The Properties of Cenospheres and the Mechanism of Their Formation During High-Temperature Coal Combustion at Thermal Power Plans†

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Abstract

A systematic analysis of the probable scenario of the supramolecular structure (texture) formation of mineral products, formed during the high-temperature combustion of pulverized bituminous coals at thermal power plants (TPP) is provided. The general physico-chemical consideration of the processes that occur at different stages (heating, burning, viscoplastic state in the hot zone, and cooling) during the combustion of bituminous coal makes it possible to allocate the following systematic transformations: coal → char → network structures (including plerospheres) → cenospheres → fly ash.

Keywords: Cenosphere, plerosphere, ash, coal combustion, thermal power plants

1. Introduction

One of the alarming environmental problems that requires an immediate solution is associated with an infinitely increasing amount of ash produced during the burning of coal, oil, and wood and other biomaterials, domestic waste, etc. The ash settling reservoirs of thermal power plants (TPP) have already transformed many tens of hectares of land into lifeless (and constantly growing) deserts. The amount of continuously produced ash is much higher than its consumption, and ash dumps continue to expand. The most insidious attendant component of ash that is formed simultaneously with it are aluminosilicate microspheres (MS), some of which have an extremely low density (0.3-0.5 g/cc) and are entrained in flue gases together with the superfine fly ash. These MS together with the ashes enter ash settling reservoirs, where due to their low density, they accumulate mainly at the external surface, and can be easily carried away by rain and wind. The most dangerous possibility is their entrainment in wind, with which they can be moved over long distances, can ingress the respiratory tracts of humans and animals, and thus promote the development of cardiovascular and respiratory illness. In addition, such MS can be generated during accidents at nuclear power plants, and they were found in the products of volcanic activity, etc.

But at the same time, MS have several unique properties that provide prospects for their effective use in many up-to-date technologies. This stimulates the necessity to improve the methods of their gathering, the deeper investigation of the properties and mechanisms of their formation, and working out the optimum conditions of utilization.

There are two main classes of MS: really “empty spheres”, in which the cavities are filled with gas only, the so-called cenospheres (CS), and plerospheres (PS) in which the cavities are filled with small mineral particles, foam, spongy or other porous framework. The term cenosphere* comes from the Greek kenos (hollow) + sphere, and reflects the most important feature of cenospheres - the presence of a cavity surrounded by a solid or perforated mineral shell. The latter type of microspheres are often called network-structured cenospheres or plerospheres - from the Greek plërës (filled) + sphere (Fisher et al.).

* The term cenosphere was proposed by F.S. Sinnatt at the second international symposium on bituminous coals in 1928, naming both products of coal combustion that quickly pass through a plastic state, followed by curing and formation of hollow spheres.
and Raask.  

Both types of MS are formed of amorphous glass-like material containing amorphous SiO₂ (~50–65 wt.%), Al₂O₃ (~20–30 wt.%), Fe₂O₃ (~3–8 wt.%), along with Ca, Mg, K, etc., phosphates, sulfates, chlorides, as well as quartz, mullite, etc. The specific composition is determined by raw coal and the transformations that occur in the burning chambers of TPPs at 1400-1700°C.²⁶,¹²,¹⁴

The structure of cenospheres defines their low density (bulk density is 0.3–0.5 g/cc), apparent density δ is 0.6–0.7 g/cc), low thermal conductivity (0.1–0.2 W/m K), which is accompanied by high mechanical strength (210–350 kg/cm²), thermal stability (sintering usually occurs at 1000-1450°C), and general chemical inertness.

The same study by Ngu et al.¹⁵ gave a numerical ratio between plerospheres and cenospheres. It was shown that this ratio increases with D₀, for example, for 45-63 μm the plerosphere fraction is ~6%, ~15% for the 75-90 μm fraction, and rises to ~90% for the greater fraction.

The specific composition of cenospheres defines their low density (bulk density is 0.3–0.5 g/cc), apparent density δ is 0.6–0.7 g/cc), low thermal conductivity (0.1–0.2 W/m K), which is accompanied by high mechanical strength (210–350 kg/cm²), thermal stability (sintering usually occurs at 1000-1450°C), resistance to acids and general chemical inertness.

Fly ash comprises 50–90% of the solid products of combustion and usually contains 1-2 wt.% of MS of all types (although a higher MS content (3.8 wt.%) was also observed). Taking into account that modern TPPs burn millions of tons of coal annually, at the same time they produce thousands of tons of CS. According to the results of technical monitoring by Drozhzhin et al.,¹⁶ the largest TPPs in Russia produce more than 120 thousand tons of CS per year.

A set of unique properties of cenospheres along with their availability opens up the prospects for a wide use as heat insulation of space ships, lightweight building materials, obtained by introducing CS into concrete, bricks, ceramics, flooring and pavements, polymer composites, metal alloys, etc., which could distinguish thin- and thick-walled cenospheres, thin- and thick-wall frame particles (that are plerospheres) and various mixtures, including the non-porous particles of ash.

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**Fig. 1.** Scanning electron microscopy (SEM) images of some MS, formed during high-temperature burning of bituminous coal (cited according to [7] and numerous publications on the Web).

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The listed areas of application are cited from the references in the Web (http://www.iccop.org). One should distinguish thin- and thick-walled cenospheres, thin- and thick-wall frame particles (that are plerospheres) and various mixtures, including the non-porous particles of ash.
simultaneously have improved mechanical, thermal and sound insulation properties. The inclusion of CS with water-impermeable shells allows creation of various frost- and water-resistant products, CS have potential as filters, seals of various kinds (from seals in windows to those for wells in oil and gas production), anti-corrosion coatings, protective layers on liquid surfaces to reduce evaporation, in energy-absorbing bumpers and other car parts, in pneumatic tires, etc. Several papers explore the prospect of their use as microcontainers for storing a wide range of diverse materials - from enzymes to liquid explosives, and for encapsulation of radioactive waste, etc. At the same time, the possibility of their use as adsorbents, catalyst supports for fuel cells, photocatalysts and catalysts operating at high temperatures in aggressive environments, etc., is also investigated.\textsuperscript{[10-29]}

Consumer properties of the CS and ash are mainly determined by their chemical composition and texture, where the texture means the structure of supramolecular level. In certain literature, most attention is paid to chemical and phase composition. The research of CS texture is usually confined to electronmicroscopic images (often the most spectacular images of defective MS are presented), their particle size and bulk density. Systematic analysis of the textural characteristics of CS and their relationship to the conditions of formation are virtually absent. This complicates the understanding of the formation mechanisms of CS with different characteristics, the development of strategies to monitor and optimize their properties, and the separation of CS with a given texture from the ash obtained at TPP using modern technologies.\textsuperscript{[11,12,20-27]}

The scenario of cenosphere formation during coal burning is generally accepted at present.\textsuperscript{[11,12,20-27]} It is based on the model of particles with a plastic or solid core and visco-plastic shell cover. The shell is formed from easy-to-melt (under combustion conditions) inorganic components (mainly silicates and aluminosilicates), and the core is formed of less easy-to-melt components. Gasification of the components in a closed volume of the shell leads to the formation of bubbles, which swell under the effect of increasing internal pressure. Swelling can destroy the shell or, after cooling and solidification, can result in the formation of cavities inside the MS. The breakthrough of gas through the shell can lead to destruction of the shell, yielding the formation of cracks or even the release of large fragments (Fig. 1a). In the case of a viscous-plastic state of the shell, the formation of craters is possible (Fig. 1b), while less plastic shells form cracks (Fig. 1c).

