Residues from fuel and power industries and glass industry as a basis of building materials

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Abstract. The most important area of resource conservation is the extensive use of secondary products of the industry as feedstock to produce building materials. Benefits of secondary products usage are to enhance the physical and mechanical characteristics and strength characteristics of the resulting building materials. By-products of different sectors of industry, such as ash and slag waste from combined heat and power systems and glass industry cullet, which provide the industry with huge sources of cheap and prepared raw materials, are used as accessory materials. They reduce the cost of producing certain materials. Three main mixtures are addressed in the article: (1) a mixture of cement, ash and slag waste and glass cullet, (2) a mixture of clay and ash and slag waste, and (3) a mixture of clay, ash and slag waste and glass cullet. The production processes of the tested materials are described: preparation and thermal treatment of raw materials. Material properties obtained after the roasting were determined: compression capacity, absorption of water and level of firing shrinkage. Not all materials are amenable to characterization techniques used in standardized ways of testing.

Keywords: ash and slag waste, glass cullet, clay, cement, construction and thermal insulating material firing.

1 Introduction
Many efforts have been made in recent years to find the best way to use various types of industrial waste in building materials production \cite{1} for the following reasons: reducing the cost of certain building materials production, and therefore, saving on capital investments for the buildings and structures, as well as the liberation of major land areas and decrease of waste exposure on the environment.

One of the most frequently used by-products in the production of building materials is ash and slag waste produced by the fuel and power industry \cite{2}. The current amount of accumulated ash and slag waste from Kazan CHPP-2 is about 600 thousand tons, covering a land area of 23 hectares \cite{3}. According to the study \cite{4}, no more than 10\% of the produced ash is disposed in the Russian Federation. Glass waste is one of the most unclaimed types of secondary raw materials used in the production of building materials. The percentage of recycled glass cullet in Tatarstan is quite small.

The use of CHPP waste and glass cullet allows us to solve both problems of building materials production at once: reduction of expensive raw materials (cement and coal), as well as the use of recycled waste.

One of the best-known options for using ASW and glass waste is the production of lightweight concrete with partial replacement of portland cement. Ash in portland cement generally improves rheological properties and durability, and also contains slight to moderate levels of calcium. Such ASWs are pozzolanic, which means they react with $\text{Ca}^{2+}$ or $\text{Ca(OH)}_2$ and form new binding compounds with the presence of water \cite{5}. Most concretes containing ASW have a degree of cement substitution with ash and slag from 30 to 70\%.

The production process of lightweight concrete consists of the particle size distribution, preparation of raw materials (ASW and glass waste), remolding, granulation and heat treatment. The particle size
distribution is responsible for important physical and chemical properties such as: mechanical bulk behavior, surface reaction, miscibility. The best-known method is particle size determination by sieve analysis. Sieve analysis is used to divide the granular material into size fractions and then to determine the weight of these fractions [6]. Glass waste can be used as partial replacement of cement and fine aggregate individually depending on the size of the fractions. It is also revealed that compressive strength of concrete made with glass waste was more than the referral conventional concrete at all the replacement levels of cement and natural fine aggregate [7].

Water absorption values were determined using two methods: 24 hours of soaking in cold water and 5 hours of boiling. Thermal conductivity was determined by the quantitative measurement of axle thermal transmission in a stationary state. The obtained value of thermal conductivity is suitable for the production of concrete blocks with improved thermal insulating properties [8].

In the works [9-10] recycling technology is offered which turns sulfur waste of oil and gas field and ash-slag waste from Thermal power stations (TPS) into silicate concrete. The technology can be used in manufacturing of concrete products. Besides, the impregnation process provides low thermal conductivity for concrete while giving the material high heat insulation [11]. It is shown that high physical-mechanical and performance properties of material are determined by chemical interaction between components in the system and by formation of sulphides [12]. It was found that the developed technology is environmentally and economically sound and allows using effectively the sulfur waste of oil and gas field and ash-and-slag waste from TPS and getting strong and aggressively steadying composite materials.

There is an attempt in the study [13] to explore alternative sources of fine aggregate by investigating the effect of incorporation of granulated blast furnace slag (GBS) as replacement of natural fine aggregate on the properties of concrete mixes. The test results show an improvement in compressive and tensile strength of concrete with the incorporation of GBS in concrete mixes. The development in compressive strength at different curing time is similar to that of normal concrete. Furthermore, the study depicts that rebound number of concrete increases with increasing percentages of GBS. It indicates the improvement in the quality of concrete with the incorporation of GBS in concrete.

