Scanning Electron Microscopy—Energy-Dispersive X-ray Spectrometry (SEM–EDS) Analysis of PM$_{1-2}$ Microspheres Located in Coal Char Particles with Different Morphologies

Elena V. Fomenko,* Vladimir V. Yumashev, Sergey V. Kukhtetskiy, Anatoliy M. Zhizhaev, and Alexander G. Anshits*

**ABSTRACT:** Scanning electron microscopy and energy-dispersive X-ray spectroscopy were used to analyze individual microspheres, 1–2 μm in size, located in coal char particles of Inertoid and Fusinoid/Solid morphological types. It was shown that PM$_{1-2}$ (where PM = inorganic particulate matter) is formed in the porous structure of the carbon matrix, which controls the microsphere size, from authigenic minerals that determine their composition. Depending on the contents of SiO$_2$, Al$_2$O$_3$, and FeO, the studied microspheres fall into various groups differing in mineral precursors. The precursor of the Group 1 microspheres with the specific composition of SiO$_2$ + Al$_2$O$_3$ > 95 wt % and FeO ≤ 1.5 wt % is NH$_4$–illite. Microspheres containing SiO$_2$ + Al$_2$O$_3$ ≤ 95 wt % and FeO in increasing content amounts up to 4, 6, and 10 wt %, included in Group 2, Group 3, and Group 4, respectively, are formed from mixed-layer K–illite–montmorillonite minerals subjected to cationic substitution with iron, followed by the entry of Fe$^{3+}$ in interlayer sites. Calcite, dolomite, gypsum, magnesite, rutile, and siderite are involved in the formation of Group 5 microspheres with a high content of Ca, Mg, Ti, or Fe. The significant part of PM$_{1-2}$ is represented by microspheres of Groups 2, 3, and 4 regardless of the type of coal char particles (62% for Inertoid ones and 75% for Fusinoid/Solid ones). About one-third of the microspheres for both char morphotypes refer to Group 5. Microspheres of Group 1 (8%) are located only in the Inertoid char particles, which results from the characteristic effect of the maceral–mineral composition of original coal. It has been suggested that Inertoid and Fusinoid/Solid char particles are formed from various macerals, semifusinite and fusinite, respectively. Due to the closed-cell structure, semifusinite contains noncation-exchanged NH$_4$–illite, the mineral precursor of microspheres with low contents of Fe, K, Na, and Mg. The fusinite structure allows cationic substitution in NH$_4$–illite with the formation of mixed-layer K–illite and montmorillonite, the mineral precursors of a significant part of PM$_{1-2}$.

**INTRODUCTION**

Inorganic particulate matter with an aerodynamic diameter smaller than 2.5 μm (PM$_{2.5}$) and 10 μm (PM$_{10}$) is the environmentally hazardous component of fly ash from pulverized coal combustion.\(^1,2\) The high level of environmental pollution with aerosols and fine suspended particulate matter makes it necessary to study the physicochemical properties of PM$_{5}$, their origin, and the ways to reduce emissions.

The physicochemical characteristics of fly ash (including its composition, structure, and particle size distribution (PSD)) depend on the type of coal and conditions of its combustion,\(^3-5\) as well as the nature of mineral components and the mechanisms of their thermochemical transformations.\(^6-9\) Intensive experimental research has shown that the PSD of PM$_{10}$ can be bimodal,\(^10,11\) trimodal,\(^12-14\) or even multimodal.\(^15-17\) A more reasonable approach is to identify the three modes of PM$_{10}$ depending on the formation mechanism.\(^18-20\) Ash particles of the ultrafine mode 0.1–0.3 μm in size\(^12-14\) are formed via the vaporization–condensation mechanism,\(^10,21\) while coarse-mode particles with the size >5.0 μm\(^12,13\) result from char fragmentation and mineral coalescence.\(^7,20\) The formation of central-mode particles (0.3–5.0 μm)\(^14,18\) depends on a combination of different mechanisms, including the char and mineral fragmentation,\(^18,19\) direct transformation, and coalescence of fine included minerals.\(^19,20\)