Formation of MS with intact shells (Fig. 1e) is usually explained by the decomposition of mineral components that provide a moderate amount of gaseous products (carbides, carbonates, sulfates and pyrosulfates, dehydration and dehydroxylation of clay-containing minerals, etc.) Fisher et al.\textsuperscript{[11,17]} Raask\textsuperscript{[12,13]}, etc. Some authors point out a special role of Fe-containing compounds.\textsuperscript{[11,13,16]} According to, e.g., Raask\textsuperscript{[12]}, at least 5% of iron oxide is necessary to form cenospheres. This idea is refuted by Ngu et al.\textsuperscript{[17]}, where the maximum yield of cenospheres (3.82 wt.\%) is observed in ash with a minimum Fe$_2$O$_3$ content (0.54 wt.%).

More controversial is the mechanism of plerosphere formation (Fig. 1d). The hypothesis of their formation in a hot zone was proposed by Fisher et al.\textsuperscript{[11]}, where this type of MS was discussed for the first time. According to this hypothesis, different components in a particle melt at different moments. This is accompanied with the release of gases from CaCO$_3$ decomposition, clay dehydration, pyrolysis and burning of carbon, present on the surface or inside the ash slag particles, etc. Raask concludes\textsuperscript{[20]} that “the plerospheres originate from coal particles with highly dispersed mineral matter during the combustion, and a fused silicate envelope, inside which the carbon residue prevents coalescence of encapsulated ash particles”.

A more detailed description includes the heat transfer from the shell to the core through small contact bridges, whose thermal conductivity is higher than the thermal conductivity of the gas. This intensifies local gas emission, allocation and moving of the core inside the cavity volume and its breaking into separate fragments.

An alternative mechanism of plerosphere formation from cenospheres at the stages after their escape from a hot zone was proposed elsewhere (Frandsen\textsuperscript{[28]} and Shibaoka and Paulson\textsuperscript{[29]}). According to this mechanism, the small particles\textsuperscript{[28]} permeate inside the cenosphere cavities from the outside through the cracks and other “windows” while they are suspended in the flue gas or during and after their collection in the dust collecting equipment. Key features of this idea are: a) formation of plerospheres from cenospheres at the cooling stage, and b) presence of fractures in the shell of MS.

According to Yu at al.\textsuperscript{[17]}, the plerospheres are formed in the hot zone. The mechanisms for their formation can be based on the simultaneous involvement of several sources of gas inside one burning
particle agglomeration and coalescence of several precursor particles. Additionally, the formation of cenospheres can be incomplete (complete coalescence of bubbles under one shell does not occur) due to the release of particles from the hot zone. The probability of implementation of these mechanisms increases with the size of particles, their viscosity and the cooling rate.

At present there is no agreement in the assessment of such an important textural characteristic as the integrity of CS shells. The majority of publications gloss over this problem, although it is considered\textsuperscript{4,9,10,16} that in typical cases, the shell of the cenospheres is perforated. This can make it suitable for a number of practical applications of cenospheres as microcontainers, but retards their usage in other applications. The situation is complicated by the fact that conventional SEM studies can only distinguish plerospheres and cenospheres if the shell is partially destroyed or by examination of polished blocks\textsuperscript{15}. Independent diagnostic methods of the MS shell integrity are not developed in detail in the known literature.

In this paper, we try to eliminate the above and several other contentious issues and ambiguities. To do that we consider a systematic analysis of texture and the mechanisms of MS formation in detail. Simple experimental methods make it possible to distinguish between MS with intact and perforated shells and between plerospheres and cenospheres with intact shells. Experimental work is based on the study of hollow MS and fly ash, obtained during the combustion of Kuznetsk coal tar (brand DG, fraction 90-450 μm) at the Novosibirsk TPP-5. These results and the analysis of data from numerous publications permit the revision of the existing ideas about the formation and properties of hollow MS. As a result, we suggest a general physical-chemical model of formation of the cenospheres supramolecular structure, which can help develop better strategies to control and optimize ash cenosphere production at TPP.

2. Experimental

Samples of MS were separated according to the hydraulic method from fly ash collected from the last in a row of four electrostatic precipitators at the Novosibirsk TPP-5, which contains MS in the largest quantity (\textasciitilde3% wt.). The first separation step was based on the fact that MS float in water, and the rest of the ash sinks. The second separation step involved a 45-minute boiling in water and was applied to remove the MS with perforated shells and ash particles that float due to small trapped air bubbles. The MS that floated after such a procedure (their content was over 80\%) were made a subject of the studies. These MS are designated here as intact MS, and are referred to hereinafter as IMS.

The studies of the internal structure of IMS were carried out after intensive grinding of the size fraction below 30 microns. This fraction was subjected to a third separation in water. The sunk particles were collected. These particles are called shredded MS (SMS).

The particle size distribution of IMS was analyzed in an ethanol suspension using a SALD-2101 (Shimadzu) instrument. The density, \( \rho_w \), of IMS and SMS was measured at room temperature by helium pycnometry using an AutoPycnimeter 1320 (Micromeritics). The bulk density \( \Delta \) of a layer of MS was measured by weighing 100 cc of a sample. To reduce the electrostatic polarization, the samples were exposed to water vapor in a desiccator. The weight of the adsorbed water vapor was taken into account during calculation. The surface area of IMS and SMS was measured from nitrogen adsorption isotherms at 77K obtained by means of an ASAP-2400 (Micromeritics) instrument. Specially manufactured large volume cells that allow the introduction of probes with a mass of 1.7 - 2.0 g made the measurements of the specific surface area reliable. However, even such large cells did not allow correct measurements of pore volume and pore volume-size distributions. The results of these measurements gave only an estimation of the total pore volume in the range below 100 nm at the level below 0.01 cc/g.

The porous structure of IMS was also studied by mercury porosimetry with an AutoPore 9200 (Micromeritics) instrument. These measurements showed the presence of pores mostly far larger than 15-20 microns, which are difficult to be reliably distinguished from the interparticle gaps. The volume of pores with a smaller size was found to be very small and close to \( \sim 0.001 \) cc/g. An additional estimation of pore volume with the size of less than 100 nm according to water adsorption gave a value of \( \sim 0.002 \) cc/g. These results allow us to believe that IMS have virtually no pores that are accessible from the surrounding bulk.

Detailed measurements of chemical and phase composition, as well as electron-microscopic studies were not carried out, because the fly ash and MS from the ashes of the same Novosibirsk TPP-5 were studied previously by means of these methods in detail in\textsuperscript{4,9,10,16} and in other publications by the same
and oxide. In the numerous measurements, the average chemical composition of main compounds in the investigated MS was as follows: \( \sim 64\% \text{SiO}_2, \sim 25\% \text{Al}_2\text{O}_3 \) and \( \sim 4\% \text{Fe}_2\text{O}_3 \) (by mass), which is close to the data given by Vereshagina et al.\(^{19}\). The residual content of combustible compounds in MS was \( \sim 3.0\% \).

