X-Ray Diffraction Analysis of Bottom Ash Waste after Plasma Treatment

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Abstract. The paper deals with the plasma-chemical synthesis of melts produced from the bottom ash waste for the production of new construction materials with enhanced performance characteristics. Phase composition of the plasma-treated bottom ash waste is detected by the X-ray diffraction analysis. The bottom ash waste is a mixture of SiO₂ minerals. The structure and phase composition of this mixture are investigated after the plasma treatment. The obtained results are compared with the original state of the mixture. The identification and the qualitative content of ash waste as a multi-phase system are complicated by the overlapped reflections and a possible existence of the intermediate amorphous phase.

1. Introduction
The treatment level of industrial solid waste in thermal power plants (TPP) is, currently, extremely low that leads to a considerable accumulation of bottom ash waste in ash-disposal areas [1–3]. The core aspect of ash waste utilization is a high melting temperature (up to 1700°C) which depends on heterogeneity of its chemical composition. Knowledge of the structural composition of the amorphous and crystal ash phases is very useful for the provision of the effective performance characteristics. To the authors’s knowledge, little publications are available in the literature that discuss investigations of the plasma treatment effect on the ash structure and phase composition.

The aim of this work is to study the processes in plasma-chemical reactor occurred during the production of ash-based silicate melt and the identification of its amorphous state after the plasma treatment.

2. Materials and methods
The bottom ash waste fraction (<150 µm) generated by Tomsk TPP–2, was used as a raw material for the production of the silicate melt. The original chemical composition of this material is presented in Table 1.

Table 1 indicates that the chemical composition of the investigated material contains 51% SiO₂. This content is similar to that of commercial glass and can be utilized to produce silicate melts, including the production of mineral fibers [4–6].
Table 1. The original chemical composition of bottom ash waste generated by Tomsk TPP–2.

| Material            | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | Ignition loss |
|---------------------|------|-------|-------|------|------|---------------|
| Bottom ash waste    | 51.16| 34.57 | 3.62  | 8.33 | 0.91 | 1.41          |

The XRD analysis was carried out by DRON-4-07 diffractometer which was modified for digital signal processing. Measurements were conducted using copper radiation (Kα) and Bragg-Brentano X-ray optical scheme. Specifications for the DRON-4-07 included 0.02° scanning step and 16.0°–92.0° range for angles to be scanned. The XRD analysis of obtained melts was based on the Rietveld refinement method [7-8]. This method is used to detect the relative phase content in compliance with the reference structure; space groups; refine the crystal parameters and the space distribution of atoms in crystal lattices. Phase transformations, chemical reactions occurring in the material under heating and cooling conditions were measured in air on the simultaneous thermal analyzer Netzsch STA 449C Jupiter (Germany) at a heating rate of 10 degrees per minute.

3. Experimental
The bottom ash waste was subjected to melting in a plasma-chemical reactor presented in [9, 10]. Its specifications included \( U=160 \text{ V}, I=220 \text{ A}, P=35.2 \text{ kW}, q=1.8 \cdot 10^6 \text{ W/m}^2 \). The operating principle of the plasma-chemical reactor is based on the interaction between the highly concentrated plasma flows and the silicate-containing powdered material. As a result of this interaction, fine particles were heated with the following formation of a homogeneous melt. The configuration of the plasma-chemical reactor allowed eliminating the loss of fine particles blowing by the plasma flow out of the melting zone. Moreover, the obtained silicate melt was homogeneous within the whole volume of the melting furnace.

4. Results and discussions
4.1. X-ray diffraction analysis
Upon completion of the experiments in plasma treatment of high-temperature silicate melts, the X-ray diffraction (XRD) analysis was performed for ash powders both before and after plasma treatment. To identify the unknown phases in the studied substances, it is advisable to address to the Crystallography Open Database [11]. The modeling of amorphous states allows identifying the quantitative phase content in ash waste after the plasma treatment. The amorphous phase predominates in the integral intensity. The number of amorphous phases is obtained on the basis of crystal lattices and the space distribution of atoms in crystal lattices. Phase transformations, chemical reactions occurring in the material under heating and cooling conditions were measured in air on the simultaneous thermal analyzer Netzsch STA 449C Jupiter (Germany) at a heating rate of 10 degrees per minute.

Figure 1 contains the plot of the XRD patterns for the certain phases. The Rietveld refinement allow the authors to list the reference phases in ash waste which contributes to the integral (experimental) intensity.
Figure 1. XRD patterns for the original state of ash waste, where experimental (1); SiO$_2$ (2); Fe$_2$O$_3$ (3); TiO$_2$ (4).

The results of the analysis, the discovered major phases and their contribution to the integral intensity in the oxide mixture are given in Table 2. The XRD analysis shows that superposition of the integral intensity is 94.47%. This amount indicates to the proper identification of phases in ash waste.