The mechanisms of PM formation significantly depend on the structure of char particles, which are formed as a result of the coal type-dependent conversions during devolatilization.\(^7,22\) Coal particles with different maceral components generate different types of char structures.\(^23-24\) The following morphological parameters of char are used in most classification systems: particle shape, wall thickness, fused and unfused structures, porosity, and voidage.\(^22-26\) On the basis of these characteristics, the Combustion Working Group in Commission III of the International Committee for Coal and Organic Petrology (ICCP) developed a detailed char classification system.\(^27\) The classification system of the ICCP\(^27\) is

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A narrow fraction of coal char particles of the granulometric class 0.16 + 0.10 mm (UE−016 grade) was used as a study object. The UE−016 fraction was isolated from fly ash produced by pulverized combustion of grade SS (low caking) Eikabust coal at the Omsk Thermal Power Station (BKZ-420-140 boiler unit; flame kernel temperature, 1700 °C; liquid slag removal). Fly ash was sampled from fields 1-2 of ESP. The narrow UE−016 fraction was separated according to the scheme that included the stages of magnetic separation and grain-size classification, followed by the splitting of the narrow fractions of the magnetic concentrate with the highest content of char particles in accordance with the State Standard GOST 16190-70 31 (0.48 g/cm³). The ash content in the fraction was determined in accordance with the State Standard GOST 11022-95, 32 where the chemical composition, including the contents of silicon, aluminum, iron, calcium, magnesium, and potassium oxides, was determined using chemical analysis methods according to the State Standard GOST 5382-91, 33 which specifies the methods for component identification and the standards of analysis accuracy.

X-ray diffraction data were obtained on an XPert Pro MPD powder diffractometer (PANalytical, The Netherlands) with a PIXcel solid-state detector. The contents of the major crystalline phases were determined by the Rietveld full-profile analysis with derivative difference minimization according to the procedure used previously for aluminosilicate cenospheres in fly ash. 34

The morphological type of coal char particles was identified using the overall SEM images of the UE−016 narrow fraction (Figure 1) for 670 carbon particles in accordance with the char classification systems. 36,27 The average diameter of individual microspheres was determined from the SEM images of local regions of char particles (Figures 2b,c and 3a,b,c) using the Image Tool v.3.0 software package (Uthscsa, USA).

The composition of single microspheres (1−2 μm in size) located in coal char particles was studied by scanning electron microscopy−energy-dispersive X-ray spectrometry (SEM−EDS) on a TM-3000 scanning electron microscope (Hitachi, Japan) equipped with a Quantax 70 microanalysis system with a Bruker XFlash 430H energy-dispersive X-ray spectrometer (EDS) at a magnification of 2500−5000x and an accelerating voltage of 15 kV. Powder coal char samples were applied to a double-coated conductive carbon adhesive tape (Ted Pella, Inc., USA) attached to a quartz plate holding a 250 μm thick and 30 mm in diameter) fabricated from DuoPur poly(methyl methacrylate) resin (Adler, Austria). To form a conductive coating, a 20 nm thick platinum layer was deposited on the surface of powder samples using an Emitech K575 Turbo sputter coater (Quorum Technologies Limited, UK). The data acquisition time was 30−1300 high-temperature furnace (Lithuania) at 815 ± 10 °C until a constant weight was achieved.

The chemical composition, including the contents of silicon, aluminum, iron, calcium, magnesium, and potassium oxides, was determined using chemical analysis methods according to the State Standard GOST 5382-91, 33 which specifies the methods for component identification and the standards of analysis accuracy.

The simple char classification summarized the basic parameters in three-group structures, Cenospheric (Tenuisphere and Tenuinetwork), Network (Crassisphere, Crassinetwork, Mixed porous, Mixed dense), and Solid (Inertoid and Fusinoid/Solid), highlighting the dominant maceral components for them. The three main maceral groups of coal are as follows (in the decreasing order of volatile matter content): liptinite > vitrinite > inertinite. Cenospheric particles are mostly formed from vitrinite; particles with the Network structure are formed from a mixture of vitrinite and inertinite, and Solid particles with a low porosity are formed from inertinite.

During combustion, coal char particles of different morphological types undergo various burnout histories, fragmentations, or coalescences of fine included minerals, 7,23,29 and produce PM with a characteristic composition and specific PSD. The lack of systematic data on the composition of individual particles with a certain size, as well as their relationship with the char structure and the maceral−mineral composition of coal, does not allow for the identification of the mineral precursors and PM formation routes.

