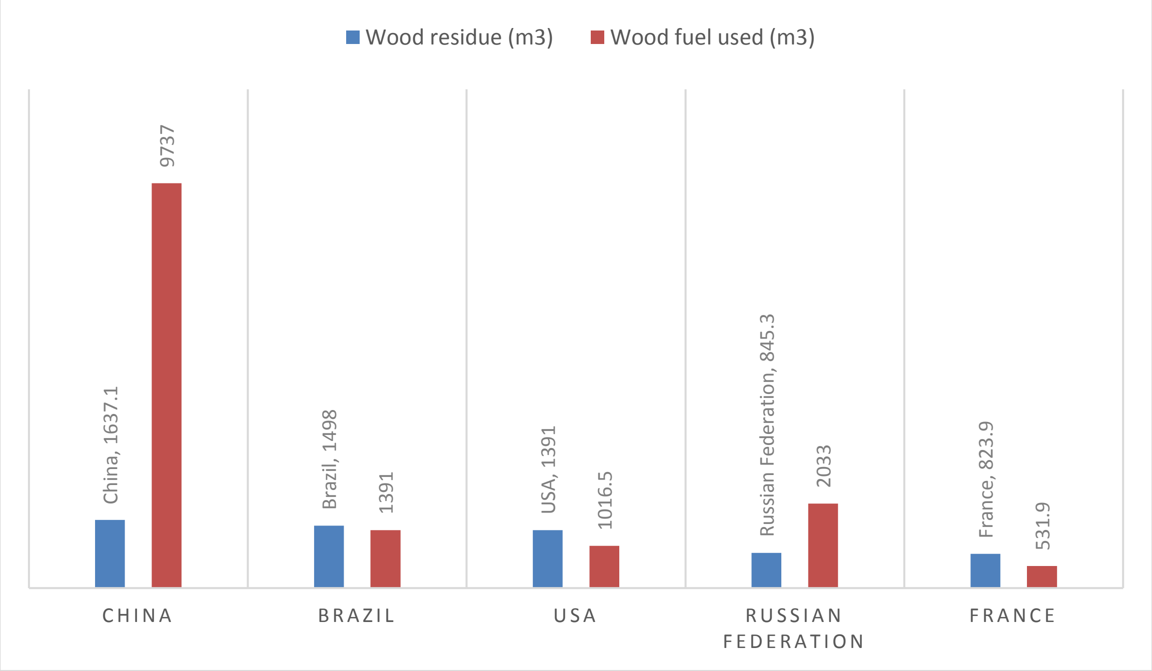

Figure 1. Wood residue and wood fuel use chart in 2010 (Source: Food and Agriculture Organization (FAO))

These remains are likely to supplement current wood-fuel consumption. “Comparing these statistics to coniferous wood-fuel used, the USA had 1,016.5 m^3 of wood-fuel, 9,737 m^3 for China, 1,391 m^3 for Brazil, 2,033 m^3 for the Russian Federation and 288,9 m^3 for France in 2010.” According to this data, it is easier to forecast the potential increase in ash production resulted from the wood-fuel usage. Wood residue ash varies with the chemical and physical properties, they depend on the origin of biomass, energy-harnessing process type, chemical reactions that occur during the high temperature in the furnace, treatment of the fuel and its storage [18].

1.4. Elements of Environmental Significance in Ash

The major characteristic ash-forming elements in biomass contain Al, Ti, Fe, Mg, Ca, Si, Na, S, K, and P [12]. Ash behavior under high heat combustion [19] depends on its composition. Chlorine and sulfur, alkali metals and alkaline earth metals as well as silicon, can cause pollutant emissions, erosion and corrosion of the ash [20] [21] [22].

1.5. Presence of Metal Compounds in Ash

In case of irrationally managed and disposed, the presence of unstable heavy metals may cause the danger to the environment due to the possible leaching into surface and underground waters [21]. According to Khan et al. [12], the existence of heavy metals, if such will be found in ash, may influence of the utilization of it, that is defined by the source of the biomass. According to Demirbas [13], the heavy metal composition of ash depends on the ash fraction as well. For example, Vamvuka [21] has suggested that due to the soil parent material, olive kernel ash was containing the high concentration of the Cr and Ni. According to the author, Ni/Cr which has been transferred from the soil to the plant through the roots. We can find more amount of As, Cd, Hg and Pb in ash produced by wood rather than, for instance, the ash from straw, wheat, etc.

Khan et al. [12] pointed out that fly ash contains much more amount of heavy metals rather than bottom ash. As mentioned above, the bottom ash generation is being increased annually, that means that its cumulative metal concentration from landfilling and deposition should be observed carefully.

1.6. BBA in cement systems

As various statistics show, per person yearly more than 1 m^3 of Portland cement concrete is being produced and globally around 3 billion tons of Portland cement is being consumed; Around 5% of all CO_2 emission is due to the cement production, that has a drastic influence on the climate changes. When it refers to the industrial by-products, we can proudly say that that the possibility of replacing Portland cement in concrete can lead to the significant improvements in workability, durability and energy and cost savings as well.

In the past years, few new plants have been installed as far as the emissions from the burning of biomass are CO_2 free [23]. Consequently, the amount of generated ashes has been significantly increased. Their common destination is supposed to be tracked. As stated by Maschio et al, it is feasible to use the biomass bottom ash in mortars, cement, or concrete, moreover, it may have a positive impact on the environment. Yet, the production must have a high durability and proper mechanical properties, while the amount of potentially hazardous elements should follow the legal standards.

One of the most important parts is an increasing global awareness about the environmental issues and the potential benefits of the use of renewable energy sources. Biomass can be used as an energy source of different scales, started from small-scale thermal projects at any institutions to the large-scale power generators. Both, human and natural activities create biomass and it is being incorporated by forestry residues, crops, timber and so on.

The power generation industry is progressively moving towards using the biomass for energy production. The thermal processes lead to the important amount of a by-product material like a wood waste ash, although the timber waste is a sustainable and renewable source of energy.

It is possible to use wood ash for a structural-grade concrete and most cement-based materials that means that the design must use a renewed approach to traditional design that incorporates the significant changes. There have been conducted several types of research to incorporate fly ash from the wood waste in cement materials. The results have been successful and have approved the fly ash for the acceptable mechanical strength and durability that is legitimate for the self-compacting concrete as well.

Unlike coal ash, generally biomass ash does not contain the toxic and hazardous metals, still, it depends on the origin and location of the biomass. In biomass fuels the elements that form ash are diverse that depends on the origin of biomass as well, the type of the harvesting and the type of the soil. Generally, the main ash-forming inorganic elements are: K, Na, Ca, Si and P. Some of these are the significant nutrients for the biomass as well. Still, there are biomass fuels that have a high silicon content, for example, rice husk, meanwhile, there are the others that have a high alkali metal content, like wood. One of the most important parameters for the element composition on biomass ash is the combustion method that is used.

It is possible to get a “greener concrete” with using the wood waste ash that also means a “greener means of disposal” of the wood waste ash [16]. Nowadays the thermal power plants are producing most of the biomass ash. They are also being recycled in forests or are being used as a supplement to fix the alkali level of the ground [16], also it is being disposed without any control to the landfills [17] that can cause several respiratory problems.

In the USA for example, around 70% of the wood ash is being distributed to the landfills and around 25% of them are being used as a soil supplement. Still, the price of the landfilling is being increased that created the need for a new way of the waste use [24].

The plants that have efficient fluidized bed furnaces can produce finer ash that would have only a small fraction of coarse ash that is left after the combustion in the chambers, when the grate-fired furnaces are being utilized, the wood ash that is produced is much coarser and tend to stay inside the chambers as bottom ash.

1.7. Portland Cement hydration process

Portland cement hydration [25] is the chemical process when the cement particles combine with water. During this process, we find changes in the rate of the reaction itself, in energy and in the material. The key reactions are the following:

Table 1. Chemical reactions during cement hydration

$2(3\ CaO \cdot SiO_2)$ Tricalcium silicate C_3S	$+ 6\ H_2O$		$= 3\ CaO \cdot 2\ SiO_2 \cdot 3\ H_2O$ Calcium silicate hydrates	$+ 3\ Ca(OH)_2$ Calcium hydroxide
$2(2\ CaO \cdot SiO_2)$ Dicalcium silicate C_2S	$+ 4\ H_2O$		$= 3\ CaO \cdot 2\ SiO_2 \cdot 3\ H_2O$ Calcium silicate hydrates	$+ Ca(OH)_2$ Calcium hydroxide
$3\ CaO \cdot Al_2O_3$ Tricalcium aluminate C_3A	$+ 12\ H_2O$	$+ Ca\ (OH)_2$ Calcium Hydroxide	$= 3\ CaO \cdot Al_2O_3 \cdot Ca(OH)_2 \cdot 12\ H_2O$ Calcium aluminate hydrate	
$4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$ Tetracalcium aluminoferrite C_4AF	$+ 10\ H_2O$	$+ 2\ Ca\ (OH)_2$ Calcium Hydroxide	$= 6\ CaO \cdot Al_2O_3 \cdot Fe_2O_3 \cdot 12\ H_2O$ Calcium aluminoferrite hydrate	

Due to its complicated composition, there are more than one reactions that are occurring simultaneously.

According to Mehta and Monteiro, [25] 2005, there are the following mechanisms of the hydration process: topochemical and through-solution. The through-solution process consists of:

1. “Dissolution of anhydrous compounds into constituents”
2. “Formation of hydrates in solution”
3. “Precipitation of hydrates from the supersaturated solution”

The through-solution mechanism is dominating in the first steps of hydration. Topochemical hydration is happening on the surface of the cement elements.

As stated by Mehta and Monteiro, [25] the hydration process goes faster in aluminates than in silicates. “To slow down the process in aluminates, it is possible to use Gypsum: gypsum can enter the solution rapidly, creates sulfate ions that causes the suppression of aluminate’s solubility. The fastest hydration process is occurring in tricalcium aluminate and water, that emits the high heat almost immediately. The setting rate is being defined by the relation of aluminate and sulfate, that means that for the normal rate of cement setting time, low number of aluminate and sulfate ions are needed. After 45 minutes [25] the water is being displaced in the pores and the cement paste starts to stiffen, from 2 to 4 hours it hardens. In case of excessive sulfate and aluminate ions, the setting may occur in 1-2 hours. In case of excessive aluminate ions and low amount of sulfate ions, the quick or immediate set might occur from 10 to 45 minutes, or even in less than 10 minutes. If it is on the contrary, and the aluminate ions are low unlike the sulfate ions, the gypsum can recrystallize in the pores in 10 minutes that will cause an immediate set. In both unbalanced cases, an immediate set will cause low ultimate strength.”

Water and calcium silicates together form C-S-H, – calcium silicate hydrate [25]. This process starts after the water is added to the cement and lasts until there are a spare water and cement particles. Calcium-to-silicate ratio varies from 1.5 to 2.0

As we can see from the Table 1, silicate hydration is producing calcium hydroxide and calcium silicate hydrate. After the full hydration [25] we get around 61% of calcium silicate hydrate and 39% of calcium hydroxide; Calcium silicate hydrate is the component that is responsible for the concrete strength, but it is easily vulnerable by sulfate and acid waters.

1.7.1. Structure development in cement paste

The successive development [25] in cement paste begins right after to cement we add water which becomes highly alkaline in around 10 minutes. Being hydrated, the cement particles decrease in volume, unlike the void in-between them, that rises. Final setting occurs after the calcium silicate hydrate phase develops a rigid structure after which the paste continues hardening and strength gaining until there are no more free cement particles and water. Time after time, the hardening speed is being decreased.