3. Results

3.1 Analysis of the experimental results

The typical textural characteristics of fly ash, intact (IMS) and shredded (SMS) microspheres are presented in Table 1.

**Table 1.** Typical textural parameters of fly ash FA, intact (IMS) and shredded (SMS) microspheres

| Sample  | Diameter, \( D_0 \), \( \mu \text{m} \) | Specific surface area, \( A_0 \), \( \text{m}^2/\text{g} \) | Density, \( \rho_{\text{ms}} \), \( \text{g/cm}^3 \) |
|---------|---------------------------------|---------------------------------|---------------------------------|
| Fly ash | 29                              | 4.9                             | 2.23                            |
| IMS     | 132                             | 1.1                             | 0.71                            |
| SMS     | 35                              | 2.6                             | 2.44                            |

The obtained values of the specific surface area, \( A_0 \), and density, \( \rho_{\text{ms}} \), for FA, IMS, and SMS are close to previously reported data\(^ {1,12,16}\). Summarizing, \( A_0 \) and pycnometric density \( \rho_{\text{ms}} \) for IMS have lower values compared with FA and SMS, the grinding of IMS is accompanied by an increase of the surface area and density. This increase can be explained by the observation that the IMS have a closed porosity. The closed pores are inaccessible for He and N\(_2\), but open up during grinding. The value of the porosity, \( \varepsilon_0 \), is equal to the ratio of the volume of all closed pores to the volume of IMS, and the value of \( \rho_{\text{ms}} \) for IMS corresponds to the apparent (or envelope) density, including the closed porosity. Let us designate this apparent density as \( \delta \) to distinguish it from the true (skeletal) density, which will be designated as \( \rho_{\text{us}} \). In turn, the \( \rho_{\text{us}} \) value for SMS corresponds to the true density. The values of \( \delta \) and \( \rho \) are interrelated by Fenelonov and Mel’gunov\(^ {29,30}\):

\[
\delta = \rho \left( 1 - \varepsilon_0 \right) \quad (1)
\]

The closed porosity value for IMS, \( \varepsilon_0 \), calculated by eq. (1) is equal to 0.71. An analogous consideration of data presented by Vereshagin et al.\(^ {16}\) gave \( \delta = 0.995 \pm 0.008 \text{ g/cc} \), and \( \rho = 2.600 \pm 0.015 \text{ g/cc} \) for IMS. The internal porosity that corresponds to these values is \( \varepsilon_0 = 0.617 \). A similar analysis of data from\(^ 1,31,32\) shows that \( \varepsilon_0 \) varies in a narrow range of 0.60-0.75.

The values of true density for SMS are slightly higher than \( \rho_{\text{us}} \) for FA. This can be explained by the presence of small amounts of IMS in FA at the level of \( \sim 3.0 \text{ wt.}\% \). Let us estimate the true density of FA according to a known equation, widely used in the studies of glass and glass-like materials (see references\(^ {33-37}\))

\[
\frac{1}{\rho_{\text{fa}}} = \sum X_i / \rho_i \quad (2)
\]

where \( X_i \) is the mass content of component \( i \) with true density \( \rho_i \), \( \Sigma X_i = 1 \). This relation was introduced by Gehlhoff and Thomas in 1926\(^ {33}\) and refined in\(^ {34-37}\). It is based on volumetric additivity.

The calculated density of FA, which contains 3.0% of IMS with apparent density \( \delta = 0.71 \text{ g/cc} \) and true density \( \rho = 2.44 \text{ g/cc} \), can be estimated as \( \rho = 1/ (0.03/0.709 + 0.97/2.44) \), which is equal to 2.27 g/cc. This is very close to the experimentally measured values. We checked the accuracy of eq. (1) for the estimation of the true density of FA obtained from different sources\(^ {2,36}\) with variable contents of \( \text{SiO}_2, \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3 \) and \( \text{CaO} \). If one uses the recommended values of \( \rho_{\text{SiO}_2} = 2.363 \text{ g/cc} \), \( \rho_{\text{Al}_2\text{O}_3} = 3.927 \text{ g/cc} \), \( \rho_{\text{CaO}} = 3.861 \text{ g/cc} \), etc. by Blanco et al.\(^ {31}\), the deviation between the calculated and measured values of \( \rho_{\text{fa}} \) does not exceed 10-15%, and decreases significantly assuming the corrections to the values of the compounds’ true density proposed elsewhere Moreno et al.\(^ {32}\) and Gehlhoff and Thomas\(^ {31}\). This confirms the applicability of eq. (2) for estimation of the true density of fly ash and shows a direct relationship between density and composition.

Our results were obtained for MS after double separation of IMS and SMS. However, they are not far from those obtained elsewhere without mentioning any additional secondary separation. This suggests that the typical MS obtained by burning coal in TPPs mostly have defect-free shells, impermeable to helium.

3.2 Interrelation between textural characteristics of cenospheres and plerospheres

Let us discuss the differences between the texture of cenospheres and plerospheres that allow their reliable identification. In this section we consider the problem of comparing the textural characteristics. Fig. 2 shows the schematic structure of spherical ash particles, cenospheres, and plerospheres with the same external diameter \( D_0 \).

Below, we attempt to formulate the dependence of porosity and specific surface area of such MS before and after destruction of their shells.

3.2.1 Porosity. The porosity of cenospheres and plerospheres can be evaluated using their geometrical characteristics. Hollow MS with external diameter \( D_0 \) have a total volume of \( V_0 = (\pi/6)D_0^3 \) and their
In our work, we dried the sediment obtained after the second separation and tried to gather the MS that floated in ethanol with a density of 0.81 g/cc. After a long exposition (exceeding 1 day), only ~12% of the particles floated, however, we could not get a quantity enough for detailed studies.

3.2.2 The specific surface area. The external specific surface area, $A_s$, related to the mass of MS with external diameter $D_0$ in general cases is:

$$A_s = \xi S_0/V_0 \delta = 6 \xi / \delta D_0$$  \hspace{1cm} (9)

where $S_0$ is the geometrical surface area of MS, $V_0$ is the geometrical volume, $\xi$ is the coefficient of surface roughness (for rough surfaces $\xi > 1.0$), and $\delta$ is equal to $\mu_0$ for non-porous particles. For non-porous MS or MS with the intact shells when the internal void is inaccessible for adsorption, $S_0$ is the same. All three types of MS shown in Fig. 2 with $D_0 = \text{Const}$, and $\xi = \text{Const}$ have the same geometrical surface area $S_0$. But the specific surface area of a unit of mass depends on $\delta$ and thus differs for MS of different types.

Disruption of intact cenosphere shells by destruction or the formation of through pores, channels or cracks makes the inner surface of the MS accessible. In such situations, the total available specific surface area $A_t$ of a crushed cenosphere shell is determined for $t/D_0 << 1$ by the equation:

$$A_t = (S_1 + S_2)/V_1 \rho \approx (2/D_0 \rho) \left[1 - 2(t/D_0)\right]/(t/D_0)$$  \hspace{1cm} (10)

where $S_1$ and $S_2$ are the geometrical surface areas of the external and internal surfaces of the shell with volume $V_1$ and $\rho$ is the true density of this shell. The increase of the specific surface area due to shredding of cenospheres can be expressed as:

$$A/A_0 = 2 \left[1 - 2(t/D_0)\right]$$  \hspace{1cm} (11)

One can assume that according to eq. (11), shredding of cenospheres should not result in more than a twofold increase of the specific surface area. Thus, if experimentally one observes a more pronounced increase of the specific surface area, this serves as an indication of the presence of plerospheres in the probe.

