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Utilization of Cinder Ash in the Ceramic Industry

Vladimir PETKOV

Bulgarian Academy of Science, Institute of Metal Science, Equipment, and Technologies
with Center for Hydro- and Aerodynamics "Acad. A. Balevski", Sofia, Bulgaria,
e-mail: vladimir2pe@yahoo.com

Abstract
During the combustion of coal in thermal power station (TPS), large volumes of technogenic waste are released in the form of cinder ash (CA). Their disposal and storage create serious technological and environmental problems. Therefore, the treatment of ash as a raw material for the production of materials with different applicability in practice would significantly alleviate the problem of disposal and storage. Cinder ash was used for the production of ceramic bricks in quantities from 20% to 40%. For quantities of CA above 30%, it is necessary to add sintering additives in order to preserve the strength characteristics of the final product. The best results were obtained with additives such as sodium polyphosphate, sodium carbonate, borax and waste glass powder. Compressive strengths in the range of 20-28 MPa and densities from 1.68 to 1.74 g/cm^3 have been achieved.

Keywords: cinder ash, ceramic bricks, waste utilization, sintering aids

1. Introduction

In our country, the waste from TPS amounts to over 6 million tons per year. In Bulgaria there are accumulated approximately 150 million tons of ashes and slag spread over tens of thousands of acres of land. The utilization of waste products from thermal power plants in our country is below 10%, while in some developed countries such as Germany and France this amount reaches 80%. In fact, they skill fully use their waste for the production of cement, lightweight concrete, ceramic and glass-ceramic products, for soil stabilization, in the laying of road surfaces, etc. The scientific and skilful operation of the ash from the TPS can lead to the realization of profits in a relatively short time.
When disposing of waste products obtained from the activity of thermal power station, a number of technical difficulties arise related to environmental protection during the operation of the constructed landfills [1-7]. At the same time, the search for new opportunities and appropriate technological solutions for efficient and cost-effective utilization of ashes obtained from the activity of thermal power plants continues [1-7].
Technologies for utilization of liquefied waste as fuel elements have been created in our country [8]. A technological way for obtaining foam glass cinder ash, applicable in heat and sound insulation in construction [9] has been developed. Cinder ash, as well as ceramic waste from the porcelain industry, is also used in the production of refractory compacts for non-ferrous metals casting, for thermal lining of various heat units, etc. [10]. The obtained products are characterized by better qualities than conventional, non-using CA and ceramic waste. They are also cheaper than ordinary products, as pre-heat treated waste is used.

2. Purpose and raw materials

The aim of the development is to study the influence of the quantitative content of ash waste and the use of different types of sintering additives on the physical-mechanical properties of ceramic products (bricks). Another challenge of this development is the use of the maximum amount of ash waste without modification (distortion) or with small adjustments to the existing production cycle. Preservation of the technological process and improvement of the properties of the final product will contribute to achieving the maximum (social) economic effect.

The properties of the obtained products largely depend on the chemical and particle size distribution of the ash. They mainly contain SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO and some other compounds including sodium, potassium, manganese, titanium and sulfur.

The following raw materials were used in the present study:

- Red clay from the village of Ovcha Mogila;
- Cinder ash from TPS "Svilosa";
- Sintering additives - glass powder, borax, sodium polyphosphate, sodium carbonate and sodium chloride.

The main methods in the production of building ceramics are:

- plastic method;
- semidry method.

The choice of the specific method depends on the properties and composition of the charge, the shapes and sizes of the products, and the requirements for the quality of the finished product [11].

The technological cycle includes sifting of the materials (ash and clay), mixing and application of the sintering additive; homogenization and moistening of the ceramic mass with water up to 17-20% humidity. This is followed by granulation and pressing of the obtained in this way charge in the form of cylinders 20 x 20 mm and tiles 50 x 50 x 8 mm. The thus obtained samples are dried for 6 hours at a temperature of 60°C, then sintered at temperatures in the range from 800°C to 950°C with 1 hour duration.

