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The Impact of Fly Ashes from Thermal Conversion of Sewage Sludge on Properties of Natural Building Materials on the Example of Clay

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Abstract: The reduction of carbon dioxide emissions, introduced by the European Union, opened the possibility of conducting experimental works on a new generation of materials—ecological and environmentally friendly ones. Such materials include those which combine raw natural resources with waste subject to disposal. The objective of the performed investigations was an assessment of the influence of fly ashes on selected parameters of building materials. The paper proposes a method of the enrichment of clay with fly ash, which would lead to the neutralization of heavy metals in the burnt matrix, possible oxidation of organic substances present in the ashes, or the destruction of pathogens, as well as an increase of the resistance of the clay ceramics to low temperatures. Clay samples were prepared with the addition of the fly ash from three sewage treatment plants. The experiments encompassed investigations of physical and chemical properties of the fly ash, as well as bending strength tests of the beam-shaped samples heated at temperatures of 20, 300, 500, and 700 °C. The beam halves, resulting from the destruction of the samples during these tests, served for testing the compressive strength. The collected results allowed a comparison of the properties of the samples. The obtained test results confirm the possibility of manufacturing a product modified with the fly ash from the thermal treatment of sewage sludge. The obtained compressive strength of the samples amounted 0.3–2.6 MPa.

Keywords: fly ash; clay-ash composite; compression strength

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1. Introduction and Literature Review

Limitations in CO_2 emissions, introduced by the EU in 2020, opened new opportunities to conduct experimental works on a new generation of materials—environmentally friendly and ecological ones.

An increase in the worldwide population due to economic development, urbanization, and industrialization evoke a dynamic development of sewerage networks and sewage treatment plants. As a result of the sewage treatment process, increasingly high quantities of sludge are being generated. At the beginning of the 21th century worldwide, ca. 45 m tons of a dry sludge was generated, of which, among the EU countries, the highest production per year was noted in Germany (1.85 m tons of the dry mass), the United Kingdom (1.14 m tons), and Spain (1.03 m tons), whereas in China, this was over 12 m tons [1,2]. In Norway, France, USA, China, Australia, Spain, and the United Kingdom, the generated sewage sludge is utilized in agriculture. Of the total production of sludge in Japan, 48% is used in the manufacturing of building materials; in Poland, Germany, and Austria, the

use of sewage sludge in agriculture is limited by binding regulations [3,4]. The use of sewage sludge, mainly its utilization and treatment, becomes then an important problem not only economically and technically, but also ecologically—a problem facing the world. In countries such as Austria, Netherlands, Germany, or the United Kingdom, the combustion constituted a significant part of the utilization of the generated sewage sludge. In Switzerland, Austria, and the Netherlands, it exceeded half of the total amount of the sludge, whereas in Japan, it amounted to 55%, and in the USA, 25% [5].

Sewage sludge management is regulated by the Council Directive 86/278/EEC of 12 June 1986, concerning the protection of the environment, particularly soils and the use of sewage sludge in agriculture. According to this document, the use of sludge in agriculture is prohibited if limit values for heavy metals are exceeded [6]. The directive 91/271/EEC, accepted 21 May 1991, obliges to monitor the municipal waste treatment [7]. The municipal sewage sludge is also addressed by the Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on wastes. According to this document, sludge, as waste, is subject to the hierarchy of waste management. Firstly, waste generation must be prevented, but if the waste has been generated, it must be prepared to be reused, and then recycled or recovered in another way and finally disposed of [8]. The Directive 99/31/WE of 26 April 1999 introduces storage limits for the sewage sludge [9]. In the United States, an analogical document is the Code of Federal Regulations [10]; in China, the 2002 "Standard for Discharging Pollutants into Urban Wastewater Treatment Plants" [11]; and in the Republic of South Africa, "Guidelines for the Utilization and Disposal of Wastewater Sludge" [12].

The municipal sewage being submitted to sewage treatment plants is a mix of domestic and industrial sewage, as well as rainwater. The quantitative and qualitative characteristics of such sewage are related mainly to the type and technical state of the sewerage system which supplies it, the living standard of citizens, the quantity of consumed water, and the industrialization level of the city. The quantity and quality of the sewage supplied varies through annual, monthly, weekly, and daily cycles [13]. The sewage sludge gathered in the treatment plant is inhomogeneous in terms of its physical and chemical composition, and it contains inorganic and organic substances, including pathogens, microbiological mass, nutritive components, phosphorus, nitrogen, and metals. A characteristic feature of the sludge is a high content of water—up to 95–99%—and a high concentration of heavy metals (Hg, Zn, Cd, Cr, Cu, Ni, Pb, As, Sb, Se, Ba, Mo) [4,14]. The main source of the heavy metals in the sludge is the sewage generated by industrial plants using galvanic processes and a recycling of lead accumulators in their technologies; additional sources are domestic sewage and the corrosion of sewerage pipes. Taking into account the disadvantageous influence of the sewage sludge on the natural environment and public health, its purification is recommended by its stabilization and volume reduction. The choice of a method of the utilization of the sewage sludge depends on its physical and chemical features, including the content of SiO_2, Al_2O_3, CaO, Fe_2O_3, SO_3, P_2O_5, and heavy metals.

Currently, the most popular utilization method for the sewage sludge is the thermal method, which is ecologically safe and economically justified. An incineration takes place in fluidal (rotational or scaffolding) furnaces [15–17]. An advantage of this method, first of all, is a reduction of waste (sludge) volume, a reduction of the quantity of sulfur and nitrogen compounds in combustion gases, and a yield of heat and electric energy. A secondary (waste) material generated in the installations of the thermal conversion of sewage sludge is fly ash, which is described as waste by code 19 01 14, and also requires appropriate management. The main legal act regulating the issues of the thermal conversion of waste, including an incineration of municipal sewage sludge with energy recovery, is the Directive of the European Parliament and Council (EU/2010/75) of 24 November 2010 on industrial emissions (integrated pollution prevention and control). The objective of this directive is, as far as possible, a limitation of the negative impact on the environment, particularly pollution through emissions to the air, soil, surface, and ground waters, as well as the resulting threats for human health evoked by the combustion and co-combustion

of waste [18]. Taking into account the near-zero-emission economy, the ashes from the combustion of sewage sludge should be treated as a potential product possible to reuse, namely in the manufacturing of building materials.