The objective of this study was to analyze the composition of individual 1−2 μm microspheres located in coal char particles with different morphologies. The small size of the microspheres makes their composition maximally similar to the composition of fine, included minerals, which are responsible for the formation of PM in a carbon matrix having a certain structure during the industrial combustion of coal with the characteristic maceral−mineral composition.

### EXPERIMENTAL SECTION

<table>
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<th>$W^{\text{r}}$</th>
<th>$C^{\text{daf}}$</th>
<th>$H^{\text{daf}}$</th>
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Table 1. Characteristics of the Organic Component and the Chemical and Phase Compositions (wt %) of the Ash Component of Coal Char Particles UE−016

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<tr>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Chemical Composition</th>
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<td>60.0</td>
<td>28.8</td>
<td>3.4</td>
<td>2.7</td>
<td>1.8</td>
<td>1.1</td>
<td>Glass phase</td>
</tr>
</tbody>
</table>

| 58.2    | 28.2        | 11.5        | 1.1 | 1.0 |       | Phase Composition   |

TM-1000_1282 D.9 x 200 500 μm

Figure 1. SEM image of the narrow fraction of coal char particles UE−016 indicating the following morphological types: (1) Cenospheric, (2) Network, (3a) Inertoid, and (3b) Fusinoid/Solid.
at least 10 min, which enabled the quantitative processing of the spectra. Figures 2 and 3 show the SEM images of individual coal char particles, indicating the areas under study, and single globules analyzed in these areas. The gross composition, including the elemental contents of Si, Al, Fe, Ca, Mg, Na, K, Ti, and Mn, was determined for each analyzed globule. The elemental composition was converted to oxides and normalized to 100%.

**RESULTS AND DISCUSSION**

**Morphology of Coal Char Particles.** According to the simple char classification, the UE−016 narrow fraction of coal char particles (Figure 1) consists of the following morphological types: Cenospheric (13%), Network (30%), and Solid (57%). A typical feature of fly ash produced by the combustion of coals from the Ekibastuz deposit is that there is a significant content of coal char particles of the Solid morphological type. That is, these coal contain a large quantity of char-forming components belonging to the inertinite group (36−45 vol %)35, which are represented by semifusinite and fusinite macerals.36

In accordance with the detailed classification of the ICCP,37 UE−016 coal char particles of the Solid morphological type are subdivided into the Inertoid and Fusinoid/Solid subtypes (Figure 1), 49% and 8%, respectively. The structure of Inertoid particles (Figure 2) has cell cavities of different sizes, which can either be empty or contain microspheres up to 10 μm in size. A characteristic feature of the structure of Fusinoid/Solid particles (Figure 3) is that they contain long cylindrical channels with individual small microspheres inside them; the size of these microspheres is confined to the channel diameter and is not greater than 3−4 μm.

The structure of coal char particles that have internal cell cavities and channels of certain dimensions is a size-limiting parameter for the multimodal PSD of the PM. The matrix of Inertoid coal char particles that have a well-developed porous structure of cell cavities with different diameters forms ash products characterized by broad PSD, which involves microspheres of a larger diameter. Dispersed microspheres, mostly characterized by having a size up to 2.5 μm and a narrow PSD, are formed in the confined channel structure of Fusinoid/Solid particles.

The char quantity in fly ash normally lies in the range 2−12%; in some cases, it can reach 25% and even increase to 57% depending on the coal’s nature and combustion conditions. The high content of char particles positively affects the reduction of emissions of PM_{10} and PM_{2.5} from coal combustion, because PMs remain localized inside the cell cavities and channels of char particles; however, this indicates an inefficiency in the combustion process.