Access to the internal space of plerospheres should be accompanied by an additional increase of the geometrical surface area due to the surface of internal spheres. For simple estimations one can apply the following equation:

$$A_{\text{ps}} = A_d X + A_t (1 - X)$$  \hspace{1cm} (12)

where $A_d$ is the specific surface area of the crashed shell, determined by eq (10), $A_d = 6/\rho_1 d$ is the specific surface area of internal spheres with mean diameter of $d$ and density $\rho_1$, $X$ is the mass of the internal spheres related to the mass of a plerosphere, and (1

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**Fig. 2** A model of a spherical particle of ash (a), a cenosphere (b), and a plerosphere (c) of one single external diameter $D_0$; $D_t$ is the cavity diameter, $t$ is the shell thickness, $d$ is an average diameter of internal spheres inside the plerosphere.
than 1-2 s, the burning of char with a residence time of no more than 1 s, the burning of combustible gases with a residence time less than 1 s, coal burning and coal or char structure is represented as a 3-D cubic network composed of different types of cells which are volatile matter, char or coal matter, ash and voids.

4. Discussion of the Mechanisms of Cenosphere and Plerosphere Formation During High-Temperature Burning of Pulverized Coal

Let us reconsider the cenosphere and plerosphere formation mechanisms and how these mechanisms are consistent with the overall scenario of pulverized coal burning and FA production. Pulverized coal combustion is a complex process with many interacting factors which are not perfectly understood. The existing overall combustion models are combinations of physical-mathematical models and empirical correlations.

The combustion usually starts in typically middle-size coal particles of 20 to 100 μm and includes the following characteristic stages: a) fast heating and de-volatilization (emission of water and volatile combustible gases) with a residence time less than 1 s, b) the burning of char with a residence time of no more than 1-2 s, c) cooling, the residence time is several seconds. The combustion of de-volatilised gases outside the coal particle occurs during stage "a", and some of the oxygen can penetrate through the flame towards the particle surface. The resultant degassed coal is usually called char. After the flame from the de-volatilised gases is extinguished, the oxygen is able to reach the particle surface and the char starts to burn (stage "b" ). The char particle temperature is highest during burning and it may exceed the surrounding gas temperature by several hundred degrees. As a result, the particle's temperature at the burning stage may exceed 2000 °C in commercial furnaces.

Let us start with "technological" mathematical models, which are focused on the kinetics of the process, the heat and mass transfer, and the resulting FA dispersion during coal combustion. Calculation of the FA dispersion is usually based on fragmentation mechanisms, including attrition, fracturing, percolation, or thermal stresses. Fragmentation due to attrition corresponds to combustion in fluidized beds with a high particle concentration. This mechanism does not explain the production of numerous small fragments, whose size by orders of magnitude is lower compared with that for the parent fuel particles. During fracturing, fragmentation to only a few pieces is possible. These pieces have a size which cannot be significantly smaller than the size of the parent particles. In its turn, the percolation mechanisms of porosity generation are more universal, they are extensively used to simulate and clarify the effects of various factors on char burn-out and fragmentation.

The percolation models are frequently used for simulation of the de-volatilization and char combustion stages. In the percolation models, usually only one coal particle is considered because it is assumed that all particles show identical behavior. Usually, the coal or char structure is represented as a 3-D cubic network composed of different types of cells which are volatile matter, char or coal matter, ash and voids. An original porosity is generated by the random and uniform introduction of cells that correspond to pores in the matrix. The percolation begins with gasification of peripheral cells, which corresponds to their transformation into ash or void cells. The direction of the gasification front from periphery to center is determined by Monte Carlo procedures. In this case the important swelling processes are not taken into account. Such processes can be accounted for when one applies Monte Carlo procedures to simulate gasification, which starts inside the particles without direct connection with their outer surface. The de-volatilization process continues until all volatile cells are depleted. Then the stage of combustion in the emptied space of pores begins. During this stage, the relation between the rates of chemical reaction of char combustion and diffusion of oxygen and reaction products is taken into account. Fragmentation takes place at a threshold porosity, defined by the theory of percolation. For example, this
threshold porosity value was determined as 0.833, corresponding to a burn-out of 25% by Arene et al.\textsuperscript{70,71}.

The adjustment of model parameters to fit data may make it possible to use all these alternative models to predict qualitatively important features of the coal and char evolution or at least to understand it. This can work well for estimation of technological parameters, but it ignores such important physicochemical mechanisms as fusion and vaporization of a significant part of inorganic components, condensation of released vapors, swell of char, appearance and disappearance of cenospheres or plerospheres, etc. Only some of the known mathematical models at least formally take into account the swelling and sintering of certain types of structures.\textsuperscript{70,71} In other models very rapid de-volatilization and total lack of swelling are assumed by Leckner\textsuperscript{69}.

However, the inevitable simplification for mathematical formalization is dangerous because "Das kind mit dem bade ausschütten"\textsuperscript{69}, i.e. one can miss significant physical and chemical mechanisms that control the formation of certain types of structures.

### 4.2 Physico-chemical mechanisms

We believe that an adequate description of fuel particle combustion should be based on the physicochemical factors that were ignored in the existing mathematical models. To start with, let us briefly discuss the properties of the major ash-forming compounds in coal\textsuperscript{1-4,12-16}, such as mineral inclusions as well as organically bound heteroatoms. The ash-forming heteroatoms can include, e.g., S, N, O, many types of metals, etc.\textsuperscript{14,12}. The composition and content of these heteroatoms and inclusions as well as the size of the mineral inclusions and their distribution vary significantly from one coal to another depending on coal rank, its geological location, separation method, etc. The typical mineral inclusions are alunosilicates and silicates (e.g. clays, quartz), carbonates (e.g. calcite, dolomite, siderite), sulfides (e.g. pyrite) and oxides\textsuperscript{1-4,12-16}, etc. The starting average size of such inclusions is approximately 1 \(\mu\)m.

The high temperature and the reducing atmosphere enhance volatilization of a portion of the inorganic ash-forming compounds. Even elements present as refractory oxides such as SiO\textsubscript{2}, CaO and MgO with very high melting and boiling temperatures can volatilize under the reducing conditions inside the burning char. This generates such volatile forms as SiO, Ca, Mg, NaCl\textsuperscript{53, 72-78}. Typically, ash precursors, which are found as included or excluded mineral oxides in coal, are not easily volatile. These precursors are the source of coarsely dispersed ash. Whereas the ash precursors, which are found as organically bound and as salts, are easily volatile during combustion. Such precursors are the source of finely dispersed ash. The resulting fine ash particles grow by coagulation, recondensation (Ostwald ripening\textsuperscript{79,80}) and agglomeration\textsuperscript{81-83}. Non-volatile components can melt and coalesce inside the char particles or on their surface. Some minerals do not fuse in the char during combustion and their composition remains almost unchanged throughout the combustion process, resulting in ash particles with compositions similar to that in the parent coal.