Research is under way concerning the possibilities of the application of such wastes as a source of phosphorus (in the chemical (mainly fertilizers) industry) [19–22], in building construction [23–26], and in mining technologies [27,28].

Fly ashes from electric and CHP plants have long been a valuable additive to ceramic masses used in the manufacturing of fired ceramics. The use of fly ashes generated in the combustion of hard coal in the manufacturing of so-called red building ceramics is because the chemical composition is close to that of the typical clay materials commonly used in the building ceramics industry. Apart from the fired building ceramics, the fly ash is also applied as an additive for clay raw materials used in the manufacturing of non-fired building materials and in wall constructions made of unprocessed clay. An example of this is the research on non-fired clay-ash composites performed by Wiśniewski and Ziółkowska (2014). Basing on this research, it was concluded that samples containing up to 10% of the siliceous fly ash show the optimum composition in terms of compressive strength, shrinkage reduction, and bending strength. If no firing is provided, then a higher content of the ash relative to the clay (20–30%) results in a reduction of the bending strength, which is undesirable if the clay-ash composite is intended to be used in the construction of supporting brickworks of buildings [29].

When applying any additives to the clay raw materials, an account should be taken of their chemical and mineralogical composition, which is determined based on a chemical and rational analysis (Table 1) [30]. As characteristic indicators, a molar content ratio of Al_2O_3 vs. SiO_2 is assumed, as well as a sum of the molar content of fluxes, generally noted as $R_2O + RO + Fe_2O_3$.

Table 1. Chemical composition of clay raw materials [30].

Chemical Composition	% of Mass
SiO_2	45–80
Al_2O_3	8–28
Fe_2O_3	2–15
FeO	2–15
CaO	0.5–20
MgO	0.0–4
K_2O	0.0–5
Na_2O	0.0–5
Loss on ignition	3–16

The first successful laboratory and industrial tests of the application of high additions of fly ashes in ceramic masses formed in a plastic method were made by Kałwa and Ropska (1986). Based on their investigations, the manufacturing technology of full and checker brick with a content of 45–60% of fly ashes in its mass was implemented. However, such a high content of the fly ashes is required to keep strict technological regimes related to mixing, drying, and firing, as well as the composition of the fly ashes themselves [31].

The fly ash generated during the thermal conversion of sewage sludge has a form of fine dust, allowing its direct introduction into a raw material mix used in the manufacturing of building ceramics. The ceramics industry mainly uses the siliceous fly ashes from CHP and conventional electric plants; however, in the fly ashes from the thermal conversion of sewage sludge, high quantities of the iron oxide and oxides of other metals can occur; thus, the addition of the fly ash can negatively affect features of the ceramic products—first of all, it can decrease the firing temperature and deform the products. As the investigations by Ferreira show [32], this problem can be solved by an optimum choice of the ash added to the clay material and an appropriate choice of the firing temperature.

The application of the ashes from the thermal conversion of sewage sludge is possible in the manufacturing of building ceramic materials (full, checker, and ceramic hollow

brick), similarly to the ashes from the coal combustion. The ash content, however, should be subjected to comprehensive investigations each time. If the ash content in the ceramic mass is high, then the maximum quantity must be related to an appropriate forming technology. As the investigations by Lin and Weng show [33,34], a significant influence on the quality of building ceramic products has the ash content in the ceramic mass and the firing temperature. In the mentioned investigations, the highest quality of bricks was obtained for 10% content of the ash from thermal conversion of sewage sludge, 24% humidity, and firing temperatures of 880 and 960 °C. The investigations by Kosior-Kazberuk and Karwowska [35] confirmed the conclusions of Lin and Weng that for ash content up to 10%, the quality of the products is comparable to that of traditionally manufactured products, and the results of strength tests are similar.

It must be noted that the ashes can be used for the manufacturing of bricks only if technical and environmental standards are satisfied [33]. The investigations on an elution of trace elements from bricks showed that such a form of ash utilization does not threaten environmental safety [36].

The objective of the performed study is an evaluation of the possibilities of a rational application of fly ashes from thermal conversion of sewage sludge in the manufacturing of clay-ash composites, as well as a determination of an influence of the ashes on the strength of these composites. The investigations have also been aimed on the determination of an impact of higher temperatures on the mechanical properties of the designed composites. The firing temperatures were selected so that they correspond to firing conditions and conditions existing in spaces on various heights. The temperatures selected to the tests are also characteristic for structural changes in the clay-ash composites. The next objective of the investigations was to determine the impact of the clay additives on the bending strength in normal conditions and after a preliminary thermal last. The firing of the samples was performed according to an assumed temperature distribution curve close to the so-called standard curve applied in fire resistance tests of the construction elements of buildings.

2. Materials and Methods

2.1. Materials and Preparation of Samples

To make the samples, we used clay and an additive—fly ash from the combustion of sewage sludge from the treatment plants in Warsaw ("Czajka"), in Cracow ("Płaszów"), and in Łodz (Figure 1). For a comparison, samples without additives were also prepared—they contained 100% clay. The samples were labeled according to the following pattern:

- 0-i—without additives (pure clay),
- 1-i—with addition of the fly ash from the combustion of sewage sludge from Łodz,
- 2-i—with addition of the fly ash from the combustion of sewage sludge from Cracow,
- 3-i—with addition of the fly ash from the combustion of sewage sludge from Warsaw,

where "i" denotes the number of a sample in the given series.