**SEM−EDS Analysis of Individual Microspheres.** Systematic studies of the compositions of individual micro-
spheres and a comparative analysis of the relationship between the major component concentrations allow one to identify the nature of mineral precursors whose thermochemical transformations result in the formation of these microspheres. This approach was used for cenospheres and ferrospheres of different morphological types and for dispersed microspheres of the nonmagnetic fraction of fly ash. A systematic study of the gross composition of individual 1–2 μm nonporous microspheres located in the main morphological types of Solid coal char particles was conducted to determine which mineral precursors are responsible for the

Table 2. Minimum and Maximum Values of Oxide Content (wt %) in PM1–2 Microspheres Located in Inertoid Coal Char Particles

<table>
<thead>
<tr>
<th>group</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>MnO</th>
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<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.06</td>
<td>0.20</td>
<td>&lt;0.01</td>
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<td>1.81</td>
<td>2.04</td>
<td>1.48</td>
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<td>11.90</td>
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<td>&lt;0.01</td>
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<td>3.03</td>
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<td>&lt;0.01</td>
<td>1.56</td>
<td>0.06</td>
<td>&lt;0.01</td>
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<td>5.90</td>
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<td>66.74</td>
<td>40.70</td>
<td>66.82</td>
<td>30.13</td>
<td>13.19</td>
<td>3.79</td>
<td>4.46</td>
<td>8.40</td>
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</tbody>
</table>

Figure 3. SEM images of individual coal char particles of the Fusinoid/Solid morphological type, indicating the areas of analysis (a, c) and the individual microspheres analyzed in these areas (b, d).
formation of environmentally hazardous fly ash aerosol particles. A total of 145 microspheres of Inertoid (Table 2) and 79 microspheres of Fusinoid/Solid (Table 3) particles was analyzed. SiO₂, Al₂O₃, and FeO were found to be the main components of the analyzed microspheres; for most globules, the total content of these components was >90 wt %. This makes it possible to represent the data for microsphere compositions as functions SiO₂ = f(Al₂O₃) with the FeO concentration discretely varied (Figure 4) and to single out several groups meeting certain criteria for the contents of major components and impurity oxides. Tables 2 and 3 list the minimal and maximal values of oxide contents in microspheres belonging to different groups:

- **Group 1**: (SiO₂ + Al₂O₃) > 95 wt %, FeO ≤ 1.5 wt %; minimal content of impurity oxides; 8% of microspheres in Inertoid char particles belong to this group; no microspheres with this composition were detected in Fusinoid/Solid char particles.
- **Group 2**: (SiO₂ + Al₂O₃) = 90−95 wt %, FeO concentration increases to 4 wt %; this group includes 28% and 29% of microspheres in Inertoid and Fusinoid/Solid char particles, respectively.
- **Group 3**: (SiO₂ + Al₂O₃) = 90−95 wt %, FeO concentration increases to 6 wt %; only single microspheres in both morphological types of char particles have this composition, 2% in Inertoid char particles and 5% in Fusinoid/Solid ones.
- **Group 4**: (SiO₂ + Al₂O₃) < 90 wt %, FeO concentration increases to 10 wt %; the contents of impurity oxides increase, MgO to 3 wt %, Na₂O and CaO to 4 wt %, and K₂O to 7 wt %. This group is the most numerous for both types of coal char particles, 32% of microspheres in Inertoid char particles and 41% in Fusinoid/Solid char particles.
- **Group 5**: (SiO₂ + Al₂O₃) < 90 wt %; the microspheres are characterized by an elevated content of individual components, FeO > 10 wt %, CaO > 4 wt %, MgO > 3 wt %, and TiO₂ > 2 wt %. This group involves a large number of microspheres in both morphological types of char particles, 30% in Inertoid char particles and 25% in Fusinoid/Solid ones.

The study demonstrated that most PM₁⁻⁻₂ compounds located in Solid coal char particles are represented by microspheres with an elevated content of iron or impurity components regardless of the carbon matrix structure. The total quantity of microspheres with FeO content monotonically increasing to 4, 6, and 10 wt % reaches 62% in Inertoid char particles and 75% in Fusinoid/Solid char particles (Figure 5; Groups 2, 3, and 4). The proportion of microspheres with the typically increased content of certain components is 1:3 for Inertoid char particles and 1:4 for Fusinoid/Solid ones (Group 5, Figure 5). The following difference between the two structures of char particles was identified: Inertoid char particles contain 8% microspheres with a low FeO content.

