Processing of ash and slag waste of heating plants by arc plasma to produce construction materials and nanomodifiers

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Abstract. The results are presented of plasma processing slag and ash waste from coal combustion in heating plants. Melting mechanism of ashand slag raw material is considered by an electromagnetic technological reactor. The analysis was conducted of temperature and phase transformations of raw material when it is heated up to the melting point, and also determination of specific energy consumption by using a generalized model of the thermodynamic analysis of TERRA. The study of materials melting temperature conditions and plum of melt was carried with high-temperature thermal imaging method, followed by mapping and 3D-modeling of the temperature fields. The investigations to establish the principal possibilities of using slag waste of local coal as raw material for the production of mineral (ash and slag) fibers found that by chemical composition there are oxides in the following ranges: 45-65% SiO2; 10-25% Al2O3; 10-45% CaO; 5-10% MgO; other minerals (less than 5%). Thus, these technological wastes are principally suitable for melts to produce mineral wool by the plasma method. An analysis of the results shows the melting point of ash and slag waste - 1800-2000 °C. In this case the specific energy consumption of these processes keeps within the limits of 1.1-1.3 kW*h/kg. For comparison it should be noted that the unit cost of electricity in the known high-melting industrial installations 5-6 kW*h/kg. Upon melting ash and slag waste, which contains up to 2-5% of unburned carbon, carbon nanomaterials were discovered in the form of ultrafine soot accumulating as a plaque on the water-cooled surfaces in the gas cleaning chamber. The process of formation of soot consists in sublimation-desublimation of part of carbon which is in ash and slag, and graphite electrode. Thus, upon melting of ash and slag in the electromagnetic reactor it is possible to obtain melt, and in the subsequent mineral high quality fiber, which satisfies the requirements of normative documents, and simultaneously to receive a condensed product in the form of carbon sublimated nanoparticles, which can be found further use in construction materials, in particular in high-strength concrete and other materials.

1. Introduction
The demand of construction industry is constantly growing in mineral fiber materials and nanomodifiers. For the production of mineral fibers, it is appropriate to use technological wastes generated during the combustion of solid fuels, due to the fact that the formation of technogenic waste tends to increase significantly in the future, which contributes to their steady accumulation [1, 2]. Processing of solid technogenic waste in fiber materials is an important scientific and technical
challenge, as these types of waste have a higher melting temperature, and therefore cannot be used for the production of mineral wool by known heat units (cupola furnaces, tank furnaces, etc.) [3].

One promising direction in this field is the use of a plasma arc to melt the raw material in order to obtain fibrous heat insulation material, as when used as a thermal energy source of the electric arc due to the high temperature sharply decreases the time of melt producing [4]. Also, in the processing of ash and slag, which usually contains up to 2-5% of unburned carbon, carbon nanomaterials were found in the form of ultrafine soot accumulating on water-cooled surfaces in gas cleaning chamber. Soot formation process consists in sublimation-desublimation of the carbon which is in ash and slag, and graphite electrode surface.

Thus, the article examined melting mechanism of ash and slag in a plasma reactor, in which is possible to obtain a mineral high quality fibers while simultaneously obtain the condensed product in the form of carbon sublimated nanoparticles that may find further application in construction materials, in particular, as additives in high-strength concrete and other materials.

2. The pilot unit and technique of researches

As noted above one of the promising methods is the use of electro-thermal melting method to melt the raw material in order to obtain mineral fiber materials.

The experimental setup was used to produce the melt and the fibers of the ash wastes, shown schematically in Fig. 1 [5, 6]. An advantage of this reactor is that the overlapping zones and release its heat absorption during the flow process, provides an intensification of heat and mass transfer from the plasma arc recyclable materials in the reaction chamber through the reactor chamber to create a large area - of the plasma volume, filling all its transverse section.

![Figure 1. Longitudinal and cross-sectional view of an electromagnetic process reactor](image)

1 - the reaction chamber; 2 - water-cooled cover; 3 - water-cooled bottom; 4 - rod electrodes (3 pcs.); 5 - electrode rod locking; 6 - pole piece; 7 - seriesnaya winding; 8 - power supply; 9 - an additional power source for heating the jet; 10 - to display the melt device (tap-hole); 11 - Lined bottom of the chamber; 12 - nozzle into the reaction chamber for supplying raw material; 13 – lining.