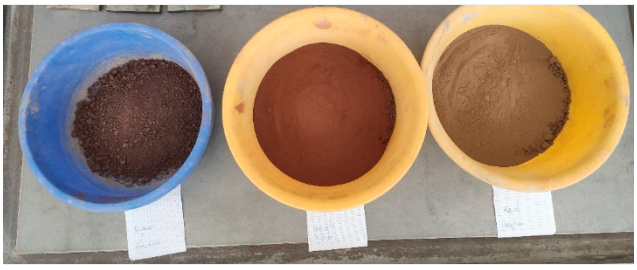

Figure 1. Fly ash from thermal conversion of sewage sludge obtained in three sewage treatment plants.

For the mixed samples (clay + ash), the proportion between the components was 60% clay and 40% ash. To determine the soakability, the samples were prepared in cubical

molds with dimensions of 4.0 × 4.0 × 4.0 cm, with 5 items per variant. For all variants, the preparation and filling of the mold were performed the same way.

The first step in the sample preparation process was a thorough drying and grinding of the clay, and then its sieving through a sieve with a mesh size of 2 mm to remove fine dirt particles. After sieving, the clay was divided into four parts to prepare a so-called "0"-sample and three samples containing the fly ashes from the treatment plants from Warsaw, Cracow, and Łodz. These three parts were supplemented by the ash in the amount of 40% of the initial mass of the clay. After a thorough mixing of the clay and ash, water was added to each sample to make the clay workable and to ensure that all samples had plasticity on a similar level. The water-clay mix was left for several hours to ensure its homogenization (uniform dampening of the clay particles). The clay was molded by hands until a homogeneous mass was obtained.

Checking the plasticity consisted of forming a 200 g clay ball and dropping it from 2 m on a flat, smooth surface. The diameter of the deformed ball after falling was 80 ± 2 mm for all parts with various fly ashes. Retaining the constant plasticity by the samples was necessary for achieving homogeneous results of measurements [37]. The deformed ball after falling is presented in Figure 2.

Figure 2. 200 g clay ball after falling from the height of 2 m.

After obtaining a clay mass fulfilling the constant plasticity criterium, the samples were molded. Due to the possibility of water evaporation from the prepared mass, the molding was performed in the shortest possible time—otherwise, measurement errors could have occurred. Each of the aforementioned parts of the plastic clay mass with the fly ashes of various types was placed in the cubical molds with dimensions of 40 × 40 × 40 mm, and in the beam-shaped molds with dimensions of 40 × 40 × 160 mm.

Before filling with the clay, the molds had been thoroughly cleaned and smeared with oil to prevent clay mix adhesion. The filling was performed in two stages. The first one consisted of filling the mold to 1/3 of its height, and a thorough beating of the mass with a wooden club. In the second stage, the remaining part of the mold was filled with the mass with an excess of ca. 2 cm, and the mass was smoothed with fingers and compacted with the club until the moment when further compaction became impossible. The clay excess was then cut off and smoothed with a knife. Before drying, each sample was numbered, and points were marked for shrinkage tests.

The drying of the clay composite samples lasted 3 days outdoors and then 2 days in a dryer with a temperature of ca. 40 °C. The slow drying was necessary to avoid an abrupt shrinkage resulting in possible fine cracks. After getting out of the dryer, the samples were left for 6 h in an ambient temperature to balance the humidity. Then, the samples were

dried in a temperature of 105 °C until mass stability was obtained. After the drying, the samples were subjected to shrinkage tests and then locked in sealed containers to avoid a possible absorption of humidity from the air. Table 2 presents the obtained results, and Figure 3 presents the samples themselves.

Table 2. Labeling and mass of the samples before weighing.

Pure Clay		Clay with Ash From					
		Łodz		Cracow		Warsaw	
No.	Mass [g]	No.	Mass [g]	No.	Mass [g]	No.	Mass [g]
0-1	136.0	1-1	114.0	2-1	120.0	3-1	120.0
0-2	138.0	1-2	119.0	2-2	118.0	3-2	119.0
0-3	134.0	1-3	114.0	2-3	117.0	3-3	114.0
0-4	135.0	1-4	119.0	2-4	120.0	3-4	116.0
0-5	132.0	1-5	120.0	2-5	118.0	3-5	116.0

Figure 3. Mixed samples.

2.2. Research Methods

To determine the physical and chemical properties of the fly ashes from combustion of sewage sludge, appropriate tests were performed. The chemical composition and morphology were determined with use of the SEM Quanta 250 FEG scanning microscope (Panalytical, Eindhoven, The Netherlands). The analysis of chemical composition was based on X-ray radiation energy dispersion—EDS (Energy Dispersive X-Ray Spectroscopy). The chemical composition of the investigated fly ashes was determined with the method of energy dispersive X-ray fluorescence (XRF) on the Panalytical's Epsilon-3 spectrometer. The tests were carried out in a measurement range for the elements Na—Am with the use of an apparatus equipped with an Rh X-ray tube (9 W, 50 kV, 1 mA), 4096-channel spectrum analyzer, six measuring filters (Cu-500, Cu-300, Ti, Al-50, Al-200, Ag), as well as the Panalytical's high-resolution solid state SDD detector (50 µm thick beryllium window), cooled with a Peltier's cell. The grain size distribution analysis was carried out on the base of a laser diffraction phenomenon, with the use of the Malvern Instruments' Mastersizer 3000 analyzer. Measurements were carried out in a dispersing liquid (deionized water) in the presence of an ultrasonic probe to break bigger aggregates of the tested samples. Grains with equivalent diameters from the range 0.1–1000 µm were analyzed. The mineral composition of the ashes was determined with the use of X-ray phase analysis (XRD). Measurements were done with the use of powder diffraction by means of the Panalytical X'pertPRO MPD X-ray diffractometer with the PW 3020 goniometer. As an X-ray radiation source, a copper tube was used (CuKα radiation, λ = 1.54178 Å). Data were handled with the use of X'Pert Highscore software. The identification of mineral phases was based on the PDF-2 Release 2010 database, formalized by JCPDS-ICDD.