Table 2. Structure and phase content refined by the Rietveld method.

| N | Chemical formula | Intensity, [%] | a, [nm] | b, [nm] | c, [nm] | α [deg.] | β [deg.] | γ [deg.] |
|---|------------------|----------------|---------|---------|---------|----------|----------|----------|
| 1 | SiO$_2$          | 56.23          | 0.49249 | 0.49249 | 0.542288| 90       | 90       | 120      |
| 2 | Al$_2$O$_3$      | 6.2            | 0.474452| 0.474452| 1.283357| 90       | 90       | 120      |
| 3 | Al$_2$O$_3$      | 14.41          | 0.513593| 0.513593| 0.513593| 57.4     | 57.4     | 57.4     |
| 4 | CaO              | 0.06           | 0.4799  | 0.4799  | 0.4799  | 90       | 90       | 90       |
| 5 | MgO              | 0.01           | 0.4217  | 0.4217  | 0.4217  | 90       | 90       | 90       |
| 6 | Fe$_2$O$_3$      | 0.01           | 0.50355 | 0.50355 | 1.37471 | 90       | 90       | 120      |
| 7 | Fe$_2$O$_3$      | 17.55          | 0.50355 | 0.50355 | 1.327161| 90       | 90       | 120      |
| 8 | TiO$_2$          | <0.01          | 0.4991  | 0.4991  | 0.2879  | 90       | 90       | 120      |
| 9 | Total            | 94.47          |         |         |         |          |          |          |

As shown in Figure 2, ash becomes amorphous after the plasma-chemical treatment. In order to identify the amorphous phases and their content using the Rietveld method, the amorphous states are simulated for SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$ phases which make the main contribution to the intensity in the original state. The calculated atomic density determines the size of the original cubic cell, in which the oxide atoms are concentrated.

Figure 2. XRD patterns for plasma-treated ash waste, where a) experimental (1); estimated (2); difference (3); b) amorphous phases Fe$_2$O$_3$ (1), O$_{22}$Al$_{20}$ (2), SiO$_2$ (3).

The optimized sizes of the cubic cells and the force-equilibrium location of atoms were then ascertained. As a result, the amorphous state of Fe$_2$O$_3$, O$_{22}$Al$_{20}$ and O$_2$Si phases was achieved as well as the space distribution of atoms in optimized cubic cells. In case these of the assignment a primary space group to cubic cells, they can be identified as the unit cells of Fe$_2$O$_3$, O$_{22}$Al$_{20}$ and O$_2$Si. For the optimized cubic cells of O$_{22}$Al$_{20}$ and O$_2$Si, the structural factors and consequently integral intensities can be calculated. The model amorphous phases of Fe$_2$O$_3$, O$_{22}$Al$_{20}$ and O$_2$Si are used to obtain the
phase composition of ash waste. Figure 2b shows the XRD patterns of plasma-treated ash waste analyzed by the Rietveld method. The convergence criterion is $R_{wp} = 5.31\%$. The refined parameters of cubic cells and the intensity of amorphous phases are presented in Table 3.

### Table 3. Amorphous structure and phase content.

| N | Chemical formula | Intensity, % | $a$, (nm) | $b$, (nm) | $c$, (nm) | $\alpha$ (deg.) | $\beta$ (deg.) | $\gamma$ (deg.) |
|---|------------------|--------------|-----------|-----------|-----------|----------------|----------------|----------------|
| 1 | $O_{22}Al_{20}$  | 43.55        | 1.3909    | 1.0361    | 1.3038    | 77.08          | 91.18          | 81.24          |
| 2 | $O_{22}Fe_{24}$  | 49.05        | 0.9750    | 1.3209    | 0.8267    | 73.69          | 80.40          | 100.10         |
| 3 | $O_{48}Si_{24}$  | 0.53         | 1.3364    | 1.6277    | 1.2900    | 78.44          | 86.10          | 69.54          |
| 4 | Total            |              |           |           |           |                |                | 93.13          |

The integral intensity superposition of the amorphous phases is 93.13% of the XRD diffraction pattern plotted in Figure 2b. The obtained results indicate that the plasma-chemical treatment leads to a complete amorphization of ash waste. At the same time, the ash melting results in a complex redistribution of the amorphous phase content. Thus, the amount of $O_2Si$ phase decreases, whereas that of $O_{22}Al_{20}$ and $Fe_2O_3$ decreases. The density of Al and O elements in $O_{22}Al_{20}$ cubic cell changes insignificantly.

### 4.2. Differential thermal analysis

The differential thermal analysis (DTA) shown in Figure 3, describes the original state of ash waste. The DTA curve indicates that the ash behavior under the heating process is similar to that of classical silicate materials.

![DTA curve](image)

**Figure 3.** DTA curve for the original state of ash waste.

Within the temperature of 100 °C, the observed endothermic process corresponds to the removal of free water. A blurred exothermic process within 300–400 °C range is caused by the formation of crystallization centers. A further temperature growth up to 600 °C leads to the removal of adsorption and chemically bound water. The exothermic process of 600–700 °C relates to the transformation of the amorphous phase to a crystal. Within 800–950 °C, the exothermic process is caused by softening of low-melting compounds and recrystallization of calcium and magnesian silicates with a complex composition.

### 5. Conclusions

The physicochemical investigations showed that the low-temperature plasma treatment of ash-based silicate melt resulted in the ordered structure of aluminosilicate glass. The experiments allowed the
authors to obtain consistent results on the ash waste phase composition both before and after the plasma treatment. SiO$_2$ mineral predominated in the ash waste. The plasma-chemical treatment resulted in amorphization of the ash waste which then transformed to a mixture of O$_{22}$Al$_{120}$, Fe$_2$O$_3$ and O$_2$Si phases. Melting products were homogeneous and ordered, i.e. the melting process of the ash waste promoted a complete homogenization of the melt. Therefore, the obtained aluminosilicate glass can be used to produce construction materials, including mineral fibers having the enhanced performance characteristics (chemical, thermal and water resistance), mechanical-and-physical properties and service life.

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