Thermal zone in the reactor chamber of the electromagnetic studied thermal imaging method for subsequent mapping with modeling of temperature fields (Figure 2) using the high-temperature thermal imager model MSC-640 by Luma Spec company.
Smelting mode is performed in a single step, consisting of the combined effects of, when starting occurs by electrical plasma heating and melting the raw material, and in the future, as the penetration and the formation of electrically conductive melt bowl comes bedding materials and the flow of current through the molten aluminum silicate mass, while electromagnetic agitation and homogenising with a series-connected series electromagnets, which significantly reduces time-to-operation and reduces the energy intensity of production. Residual carbon in the form mechanical underburning in melting ash and a part of graphite from the surface electrodes in electrothermal erosion under the influence of high temperature and uniform melt density actively evaporate and form ultrafine carbon black is removed from the reaction zone of the reactor in the gas cleaning chamber where their accumulation with further collection and treatment in non-polar solvents for use in the form of carbon nanomodifiers. Some practice expended power required to produce a melt with a weight up to 150 kg / h of 1.1-1.3 kWh / kg (for comparison, the power expended working induction furnaces - 6 kW / kg).

3. The analysis of temperature transformations of raw materials in the melting

Mineral fiber production process includes two major stages - preparation of a homogeneous melt and feed it into the fiber blowing. For computational and theoretical results on the melting of ash and slag waste from the definition of technological conditions in the preparation of the melts and the fiber necessary to carry out calculations of the process of high-temperature melting raw materials. In the study of the mechanism of melting raw materials used TERRA modeling environment for calculation of melting slag waste processes [7, 8].

The described software package allows you to simulate the maximum equilibrium states and markets created for his method and algorithm calculations. For each material property set should consist of its chemical formula, the limits of approximation of the thermodynamic functions Tmin, Tmax, the seven factors for the reduced thermodynamic potential Φi (T) (φ1 - φ7), standard enthalpy of formation Hf0 (298).

Specific energy consumption in the heat treatment process consists of heating energy costs for raw materials to a predetermined temperature and melting resulting in chemical reactions, thermodynamic to establish equilibrium in the system. The expression for \( Q_{\text{spec}} \) is:

\[
Q_{\text{spec}} = I_{\text{eq}} - I_{\text{origin}}, \text{kW·h/kg},
\]

where \( I_{\text{eq}} \) and \( I_{\text{origin}} \) - total enthalpy, referred to 1 kg of the working fluid (batch + oxidizer) which is in the initial and equilibrium (after all transformations) states.

For specific thermodynamic systems \( I_{\text{eq}} \) value calculating methods of chemical thermodynamics of multicomponent heterogeneous systems using the TERRA program.

The enthalpy of the feedstock can be written expression:

\[
I_{\text{origin}} = \Delta H_f^0(T_0)_{\text{origin}} + \int_{T_{\text{origin}}}^{T_0} C_p(T) dT,
\]

where \( \Delta H_f^0(T_0)_{\text{origin}} \) - the standard heat of formation of a working body, \( T_0 = 298.15 \text{ K} \) - standard temperature; \( T_{\text{origin}} \) - initial process temperature at which the reactants enter the reaction zone.

At equality \( T_{\text{origin}} = T_0 \), the expression will be:
\[ \Delta H^\circ_{\text{of}}(298)_{\text{origin}} = \Delta H^\circ_{\text{of}}(298)_{\text{SiO}_2} + \Delta H^\circ_{\text{of}}(298)_{\text{Al}_2\text{O}_3} + \Delta H^\circ_{\text{of}}(298)_{\text{TiO}_2} + \Delta H^\circ_{\text{of}}(298)_{\text{Fe}_2\text{O}_3} + \Delta H^\circ_{\text{of}}(298)_{\text{CaO}} + \Delta H^\circ_{\text{of}}(298)_{\text{MgO}} + \Delta H^\circ_{\text{of}}(298)_{\text{Na}_2\text{O}} + \Delta H^\circ_{\text{of}}(298)_{\text{K}_2\text{O}} + \Delta H^\circ_{\text{of}}(298)_{\text{MnO}} + \Delta H^\circ_{\text{of}}(298)_{\text{P}_2\text{O}_5} + \Delta H^\circ_{\text{of}}(298)_{\text{SO}_3} \]

The enthalpy of formation of the above, depending on the system components get value \( I_{\text{origin}} = 112074.3 \text{ kJ/kg} \).