The use of waste materials in bricks can lessen the consumption of clay material and reduce the environmental burden due to accumulation of waste materials. Furthermore, addition of recycled materials can decrease the high carbon footprint. Reduction in weight was observed in the fly ash bricks which would lead to overall weight reduction of the structures. Furthermore, less efflorescence was observed in bricks incorporating fly ash [14].

The additives of clay and fly ash, hematite tailings were added to the raw materials to improve the brick quality in [15] work. The suitable firing temperature was ranged from 980 to 1030 °C for 2 h. In [16] work also the sintering temperature of bricks with high replacing ratio of fly ash was about 1050 °C, which is 50-100 °C higher than that of clay bricks. The compressive strength increases with increasing heat energy up to a certain level. Beyond this level, the specimens shrink and crack due to the reduction in pore fluid, which results in the strength reduction [17].

But clay brick incorporating waste glass allowed the use of low firing temperature of 900 °C instead of the normally used 1000 °C [18].

The objective of [19] study is to explore the potential of using waste glass sludge (WGS) as a secondary material in clay brick manufacturing. A range of mechanical and durability tests were performed on the bricks to quantify their performance. Clay bricks incorporating WGS exhibited higher compressive and flexural strength as compared with that of control traditional clay bricks. The unit weight of bricks was reduced owing to WGS addition, which can lead to lighter and economical structures. Furthermore, the resistance against efflorescence, sulfate attack, and freeze-thaw was enhanced for all the clay bricks incorporating WGS.

Active research for the production of building materials using glass cullet is led by Russian scientists. Methods for producing facing brick, wall ceramics, facing tile, etc. of the plastic mixture and earth-moist mixture, containing from 10 to 85 % glass waste, have been developed [20].
Chemical activation based on a non-fired or low-temperature approach for the production of binders from glassy aluminosilicates is an intensively developing and promising clean technology that finds application in construction and building materials. The resulting materials in turn improve engineering performance and aid the valorisation of different types of wastes and by-products. This is one of the main trends in the development of the modern cement industry, including the alkali activation technology. Coal fly ash is one of the large-tonnage wastes that are effectively converted by alkali activation in binders and compatible with many mineral supplementary materials. The [21] paper reviews the supplementary mineral materials of natural and waste origin from different industries for alkali activated fly ash cements; the composition, structure, and properties formation process of incorporated with blending and modifying materials, and the feasibility for improvement of the structures and properties of mixture.

Replacement of some components with ash and slag waste in the production of building materials increases its thermal-insulating properties. And the modification of such materials by various activators [22] significantly improves the mechanical strength characteristics and water-resistibility, which in turn expands the application of the produced composite materials [23].

The main aims of this research are the following: the production of materials made of clay and concrete using ash and slag waste from the fuel and power industry and glass cullet from the glass industry; the analysis of the properties obtained during firing; the study of the possibility of their use in construction.

The study of the produced materials properties is one of the main goals, because it was revealed that the produced materials have high strength, mechanical and physical, waterproof and heat-insulating characteristics. Also, the advantages of such materials are low marketing costs, building materials conservation, environmental improvements.

2 Materials and methods
2.1 Material based on cement
In this experiment the following materials have been used:
- portland cement, compliant with GOST 10178-85 (Russian state standard);
- ash and slag waste from Kazan CHPP-2 [9];
- glass cullet from Kazan glass industry;
- carboxymethylcellulose (CMC) as a polymeric material.

The first stage of production is a sieve analysis of raw materials. After the particle size distribution, particles of materials with a size of 0.03 mm were selected [6]. The second stage was the mixing of glass cullet, ash and slag waste, cement in the presence of carboxymethylcellulose (CMC) as a polymer material and mixing the received composition with water [8]. The blend ratio in the resulting mixture is presented in Table 1:

| Material          | Allotment of materials (mass), g |
|-------------------|----------------------------------|
| Glass cullet      | 81                               |
| Ash and slag waste| 35                               |
| CMC               | 0.02                             |
| Cement            | 25                               |
| Water             | 45                               |

After mixing all the components, the resulting mass was formed into cubes of 2x2x2 cm in size. The next step was drying the material in a laboratory oven at a temperature of 105 °C for 8 hours in a day. The final stage of production was heat treatment; the firing thermal conditions are shown in Figure 1. Material aging for an hour at a temperature of 350 °C and 1100 °C is a prerequisite.