The volatilized ash compounds (especially K, Na, S, Ca, Mg, Sr, Ba, Zn, Si, chlorides, sulfates, etc.\textsuperscript{12,13,40,51,54,74,86,97}) form new fine particles by homogeneous nucleation outside the burning zone, but inside this zone they form residual ash particles inside the char particles and on the char surface by heterogeneous condensation\textsuperscript{51, 88,92}. The amount of vaporized ash strongly depends on the char combustion temperature, since a higher temperature leads to more vaporization of ash materials\textsuperscript{74,91,92}. If the parent coal contains more easily volatile elements, the production of submicron particles also increases\textsuperscript{68,72}. The concentration of submicron particles is affected by the furnace wall temperature, fuel/air ratio, preheat temperature and the furnace aerodynamics\textsuperscript{74,93}.

The scenario of FA formation based on such an approach can include four main mechanisms whose action results in the formation of a bimodal (or trimodal by Yu et al.\textsuperscript{95}) ash particle size distribution. The fine particles (<1 \(\mu\)m) are produced via vaporization/condensation of easily volatile ash compounds. The large particles (>1-5 \(\mu\)m) are produced from fragmentation of char and excluded mineral particles \[53, 94\]. The extent of char fragmentation depends on the char swelling behavior\textsuperscript{53, 95-101}. If the char fragments are large and contain large mineral particles, this mineral will coalesce. The occurrence of a trimodal distribution identified by Yu et al.\textsuperscript{95} results from agglomeration of the coarse particles.

It is obvious that along with the development of modern variants of mathematical modeling, which gradually scramble out from Procrustes’ bed of model restriction and are helpful for technological appreciations, fundamental research is necessary to account for possible combination mechanisms and physical simulation with minimum restrictions, assumptions, and simplifications. Such models are unavoidable at today's stage of development of math-

\footnote{Throw the babe out with the bathwater.}
The results of such fundamental physicochemical research can be used to develop more adequate mathematical models of solid fuel combustion.

4.3 The general scheme of supramolecular structure formation

Let us discuss the generalized physicochemical scenario of the appearance and disappearance of cenospheres as well as plerospheres during fly ash production during high-temperature coal combustion at thermal power plants. Our scenario should include all models and mechanisms considered above on the sequential characteristic stages of heating of coal, burning of char, and cooling of ash as well as the fact that the ongoing transformations strongly depend on the type, content, form and distribution of inorganic and other components in the coal. The following discussion relates to bituminous carbons (solid fuel, or SF) that swell during burning and can be assumed as a source for cenospheres and plerospheres.

Fig. 3 shows a generalized schematic of the formation of the supramolecular structure of the MS and FA during the high-temperature combustion of pulverized SF. The transfer “a” → “b” corresponds to de-volatilization at fast heating. The de-volatilization occurs from the outer surface to the center of a particle and is accompanied by a movement of a temperature front. Removing the volatile compounds should result in the formation of microporosity, but simultaneous high-temperature heating results in plasticization of the residual phase and its sintering with formation of large pores [46,47, 102-105]. The formation of porosity occurs according to the percolation mechanism and can result in fragmentation.

Fig. 3c corresponds to the starting of the char

![Diagram of MS and FA formation](image-url)
burning stage inside pores and on the surface. Gas can be removed from the volume of the particles through the pores, connected to the outer surface, so the combustion reaction shifts to the diffusion regime. In parent SF particles, various mineral forms are distributed randomly (Fig. 3a). The burning-out of char is accompanied by a concentration of mineral components on the surface, decomposition and consolidation of the chemically bound species, melting and sintering of the most fusible forms (e.g. congruent melting of metasilicate and sodium metasilicate occurs, respectively, at 1090°C, and 875°C, according to Bryers). So the coarsely dispersed minerals, which are relatively weakly associated with carbon, can melt and coalesce. Mineral substances in bonded forms break bonds with carbon and convert to volatile products that condense according to the mechanism of homogeneous nucleation in the cooling zone (Figs. 3e’ and 3e) or deposit on the surface of the existing particles via heterogeneous nucleation. Nucleation via the “e’→“e1” pathway results in formation of the fine FA fraction, although the average particle size can increase due to Ostwald ripening.

Simultaneously, the fragmentation occurs at this stage (Fig. 3c→Fig. 3d). The increase in temperature results in pyrolytic breaking of a part of the bonds between the atoms of carbon. As a result, the remaining carbon fragments become labile, and a certain part of them transforms to the mobile form of pitch. The overall lability of the forming plastic meta-plast or mesophase (by Marsh) depends on the temperature and volume ratio of liquid to solid. When the latter ratio exceeds a certain threshold value, the metaplast transforms from visco-plasticity to the fluid-viscosity state [-], e.g. according to Raask and Spiro, 50%wt. of pitch in parent SF particle is necessary to form a viscous state.

The labile metaplast at this stage consists of the products of carbon pyrolysis and labile mineral forms. Under the influence of the surface capillary forces, the metaplast modifies the surface of char particles, fills the remaining pores, and distributes evenly on the surface, forming an intact shell. Under equilibrium conditions, such shells should have a constant curvature. This contributes to the transformation of particles of arbitrary shape into spheres (Figs. 3d→Fig. 3f), and provides a constant curvature and thickness of the shell. A violation of this requirement is accompanied by a spontaneous redistribution of matter in shells until their thickness and curvature becomes constant. More refractory mineral components and unburned solid carbon form the core of the corresponding hybrid particles (Fig. 3g) with viscoplastic shells and less plastic cores. The dynamics of the further transformation includes interrelated processes on the surface and inside such hybrid particles. The driving force behind these processes is governed mainly by the action of surface tension σ and surface curvature, while resistance to these processes is provided by viscosity η of the metaplast.

The increase in temperature reduces the viscosity of the components forming the core, thus facilitating their gradual transition from the core to the shell. Direct contacts between particles cause the formation of a meniscus in the zones of contact and the appearance of capillary forces that bring the particles together (Fig. 3f). The intensity of these processes is determined by the balance of forces of surface tension and viscosity. The detailed mechanisms of such processes is considered, for example, in [111-115]. For simple estimations, one can consider the dimensionless parameter ψ = στ/ηR₀, where σ is the surface tension of the metaplast, τ is the time, η is the viscosity of the core or shell, and R₀ is the particle radius, or effective pathway of a transfer. Growth of ψ increases the depth of transformation. For example, a high value of ψ can lead to complete coalescence of a pair of particles in Fig. 3f with the formation of a single spherical particle (Fig. 3g), and a small value of ψ more likely corresponds to particles sintering in the contact zones with the formation of aggregates (Fig. 3h).

As a result, easy-to-melt mineral inclusions contribute to the growth of particle size due to sintering and coalescence, but volatile forms can deposit at contact zones accompanied by the formation of intergrown assemblies of particles, or can precipitate outside the burning zone, resulting in the formation of the small particles. These effects are controlled by diffusion and kinetics, variation of “lifetime” in different zones, etc. Therefore, multiple collisions between particles and aggregates are accompanied not only by the destruction of the least stable (loose) particles according to the mechanisms of abrasion and splitting, but also the agglomeration with the formation of new aggregates, and as a result persistence and growth of the most densely packed, i.e. strong, ones.