When calculating \( Q_{\text{spec}} \) necessary to consider mass fractions are part of the components [5], so partite composition of the ash on the basis of the chemical (in the capture of 100% per unit) distributed as follows: \( \text{SiO}_2 = 0.565; \text{Al}_2\text{O}_3 = 0.2087; \text{TiO}_2 = 0.0071; \text{Fe}_2\text{O}_3 = 0.1438; \text{CaO} = 0.0380; \text{MgO} = 0.0186; \text{Na}_2\text{O} = 0.0057; \text{K}_2\text{O} = 0.0082; \text{P}_2\text{O}_5 = 0.0028; \text{SO}_3 = 0.0021. \)

Defining \( Q_{\text{spec}} \) (kWh/kg), calculated the minimum de- posited electrical power \( P_{\text{el}} \) in kW:

\[ P_{\text{el}} = Q_{\text{spec}} \times G_{\text{charge}}, \quad (4) \]

Where \( G_{\text{charge}} \) - the batch weight, kg.

As a result of the melting of the charge in electric plasma airdoes not participate. Weight average loaded batch of 150 kg, the melting time and tentative - 1 hour.

The results of thermodynamic calculation of the total enthalpy \( I_{\text{eq}} \), condensed phase amount \( Z \) (%), and the equilibrium composition via TERRA program shown in Figures 3 a, b; energy dependence on the temperature is shown in Table 1.

![Figure 3. Complete melting enthalpy (A) and the amount of the condensed phase (B) Okino-Kliuchevskoi ash.](image)

| Table 1. Dependence of specific energy consumption from ash melting point. |
|---------------------------------|---|---|---|---|---|---|---|---|---|
| \( T \), °C | 1000 | 1200 | 1400 | 1600 | 1800 | 2000 | 2200 | 2400 | 2600 | 2800 | 3000 |
| \( Q_{\text{spec}} \), kW*h/kg | 0,285 | 0,34 | 0,424 | 0,68 | 0,96 | 1,23 | 1,58 | 2,42 | 2,91 | 3,02 | 3,18 |
| \( P \), kW | 37 | 48,1 | 64,8 | 75,9 | 92,5 | 120,3 | 137 | 165 | 181,4 | 204,8 | 235 |

4. The research results

Earlier studies were conducted by authors to obtain high-strength concrete with the introduction of carbon nanomaterials, simultaneously obtained upon melting carbon-containing wastes in the form of unburned carbon in electromagnetic reactor [9, 10]. According to the research the nature of the impact is identified of carbon nanomaterials on processes of hydration and hardening of cement and composite binders. Compositions are developed of modified concrete on cement and composite binders using carbon nanomaterials. Another promising direction of research is the use of mineral fiber which is obtained from the ash and slag waste to disperse reinforcement of concrete. It is known that concrete structures are not having sufficiently high tensile strength in flexure. This problem can be solved by...
Disperse reinforcement of concrete by various fibers [11-13]. Disperse reinforcement by metal and non-metallic fibers allow qualitatively improves the indicators of composites. It is necessary to consider the possible negative impact of hardening cement environment when using non-metallic mineral fibers.

The most effective of non-metallic mineral fibers for concrete dispersed reinforcement is the basalt roving and finely staple fiber. However, the technologies of production of these types of mineral fibers are characterized by high energy costs. Use of these mineral fibers with less stable and homogeneous properties compared to the roving and staple fibers for dispersed reinforcement of cement composites is a promising direction in the technology of their production.

The introduction of the mineral fibers increases the compressive strength after 28 days by 16%, the flexural strength by 50% compared to control composition. Noticeable increase of flexural strength is associated with the reinforcing action of mineral fibers (fig.4).

![Figure 4](image-url)

Figure 4. Compressive (A) and flexural (B) strength of cement stone:
1 – without mineral fiber, 2 – with mineral fiber on the basis of ash and slag waste, 4 wt. %.

Studies have been conducted on the definition of physical, mechanical and performance properties of the fine fiber-reinforced concrete using ash and slag fibers (Table. 2, 3).