The compressive strength, which is the main mechanical indicator, is most often determined in building ceramic products [12]. The compressive strength is the maximum stress at which the material breaks under the action of compressive force. The test bodies are in the form of a cube or cylinder with a diameter equal to their height. The upper and lower bases must be completely parallel and the test speed shall be gradually increased by 2 MPa/sec. The mechanical strength of building ceramics is determined differently according to their type. In the case of hollow clay brick with round holes (60 x 120 x 250 mm), the compressive strength is determined on the whole brick according to (Table 4) of BDS 626-78. The boards on which the brick rests are leveled with gypsum mortar. The pressure is applied in the direction of the applied stress in the wall. The hollow ceramic blocks (250 x 250 x 120 mm) are tested according to (Table 2) of BDS 9338-83. Strength is calculated on the gross area together with the holes. Depending on the purpose of the bricks, the chemical resistance and frost resistance are determined [5]. The brand of bricks corresponds to the ultimate compressive strength: 7.5; 10; 12.5; 15; 20; 25 and 30 MPa. Lime inclusions and mechanical defects are not allowed [11].

3. Results and discussion

Table 1 shows some of the tested compositions with different ratios of the main component clay and cinder ash. The influence of various sintering aids on the density and strength of the final product is determined. The highest compressive strength was found in composition No 2 without sintering aid - 25.8 MPa and composition No5 with addition of sodium polyphosphate $(NaPO_3)_n$ - 27.9 MPa.

Table 1. Determination of the compressive strength of samples with different content of cinder ash, clay and sintering aids

Sample No	Cinder ash, wt. %	Clay, wt. %	Sintering aids	Density, g/cm^3	Compressive strength, MPa
1	20	80	-	1.63	25.1
2	25	75	-	1.64	25.8
3	30	70	-	1.62	19.3
4	35	65	-	1.63	14.7
5	25	75	$(NaPO_3)_n$	1.69	27.9
6	30	70	$(NaPO_3)_n$	1.74	24.9
7	35	64	$(NaPO_3)_n$	1.72	19.3
8	40	59	$(NaPO_3)_n$	1.70	9.2
9	25	75	Na_2CO_3	1.67	22.8
10	30	70	Na_2CO_3	1.66	21.2
11	35	64	Na_2CO_3	1.68	17.5
12	40	59	Na_2CO_3	1.69	14,3
13	25	75	$Na_2B_4O_7$	1.62	18.6
14	30	70	$Na_2B_4O_7$	1.64	16.0
15	35	65	$Na_2B_4O_7$	1.59	13.8
16	40	60	$Na_2B_4O_7$	1.61	21.3
17	25	75	Waste glass powder	1.67	20.5
18	30	70	Waste glass powder	1.66	17,6
19	35	65	Waste glass powder	1.69	14,7
20	40	60	Waste glass powder	1.69	11,0

Additives like sodium chloride (NaCl), aluminum disulfate ($Al_2(SO_4)_3$), ammonium chloride (NH_4Cl) and their combinations were also tested. They don’t have significant effect on the properties of the ceramic samples.