The advantage of such thermal operating conditions of heat treatment is an almost continuous process [8]. On firing at a temperature of 1100 °C, concrete gets destroyed. However, due to the
presence of CMC and glass cullet particles that melt at a given temperature, the material does not get destroyed, but changes its shape and «flows back» (see Figure 2). Also, the «boiling» of the material was observable when it was fired at maximum temperature.

![Figure 1. Thermal regime of material firing.](image1)

![Figure 2. The macrograph of the obtained material structure.](image2)

When firing, ash and slag waste makes the material more firmer and dense, forming micropores [1]. When cooling, the glass forms a thin strong layer on the surface of the material and the surface of each pore.

The obtained material is not determinable for characteristics necessary for building materials, because the material has changed its initial shape when firing. A porous dense aggregate for concrete was obtained based on ash and slag waste from a CHPP, glass cullet and CMC as a polymeric material that cannot be used as an independent composite concrete.

2.2 Material based on clay
To create a composite material that can be used as a final independent product, it was decided to replace the cement with clay in the mixture. It is a well known fact that clay bricks containing ash and
slag waste from CHPP are more resistant than ordinary clay bricks, and have higher compressive strengths as well [14]. Also, bricks that are made using of ash and slag are economically beneficial.

**A mixture of clay and ash and slag waste.** In this experiment the following materials have been used:

- clay, compliant with GOST 3226-93 (Russian state standard);
- ash and slag waste of Kazan CHPP-2 [9].

Raw materials were forced through a sieve with a cell size of 0.03 mm [6]. Particles of materials of this size were selected for the mixture under investigation. The second stage of the production process was the mixing of ash and slag waste, clay and mixing the resulting mixture with water. The blend ratio in the mixture is presented in Table 2:

| Material                 | Allotment of materials (mass), g |
|--------------------------|----------------------------------|
| Clay                     | 60                               |
| Ash and slag waste       | 40                               |
| Water                    | 25                               |

After mixing all the components, the resulting mass was formed into cubes of 2x2x2 cm in size. 6 samples were obtained. The cubes were dried in a laboratory oven at a temperature of 105 °C for 24 hours. The final stage of production was heat treatment; the firing thermal conditions are shown in Figure 3. Material aging at a temperature of 300 °C and 600 °C; at a temperature of 1000 °C for 30 minutes is a prerequisite because the suitable temperature for ASW and clay brick firing is 980–1030 °C [15-16]. With this heat treatment, the firing time in the oven is reduced in comparison with the material that is made with the use of cement. The firing time is reduced from 160 to 95 minutes, which is more economically beneficial and less energy consumption.

![Figure 3. Thermal regime of material firing.](image-url)
Figure 4. The macrograph of the obtained material structure.

The material obtained after firing has a porous structure, the maximum size of open pores in diameter is 2 mm. There is also a huge amount of micropores, the material has a dimmer and more unevenly distributed color than before firing. The macrograph of the material (Figure 4) shows a color change and deformation of the cube faces, which is due to the non-uniform fire shrinkage of the ceramic mass.

To calculate parameters such as volume density, fire shrinkage, water absorption, formulas (1), (2) and (3) were used. The obtained results are presented in Table 4, the mass and volume of all 6 samples, as well as their average amounts (Table 3).

The average density for brick compression with the use of ash and slag waste was 5.5 MPa, which corresponds to the brick grade M75 according to GOST 530-2012 (Russian state standard).