1.7.2. Hydration progress evaluation

According to Neville, 1996, there are several methods with which we can evaluate the cement hydration. For this, should be measured the following:

- “the heat of hydration;
- the amount of calcium hydroxide in the paste developed due to hydration;
- the specific gravity of the paste;
- the amount of chemically combined water;
- the amount of un-hydrated cement paste using X-ray quantitative analysis;
- the strength of the hydrated paste, an indirect measurement.”

Voids greatly influence concrete strength [25], durability, and volume stability. During hydration, we find two types of voids:

- Interlayer hydration space voids
- Capillary voids

We find the interlayer hydration space between the layers of calcium silicate hydrate, its width is approximately 0.5-2.5 mm, that is not enough to have any influence on the strength of the concrete. Still, these voids play a significant role (28%) in the porosity.

If the hydrated cement paste [25] has a lower bulk gravity than the cement particles itself, we find the capillary voids in the paste, amount, and size of which depends on the primary separation of the cement particles and water ratio. If these voids are bigger than 50nm then the strength of the concrete is being decreased. Shrinkage may occur in case of water removal from the small voids (less than 50nm), but not from the bigger ones.

In both types of voids, air may appear by the mixing of the cement paste [25], that reduces the strength of the concrete and raises the permeability. Well-distributed air bubbles can significantly raise the durability of the paste.

Right after mixing [26], the consistency of cement paste does not change for a while. When the initial setting time begins, the paste starts to stiffen faster, unlike before the initial setting, when this process was almost unrecognizable. Still [26] the paste does not have any strength until the final setting time that comes after some hours. During the next few days, the paste gains strength rapidly but this rate is steadily being decreased for a few months.

Setting time is being measured by standardized methods that means defining the depth of the needles or plungers that penetrate the paste. Not much [26] but the limit of placing time of the concrete is being defined by the initial setting time, this limit is standardized, but the gaining of the mechanical strength is being defined by the final setting time, for which there are standard limits as well.

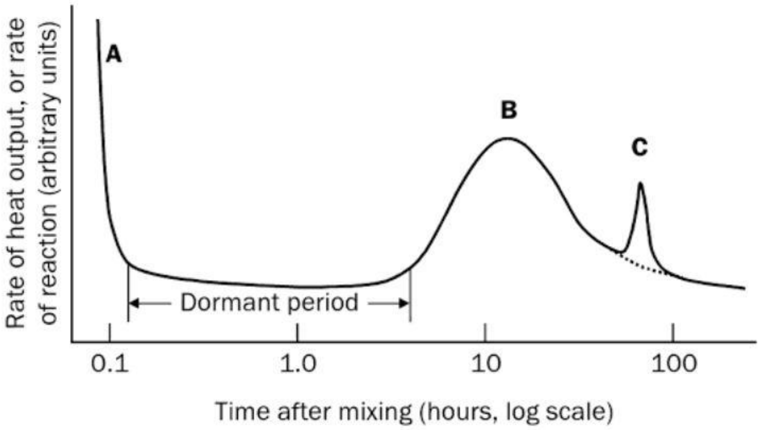

Figure 2. Heat releasing after cement paste mixing (Source: Construction materials: their nature and behavior – Domone et al.)

During the early hardening and early setting time, the cement paste becomes outstandingly warm, that means that the exothermic hydration reactions take place. If the paste is left in an adiabatic state, that means that in that condition there will be no heat loss, the amount of the released heat will be enough to bring the temperature to the 100°C or even more approximately in one day. [26] Fig 2 shows that “right after the mixing, short but the highest rate of heat releasing takes place (peak A) that is caused by the dehydration of calcium sulfate hemihydrate, that is caused by its own by the gypsum. After that the state of the paste rapidly it transfers into a dormant period that lasts for around 2-3 hours, then after a final setting time it reaches a lower peak (B) again, comes back to a short dormant period and after 1-2 days it reaches again a narrow peak C.”

The physical process in the cement grain during the hydration process is being schematically described in the fig. 3.

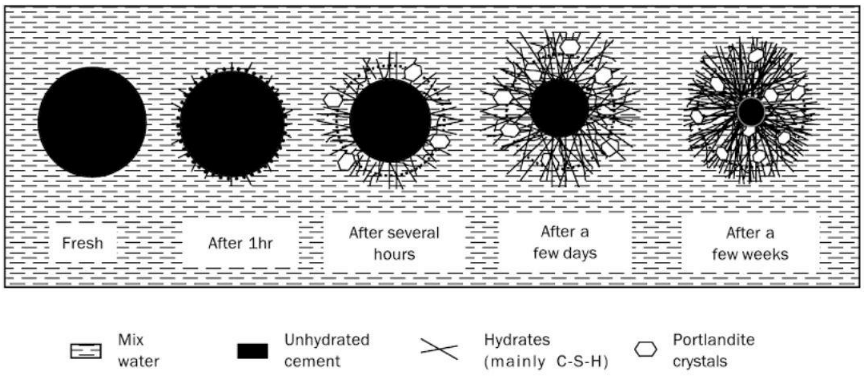

Figure 3. Hydration process in cement particles (Source: Construction materials: their nature and behavior – Domone et al.)

The moment when the pressure of osmosis or/and portlandite (Ca(OH)$_2$ disrupts the layer, can be considered as an end of the dormant period. This process [26] lets a hydration process be faster. The gel after hydration is composed of ettringite crystals of a needle shape and an amorphous mass that is mainly calcium silicate hydrate and portlandite crystals of the hexagon shape. It contains a lot of small pores of 0.5-5 nm width that decreases with the hydration process. At complete hydration, the porosity stays at 28%. The volume of the final product is about twice more than not hydrated cement.

1.8. The effect of adding Calcium Chloride or Magnesium Chloride to the cement hydration process

Several investigations have been conducted about the addition of $CaCl_2$ to the cement pastes, using the isothermal calorimetry and in-situ small angle neutron scattering. There have been conducted many experiments with isothermal calorimetry over the tricalcium silicate and tricalcium silicates accelerated by calcium chloride. These experiments showed that $CaCl_2$ meaningfully increases the hydration rate, still, it does not change the density the composition of calcium silicate hydrate. Wiltbank et al. conducted these experiments over the hydration temperatures varied from 10°C to 40°C. It was found that CaCl2 decreased the setting time of Portland Cement.

Later Bortoluzzi et al. provided a test on white Portland cement with the 10% of calcium chloride addition, in which the results showed that it decreased the setting time with about 50%, moreover it reduced the paste's solubility and increased the pH level of it.

There is a direct proportionality between the cement composition and the heat emission during the hydration process. The results are shown in Table 2, [27] namely we can see that the most heat is evolved by the C3A, after which comes C3S (tricalcium silicate). Calcium chloride also increases the heat evolved by C4AF (tetracalcium aluminoferrite) and C2S (dicalcium silicate). The variables for the real concrete mixes might be utilized to get a genuinely exact estimate of the expansion in the rate of advancement of warmth and the aggregate warmth developed up to 24 hours for a specific bond in case of $CaCl_2$ addition.

Table 3 represents the impact of an adjustment in a compound composition of the paste [27] upon the temperature released when calcium chloride is added. The column 1 of the table gives the assembly, column 2 gives the average change in the warmth created in 24 hours delivered by the expansion of 1 % of calcium chloride. From this table it can be seen for the trial bonds that an expansion in the warmth advanced from gathering to bunch was joined by an expansion in a level of both the tricalcium aluminate and the tricalcium silicate, the two mixes appeared from table 2 to be those contributing the more noteworthy amounts of the heat released during the hydration.

Table 2. Released heat in cement pastes (Source: Effect of calcium chloride on Portland cements and concretes - Rapp, P. et al.)

	Calories for each percent in 1 gram of cement	
Compound	Without $CaCl_2$	With 1% of $CaCl_2$
Tricalcium silicate	0.80	0.78
Dicalcium silicate	0.19	0.26
Tricalcium aluminate	1.62	1.47
Tetracalcium alumino-ferrite	0.01	0.25

Moreover, [27] the growth in the heat developed due to the addition of 1% of calcium chloride is the highest in the first group, the succeeding groups appear to develop less heat, reaches zero in the fourth group, and we find a definite decrease of 2 calories per gram in the 5th group. The abovementioned changes of the heat released those modifications in heat developed due to the addition of calcium chloride cannot seemingly be assigned to the tricalcium silicate content in each group, because it has been proven in table 2 that every percent of tricalcium silicate found in 1 gram of cement evolves the identical quantity of calories with or without calcium chloride. The modifications do, but, are inversely associated with the quantities of tricalcium aluminate, and directly associated with of dicalcium silicate and tetracalcium alumino-ferrite found in every group, and in this respect, are in the settlement with the records of table 2.

Table 3. Changes in the total heat evolved at 24 hours by the addition of 1% of CaCl2 to the cement pastes (Source: Effect of calcium chloride on Portland cements and concretes - Rapp, P. et al.)

Heat evolved in 24 hours without $CaCl_2$	Average changes produced by 1% of $CaCl_2$	Average compound composition			
		Tricalcium aluminate	Tetracalcium aluminoferrite	Dicalcium silicate	Tricalcium silicate
30-40 cal/g	+7 cal/g	3%	15%	47%	30%
40-50 cal/g	+5 cal/g	4%	14%	35%	42%
50-60 cal/g	+4 cal/g	10%	12%	34%	42%
60-70 cal/g	0 cal/g	10%	11%	25%	52%
70-80 cal/g	-2 cal/g	15%	7%	21%	53%

The impact of the addition of $CaCl_2$ [27] on the warmth evolved by using an ordinary Portland cement (B) is expressed in fig. 4. When the quantity of calcium chloride is expanded, the preliminary speed of heat release is expanded as well, however, the quantity of warmth evolved during a day is only slightly different.

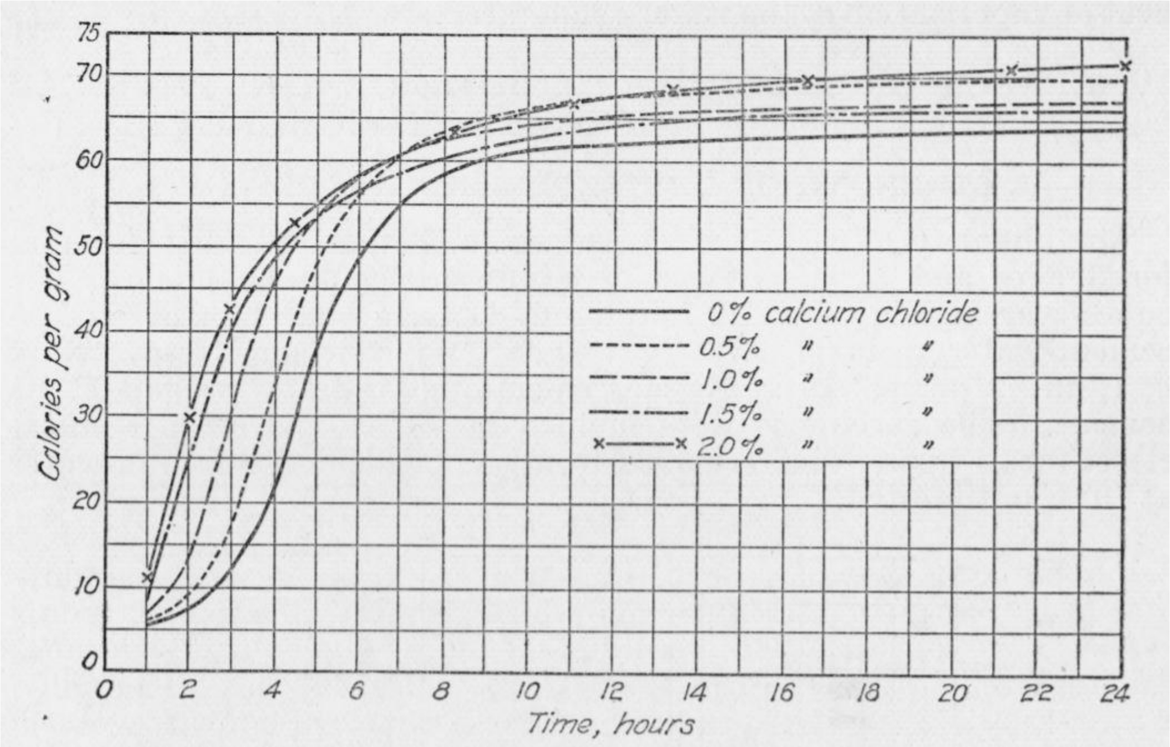

Figure 4. Typical heat curves of CaCl2 addition (Source: Effect of calcium chloride on Portland cements and concretes - Rapp, P. et al.)