4.4 Formation of cenospheres and plerospheres

Even more significant events occur due to the fact that the direct link of the core with the outer space is absent due to the presence of an intact shell of
metastable at this stage. Therefore, the gas released in the cores leads to the formation of bubbles (Fig. 3i).

The sources of this gas are the products of pyrolysis and gasification of unburnt solid fuel, decomposition of minerals as well as other volatile forms. Under equilibrium conditions, the pressure of gas in such bubbles depends on their radii r according to the Laplace-Young law \( \Delta P = 2 \sigma / r \). The difference of \( \Delta P \) between bubbles with different r promotes the growth of large bubbles due to diffusion of gas from the bubbles of small size, and coalescence of contacting bubbles with the formation of one or several bubbles in the bulk surrounded by the shell. The pressure in the bubbles can exceed the equilibrium under real conditions of fast temperature increase.

But in any case, gas release is accompanied by swelling of the hybrid particles with an increase of the external size, D0, and reduction of wall thickness t (the transition from Fig. 3i to 3j). Such hybrid spherical particles with gas-filled cavities are the direct precursors of MS. To form MS they must withstand swelling in the hot zone, solidification during cooling, as well as survive in collisions with other particles.

Let us make estimations. Changing the relative thickness of the shell \( t/D_0 \) with swelling of microspheres is derived from equation (4) at \( V_i \approx \text{const} \) in the form

\[
\frac{t}{D_0} = \frac{V_0}{V_0} \left( \frac{t}{D_0} \right)
\]

where \( t_0, D_0, \) and \( V_0 \) are the shell thickness, external diameter, and volume of an initial sphere (state 0), and \( t, D_0, \) and \( V_0 \) are that for a swollen sphere (state i). Thus, an increase of volume is accompanied by a decrease of \( t/D_0 \). For example, a twofold increase of volume results in a twofold decrease of \( t/D_0 \), while the external diameter increases by only 26%.

Blowing up of the shell as a result of the increase of the internal gas pressure is accompanied by an increase in stress in the shell to maximal critical values of \( \sigma_{t, \text{max}} \). Above this critical value the shell destructs. The theory of thin spherical shells’ stability is a classic problem of the elasticity theory\(^{[116,117]} \). According to one of the basic equations of this theory, introduced by Laplace, in the simplest case of a thin-walled spherical shell with \( (t/D_0) \rightarrow 0 \), the critical gas pressure inside the cavity \( P_{\text{max}} \) is defined as

\[
P_{\text{max}} = 4 \sigma_{t, \text{max}} (t/D_0)
\]

where \( \sigma_{t, \text{max}} \) is expressed in units of pressure.

The problem of the strength of hollow microspheres of glass-like materials is intensively investigated in connection with the prospects of use of such materials for the storage of compressed hydrogen as fuel for cars\(^{[118,119]} \), in problems of volcanology\(^{[120-127]} \), during the studies of properties of inorganic and polymeric glassy materials\(^{[128-129]} \), in general fracture mechanics\(^{[116,117]} \), etc. For glass and ceramic MS that are considered for hydrogen storage, \( \sigma_{t, \text{max}} \sim 10^5 \text{atm}^{[118,119]} \). The results of numerous studies of the strength limit of glass-like materials in various forms (microspheres, microbubbles, vesicles, etc.) at temperatures up to the temperature of vitrification T\(_G\), give the values of \( \sigma_{t, \text{max}} \), in the range of \( 10^5 - 10^6 \) atm\(^{[120-122]} \). According to Mungall et al.\(^{[123]} \) and Romano et al.\(^{[124]} \), the strength practically does not change if the cavity is filled with CO\(_2\) or Xe, but may be reduced by 1-2 orders of magnitude in the presence of water vapor. The authors explain this effect with the appearance of micro-cracks in the shell due to volume changes caused by the processes of hydration-dehydration during temperature changes. It is essential that this effect is weakened when the cooling rate is high (200°C/s), which is characteristic for the conditions of a TPP, as well as with an increase of the size of MS at \( D_0 \geq 50 \text{ microns}^{[21]} \). The problem of thermal stresses in hollow spheres of glass is discussed in detail by Nowacki\(^{[125]} \) (p.219). In general, the strength decreases with the loss of sphericity, the presence of microcracks, surface roughness and other defects that contribute to stress concentration\(^{[128,129]} \). These stresses decrease the strength of individual MS and lead to some statistical distribution of probability of their destruction\(^{[128,129]} \).

Similar relationships are known for the viscoplastic or viscoelastic membranes and films at T > T\(_G\) (vitrification temperature) at much smaller values of \( \sigma_{t, \text{max}} \). The values of \( t/D_0 = 0.06 \pm 0.04 \) obtained in [15] can be considered as critical \( (t/D_0)_c \). Further swelling with an increase in \( D_0 \) and a corresponding decrease in \( t \) leads to destruction of the shell. Some spread in \( t/D_0 \) values is easily explained by, for example, variations in the values of \( \sigma_{t, \text{max}} \), which depends on the chemical and phase composition, plasticity, the rate of gas emission and other factors determining the mechanical, rheological and other properties of the shell\(^{[20,97,98]} \). It is essential that the values of \( t/D_0 \) that were obtained in by Ngu et al.\(^{[23]} \) for intact MS after polishing are close to the usually observed values for shredded MS. Apparently in the hot zone, MS with \( t/D_0 < (t/D_0)_c \) continue to swell, and those with \( t/D_0 > (t/D_0)_c \) crack or transform by an oscillation mechanism, which is discussed below. As a result, only MS with \( t/D_0 < (t/D_0)_c \) can escape the hot zone and survive. The situation of \( t/D_0 << (t/D_0)_c \) is not realistic due to extremely high internal pressures in small bubbles, according to the Laplace-Young law.
This tough condition can be the cause of the small fraction of MS in the products of combustion in TPPs, as well as the experimentally observed narrow range of values of $t/D_0$ in cenospheres and plerospheres.

In general, the destruction may occur both during the viscoplastic state in the hot zone, and during cooling to $T < T_G$ in transition to the brittle state typical for glass-like materials. The trigger for destruction can be the growing internal pressure during a plastic stage, the external pressure, which can exceed the internal one when MS are cooled down, and the kinetic energy of a collision.

The variants of destruction with the formation of cracks (Fig. 1c) and the ejection of large fragments of shell (Fig. 1a) were shown earlier. The complete disintegration of MS into separate fragments (not shown) is also possible. All these options are typical for brittle fractures that most likely start at the stage of cooling down to $T < T_G$. The problem of the formation, growth and destruction of MS with viscoplastic or viscoelastic shells is considered, for example, by Sheng and Azevedo, who studied the formation of fly FA and MS, Yao et al., and Ribe, who attempted to develop a general theory of the dynamics of thin viscous films, Mungall et al., who studied the cooling of volcanic lava or by van der Schaaf and Beerkens, who examined the behavior of glass spheres in the molten metal.