### Table 3. Values of volume and mass of the samples.

| Name     | №  | Cubic capacity, cm³ | Mass, g | Average density ρ₀, g/cm³ |
|----------|----|---------------------|---------|--------------------------|
|          | 1  | 7.22                | 8.89    |                          |
|          | 2  | 7.41                | 8.81    |                          |
|          | 3  | 7.8                 | 9.07    |                          |
|          | 4  | 7.22                | 8.79    |                          |
|          | 5  | 7.22                | 8.77    |                          |
|          | 6  | 7.4                 | 9.01    |                          |
|          | Aver. value | 7.38              | 8.89    |                          |

Average density ρ₀, g/cm³, is calculated upon the formula:

$$ ρ₀ = \frac{m}{V} $$  \hspace{1cm} (1)

Fire shrinkage $V_{\text{fire shrinkage}}$, %, is calculated upon the formula:

$$ V_{\text{fire shrinkage}} = \frac{V_{\text{before firing}} - V_{\text{after firing}}}{V_{\text{before firing}}} \cdot 100\% $$  \hspace{1cm} (2)

Water absorption $B$, %, is calculated upon the formula:

$$ B = \frac{m_1 - m}{m} \cdot 100\% $$  \hspace{1cm} (3)
Table 4. Values of average density, fire shrinkage, water absorption and compression capacity of the samples.

| Name of parameter | Average density | Fire shrinkage | Water absorption | Compression capacity |
|-------------------|-----------------|----------------|------------------|---------------------|
| Value             | 1200 g/cm³      | 12 %           | 19 %             | 5.5 MPa             |

A mixture of clay and ash and slag waste. To improve the physical strength characteristics in this experiment, the following materials have been used:
- clay, compliant with GOST 3226-93 (Russian state standard);
- ash and slag waste of Kazan CHPP-2 [9];
- glass cullet from the Kazan glass industry.

Raw materials were also forced through a sieve with a cell size of 0.03 mm [6], particles of materials of this size were selected for the mixture under investigation. The second stage of the production process was the mixing of ash and slag waste, clay and mixing the resulting mixture with water [18]. The blend ratio in the mixture is presented in Table 5:

Table 5. The blend ratio in the mixture.

| Material                | Allotment of materials (mass), g |
|-------------------------|----------------------------------|
| Clay                    | 80                               |
| Glass cullet            | 75                               |
| Ash and slag waste      | 45                               |
| Water                   | 50                               |

After mixing all the components, the resulting mass was formed into cubes of 2x2x2 cm in size. 12 samples were obtained. The cubes were dried in a laboratory oven at a temperature of 105 °C for 24 hours. The final stage of production was heat treatment, the firing thermal conditions are shown in Figure 5. Material aging at a temperature of 300 °C and 600 °C for 15 minutes; at a temperature of 1000 °C for 30 minutes is a prerequisite because the suitable temperature for ASW and clay brick firing is 980-1030 °C [15-16].

With this heat treatment, the firing time in the oven is reduced in comparison with the material that is made with the use of cement. The firing time is reduced from 160 to 95 minutes, which is more economically beneficial and less energy consumption. The amount of water required for mixing 100 g is reduced, which is also economically beneficial.
Figure 5. Thermal regime of material firing.

Figure 6. The macrograph of the obtained material structure.

The material obtained after firing has a porous structure, the maximum size of open pores in diameter is 1 mm. There is also a huge amount of micropores. Glass shine has appeared, the color of the material remains plain and bright (Figure 6). The deformation of the faces of the cube has appeared. It is due to the unevenness of the fired shrinkage of the ceramic mass, however, the material retained its original shape.

To calculate parameters such as volume density, fire shrinkage, water absorption, formulas (1), (2) and (3) were used, the obtained results are presented in Table 6, the mass and volume of all 12 samples, as well as their average amounts (Table 7).

The average density for brick compression with the use of ash and slag waste was 22.5 MPa [7], which corresponds to the brick grade M250 according to GOST 530-2012 (Russian state standard). The increase in material strength is due to the presence of the glass cullet in the mixture.
Table 6. Values of volume and mass of the samples.

| Name | № | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------|---|---|---|---|---|---|---|---|
| Cubic capacity, cm³ | 8.19 | 8.2 | 8 | 7.79 | 8.2 | 7.61 | 7.8 |
| Mass, g | 10.91 | 10.86 | 10.82 | 10.98 | 11.04 | 10.72 | 10.90 |

| Name | № | 8 | 9 | 10 | 11 | 12 | Aver. value |
|------|---|---|---|---|---|---|-------------|
| Cubic capacity, cm³ | 7.61 | 7.61 | 7.8 | 8 | 7.6 | | 7.88 |
| Mass, g | 11.04 | 10.67 | 10.94 | 10.82 | 11.10 | | 10.9 |

Table 7. Values of average density, fire shrinkage, water absorption and compression capacity of the samples.