Time-heat curves designed from the temperature statistics of those sorts of cement show that calcium chloride commonly rises the initial speed of temperature growth and reduces the time required to attain the most temperature. Still, with the high-early-energy cement (fig. 5), in each case, with CaCl2 and without, the maximum temperature attained got close to the water's boiling temperature [27].

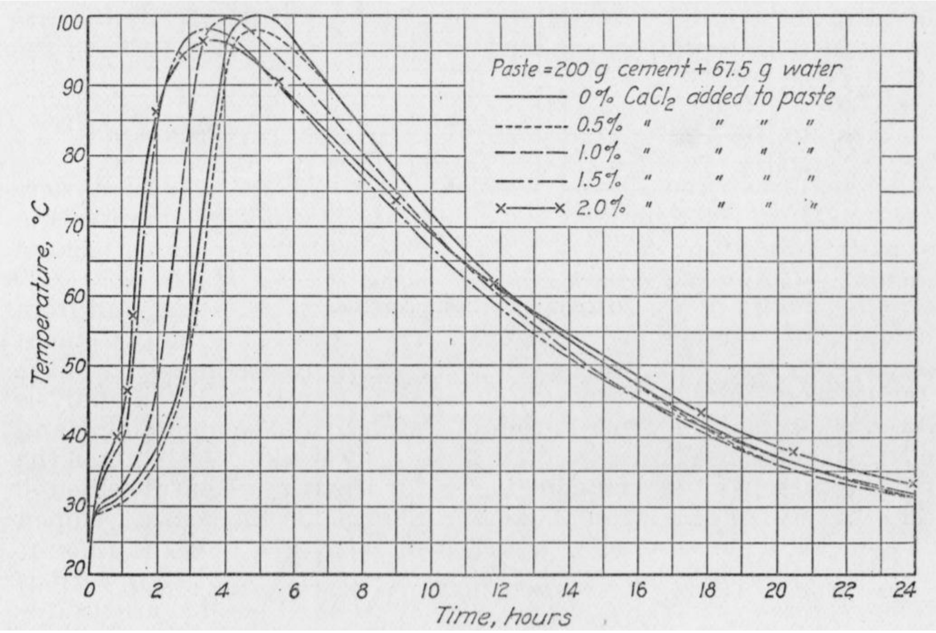

Figure 5. Temperature curves for high early strength cement (Source: Effect of calcium chloride on Portland cements and concretes - Rapp, P. et al.)

The strength results in figures 4, 5, and 6, and issued experiments show that the chemical composition of the cement significantly effects the mortars' compressive strength.

It is to be predicted that since the character compounds have totally unique strength traits, their proportions inside the cement influence the strength of the entire. The findings of this research support the outcomes suggested by Gonnerman (7) on almost the equal types of cement, specifically, *"(a) Tricalcium and dicalcium silicates are the main strength contributing compounds of Portland cement. Tricalcium silicate not just contributed a lot of the strength at the early ages, it also increased the strength in later ages. Dicalcium silicate contributed little to the strength up to twenty-eight days, however it significantly increased the later strength of the cement; (b) tricalcium aluminate contributed strength to a crucial degree up to twenty-eight days, but its impact then faded and have become zero or negative at 1 and 2 years, and (c) the function of tetracalcium alumino-ferrite stays vague for the cement paste. It affected the compressive strength of cement paste and concrete at some point at 28 days and later ages."*

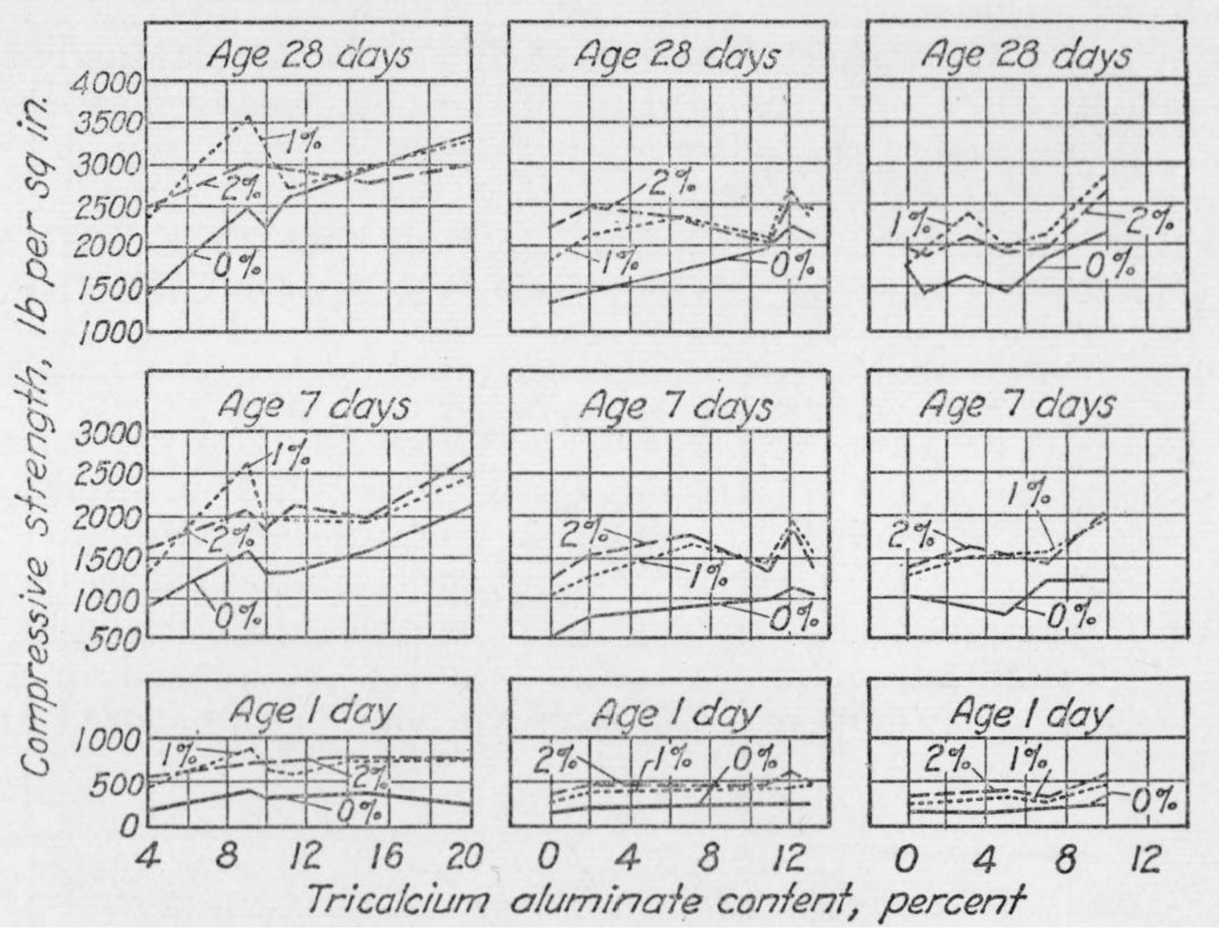

Figure 6. Compressive strength with and without calcium chloride with variable tricalcium-aluminate content (Source: Effect of calcium chloride on Portland cements and concretes - Rapp, P. et al.)

The addition of $CaCl_2$ improved the mortar compressive strength at every age of all the types of cement covering the incredibly wide ranges of silicate content stated above.

The flows of the concrete containing white cement have been in the identical range because the flows with general types of cement, and the calcium chloride had [27] about the equal impact. The flow of the concrete containing excessive-early-strength cement was similarly improved after using calcium chloride.

This growth in flow indicates improved workability, therefore, it is possible to use less water after adding calcium chloride, so that the flow of the plain concrete will remain unchanged. Consequently, it is possible to acquire both the early age and the later strength improvements because of a reduced water content.

There can be one more benefit [27] of the use of calcium chloride in a cold climate because of the increased heat development. The constructions under a low temperature need unique measures to guarantee a rate of hydration of the cement which assures an early strength. In thin concrete slabs, in which the heat can readily degenerate, this increased rapidity of heat development will compensate for much loss of the heat and will lower the curing time and the essential time for the usage of coverings, or diverse ways of keeping an appropriate temperature for hydration. Too great a growth in either, or both, of the accelerating factors, consequently, is probably to cause a time set so rapid that finishing of the placed concrete might be difficult.

It was found that [27] adding 2% of commercial calcium chloride to the standard and white Portland cement pastes is the optimum amount under 5°C and 20°C; at 30°C, it is recommended to use less - 1.5%. As far as it is being approved that the acceleration of both grown initial temperature and $CaCl_2$ is bigger for the high-early-strength cement, it is advised to use not more than 1.5% of commercial calcium chloride under 20-30°C for a better early strength.

(a) Verifying the results of experiments, the strength of Portland cement is significantly affected by its compound composition. The strength contribution of C3S, C3A, C2S and C4AF has been investigated.
(b) $CaCl_2$ improved the strengths of cement pastes, especially for the commercial Portland cement pastes.
(c) $CaCl_2$ improved the strength with the help of dicalcium and tricalcium silicates.
(d) For the first days, tricalcium aluminate increased the strength of the cement paste after calcium chloride addition, though after these days it tended to decrease.
(e) Tetracalcium alumino-ferrite has a very vague effect on the strength of cement. Calcium chloride addition makes this effect to be even slightly negative.

- As the amount of calcium chloride is being increased, the setting time of a cement 20°C is being decreased.
- Up to one-year age, the strength of the types of cement has been increased after the addition of calcium chloride, however further tests for the later ages were not performed. Moreover, calcium chloride increased not only the early strength, but it greatly improved the one-year strength as well. The experiments showed that calcium chloride improves the compression strength even up 90 days under the condition from 5 to 30°C.
- The addition of 3% of commercial calcium chloride improved the workability and the flow of the concrete under 20°C.
- The experiments under 5°C, 20°C and 30°C showed that calcium chloride can increase the early strength of the cement paste better if the initial curing temperature is lower.
- Tests approved that fundamental use of $CaCl_2$ is effective to increase the curing of all types of cement. It is significantly useful for the construction in the wintry weather as far as it greatly decreases the time that keeps the concrete strength.

There are different curing temperatures for concrete with an addition of calcium chloride and without [27]. There was found the optimal percentage of calcium chloride that should be used for the cement paste treatment under three different temperatures that are given in table 4:

Table 4. The optimum amount of CaCl2 which should be used at the three curing temperatures (Source: Effect of calcium chloride on Portland cements and concretes - Rapp, P. et al.)

Temperature, °C	Commercial $CaCl_2$	Type of cement
5	2%	All cements
20	2%	Normal and white
	1.5%	High early
30	1.5%	All cements

[28] Experiments show that magnesium chloride ($MgCl_2$) is the most effective accelerator among many others like calcium chloride, aluminium chloride ($AlCl_3$) and ammonium chloride (NH_4Cl). It showed also positive effects on the mechanical properties but negative ones on the expansion and shrinkage and the reinforcement corrosion.