The simplest scenario of the MS destruction at this stage involves breakthrough in the shell at $t/D_0 < (t/D_0)_s$ accompanied by gas emission, possible loss of part of the shell, the subsequent collapse and reformation of an intact shell over a preserved core. In the newly formed shell, the diameter of the particle $D_0$ becomes significantly smaller, and the value $t/D_0$ increases to values that allow the re-formation and growth of new bubbles up to values of $(t/D_0)_s$ followed by repeated re-destruction (Fig. 3j–3k). These stages of swelling and collapse of the particles can be repeated many times, until the depletion of the source of gas or the moment of transition of particles in the cooling zone happens.

During such oscillations, the plastic components that form the core can move as a whole in the mesoplastic of a shell or can gasify. The transport of such MS into the cooling zone leads to the formation of cenospheres (Fig. 3l), while an incomplete transition of components in the shell can be a cause of plerosphere formation (Fig. 3m). Fig. 3n shows a hypothetical schematic for plerosphere formation with hollow particles within a single shell. This can be implemented if the processes such as $3j=3k$ proceed at the level of “internal” particles inside a mutual large sphere. Brittle fracture of MS with parameter $t/D_0 < (t/D_0)_s$ leads to the formation of fragments (Fig. 3o), which can sinter and transform into nonporous spheres or aggregates of FA (Fig. 3p). This allows the formation of intact particles of FA with a wide size distribution and various types of morphology starting from the spherical particles formed during sintering and coalescence in the hot zone, and ending with a variety of products whose transition to an equilibrium spherical form was not finished (Fig. 3p). According to Seames and many others, the majority of FA particles are spheroidal. This indicates their preferential formation and an intense sintering in the hot zone. Frequently, observed particles with a typical acute-angle shape and a size of less than 1-2 microns are clearly fragments - the products of brittle fracture in the cooling zone. One can believe that in typical situations, the formation of different forms of fly ash from bituminous coal passes through a stage of formation of the MS.

The case shown in Fig. 1b can be regarded as the consequence of an additional special type of fracture of viscoplastic shells in the hot zone. The actual conditions of the combustion of the fuel particles do not match the equilibrium. This might cause the formation of individual damaged areas in the shell with local volcano-like gas release without destroying the entire shell. The reduction of pressure to equilibrium is accompanied by a contraction of the shell and its “healing” due to the action of surface-capillary forces. This mechanism is similar to excess gas pressure discharge in wheat dough studied by Hailemariam, or volcanic lava followed by “healing” the formed craters. This explains the presence of “craters” or their traces on the surface of MS as clearly observed in Fig. 1b. Such craters serve as emergency pressure relief valves.

The conventional ideas on the mechanism of cenosphere formation proposed by Fisher et al. and Raask attribute the main source of gas to only the mineral inclusions of types of carbonates, sulfides, sulfates, and clay minerals, the decomposition of which gives a moderate amount of gaseous products. The mechanisms “periodic shell collapse” and “pressure relief valve” (subsequently referred to as oscillation mechanism) remove this restriction. Any compounds of fuel that are suitable to gas emission can be involved. Plerospheres can be formed in the hot zone as cenosphere precursors as the result of the incomplete transfer of mineral components from the core to the shell (Figs. 3k, 3n, 3m), and much
less likely as a result of filling of the MS cavity with small spheres through cracks at the stage of cooling (the mechanism proposed by Goodarzi and Sanai\(^\text{20}\) and Shibaoka and Paulson\(^\text{21}\)). So, the mechanisms proposed by Ngu in [15] seem to be the most probable.

4.5 Cooling stage

The cooling stage finishes the formation processes and states the molecular and supramolecular structure of the resulting materials. The formation of crystalline and amorphous solid phases sharply increases the viscosity. Simultaneously, the chemical and phase composition of the inorganic products of coal burning can significantly differ from the starting material due to the transformations that occurred and the redistribution of all mineral compounds noticed by Bryers\(^\text{10}\).

The cooling starts from the external surface. As a result, the temperature of the shell can be lower than that of the core, which is filled with gas in the case of cenospheres, or with solid untransformed compounds and gas in the case of plerospheres. The following events are determined by the balance between the changes of internal pressure \(P\) and the strength of the shell, which also changes according to the rheological properties of glass-like materials.

To illustrate these features, the typical dependence of the specific volume, \(v\), of a glass-like material with temperature, \(T\), is shown in Fig. 4. The increase of \(T\) results in thermal expansion and increase of \(v\). The corresponding density, \(\rho\), decreases. The high-temperature region (region \(A\) in Fig. 4) corresponds to the viscous state of a melted matter. In the case of normally crystallizing compounds, a decrease of \(T\) to some critical \(T_c\) results in their crystallization (curve \(I\cdot(AEF)\)). But glass-like compounds are characterized by a high viscosity, which inhibits formation of a regular crystalline structure. Thus, curve \(I\) can be obtained for these compounds only during infinitely slow cooling down. More common are the curves of type \(II\cdot(ABCD)\), when transition from liquid to solid occurs within an interval of vitrification \((BC)\) after some supercooling, which corresponds to an interval between \(T_G\) and \(T_I\). The vitrification temperature \(T_G\) (point \(G\) in Fig. 4) lies within this interval of \(\Delta T_G = T_1 - T_2\).

The softening temperature \(T_1\) corresponds to a transition from the viscous to plastic state, and the solidifying temperature \(T_2\) from the solid state. For many typical compositions of mineral compounds, the values of \(T_2 \approx 1250 \pm 250^\circC\), and \(T_1 \approx 1450 \pm 150^\circC\) apply, although in general \(T_2\) can vary from \(480 - 500^\circC\) for some aluminosilicates to \(\approx 1500^\circC\) (quartz) and \(1700^\circC\) (crystalballite)\(^\text{41}\). Usually, \(\Delta T_G \approx 100 - 200^\circC\) and, as well as \(T_G\), is determined by chemical composition. \(\Delta T_G\), \(T_1\), and \(T_2\) increase with the cooling-down rate of the system.

The most essential point is that within the vitrification interval, the viscosity increases with several orders of magnitude, e.g. from \(\eta \sim 10^{12} \text{ Pa} \cdot \text{s (liquid melt)}\) to \(10^{16} \text{ Pa} \cdot \text{s (solid phase)}\), while the specific volume changes with \(8 \div 12\%\) and the rate of gas release decreases with temperature not as significantly. According to Frank-Kamenetsky\(^\text{139}\), with the value of carbon burning activation energy at 80-170 kJ/mol, a temperature decrease of 300 - 500°C results in only a tenfold decrease of the rate of carbon burning. Other reactions give similar estimations of the gas release rate.

The significant changes of rheological and, correspondingly, mechanical properties inhibit the action of the oscillating mechanism with shell regeneration and result in the increase of \(\sigma_{\text{max}}\) in equation (16). This increase is more considerable at \(T < T_G\). Let us discuss possible scenarios of the events occurring during cooling down in more detail, assuming the mentioned features.

In the case of only volatile compounds, the decrease in temperature results in their supersaturation followed by rapid precipitation on the surface of neighboring particles, or nucleation of new particles. Nucleation increases the fraction of small particles with the size of 0.1 - 1.0 \(\mu\)m that can hardly be captured with electrostatic precipitators, and which are just as dangerous for ecology as cenospheres. These fine particles can be easily spread with the wind.