The bending and compressive strength was tested for the samples, with dimensions of 40 × 40 × 160 mm in a mortar testing machine equipped with an arm exerting a pressing force up to 250 kN (Advantest 9 of the Controls company).

The thermal resistance of the clay-ash composite against high temperature was investigated in a special furnace, PK 1100/5 from Termolab S.C. (Warsaw, Poland), with electrically supplied heating sections. The samples were held in a temperature of 300–700 °C. The rig is equipped in the dedicated program ThermoPro, which enables programming of the heating process. The temperature distribution in the tested element was monitored with the use of the thermocouples NiCr-Ni, fulfilling the standard requirements [38].

Before starting the heating, all samples were dried to a constant mass in a temperature of 105 ± 5 °C. A signal from thermocouples was registered by a computer equipped with dedicated software. The elements were heated according to the standard temperature–time curve for a determined combination of temperature loads and in a predetermined time. The temperature distribution is presented in Figure 4. The analysis and evaluation of the temperature impact on the elements made of the clay-ash composites were carried out in a predetermined time excluding a cooling phase. After reaching the assumed temperature, i.e., 20 °C, 300 °C, and 700 °C, the samples were additionally soaked for 30 min. The purpose was to equalize the temperature in the whole volume of the composite before cooling until the ambient temperature. The total time of the load of the element with the temperatures of 300 °C and 700 °C was equal to 60 and 180 min, respectively. Then, the samples were tested with regard to selected mechanical properties.

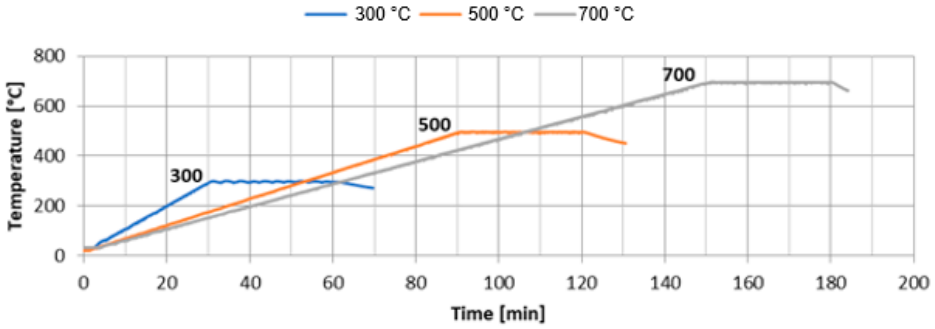

Figure 4. Temperature distribution in the elements.

The tests were carried out in the Warsaw University of Life Sciences (Institute of Civil Engineering, Warsaw, Poland), in Main School of Fire Service in Warsaw, and in the Lublin University of Technology.

2.3. Characteristics of the Clay Used in the Research

The clay used in the tests came from excavations in the vicinity of Szkucin in Świętokrzyskie voivodship. It is a medium fat clay; its chemical composition is presented in Table 3, and the mineral compositionis presented in Table 4.

Table 3. Chemical composition of a medium fat clay.

Chemical Composition	Content [%]
SiO_2	55.00–67.40
Al_2O_3	13.60–17.30
TiO_2	0.70–0.85
Fe_2O_3	6.20–7.90
MnO	0.06–0.17
MgO	1.65–2.70
CaO	0.25–0.75
Na_2O	0.05–0.30
K_2O	2.35–3.40
P_2O	0.05–0.15

Table 4. Mineral composition of the clay used for the investigations.

Mineral Composition	Content [%]
Quartz	17–23
Kaolinite	3–10
Illit	3–10
Hematite	3–5
Plagioclase	<3
Potassium feldspar	<3
Goethite	<2
Anataz	3–5
Packaged minerals (vermiculite/chlorite, smectite/illite)	47–68
amorphous phase	-

The chemical and mineral composition were determined in a laboratory of the Institute of Glass and Ceramics in Warsaw, basing on the samples taken from a deposit in the clay mine and brickyard in Szkucin. Comprehensive mineralogic tests encompassed microscopic, derivatographic, thermogravimetric, and X-ray tests, which showed that the main components of these formations are clay minerals, e.g., feldspars, etc. Among the clay minerals, the basic component is the kaolinite, and to a lesser extent, illite. They are accompanied by feldspar-type minerals and mixed-layer minerals. Among the non-clay minerals, the quartz and hematite are prevailing.

Results (obtained excluding loss on ignition) of the chemical analysis of the abovementioned minerals allowed the determination of two indicators:

- silica indicator:

$$\frac{SiO_2}{Al_2O_3 + \text{fluxes (oxides)}} = \frac{67.40}{17.30 + 16.22} = 2.01$$

- alumina indicator:

$$\frac{Al_2O_3}{\text{fluxes}} = \frac{17.30}{16.22} = 1.07$$

The obtained indicators confirm a usefulness of the clay in the manufacturing of building ceramics.

3. Results and Discussion

3.1. Physical and Chemical Properties of Fly Ashes from Thermal Conversion of Sewage Sludge

The pozzolanic activity index of the fly ashes from the combustion of sewage sludge, determined according to the standard PN-EN 450-1:2012 after 28 days of curing, amounted 58.4% for the ash from Łodz (L), 71.6% for the ash from Cracow (C), and 68.5% for the ash from Warsaw (W); whereas after 90 days of curing, the respective values of the index amounted to 66.3% (L), 83.4% (C), and 79.3% (W). The activity index after 28 days of maturation should reach a value $\geq$75%, and after 90 days, should reach a value $\geq$85% [39]. Additionally, the pozzolanic activity determined as the total content of reactive Al_2O_3 and SiO_2 based on ASTM C379-65T [40], slightly exceeded 20% for all ashes. The ash shows a pozzolanic character when the total content of oxides is over 20%.

The chemical composition of the fly ashes from the thermal conversion of sewage sludge is presented in Figure 5.