2. Experiment materials and methods

In this work, three types of bottom ashes were collected from the Lithuanian factories after wood combustion. They have been studied using several analytical techniques to characterize and compare samples from different plants and determine its usage value in the concrete systems.

2.1 The used experimentation methods

To achieve the objectives of this work we did the following tests:

- X-ray powder diffraction (XRD)

  This test was performed to identify the unknown minerals and inorganic compounds of biomass bottom ash; X-ray diffractometer DRON-6 was used for the X-ray diffraction analysis with the help of CuKα radiation and Ni filter. The powder X-ray diffraction patterns were identified with references available in the PDF-2 database (PDF – 2 International Centre for Diffraction Data, 12 Campus Boulevard Newtown Square, PA 19073-3273 USA).
- X-ray fluorescence (XRF)

  This test was conducted for elemental and chemical analysis of the biomass bottom ash used in our experiments, that let us check the existence of hazardous materials in BBA. For ecological and health reasons, it is important that the building materials did not contain heavy metals;
- Ph meter

  For the better properties and human health reasons as well, it is important to make a cement paste that is pH neutral; For pH level definition in the used water suspensions we use the pH-meter EDGE, 230V
- The measurement of the hydration temperature of the BBA cement pastes was performed with 8-channel USB TC-08 Thermocouple Data Logger (temperature measurement ranges from -270 to +1820 °C).
- The compressive strength of hardened cement paste samples. (Fig. 7)

Compressive strength is one of the most important mechanical properties of concrete thus this test can greatly help to define the cons and pros of the addition of the biomass bottom ash to the cement paste; The water/solid material ratio was 0,35. The press Toni Technik 2020 was used to compress the sample cubes. The density of samples was determined according to EN 12390-7.

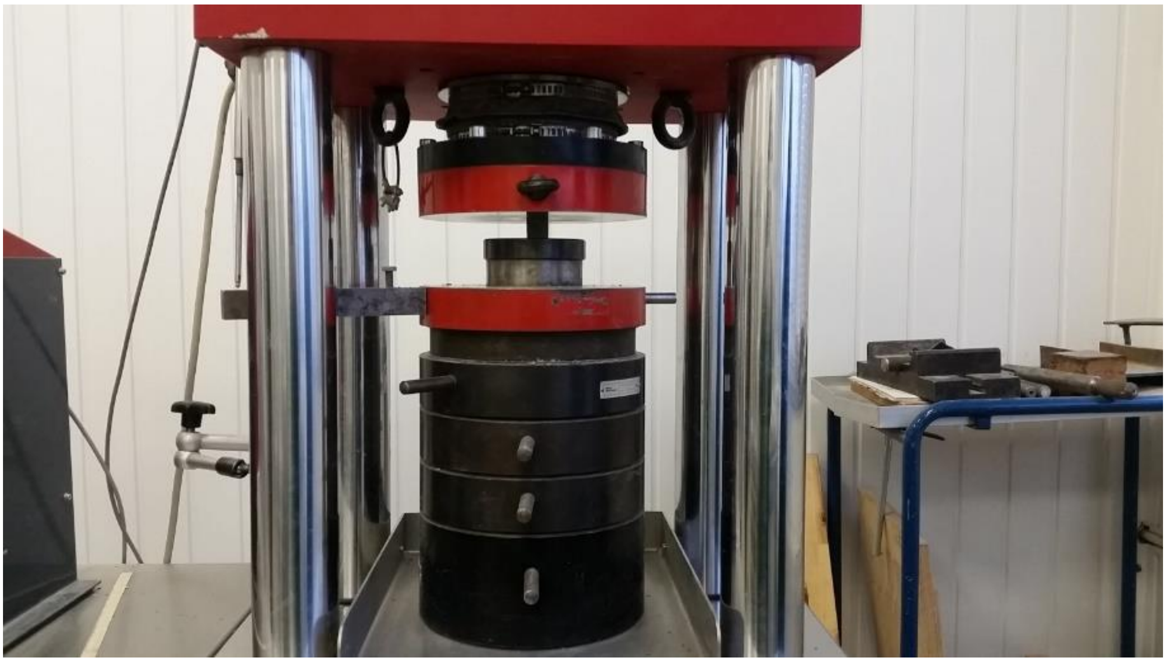

Figure 7. Compressive strength test on the final cement samples

After having checked the properties of the primary materials, the chemical modification was done according to the scheme shown in figure 8.

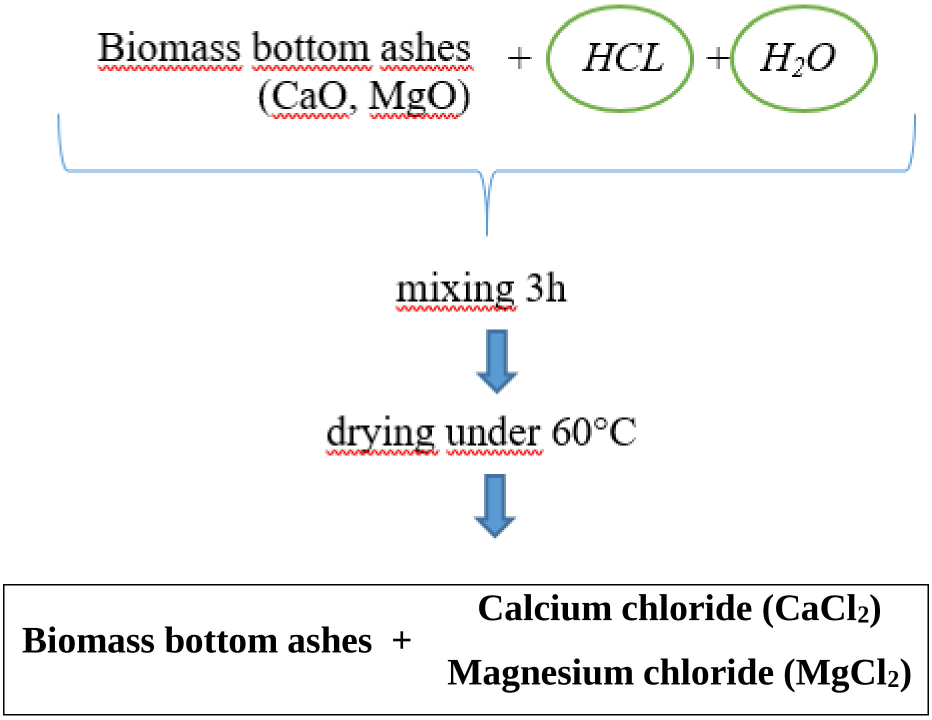

Figure 8. Method of the preparation of the biomass bottom ashes samples

In this case, the 10 % Hydrochloric acid (HCl) was used. The Ph values of investigated ashes were measured before the chemical modification and after the chemical treatment of the biomass bottom ash paste. After the chemical modification, the BBA powder was dried at 60°C until the complete drying.

2.2. Initial materials

In the experiments we have used the CEM I 52.5R type Portland cement. The commercial Portland cement type CEM I 52.5R was used for the tests. Table 5 represents the oxide composition of the cement paste, where we find that CaO and SiO_2 has the highest ratio.

Table 5. Oxide composition of the Portland cement

Chemical composition, %	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	MgO	K_2O	Na_2O
Portland cement clinker	20.61	5.45	3.36	63.42	0.80	3.84	1.31	0.94

Biomass bottom ashes were collected from three different combustion plants of Lithuania. The powders of the experiment biomass bottom ashes differ from each other with the color and texture (Fig. 9)

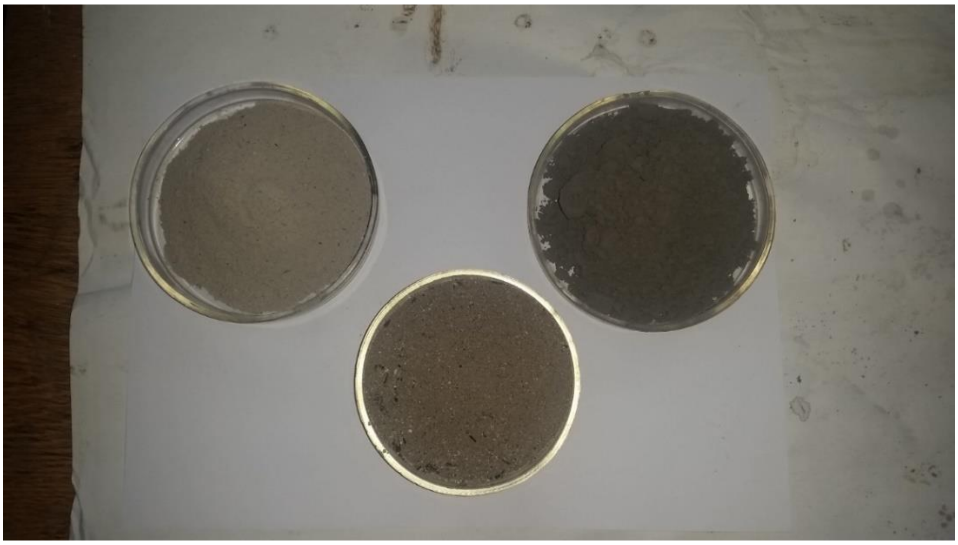

Figure 9. Type 1, Type 2, Type 3 BBA

The X-ray diffraction (XRD) spectroscopy test was conducted with the DRON-6. X-rays are the transverse electromagnetic waves of a wavelength of 10^{-12}-10^{-8}. The main principle of the method is that the structural characteristics of the substances can be determined by reflection and diffraction.

$$n\lambda=2\cdot d\cdot \sin\theta$$

where λ is an x-ray wavelength; n - is an integral, called a spectrum, or reflection.

The first effect that chlorine is responsible for is the corrosion of ash in the boilers, furnaces and on metal surfaces, moreover for the emission of NaCl, HCl, KCl, $ZnCl_2$ [29] „Chlorine related corrosion problems are predictable when the fuel concentrations is more than 0.1 w-% (d.b.) and is possible to be of significance for hay, cereals and grasses" [30].

The biomass burning type, changes during the combustion process and some other factors have an influence on the chemical characteristics of the ash.

On the Fig.10 can be found the chemical composition of all the types of the biomass bottom ashes that were used for the experiments.

As the curves show the ashes, used during the experiments, are heterogeneous products the composition of which consist of primarily of few main components, that are: quartz (SiO_2), synthetic calcite ($CaCO_3$), Halite (NaCl), calcium sulfate ($CaSO_4$), other components are shown in lower rates.