### Table 2. Minimal and Maximum Values of Oxide Content (wt %) in PM₁⁻⁻₂ Microspheres Located in Inertoid Coal Char Particles

<table>
<thead>
<tr>
<th>group</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>FeO</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>MnO</th>
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<tr>
<td>min</td>
<td>51.13</td>
<td>8.18</td>
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<td>max</td>
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<td>2.84</td>
<td>4.86</td>
<td>1.73</td>
<td>1.06</td>
</tr>
<tr>
<td>2</td>
<td>SiO₂ + Al₂O₃ &gt; 95 wt %; These Microspheres Were Not Detected</td>
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<td>3</td>
<td>SiO₂ + Al₂O₃ = 90−95 wt %, FeO &lt; 4 wt %; 23 Microspheres</td>
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<tr>
<td>min</td>
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<tr>
<td>4</td>
<td>SiO₂ + Al₂O₃ &lt; 90 wt %, FeO &lt; 10 wt %; 32 Microspheres</td>
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<td>7.38</td>
<td>1.81</td>
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### Figure 4. Dependence of the SiO₂ content on the Al₂O₃ content for PM₁⁻⁻₂ microspheres located in coal char particles with different morphologies: (a) Inertoid and (b) Fusinoid/Solid. Compositions of dehydroxylated minerals correspond to their stoichiometric formula from refs 47 and 48.
(<1.5 wt %), while the Fusinoid/Solid char particles do not contain them (Group 1, Figure 5). The formation of microspheres with a specific composition in the carbon matrix that have a certain structure is indicative of the typical location of mineral precursors of microspheres with a low iron content and their relationship with the mineral–maceral composition of the original coal.

It was demonstrated\textsuperscript{42} that 1–2 μm microspheres from the nonmagnetic ash fraction form similar groups meeting the aforedescribed criteria for composition. This fraction of dispersed microspheres was isolated at the stage of magnetic separation from the narrow fraction of ash produced during the combustion of Ekibastuz coal.\textsuperscript{42} The difference is in the percentage distribution of microspheres by groups (Figure 5). The nonmagnetic ash fraction is represented by microspheres with a low iron content, which belong to Groups 1 and 2 by more than two-thirds; together with Group 3, they form 90% of the PM\textsubscript{1–2} (Figure 5, histogram column "Narrow fraction"). The microspheres, having an elevated iron content (dispersed ferrospheres meeting the composition criteria for Groups 4 and 5), were isolated in the magnetic fraction. However, the yield of the magnetic fraction is sufficiently low (0.2 wt %).\textsuperscript{42} Therefore, its isolation could not noticeably affect the rise in the concentration of nonmagnetic microspheres in groups characterized by a low iron content.

The difference in the percentage distribution of PM\textsubscript{1–2} in identical groups between the nonmagnetic narrow fraction of fly ash\textsuperscript{42} (Figure 5, histogram column "Narrow fraction") and Solid char particles (Figure 5, histogram columns "Inertoid and Fusinoid/Solid") is a consequence of the various burnout histories of the initial coal char particles and routes leading to the microsphere formations. Fly ash microspheres originating from the more reactive coal char particles of the Cenospheric or Network morphological types were obtained from vitrinite macerals. During combustion, Cenospheric char particles undergo significant fragmentation, which reduces the extent of the coalescence of the included minerals. Network char particles are less prone to fragmentation; coalescence of the included minerals may occur on the particle surface. Solid char particles exhibit the least fragmentation; coalescence of the included mineral is the dominant mechanism of their thermal transformation.\textsuperscript{7,20,22}

**Identification of PM\textsubscript{1–2} Mineral Precursors.** Kaolinite clay minerals in combination with quartz are the predominant mineral components of hard coal from the Ekibastuz deposit; hydromicas, feldspars, siderite, pyrrite, calcite, dolomite, gypsum, and magnesite are also present.\textsuperscript{36,43–45} Individual carbonaceous rocks include nonstoichiometric mixtures and contain montmorillonite,\textsuperscript{44} which can be associated with kaolinite, quartz, or illite/montmorillonite mixed-layer minerals,\textsuperscript{43} as well as be present within hydromicas (illite/smectite minerals with a low smectite content).\textsuperscript{46} The conditions of groundwater recharge and accumulation in the Ekibastuz coal basin are responsible for the stagnant nature and high mineralization of groundwater;\textsuperscript{56} the cationic exchange in clay minerals gives rise to mixed-layer phases with diverse compositions.