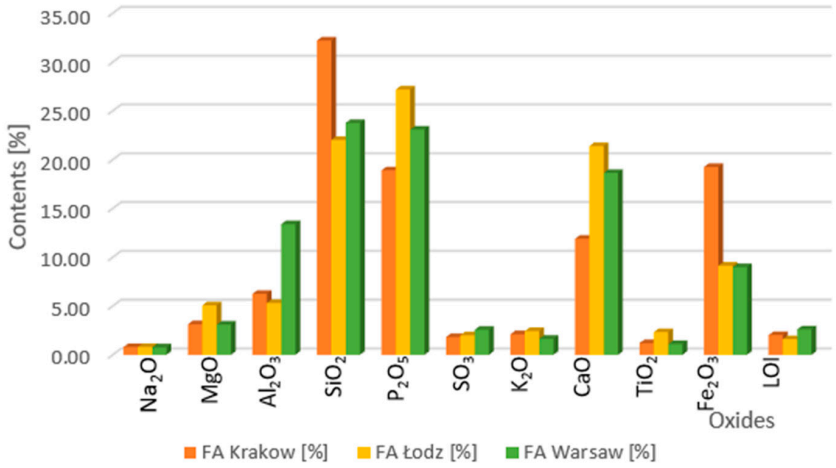

Figure 5. Chemical composition of the sewage sludge fly ashes.

In all ash samples, the highest percentage share was for SiO_2 (L–22.01%, C—32.21%, W—23.76%), CaO (L—21.39%, C—11.90%, W—18.64%), and P_2O_5 (L—27.19%, C—18.91%, W—23.09%). Additionally, the sum of content of the silica, aluminum oxide, and iron oxide did not satisfy the requirements of the standard PN-EN 450-1+A1:2012 (65%). The total content of these oxides was equal to 36.4% in the ash from Łodz, 46.1% in the ash from Warsaw, and 57.7% in the ash from Cracow. The share of Al_2O_3 in the ash from Warsaw (13.39%) significantly differed from that in the ash from Cracow (6.25%) and Łodz (5.31%), and the share of CaO fluctuated within the range of 11.9–21.39% and MgO—3.10–5.07%. The loss on ignition, describing the amount of the non-combusted coal in the tested sample in a fluidal furnace with a temperature over 850 °C, was only 0.5%. When compared to the ashes from the combustion of hard and brown coal, the fly ashes from sewage sludge contained less SO_3 and more P_2O_5. According to the investigations [39,41–44], the low loss on ignition and phosphate ions occurring in the fly ash affect the compressive strength of the composites manufactured with this additive. The high quantity of P_2O_5 is related to the type of municipal sewage supplied to the treatment plant. For the ashes from coal combustion, this content is lower than 5% [45,46]. Hence, the fly ash from sewage sludge does not satisfy the requirements concerning the content of soluble phosphorus compounds contained in the standard [39], and presented in the literature [45,46]—no higher than 100 mg per 1 kg of ash.

Figure 6 presents an example of the volumetric distribution of individual grain fractions for the ashes from Łodz. With regard to all the treatment plants, the prevailing grain fractions are 20–50 µm (L—20.18%, C—27.25%, W—25.01%), 50–100 µm (L—25.88%, C—29.39%, W—28.12%), and 100–250 µm (L—34.79%, C—22.89%, W—27.75%). The grains with diameters 2–250 µm have the highest share.

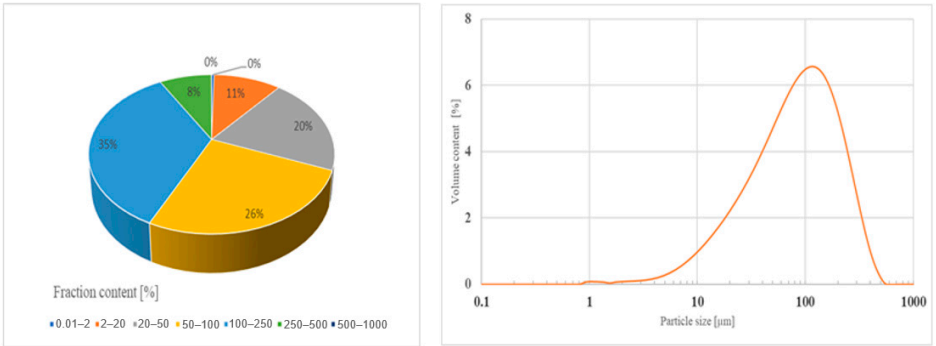

Figure 6. Volumetric distribution of grains of the fly ash from sewage sludge from the treatment plant in Łodz.

The fineness-determined acc. PN-EN 451-2:2017-06 amounted to 59.5% (L), 46.2% (C), and 50.3% (W). The volumetric density acc. PN-EN 1097-07:2008 amounted to 2620 kg/m^3 (L), 2780 kg/m^3 (C), and 2530 kg/m^3 (W); the bulk density—710 kg/m^3 (L), 810 kg/m^3 (C), and 820 kg/m^3 (W). The fly ash of this type is characterized by a high content of grains (grain conglomerates) with a high open porosity that evokes a high water demand. The porosity index was equal to 72.90% (L), 70.86% (C), and 67.59% (W) [41,42].

The chemical analysis of the additive in the microrange (SEM-EDS) presented a diversified element composition. Grains containing silicon, iron, aluminum, and phosphorus were prevailing. Magnesium, calcium, and potassium were also observed (Figure 7). In the mineral composition of the fly ashes from sewage sludge, quartz and anhydrite, as well as the phosphates in the form of apatite and fluorapatite, were prevailing.