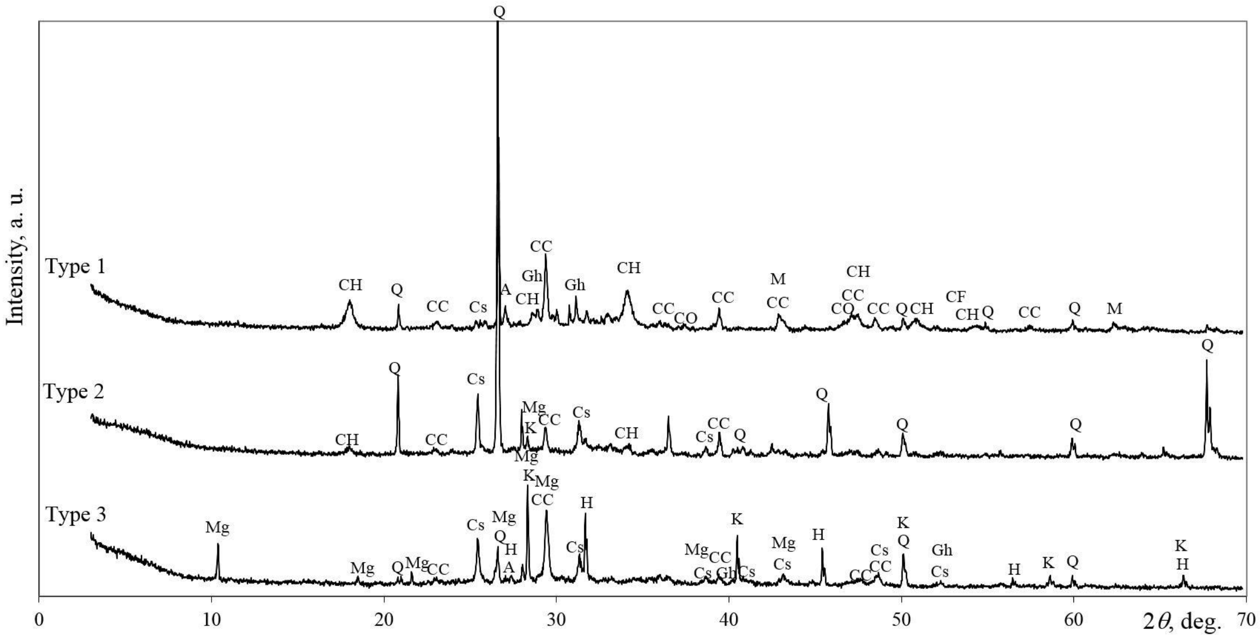

Figure 10. X-Ray diffraction pattern of biomass bottom ashes. Notes: Q–quartz SiO2 (83-539), CH –calcium hydroxide Ca(OH)2 (44-1481), M – periclase MgO (45-946), CC – calcite $CaCO_3$ (5-586), A – allophane $Al_2O_32SiO_23H_2O$ (38-449), Gh – gehlenite Ca_2 Al($AlSiO_7$) (79-1726), Cs – calcium sulfate $CaSo_4$ (80-787), CO – lime CaO (3-1123), H – halite NaCl (75-306), K – potassium chloride KCl (75-296), Mg – cordierite $Mg_2Al_4Si_5O_{18}$

Aluminium (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), phosphorus (P), silicon (Si) are the major elements that form the ash and that have the significant effect on ash melting and deposit formatting behaviours. Unstable elements such as chlorine (Cl), sulfur (S), sodium (Na), potassium (K), arsenic (As), cadmium (Cd), mercury (Hg), lead (Pb), zinc (Zn), are responsible for gas emissions and the deposit formation, oxidation and utilisation or disposal creation.

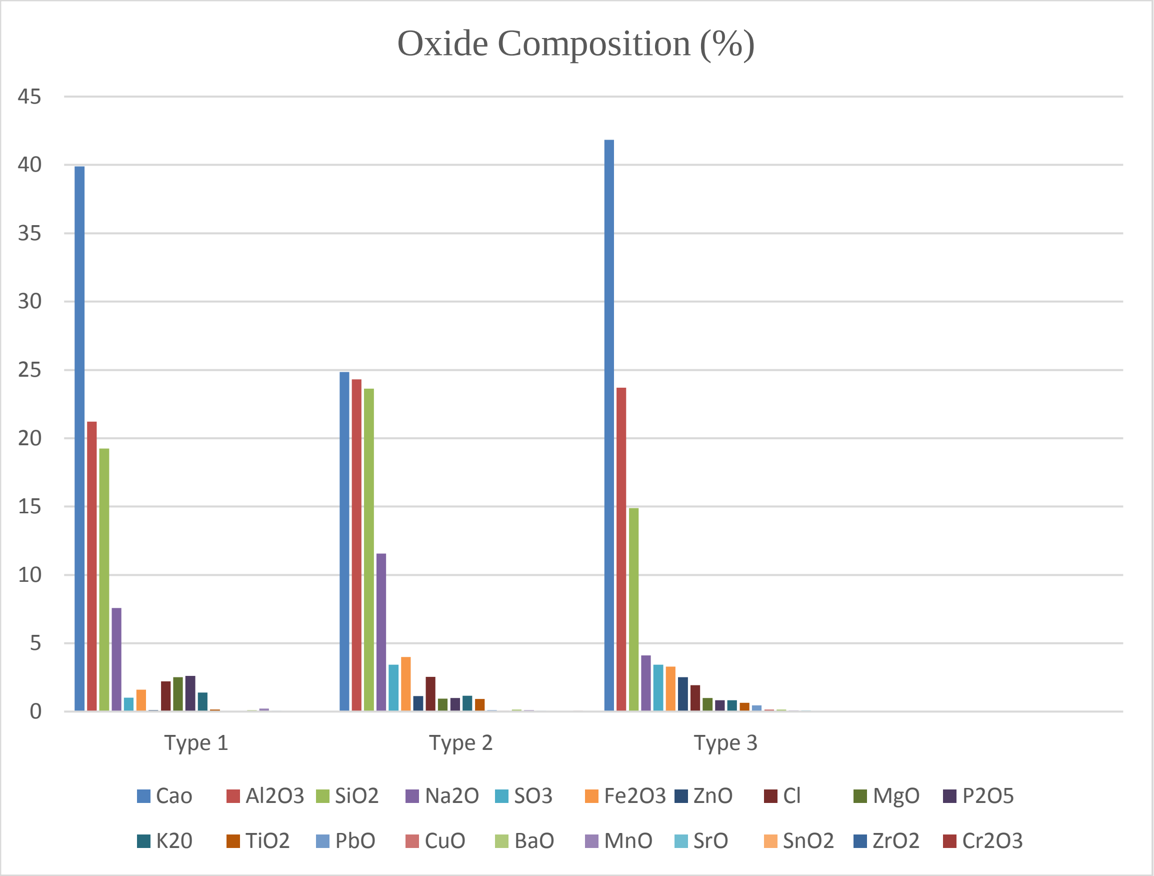

Figure 11. BBA oxide composition

As we can see from the diagram (Figure 11), oxide composition levels vary from type to type. In all the samples calcium oxide, known as “burnt lime” is the dominant one, but the most amount of this oxide is in the Type 3 bottom ash (41.84%), then comes Type 1 (39.89%) and in the end - Type 2 (18.4%).

After Calcium oxide, the significant part is being taken by aluminum oxide, silicon dioxide, sodium oxide. BBA Type 2 stands out with the almost even amounts of CaO, Al_2O_3 and SiO_2 (about 18%).

BBA Type 2 and 3 contain small amount of toxic oxides - Lead oxide (PbO)(Type 2 - 0.11%, Type 3 – 0.45%). All types of BBA contain toxic BaO (Type 1 – 0.11%; Type 2 – 0.15%; Type 3 – 0.15%)

Unlike Type 3 BBA (0.05%), we do not find the tin dioxide (SnO_2) in the other two types. Chromium oxide takes 0% of the Type 1 BBA, Type 2 – 0.05%, Type 3 – 0.03%.

3. Results and discussion

In this work, three types of biomass bottom ashes were studied that were gathered from the three-different wood combustion power plants in Lithuania. The study was conducted to find out the potential use of BBA in construction materials, providing the “greener” environment with the help of elimination of CO2 emission and sustainable energy strategy.

3.1 Hardened cement paste samples with BBA

By replacing 0, 5, 10 and 15% of Portland cement to biomass bottom ashes 4x4x16 cm samples from this cement paste were made. It was found that micro and macro cracks opened while these samples were hardening (Fig 16.). The reason can be calcium and magnesium oxides hydration reaction (1 and 2). It causes volume expansion, internal stresses, and the cracking in the solid sample. Therefore, in cement systems, biomass bottom ashes cannot be used without additional processing.

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (4)$$
$$MgO + H_2O \rightarrow Mg(OH)_2 \qquad (5)$$

Figure 12. Hardened cement paste with biomass bottom ashes

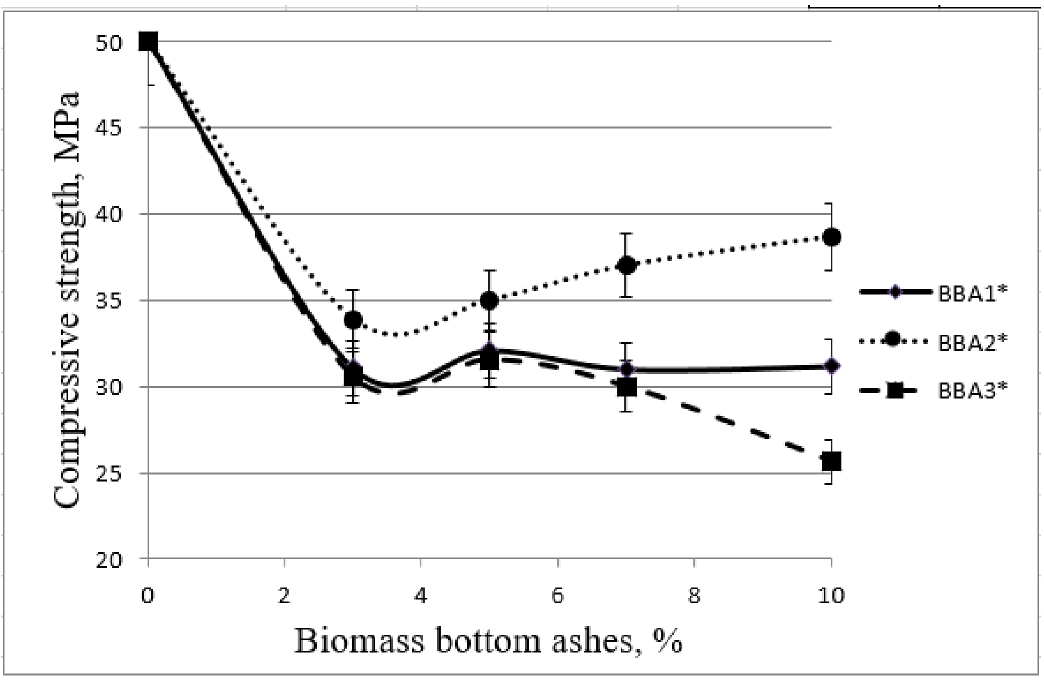

Figure 13. Compressive strength of the concrete samples with unmodified BBA

Figure 13 describes that the use of the unmodified biomass bottom ash in the cement, showed that is disgrading for the compressive strength of the samples. All these three kinds of the biomass bottom ashes decreased the compressive strength with about 50%.

For example, Type 3 BBA decreased the compressive strength from 50 MPa to 25 MPa. Unlike the further experiments, where BBA Type 2 showed the best result, here we can see that this type has decreased for the least percentage, however, still, it worsened the compressive strength of concrete sample from 50 MPa to 39 MPa.

3.2 The chemical modification of BBA

pH value is one of the most important aspects to evaluate the calcium and magnesium compounds in the BBA.

In the initial pH values of untreated biomass bottom ashes used for experiments were highly alkaline: 12.61, 12.42, and 9.58, fig 12.