| Name of the parameter | Average density, g/cm³ | Fire shrinkage, % | Water absorption, % | Compression capacity, MPa |
|----------------------|------------------------|------------------|--------------------|-------------------------|
| Value                | 1380                   | 6.2 %            | 7.2 %              | 22.5 MPa                |

3 Results and discussion

The use of waste from various industries in the manufacture of building materials improves strength, physical and mechanical characteristics. When ash and slag waste from the fuel and power industry is added to a mixture with cement or clay, the sponginess of the material improves, and therefore the thermophysical properties of the material improve; the stableness of the material and its strength increase. The use of glass cullet also increases the strength characteristics of the material during its firing and reduces water absorption. However, with the addition of glass cullet, the material is supposed to be fired at temperatures above 1000 °C [15-16], which has a beneficial impact on the mixture of clay and ASW and negatively affects the mixture of cement and ASW. As was mentioned before, the material obtained from a mixture of cement, ash and slag waste, glass breakage and CMC as a polymeric material is not amenable to determining methods of characteristics necessary for building materials, because the it changed its original shape when firing. A porous, dense aggregate was obtained for irregularly shaped concrete, which cannot be used as an independent composite concrete.

Based on the information we have received, only samples (2) and (3) can be analyzed comparatively. Table 8 shows the results of the obtained characteristics for the samples. Mixture (2) is a brick made of clay and ASW from a CHPP, mixture (3) is a brick made of clay, ASW, and glass cullet.

Table 8. Values of the samples.

| Characteristic Name | Cubic capacity, cm³ | Mass, g | Density, g/cm³ | Fire shrinkage, % | Water absorption, % | Compression capacity, MPa |
|---------------------|---------------------|---------|----------------|-------------------|---------------------|--------------------------|
| Mixture (2)         | 7.38                | 8.89    | 1200           | 12                | 19                  | 5.5                      |
| Mixture (3)         | 7.88                | 10.9    | 1380           | 6.1               | 7.2                 | 22.5                     |

The addition of glass cullet to a mixture of clay and ASW leads to an increase in the weight of the material, as well as its density. However, this reduces the fired shrinkage of the material twice, water absorption decreases by 2.6 times, and compression capacity increases by 4 times. Besides, the use of glass cullet reduces the cost of raw materials, but energy efficiency remains unchanged.

According to GOST 530-2012 (Russian state standard), the resulting materials can be used as construction materials during the construction. The Compression capacity of 22.5 MPa is compliant to the brick M250, the density of 1380 kg/m³ is compliant to class 1.4 of the average density of the
product, the water absorption of 7.2% meets the requirements (at least 6%) for material with the use of ash and slag waste and glass cullet. Material with the use of only ash and slag waste has a compression capacity of 5.5 MPa, which refers to the M75 grade. The average density of the product is 1.2 (1200 kg/m³), the product's water absorption of 19% also meets the requirements (at least 6%).

Improvement of these parameters is possible by adding various superficially active substances (SAS) [2, 17, 22, 24], but this will lead to an increase in the cost of the raw material mixture.

4 Conclusion

Given the desire of the world community for resource and energy conservation and the ever-increasing accumulation of industrial waste, we can talk about the increasing role of ASW, as well as glass industry waste, as a partial replacement of components in the manufacture of aggregates for concrete and bricks.

Based on the necessary performance property when choosing materials with the use of ASW and glass cullet, one should take into account density, compression capacity, and water absorption. The opportunity of studying these characteristics was possible for materials of a mixture (2) and (3). The brick made of ASW and glass cullet (1380 kg/m³) has a higher density among all the materials. The brick made with the addition of ash and slag waste (1200 kg/m³) has lower density, and also has lower compression capacity (15.5 MPa). The bricks made with the use of ASW and glass cullet (22.5 MPa) has the highest compression capacity.

Taking into account the possibility of replacing the already known wall materials with materials made with the use of ASW and glass waste in multilayered enclosing structures as a structural material, it is possible to reduce the capital costs for the construction of exterior structures, which is economically efficient.

The choice of the most suitable option for the necessary application domain is possible due to the variety of materials, which are not only cheaper, but also better than existing analogs in their performance property. Besides, the use of these materials solves the problem with the disposal of ash and slag waste from CHPP and glass production.

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