The systematic study of the compositions of PM\textsubscript{1–2} located in coal char particles with different morphologies (Tables 2 and 3) and the comparative analysis of the relationship between major component concentrations (Figure 4) demonstrated that the aluminosilicate compositions of individual microspheres in separate groups are described by regression equations SiO\textsubscript{2} = f(Al\textsubscript{2}O\textsubscript{3}) with high correlation coefficients:

\[
\text{Group 1 of Inertoid morphotype: } [\text{SiO}_2] = 96.92 - 1.05[\text{Al}_2\text{O}_3] \quad r = -0.98
\]

\[
\text{Group 2 of Inertoid morphotype: } [\text{SiO}_2] = 92.33 - 1.02[\text{Al}_2\text{O}_3] \quad r = -0.99
\]

\[
\text{Group 2 of Fusinoid/Solid morphotype: } [\text{SiO}_2] = 90.98 - 0.99[\text{Al}_2\text{O}_3] \quad r = -0.99
\]

The aluminosilicate compositions of dehydroxylated clay minerals lie in the immediate vicinity of the trends (Figure 4): NH\textsubscript{4}–illite = (NH\textsubscript{4}0.67K0.11)(Al\textsubscript{1.90Fe0.06Mg0.04})\textsubscript{4}–(Al\textsubscript{0.85Si\textsubscript{3.32}}O\textsubscript{10}OH)\textsubscript{4.74} \text{ montmorillonite = } Na\textsubscript{0.33}(Al\textsubscript{1.67}Mg\textsubscript{0.33})\textsubscript{2}Si\textsubscript{10}(OH)\textsubscript{2} \text{ and } K–illite = K\textsubscript{2}Al\textsubscript{2}Si\textsubscript{13}O\textsubscript{26}(OH)\textsubscript{6} \text{. The thermochemical transformations of these authigenic minerals and their coalescence with dispersed SiO\textsubscript{2} in the carbon matrix, which has a certain structure, give rise to most of the PM\textsubscript{1–2} located in Solid char particles. The quite different composition of kaolinite, Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}(OH)\textsubscript{4} (Figure 4), gives support for inferring that this mineral is not directly involved in the formation of the 1–2 μm microspheres and is a structure-forming mineral precursor of coarse particles that have a cellular structure.\textsuperscript{39}

The characteristic relationship has been established between the composition of individual microspheres located in Solid char particles, the char structure, and the maceral–mineral composition of the original coal. Inertinite is the predominant maceral forming the Solid coal char particles.\textsuperscript{25–28} Ekibastuz coals contain semifusinite and fusinite,\textsuperscript{36} the macerals with preserved plant cell structures belonging to the inertinite group.\textsuperscript{49} According to its framework and properties, semifusinite is an intermediate structure between vitrinite and fusinite.\textsuperscript{39} During combustion, when macerals lose their volatiles, semifusinite generates more porous char particles with the cellular structure of the Inertoid morphological type, while fusinite produces low-porosity char particles with the channel structure of the Fusinoid/Solid morphotype.
The cell cavities of semifusinite and fusinite may be either empty or filled with clay and other minerals. A characteristic feature of clay minerals is that they can undergo isomorphic substitution and interlayer cation exchange due to their layered structure, giving rise to mixed-layer phases that have rather diverse compositions. Due to the closed-cell structure, semifusinite contains noncation-exchanged NH4−illite, which is an authigenic mineral resulting from the transformation of other clay minerals (e.g., kaolinite) during diagenesis. The proportion of NH4−illite within the total clay minerals tends to rise with the increasing Vdaf of the associated coal, and the Vdaf of semifusinite is higher than that of fusinite. The thermochemical transformations of NH4−illite and coalescence with dispersed SiO2 lead to the formation of microspheres with a low content of iron and impurity components belonging to Group 1 in coal char particles with the cellular structure of the Inertoid morphotype.