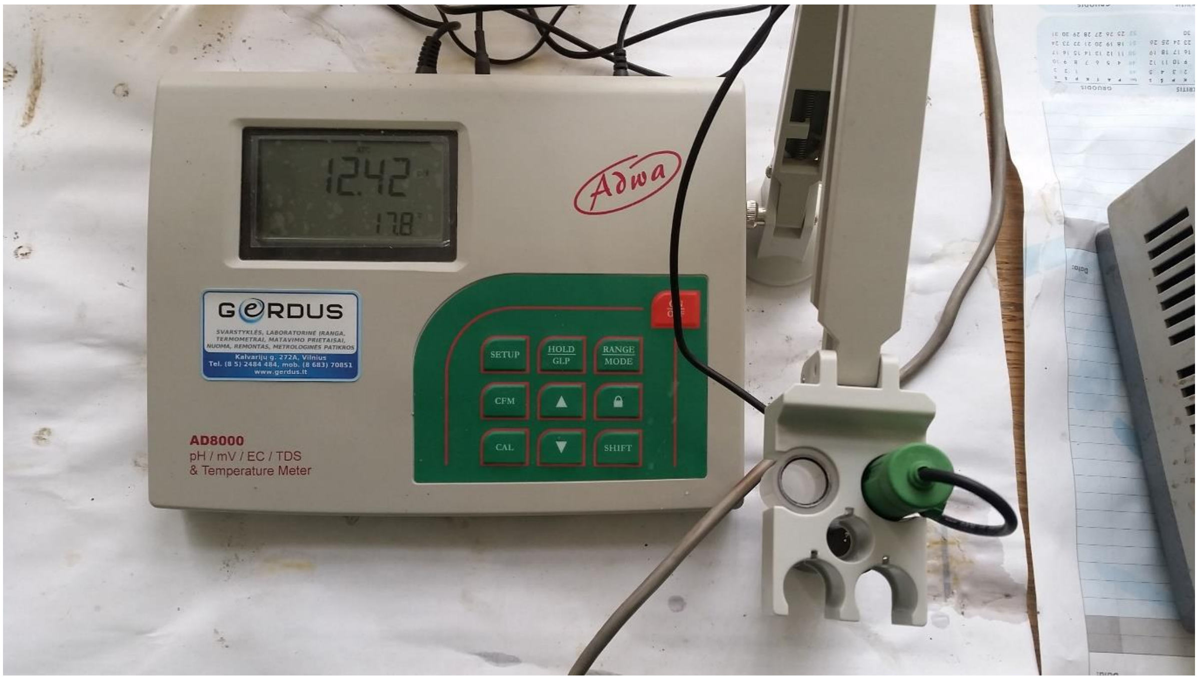

Figure 14. pH level in BBA before HCl treatment

By adding the hydrochloric acid to BBA neutralization reaction appears and $CaCl_2$ with/or $MgCl_2$ form in the mixtures (equation 3).

$$CaO + HCl \rightarrow CaCl_2 + H_2O \qquad (3)$$
$$MgO + HCl \rightarrow MgCl_2 + H_2O$$

The aim was to make a BBA paste to be pH neutral and to bind dangerous CaO and MgO that was possible with adding the hydrochloric acid to the paste. The amount of hydrochloric acid was different, and it depends on calcium and magnesium compounds.

Type 1 – 150g ash + 100ml H_2O + 370ml HCl;

pH before HCl treatment - 12,61

pH after HCl treatment - 7,18

Type 2 – 150g ash + 100ml H_2O + 200ml HCl;

pH before HCl treatment - 12,42

pH after HCl treatment - 7,03

Type 3 – 150g ash + 100ml H_2O + 110ml HCl;

pH before HCl treatment – 9.58

pH after HCl treatment - 7,23

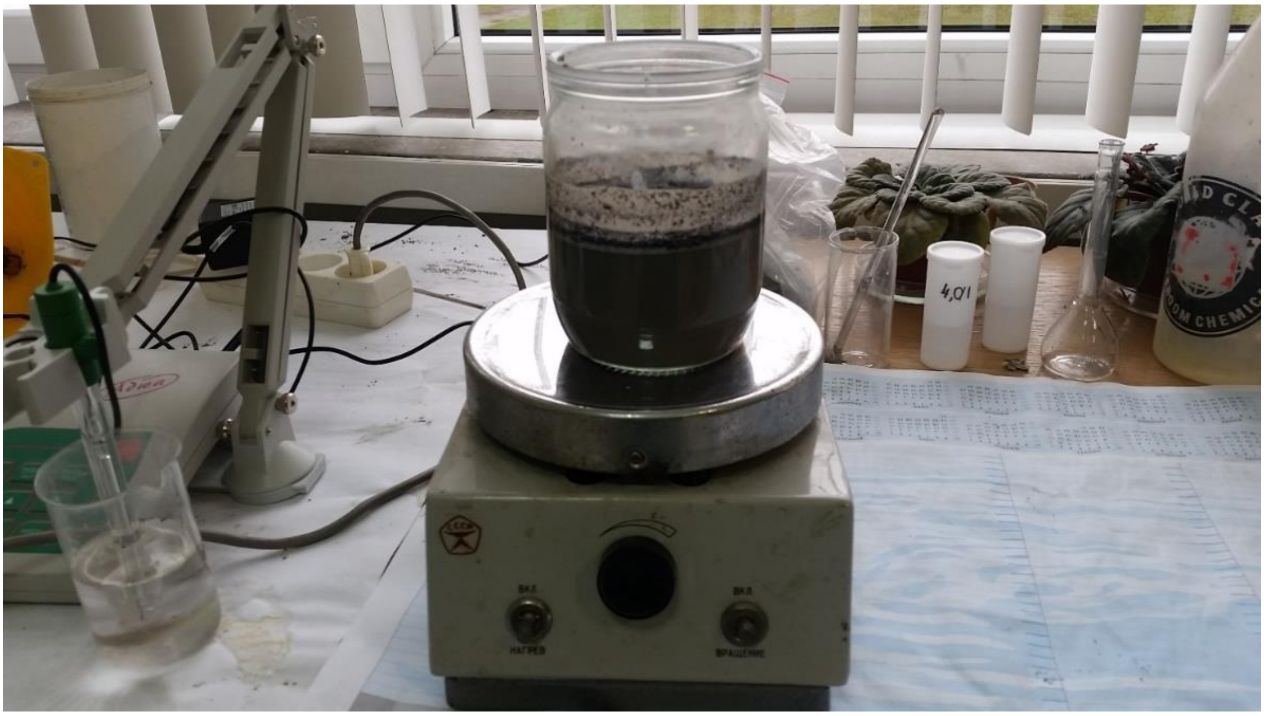

Figure 15. BBA mixing and HCl treatment process

The process of lowering the pH level in the biomass bottom ash Type 1 took longer time and needed more hydrochloric acid treatment than Type 2 and Type 3.

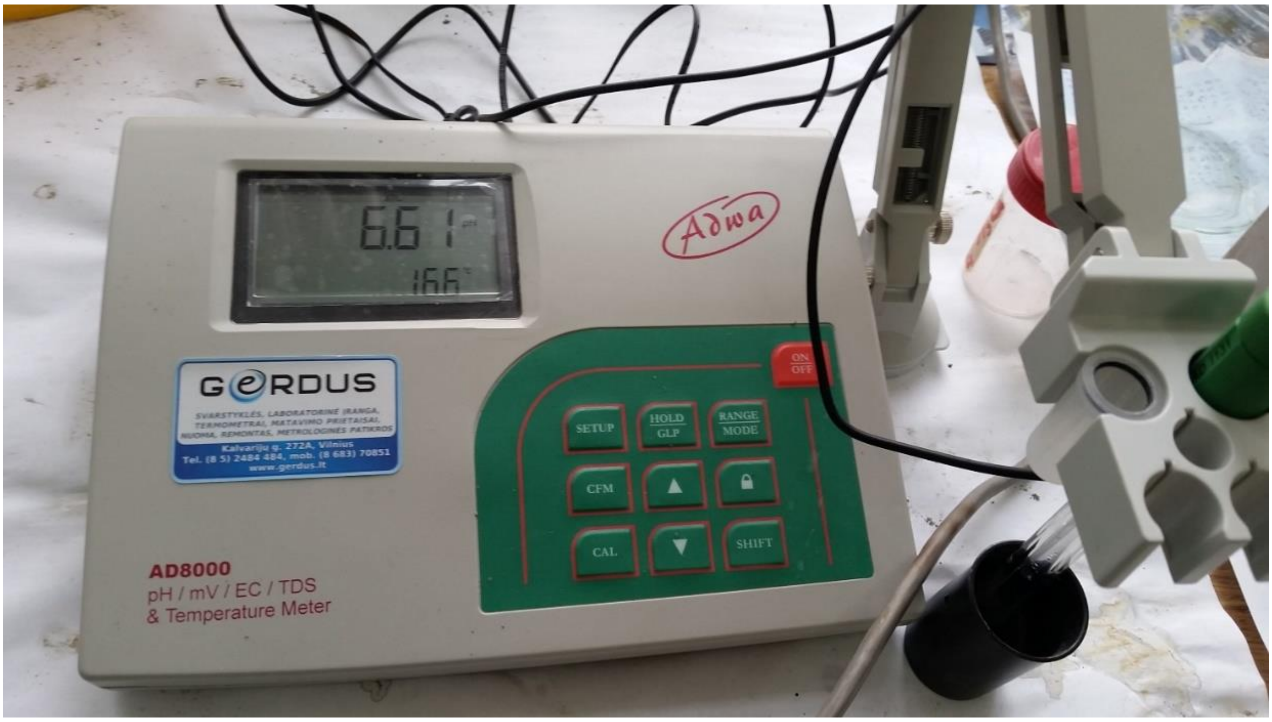

Figure 16. pH level in BBa after HCl treatment

Figure 17. Type 1, Type 2, Type 3 BBA after chemical treatment and drying at 60 °C temperature

Calculations showed that the biomass bottom ash Type 1 contained 12.82% of CaC_2, BBA Type 2 contained 7.14% of CaCl2, while BBA Type 3 – 3.99%.

3.3 Hardened cement paste samples with modified BBA

Five samples were prepared for the experiment (Table 6) with three types of BBA.

After chemical treatment of biomass bottom ashes, they were inserted in cement paste and hydration temperature was measured (Fig. 17). It was determined that the highest hydration temperature was shown by the sample with 5% of the modified BBA. By increasing the modified biomass bottom ash, the duration of maximum hydration peak was shorter. It could be explained by the higher amount of acceleration compounds ($CaCl_2$ and $MgCl_2$) in the system.

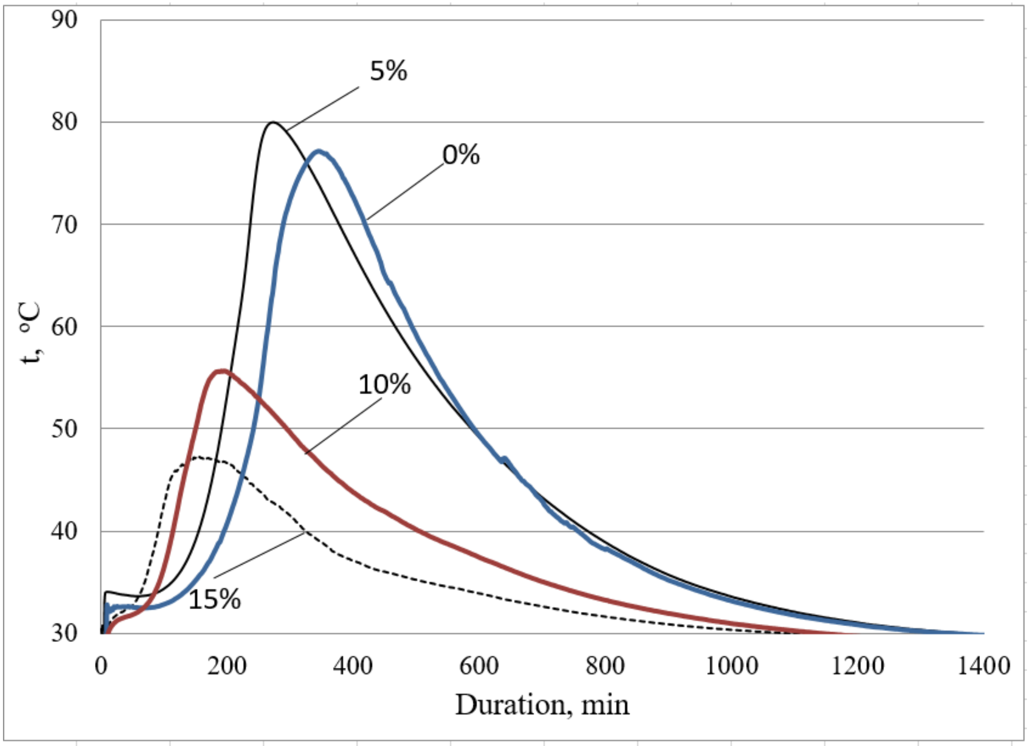

Figure 18. The dependence of hydration temperature of Portland cement paste on the quantity of modified biomass bottom ash Type 1.