Table 2. The composition and technological parameters of fiber-reinforced concretes with mineral fiber.

| Material consumption per 1 m³ of concrete, kg | W/C ratio | Segregation by water separation, % |
|---------------------------------------------|-----------|----------------------------------|
| cement                                      | sand      | fiber                            |
| 550                                         | 1375      | -                                |
| 550                                         | 1375      | 22                               |

Table 3. Mechanical and performance and technological properties of fiber-reinforced concrete.

| Properties                | Units | Indicators | Reference composition of concrete | Fiber-reinforced concrete |
|---------------------------|-------|------------|----------------------------------|--------------------------|
| The average density       | kg/m³ | 2400       | 2460                             |
| Compressive strength      | MPa   | 44         | 50                               |
| Flexural strength         | MPa   | 9          | 13                               |
| Water absorption          | % by weight | 4.0     | 3.5                               |
| Frost resistance          | cycles| 150        | 200                              |
| Shrinkage                 | mm/m  | 2.7        | 1.6                               |
3. Conclusions
Presented electric smelting reactor, which is a type of plasma reactors, allowed to regulate smoothly of melt temperature and maintain it at the exit of the jet from the tap hole, which made it possible to lower the viscosity and increase the melt flow. It may be recommended ash and slag waste heating plants to process plasma method in the melt for mineral casting and thin fibers as a component of composite materials, as well as for the production of carbon nanoparticles for modification [14].

Introduction of mineral fibers increases the strength characteristics for compression strength at 13%, flexural strength - 40%. The use of mineral fiber, obtained using plasma arc and characterized by inhomogeneity of on the main characteristics, it allows obtaining high-strength fine fiber-reinforced concrete with improved properties. In the Baikal region the use of fiber-reinforced concrete will improve the quality and reduce resource consumption in construction, such as road and bridge construction. Electric smelting reactor allows obtaining from ash and slag waste sublimated at a high temperature carbon nano sized additive, which make it possible to receive high strength properties of concrete and other construction materials.

References
[1] Buyantuev S L, Sultimova V D 2004 Production of thermal insulation materials made of ash and slag waste TPP using low-temperature plasma Construction Materials 10 51-53
[2] Buyantuev S L, Sultimova V D, Dondokov A T, Volokitin G G, Zayahanov M E, Tsyrenov S A 2006 Manufacture of heat-insulating building materials using elektroplazmennoy processing Building Complex of Russia: science, education, practice: Proceedings of the Intern. scientific. Conf. Ulan-Ude 90-93
[3] Bobrov Y L, Ovcharenko E G, Shoikhet B M, Petukhova E J 2003 Thermal insulation materials and construction. M.: INFRA-M 268
[4] Sergeev P V 1978 An electric arc in electric reactors Alma-Ata. The science 140
[5] Buyantuev S L, Sultimova V D 2010 The use of low-temperature plasma to produce fibrous thermal insulation materials from ash and slag waste of thermal power plants Ulan-Ude: VSGTU 132 p
[6] Buyantuev S L, Malikh A V, Pashinsky S G, Ivanov A A, Kitaev V V Russian patent for invention №2432719 Electromagnetic Technology reactor, published 27.10.2011 Bull. №21
[7] Vatolin N A, Trusov B G, Moiseev G K 1994 Thermodynamic modeling in high-inorganic systems. M.: Metallurgy
[8] Trusov B G 2002 TERRA program complex for calculation of plasma-chemical processes Mater. 3 Intern. Symp. in Theoretical and Applied Plasma Chemistry. Ples 217-218
[9] Buyantuev S L, Kondratenko A S, Khmelev A B 2013 The use of carbon nanomaterials produced plasma treatment of coal as modifying additives in concrete Wschodnie Partnerstwo - 2013: materiały IX międzynarodowej naukowo-praktycznej konferencji, 07-15 września 2013 roku. - Przemysł: Nauka studia. 34: Techniczne nauki 49-55
[10] Urkhanova L A, Buyantuev S L, Lkhasaranov S A, Kondratenko A S 2012 Concrete on composite binders with nanostructured fullerene additive Nanotechnology in construction 1 22-25
[11] Pukhareno Y V 2012 Restoration and construction of: the potential fiber reinforced materials and products Modern problems of science and education 4
[12] Borovskikh I V, Khizin V G 2009 Changing the length of basalt fibers in its distribution in the composite binder of high bazaltfibrobetonov Proceedings of Kazan State Architectural University 2 (12) 233-237
[13] Stepanova V F, Buchkin A V 2011 Corrosion behavior of basalt fibers in the cement matrix of concrete Building materials, equipment, technologies of XXI century 9 22-26
[14] Buyantuev S L, Kondratenko A S 2014 Thermal insulation materials of the fibrous structure of the rock melts and technogenic waste of ash: monograph Ulan-Ude: VSGUTU 180