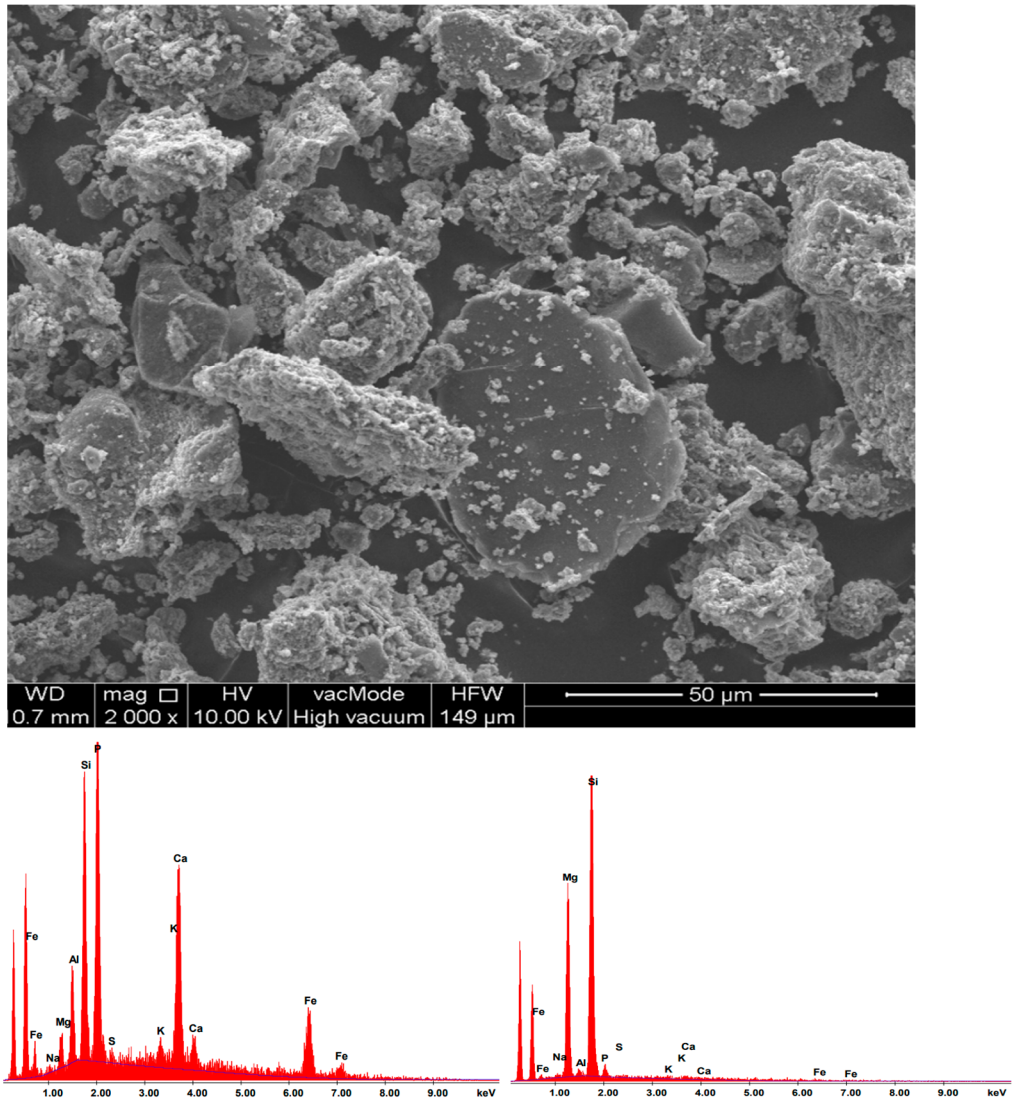

Figure 7. SEM image of the fly ash from Cracow and its EDS analysis.

3.2. Properties of the Clay-Ash Composite with Addition of the Fly Ash

To investigate the strength, the beams with dimensions of 40 × 40 × 160 mm were heated: six pieces per each test. A real example temperature distribution is presented in Figure 8. This distribution enables observations of the composite behavior in a situation of temperature increase. After the visual evaluation and measurement of characteristic parameters, the samples were tested to determine the compressive strength. The temperature

increase weakens the material structure. Crazing and cracks were visible at the sample surface. The samples were being observed during tests in the testing machine.

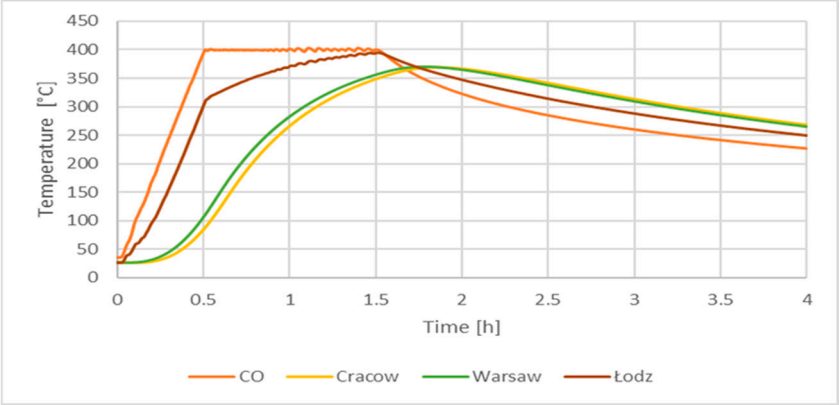

Figure 8. Temperature distribution in the clay-ash composite samples.

The analysis of the impact of high temperatures on the clay-ash composites was performed in a predetermined time range without a cooling phase. After reaching the assumed temperature, i.e., 20 °C, 300 °C, and 700 °C, the samples were soaked (maintained) in these temperatures for 30 min. The purpose of this was to homogenize the temperature in the whole volume of the composite. Then, the samples were slowly cooled until they reached ambient temperature. The total time of the thermal loading of the elements with temperatures of 300 °C and 700 °C was equal to 60 and 180 min, respectively. Then, the samples were tested with regard to the selected mechanic properties. The results of the tests of the compressive strength of the individual clay-ash composites are presented in Figure 9. The 5% error bars have also been marked in the bar graphs.