Table 6. Measurements and compressive strength data of final concrete samples after 7 days

No BBA		**mm**	**mm**	**mm**	**g**	**kN**
0%	1	21.20	19.60	19.20	18.22	33.13
	2	21.50	21.40	20.00	18.63	32.33
	3	21.40	22.70	19.30	18.22	22.84
Type 1						
3%	1	20.20	20.00	20.10	16.27	34.21
	2	20.10	20.00	20.00	16.01	32.80
	3	20.00	20.20	20.10	16.18	30.18
5%	1	20.00	20.80	21.10	17.32	30.84
	2	19.80	20.50	21.40	17.62	33.42
	3	21.30	19.60	20.60	17.23	24.14
7%	1	19.80	20.00	19.70	15.91	28.09
	2	20.00	19.80	19.80	15.86	32.46
	3	19.80	19.80	20.00	16.06	36.91
10%	1	20.50	20.00	21.00	17.49	34.45
	2	19.50	21.00	21.00	17.41	29.09
	3	19.60	20.50	20.40	16.75	32.33
Type 2						
3%	1	21.80	21.20	20.10	17.95	18.01
	2	21.20	20.50	19.70	17.07	21.15
	3	20.60	21.00	20.00	17.23	23.03
5%	1	20.70	21.50	20.50	17.14	9.25
	2	21.20	22.30	20.40	18.77	17.70
	3	21.00	20.50	21.70	17.93	17.98
7%	1	20.20	20.70	20.10	15.94	11.25
	2	20.20	20.80	20.20	16.56	9.28
	3	20.80	20.20	20.20	16.49	16.75
10%	1	20.20	21.10	20.20	16.15	17.15
	2	20.00	21.40	20.00	16.33	16.46
	3	20.20	21.30	20.10	16.17	16.01
Type 3						
3%	1	20.20	20.20	20.20	16.35	35.45
	2	20.30	20.10	20.20	16.36	26.34
	3	20.50	19.80	20.30	16.49	25.26
5%	1	20.40	20.50	20.20	16.48	23.56
	2	20.40	19.90	20.40	16.41	28.61
	3	20.30	20.50	20.40	18.77	33.19
7%	1	19.70	20.10	19.80	15.95	27.90
	2	20.20	20.20	19.90	16.29	25.07
	3	20.10	20.20	19.80	16.17	32.74
10%	1	19.90	19.90	20.00	15.16	21.66
	2	20.00	20.10	19.80	14.96	18.30
	3	20.10	19.40	20.10	14.86	19.52

As the table 6 and figure19 shows the best compressive strength properties after 7 days were shown by the Type 1 and Type 3 BBA concrete samples. We can see that the hardened cement paste samples that contained BBA Type 1 with each percentage (3%, 5%, 7%, 10%) showed the top 10 best results. As for the Type 3 concrete, only the concrete sample that contained only 3% of BBA showed the superior results.

The lowest results were shown only by the samples that contained BBA Type 2. It could be explained that in this type biomass bottom ashes there is a small number of accelerating compounds.

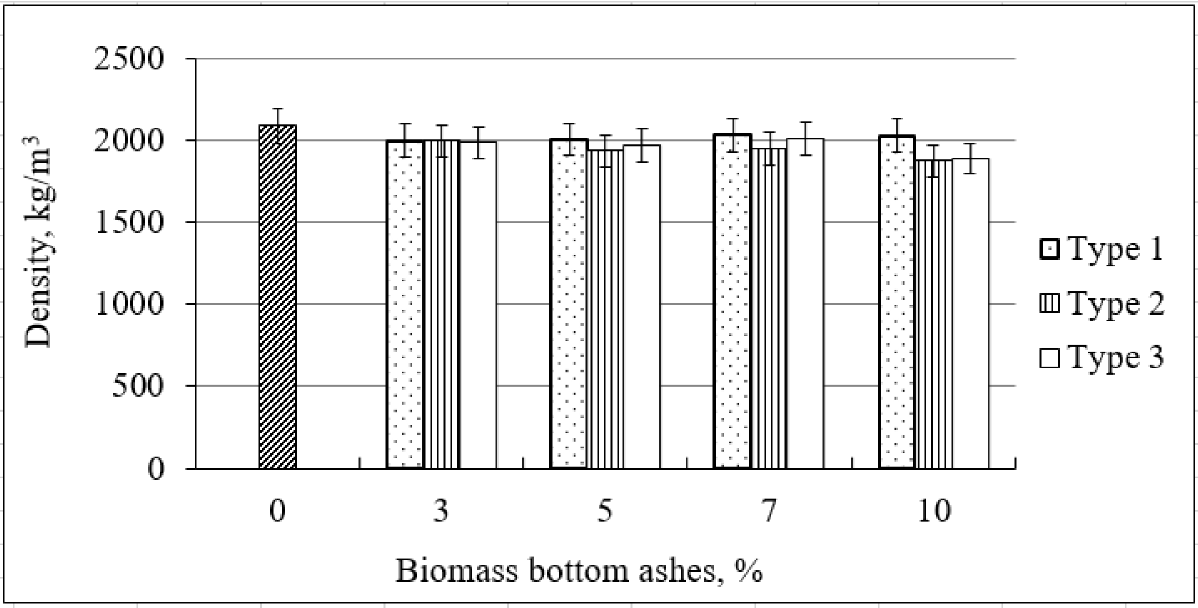

Figure 19. Density of hardened cement paste samples after 7 days

The density of hardened cement paste samples was like the reference sample density. The reference samples density was slightly higher than samples with biomass bottom ashes.

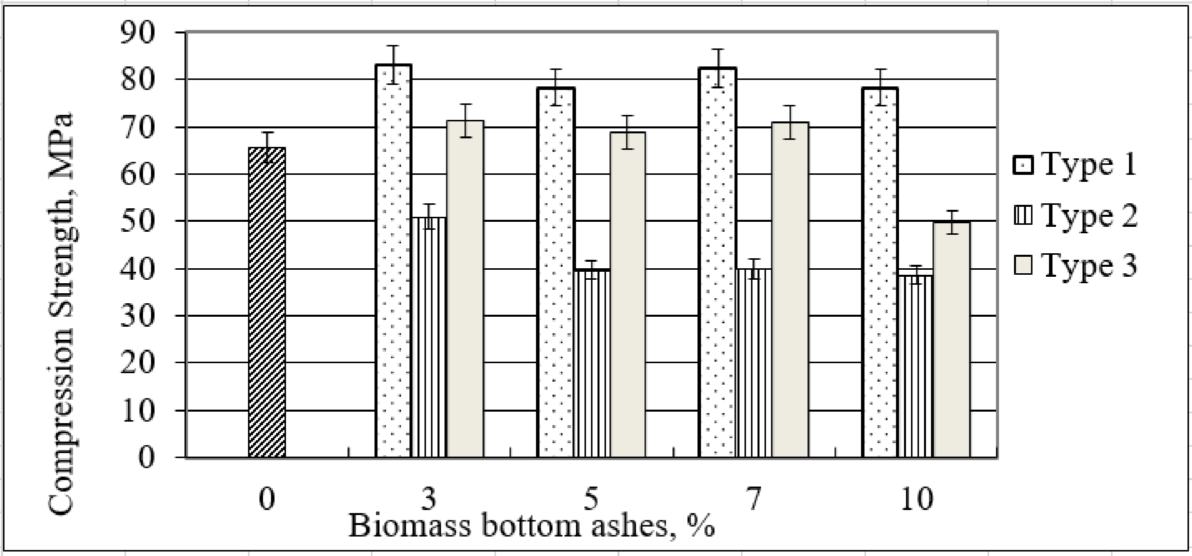

Figure 20. Compressive strength of hardened cement paste samples after 7 days

Figure 19 shows that the best result is being shown by the concrete sample with Type 1 BBA content of 7% - 36.91kN. Which is followed by the sample that contained 3% of Type 3 BBA.

The best result of the Type 2 BBA is only in the sample which contained only 3% of this type – 23.03kN.

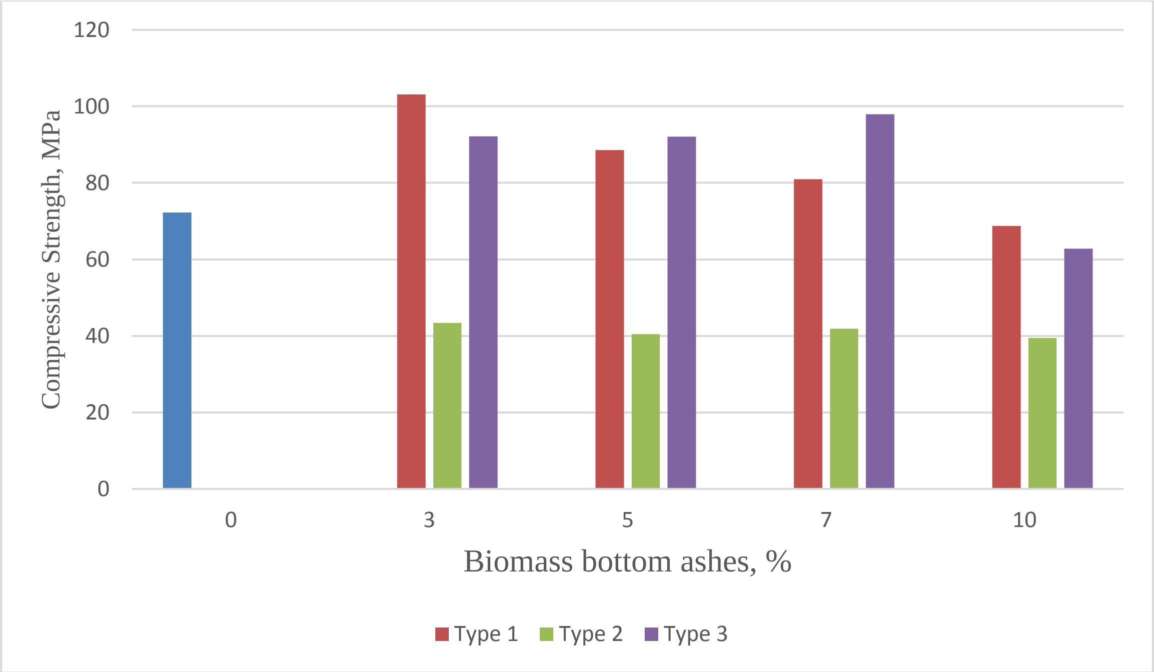

Figure 21. Compressive strength of hardened cement paste samples with modified BBA after 28 days

Table 7. Measurements and compressive strength data of final concrete samples after 28 days