![Fig. 4 Typical dependence of a specific volume \(v\) (reciprocal to true density \(\rho\)) on temperature, \(T\), for normally crystallizing (curve \(I\cdot(AEF)\), and glass-like (curve \(II\cdot(ABCD)\)) compounds.](image)

The following events are determined by the balance between the changes of internal pressure \(P\) and the strength of the shell, which also changes according to the rheological properties of glass-like materials.
penetrate into respiratory paths, etc. On the other hand, the larger particles can serve as distinctive collectors that can capture such volatile components and reduce their concentration. From this point of view it would be useful to develop various technologies that would facilitate the effect of deposition of volatile compounds on such “collectors”.

The transformation of all forms of particles at $T < T_2$ to a brittle state must intensify their mechanical destruction. Cooling leads to fixation of the cavities, and the parameter $t/D_0$. Microsphere shells completely lose their ability to regenerate after depressurization at $T \approx T_2$. The condition of maintaining the integrity of the intact shell MS can be written as

$$P(T) < 4 \sigma_{\text{max}}(T) [t/D_0] \quad (17)$$

where $P(T)$ is the pressure inside the cavity, which depends on $T$ and gas source, $\sigma_{\text{max}}$ is the parameter in equation (16), which also depends on $T$, as well as on other parameters. The shell is viscoplastic at $T > T_1$, it is plastic within $\Delta T_0$, and becomes brittle at $T < T_2$ having high value of $\sigma_{\text{max}}$.

The cooling of cenospheres which do not have an internal gas emission source, is accompanied by the decrease of $P(T)$ (up to a 5 or 6-fold decrease). This allows fulfillment of the condition determined by eq. (17) when $T > T_1$, and moreover at $T < T_1$. One can explain the frequently observed brittle cracking of cenospheres to the pieces of various size with a non-uniform distribution of stresses in the shell that happens mainly at $T < T_2$.

The case of plerospheres, which can contain gas emission sources, is more complicated. If the gas emission at $T \geq T_1$ (or $T \geq T_0$) is not compensated by a reduction of the internal pressure due to the reduction of $T$, then this MS is most likely doomed to be destroyed. Experimentally, one can observe only plerospheres whose shells are partially destroyed. We believe this destruction is caused by the mechanism of brittle fracture (Fig. 1d) at $T < T_c$. Plerospheres with intact shells can be observed by applying the technique of electron-microscopic analysis of thin sections. But the detection of such plerospheres requires a pre-selection of MS with whole and broken shells, or additional measurements of the density and the accessible surface before and after crushing of the MS. Unfortunately, such additional studies were not carried out by Ngu. Analysis of the changes in density and specific surface area in section 3.2 shows that even if plerospheres with intact shells are preserved, then their contribution is small. However, the general problem of the existence of the plerospheres with intact shells remains debatable, and also options for their efficient utilization are questionable.

5. Conclusion

Based on the presented analysis one can provide a probable sequential scheme of plerospheres, cenospheres and fly ash formation during the burning of pulverized bituminous coals with a typical composition of mineral admixtures at thermal power plants. De-volatilization transforms the initial coal to char and shifts burning to the volume of char particles through pores. The char combustion is accompanied by the increasing concentration of all mineral forms plus the formation of volatile and condensed phases. When the burning-off degree is high, the percolation scenario proposed in mathematical models become less probable and can be used for non-swelling forms of fossil fuel (peat, lignite, etc.) only. The formation of a supramolecular structure of the products of bituminous coal burning is governed by a joint action of burning and pyrolysis of carbonaceous material and the behavior of mineral fractions: volatility of bound forms and melting of non-volatile forms. The general schematic of the main processes is shown in

**Fig. 5** The general schematic of transformation of pulverized bituminous coal during combustion in the furnaces of thermal power plants.
An intensive sintering of the products of incomplete carbon burning results in the formation of heavy residues in the form of slag (bottom ash) which precipitates mainly at the bottom of the furnaces. Another part of the matter is made up of slightly aggregated fine particles that are carried out by the air-gas flow and which deposits in electrostatic precipitators or ends up in the exhaust gases. The fly ash formation most likely goes through skeletal structures similar to that of plerospheres with the possible coexistence of multiple-cavity bubbles within a single particle. They are then transformed into “normal” plerospheres with one or more interior particles which can serve as the contributors of gasification. The above-discussed oscillation mechanism can start its action at this stage, resulting in the formation of microspheres or their fragmentation. The destruction of the MS in the hot zone or at the beginning of cooling, followed by sintering and aggregation of the resulting fragments leads to the formation of non-porous fly ash. So, fragmentation is possible during all sequential stages simultaneously with mechanical breakage due to collisions. The destruction at the cooling zone is accompanied by the formation of defective MS and fragments, which also partially sinter, giving a contribution to the FA. Preservation of many plerospheres with intact shells has a low probability. However, they can persist in the form of the largest MS, which successfully escaped destruction. This corresponds, for example, to data about the dependence of the content of plerospheres on their size obtained by Ngu. So it can be assumed that the main FA precursors are the volatile mineral species and products of damage of plerospheres and cenospheres, while the main cenosphere precursors are plerospheres. Apparently, the same concept with minimal modification can describe the origin of typical swelling products of the high-temperature combustion of heavy oil, garbage, biological materials and domestic waste according to Bryers. The proposed scenario explains reasons for a weak dependence of the shell thickness, \( t \), on the MS diameter \( D \) (\( t/D \) values are defined by temperature and chemical composition), and why the plerosphere size is large and their relative fraction is low compared with cenospheres. This scenario emphasizes the important role of the cooling stage for the fragmentation processes, which is usually ignored. It also includes a general picture of physico-chemical concepts, which is absent in previous well-known publications.

We hope that this analysis of the properties and genesis of the supramolecular structure of cenospheres and other products of high-temperature combustion of pulverized coal based on the mechanisms assumed here are useful from a technological point of view.

List of symbols and acronyms

- **CS**: cenosphere
- **FA**: fly ash
- **IMS**: intact microsphere
- **MS**: microsphere
- **PS**: plerosphere
- **TPP**: thermal power plant
- **SF**: solid fuel
- **SMS**: shredded microsphere
- **\( t \)**: microsphere shell thickness
- **\( D_0 \)**: microsphere external diameter
- **\( \Delta_0 \)**: specific surface area of intact microsphere
- **\( \Delta \)**: specific surface area of shredded microsphere
- **\( \rho_\text{Hu} \)**: density, measured by means of helium pycnometry
- **\( \varepsilon_0 \)**: porosity of void sphere (for example, cenosphere)
- **\( \varepsilon_\Delta \)**: porosity of sphere filled with internal spheres (for example, plerosphere)
- **\( \varepsilon_\Delta / \varepsilon_0 \)**: is the porosity between internal spheres and the inside filled sphere
- **\( \delta \)**: apparent density
- **\( \sigma \)**: surface tension
- **\( \sigma_{\text{c}, \text{max}} \)**: critical stress values
- **\( \eta \)**: viscosity
- **\( P \)**: pressure
- **\( V_0 \)**: total microsphere volume
- **\( V_t \)**: shell volume
- **\( V_\Delta \)**: volume of internal spheres in plerosphere
- **\( T_v \)**: vitrification temperature
- **\( X \)**: mass of internal spheres related to total mass of plerosphere (eq. 12,13)
- **\( X_i \)**: related mass of component \( i \) (2)

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