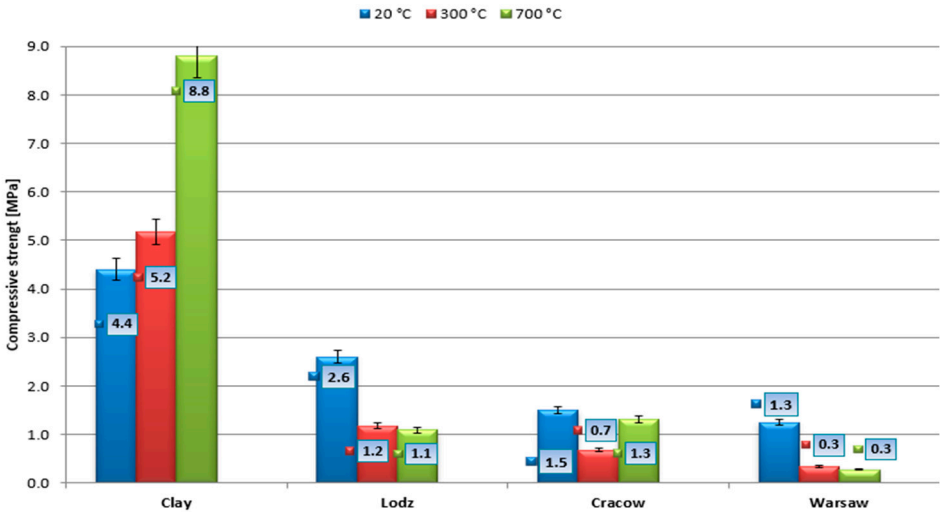

Figure 9. Average compressive strength with marked 5% error bars.

The results from the performed investigations on the samples fired in the temperature of 700 °C were spontaneously damaged—hence, they were not tested for bending strength, and only their surviving pieces were tested for compression. The damage could have arisen as a result of the abrupt rising and dropping of the temperature during firing, which, in turn, resulted in material changes in quartz (transition from the α to β form). When the temperature increases and exceeds 250 °C, the quartz changes its structure from the β to α form and changes its volume, which—if the temperature rise is abrupt—can evoke microcracks, whereas during an abrupt cooling, the fast transition from the α to β form can evoke bursting of the examined samples. Therefore, the initial increasing of the temperature

within the range of 250–500 °C should be slow, and it can accelerate beyond this range. The cooling from 500 to 250 °C should be slow as well—it should last several hours—so as not to cause excessive stress. Supposedly, the low compressive strength of the tested clay-ash composites based on the ashes from thermal conversion of sewage sludge from sewage treatment plants results mainly from a relatively low firing temperature—300–700 °C—as well as too short a soaking time in the temperature of 700 °C. This is especially visible in the case of the reference samples (without ash) where even the strength of 7.5 MPa was not achieved in the temperature of 300 °C. The remaining samples achieved a compressive strength within the range of 0.30–1.12 MPa, wherein, for the samples with the ash from Cracow, it is evident that the samples fired in the temperature of 700 °C have higher compressive strength, and for the remaining cases (Warsaw and Łodz), the results for both of these temperatures are close to each other. Hence, further investigations should be focused on samples fired in a higher temperature range, e.g., 850–1050 °C, i.e., the range of temperatures used in the firing of building ceramics. If the ash amount is high (over 20%), then the firing temperature plays an important role in achieving an appropriate compressive strength.

Figure 10 presents values of the average compressive strength as a temperature function. A strengthening effect is visible for the composite heated to 300 °C and 700 °C without ash addition, and is equal 1.1 and 2.0 MPa, respectively.

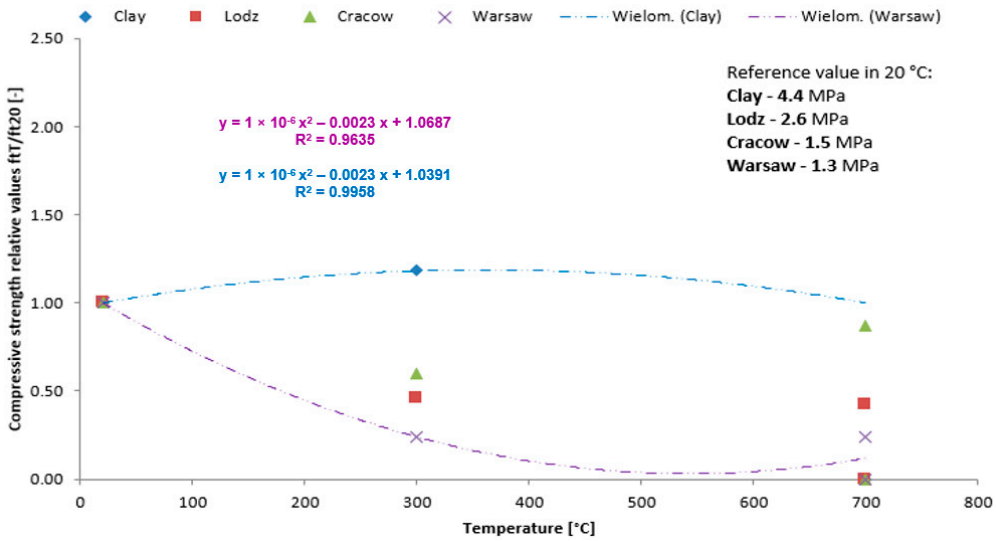

Figure 10. Changes in compressive strength for the samples after the thermal load. Relative compressive strength fcT/fc20 (i.e., related to the strength in the temperature 20 °C) is presented.

Figure 11 presents results for the water absorbability.

Figure 11 presents results for the water absorbability. The high absorbability results mainly from an inappropriate firing which does not finish with the generation of a liquid glass phase (quartz, feldspars), which would fill empty spaces between grains or reduce capillary magnitudes. Due to that, it should be considered to fire samples in a higher temperature range with a simultaneous longer soaking time in the maximum temperature. It is also recommended to reduce the cooling velocity of the samples in the temperature range of 250–500 °C, due to changes in the quartz structure (transition from the α to β form, so-called cristobalite jump), which can evoke damages (breaks). Reduction in the strength of the fired samples can be affected by changes occurring during firing (loss of chemically bonded water), as well as by additional chemical compounds included in the ashes from the combustion of active sewage sludge, e.g., P_2O_5. An exact examination of the influence of additions of the mentioned ashes on the strength of the clay composites should also encompass the higher firing temperatures—until a softening range—which should help in establishing the most advantageous firing temperature.