No BBA		**mm**	**mm**	**mm**	**g**	**kN**
0%	1	21.60	19.50	21.30	19.19	34.03
	2	21.00	19.70	21.20	18.33	31.00
	3	21.50	19.50	21.10	18.68	25.47
Type 1						
3%	1	20.00	19.60	20.00	16.47	41.10
	2	20.10	19.80	20.20	16.36	40.96
	3	19.90	19.60	20.30	16.11	39.66
5%	1	21.60	20.00	21.00	18.26	39.81
	2	20.80	20.00	21.60	18.18	33.57
	3	19.70	21.00	20.60	17.74	38.43
7%	1	19.80	20.00	20.00	16.24	36.15
	2	20.00	20.00	20.00	16.25	31.83
	3	20.00	20.00	20.00	16.00	28.81
10%	1	20.80	20.00	21.40	17.40	30.60
	2	21.00	19.80	21.30	17.88	28.79
	3	21.00	19.50	20.70	17.17	25.94
Type 2						
3%	1	21.00	20.00	21.20	17.89	17.26
	2	21.20	20.00	21.50	18.13	19.24
	3	21.00	19.80	21.40	17.68	18.20
5%	1	22.20	20.40	21.30	18.94	20.11
	2	21.90	20.50	21.40	18.84	20.73
	3	21.30	22.30	20.50	19.26	14.67
7%	1	20.30	21.20	20.10	16.70	17.69
	2	20.50	21.00	20.10	16.67	17.37
	3	20.20	21.30	20.40	16.75	18.99
10%	1	20.00	21.40	20.20	16.37	18.84
	2	20.20	21.00	20.10	16.14	14.37
	3	20.20	21.50	20.00	16.43	17.57
Type 3						
3%	1	20.00	20.00	20.40	16.05	38.23
	2	20.00	20.30	20.00	15.98	39.35
	3	20.50	20.10	20.00	16.41	34.65
5%	1	20.50	20.40	19.80	16.55	37.80
	2	20.00	20.20	20.40	16.63	41.91
	3	20.20	19.80	20.20	16.65	32.88
7%	1	20.30	19.90	20.00	16.49	40.08
	2	20.10	20.00	20.00	16.31	41.80
	3	20.10	20.10	20.00	16.57	36.61
10%	1	20.10	20.30	20.20	15.29	28.98
	2	20.00	20.10	20.10	15.03	27.55
	3	20.00	20.30	20.00	15.23	19.82

The figure 21 shows that the after addition of modified BBA to the cement systems, compressive strength of the samples icreases with around 40%. After 28 days, the biomass bottom ash type 1 showed the best results again. Addition of the 3% of the Type 1 BBA appeared to be the optimal option.

From figure 22, we can clearly find out that after 28 days, the compressive strength of the sample increases, though, as the content of BBA increases, we see that the compressive strength decreases, moreover, in case of 7% and 10% use of BBA, the compressive strength becomes less than it was after 7 days.

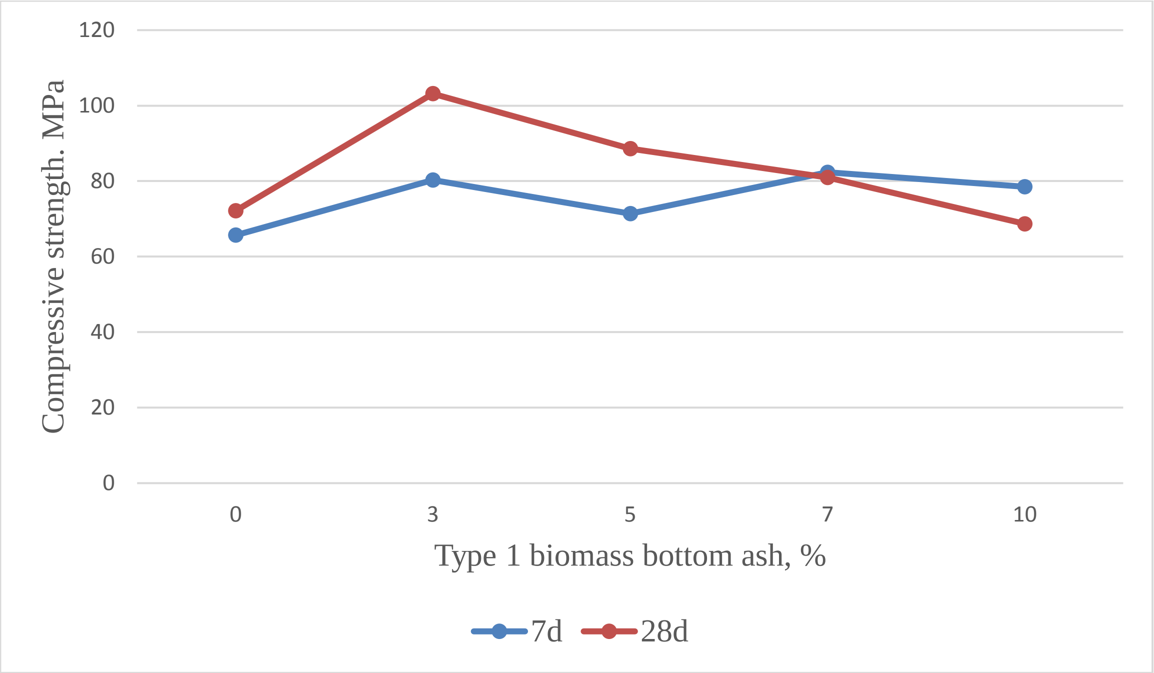

Figure 22. Difference of compressive strength between 7 and 28 days (using Type 1 BBA)

Figure 23 describes the same change of the BBA Type 2. As we can see, after 28 days the compressive strength of cement pastes improve in cas of 5% and 7% use of it, still the level is lower than the compressive strength level of the ordinary portland cement without biomass bottom ash.

According to figure 24, we can conclude that BBA Type 3 can be used with any amount, up to 7%. 10% of BBA Type 3 showes the decreased compressive strength of the hardened cement paste. 7% of type 3 biomass bottom ash sows the best result from this type. Up to 7 days the compressive strength almost does not change between the cement paste with BBA and without it, but as we can see, at 28 days of hardening, it gains around 7% improvement.

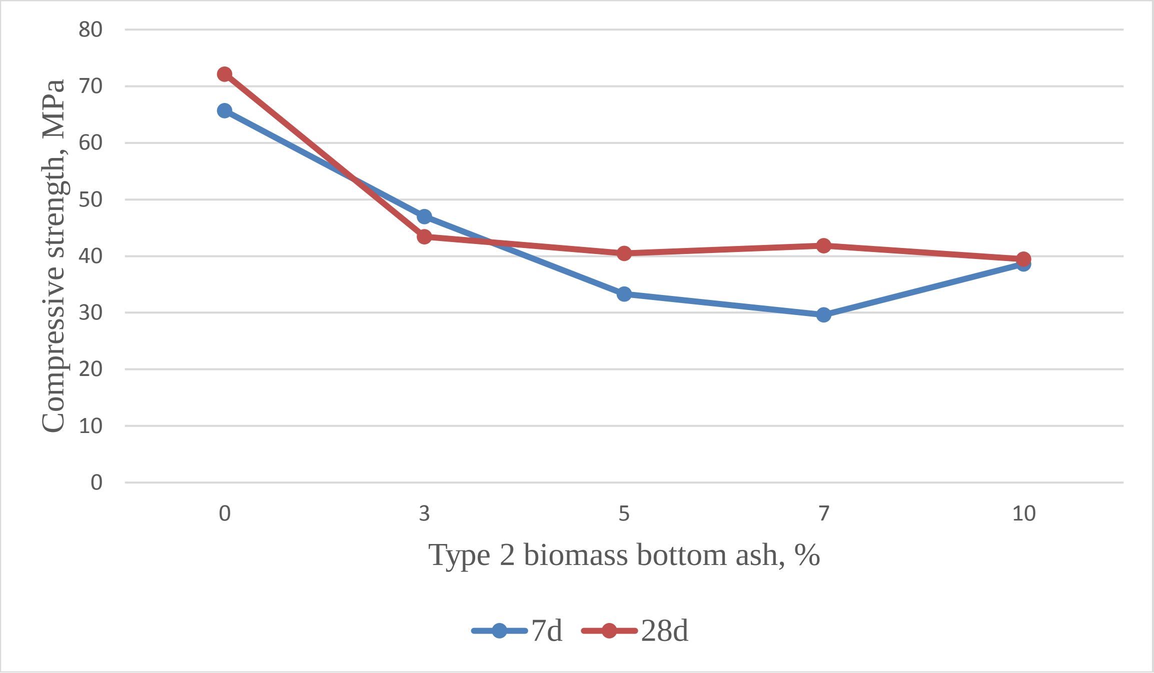

Figure 23. Difference of compressive strength between 7 and 28 days (using Type 2 BBA)

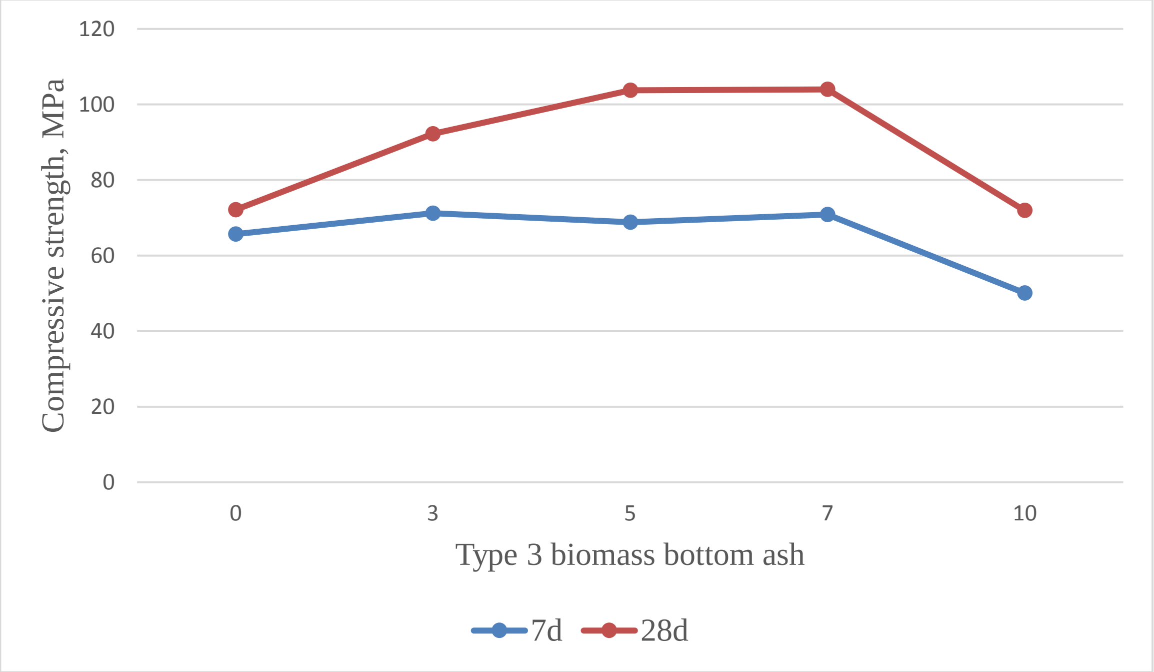

Figure 24. Difference of compressive strength between 7 and 28 days (using Type 3 BBA)

4. Conclusions

In this work tree types of biomass bottom ashes were studied that were gathered from the three-different wood combustion power plants in Lithuania. The study was conducted to find out the potential use of BBA in construction materials, providing the “greener” environment with the help of elimination of CO_2 emission and sustainable energy strategy.

- It has been found that biomass bottom ashes cannot be used as a direct substitute for Portland cement due to the hydration reactions of magnesium and calcium oxides in hardened cement paste.
- The above-described experiments proved that the unmodified biomass bottom ash decreases the compressive strength of the ordinary concrete sample for around 50%.
- By adding the hydrochloric acid to BBA neutralization reaction appears and $CaCl_2$ with $MgCl_2$ form in the mixtures.
- Hardened cement paste samples, where part of the Portland cement was replaced with chemical modified biomass bottom ashes, had a compressive strength ranging from 38.64 to 83.10 MPa at an early age. The maximum compressive strength was determined at 83.10 MPa for hardened cement paste samples with 1 type ash. It was approximately 21% higher than reference hardened cement paste samples.
- The compressive strength of hardened cement paste samples with modified BBA of Type 1 and Type 3 improved after 28 days with almost 40% than the compressive strength at an early age.

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