For fusinite, the cell walls are often thin, and the cavities are usually larger than those of semifusinite. The fusinite layer is more permeable for groundwater compared to the semifusinite layer, which has a denser structure. The internal structure of fusinite is accessible for highly mineralized aqueous solutions containing K, Na, and Mg exchangeable cations, so NH4−illite gets completely substituted, and the mixed-layer structures characterized by different K−illite/smectite ratios are formed in fusinite cell cavities. Most of the Group 2, 3, and 4 microspheres are formed from the isomorphic mixtures of mixed-layer illite/montmorillonite minerals. They contain iron (Tables 2 and 3), because cationic substitutions occur in the layered structure of mineral precursors via the isovalent and heterovalent mechanism (first, Mg2+ at octahedral positions; subsequently, Al3+ in octahedra and partially Si4+ in tetrahedra are replaced with Fe2+/Fe3+ cations). The iron content was further increased as Fe3+ entered the interlayer positions.

The limiting FeO content for microspheres of various groups (Tables 2 and 3) is determined by the iron content in natural mixed-layer illite/montmorillonite minerals. For Group 2, the microsphere FeO content is consistent with that of the data for little substituted illites, which is less than 4 wt % of iron (calculated as FeO). The increase in the FeO content to 6 wt % for Group 3 microspheres is associated with the illite−montmorillonite mineral characterized by a higher degree of isomorphic heterovalent substitution. In the case of Group 4 microspheres, the FeO content increases to 10 wt % due to the additional incorporation of iron in the interlayer positions of the mineral precursor.

The elevated contents of Na2O and K2O observed for some Group 4 microspheres (Tables 2 and 3) are possibly related to the fact that feldspars are partially involved in their formation (Figure 4). Impurity minerals of coal char (such as calcite, dolomite, gypsum, magnesite, rutile, and siderite) are involved in the formation of Group 5 microspheres with typically high contents of calcium, magnesium, titanium, and iron (Tables 2 and 3).

CONCLUSION

The present study leads to the following conclusions. Individual microspheres with the size of 1−2 μm, located in Solid coal char particles, are formed in the internal porous structure of the carbon matrix from authigenic fine included minerals. Mineral precursors of most PM1−2 microspheres, which are responsible for their composition, are the isomorphic mixtures of illite/montmorillonite mixed-layer minerals characterized by different levels of substitution with ion cations and the possession of Fe3+ in the interlayer sites. The size-control parameter of microspheres is the cellular structure of the Inertoid and channel structure of the Fusinoid/Solid char particles, which is generated during devolatilization and depends on the coal macerals. There exists a characteristic relationship between the composition of PM1−2 microspheres, the char structure, and the maceral−mineral composition of the original coal. The Inertoid char particles are formed from the semifusinite maceral, which contains noncation-exchanged NH4−illite, the mineral precursor of microspheres with a specific low content of iron and impurity components: SiO2 + Al2O3 > 95 wt %, FeO ≤ 1.5 wt %. The Fusinoid/Solid char particles are formed from fusinite maceral. The internal structure of fusinite is available for cationic exchange, so NH4−illite is substituted, giving rise to mixed-layer minerals with different ratios between the K−illite and smectite layers, precursors of microspheres with elevated contents of K, Na, and Mg: SiO2 + Al2O3 < 95 wt %, FeO increases to 10 wt %.

AUTHOR INFORMATION

Corresponding Authors

Elena V. Fomenko − Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center “Krasnoyarsk Science Center SB RAS”, Krasnoyarsk 660036, Russia; orcid.org/0000-0003-0929-807X; Email: fom@icct.ru
Alexander G. Anshits − Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center “Krasnoyarsk Science Center SB RAS”, Krasnoyarsk 660036, Russia; Siberian Federal University, Krasnoyarsk 660041, Russia; orcid.org/0000-0002-5259-0319; Email: anshits@icct.ru

Authors

Vladimir V. Yumashev − Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center “Krasnoyarsk Science Center SB RAS”, Krasnoyarsk 660036, Russia
Sergey V. Kukhtetskiy − Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center “Krasnoyarsk Science Center SB RAS”, Krasnoyarsk 660036, Russia; orcid.org/0000-0001-6606-8241
Anatoliy M. Zhizhaev − Institute of Chemistry and Chemical Technology SB RAS, Federal Research Center “Krasnoyarsk Science Center SB RAS”, Krasnoyarsk 660036, Russia

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.energyfuels.0c01345

Notes

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