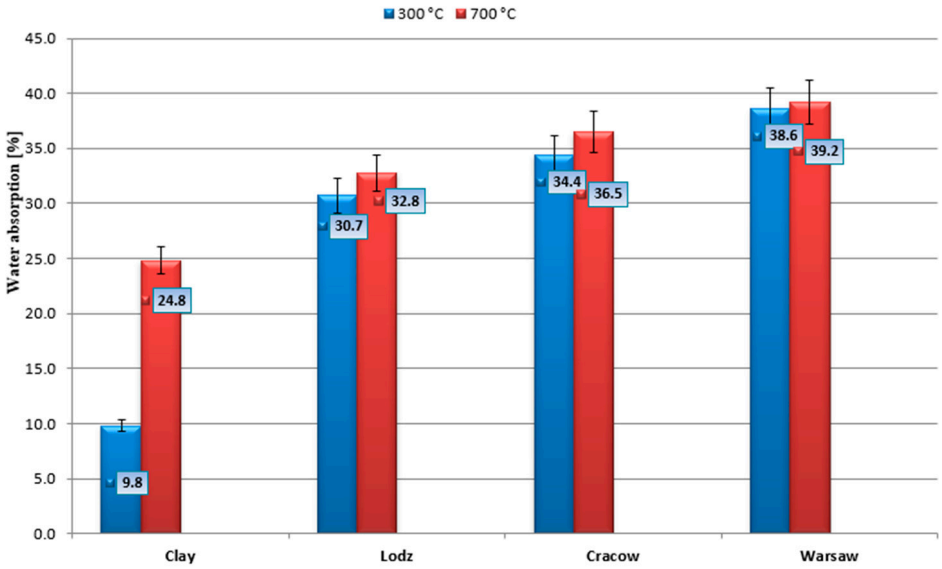

Figure 11. Water absorption.

3.3. Statistical Analysis

In order to compare two average values between each other, the t-Student test was used for trials unrelated to each other. The Statistica 2020 software package, version 2.0 (TIBCO Software Inc., Palo Alto, CA, USA), was used. Whether the value of the t-Student statistics indicates a statistical significance was checked. For this purpose, the t-Student test was used for trials unrelated to each other, with a comparison of two different observation trials. According to a zero hypothesis of the test (H_0), the differences between the average values are statistically equal to each other ($\beta_1 = \beta_2$), and according to an alternative hypothesis (H_1), these differences are statistically different ($\beta_1 \neq \beta_2$). If the obtained value of the test statistics falls into a critical area, then the hypothesis H_0 is rejected, and the hypothesis H_1 is assumed. Otherwise, if this value is outside the critical area, there is no reason to reject the hypothesis H_0 [47].

The relevance of the adopted statistical model was set at a significance level of $\alpha = 0.05$. It was assumed:

- df = 6 and $\alpha = 0.05$ => critical value: t = 2.446912
- df = 5 and $\alpha = 0.05$ => critical value: t = 2.570582
- df = 4 and $\alpha = 0.05$ => critical value: t = 2.776445.

Having the t-Student test performed at the significance level of 0.05, the zero hypothesis was rejected in favor of the alternative hypothesis. The absolute values of t obtained in the t-Student test are statistically significant. In each analyzed case, they are greater than the critical values. Table 5 presents the basic statistical characteristics.

Table 5. Basic statistical characteristics of clay-ash composite—t-Student's test for temperature.

	T-Test for Independent Samples (Spreadsheet24) Note: Variable Were Treated as Independent Samples									
Group 1 vs. Group 2	**Mean Group 1**	**Mean Group 2**	**t-Value**	**df**	***p***	**Valid N Group 1**	**Valid N Group 2**	**Std. Dev. Group 1**	**Std. Dev. Group 2**	**F-Ratio Variances**	***p* Variances**
Cracow vs. Temp.	1.207273	340	−3.84769	21	0.000935	11	12	0.358834	291.4540	659,710.0	0
Warsaw vs. Temp.	0.608417	340	−4.03386	22	0.000555	12	12	0.521950	291.4540	311,804.4	0
Clay vs. Temp.	5.695917	340	−3.97323	22	0.000644	12	12	2.675164	291.4540	11,869.7	0
Lodz vs. Temp.	1.525917	340	−4.02294	22	0.000570	12	12	0.863062	291.4540	114,039.7	0

4. Conclusions

Based on the performed investigations, the following conclusions and plans concerning further works can be formulated:

- The collected results of the investigations enabled a comparison of the properties of clay samples produced with the fly ash from three wastewater treatment plants.
- The obtained test results confirm the possibility of manufacturing clay-ash composites using the fly ash from thermal conversion of sewage sludge.
- The main objective of the investigations is the utilization of wastes coming from the thermal conversion of sewage sludge, and the determination of the possibility of its use in clay-ash composites.
- With large amounts of fly ash addition (above 20%), the firing temperature plays a significant role in achieving the appropriate compressive strength.
- It is proposed to reduce the ash quantity (5, 10, 15, 20%) in the samples, and to re-fire in the temperature of 300 and 700 °C to check an effect of this reduction (positive or negative) on the strength. Such a test should be performed in a temperature of 850–1050 degrees.
- In the next stage, the tests should be repeated with the previously assumed proportions between ash and clay, but with the samples fired at higher temperatures, in the range 950–1050 degrees.
- The assumption of a higher firing temperature for the clay-ash composite samples is justified by the results of the statistical analysis (t-Student test) which showed that the temperature significantly affects the mechanical and physical parameters of the clay-ash composite samples.

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