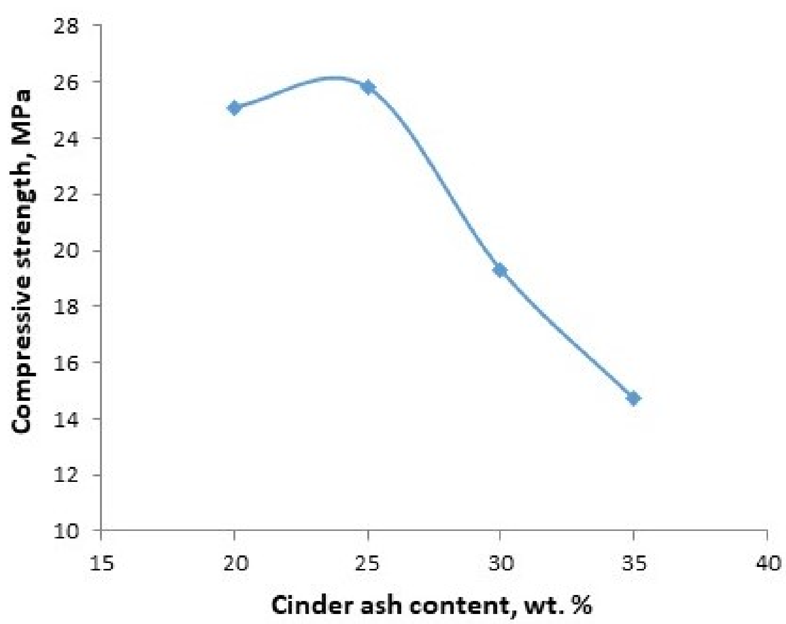

Fig. 1. The influence of the cinder ash content on the compressive strength

Figure 1 shows the influence of the cinder ash content on the compressive strength without any additive. It shows that the best physical-mechanical parameters of the ceramic samples are obtained using 20-25 wt% of cinder ash.

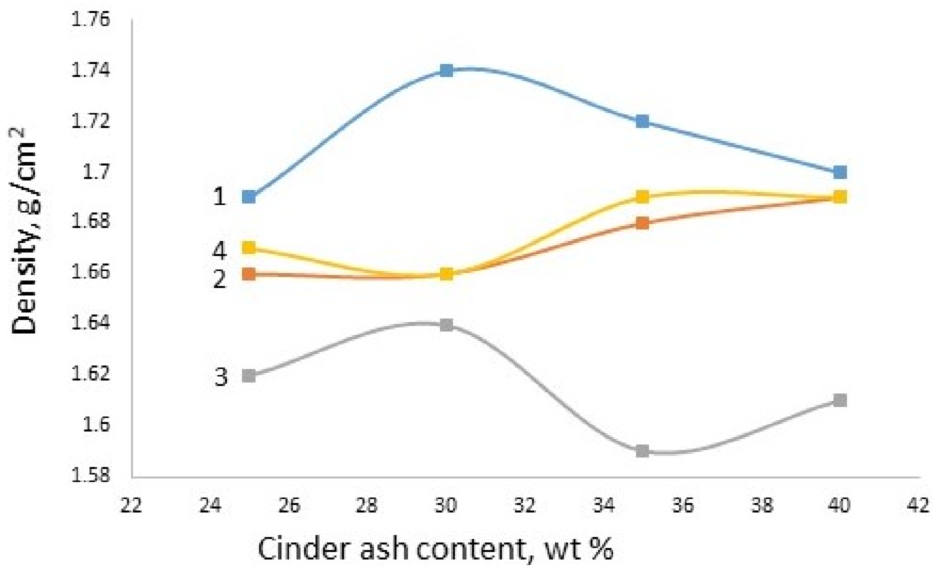

Fig. 2. The influence of the cinder ash content on the density with different sintering aids
1. sodium polyphosphate; 2. sodium carbonate; 3. borax; 4. waste glass powder

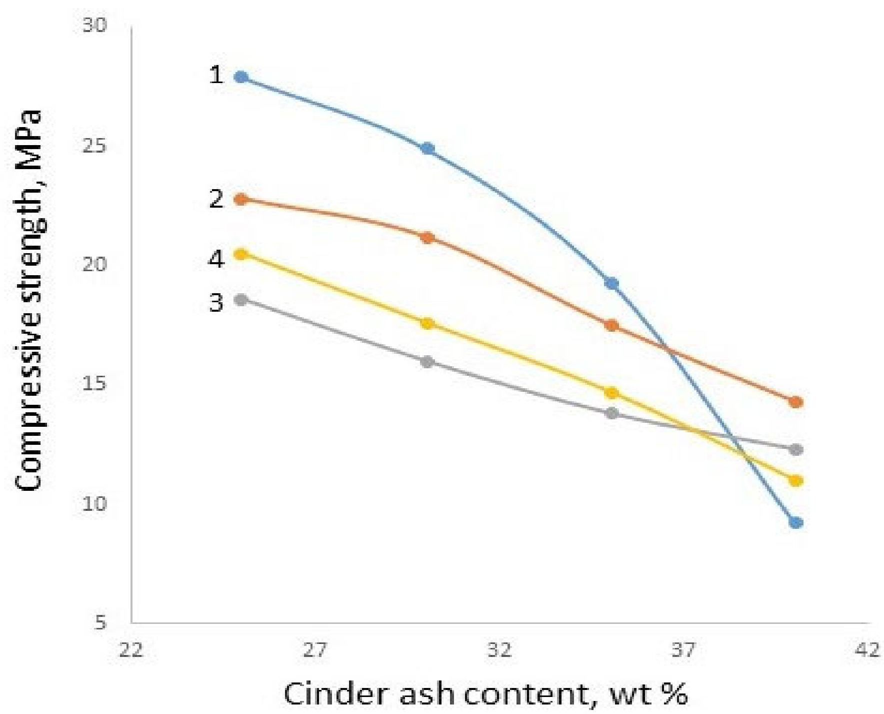

Fig. 3. The influence of the cinder ash content on the compressive strength with different sintering aids
1. sodium polyphosphate; 2. sodium carbonate; 3. borax; 4. waste glass powder

The research explores the influence of the cinder ash content on the density and the compressive strength when using different sintering aids. The ceramic products (bricks) with the highest densities were obtained when sodium polyphosphate - 1.74g/cm^3 and sodium carbonate - 1.69g/cm^3 were used as sintering aids (Fig. 2). By adding the same additives compressive strengths between 20-28 MPa were obtained using 25 - 35 wt.% cinder ash in the compositions (Fig. 3). The graphs show that it is possible to use a significantly larger amount of ash (35 - 40%), as the mechanical parameters remain within the acceptable limits for ceramic production, i.e. above 10 MPa. It is also evident that the best qualities of the ceramic samples are obtained where sodium polyphosphate and sodium carbonate are used as sintering aid in the composition. It is known that in quartz-rich masses there are polymorphic transformations connected with volumetric expansions. At 573℃ β-quartz converts into α-quartz and at 870℃ α-quartz into α-tridymite, etc. These expansions can lead to cracking and destruction of the ceramic products. The technological regime of drying and sintering with proper temperature hold for the separation of residual moisture of the clay materials and for the quartz transformations before the final sintering temperature is reached are essential.

4. Conclusions

- It has been proven that the cinder ash can be introduced into the ceramic mass in quantities of 25-40% as per the basic mass.
- It has been found that when the content of the cinder ash is more than 30% it is recommended to add sintering aids in the range of 0.5 to 5% to preserve the physical and mechanical properties of the ceramic products.
- Sodium polyphosphate and sodium carbonate as sintering aids have been found to be most effective.
- The effects of using cinder ash are:
  - A cheaper raw material than clay;
  - Utilization of waste material;
  - Freeing up of large areas of land and respectively protection of the environment from accumulation of dust;
  - Saving electricity (fuel) in the production of ceramic products, as the cinder ash has already undergone heat treatment;
  - Decreasing the final sintering temperature with 50-60℃, which saves fuel and time;
  - Improving the quality of ceramic products (bricks, tiles) and improving their appearance (colour);
  - Reducing the time of the whole technological regime (drying and sintering);
  - Reduction in the prices of the final product with about 25%.

The recovery of waste from industry and in particular from solid fuel leaks is extremely important for the protection of the environment. Such developments can solve much of this problem with the accumulation of inorganic waste materials from industry.

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