Abstract: Aluminum-silicate cenospheres are the most valuable residue present in fly ashes after combusting stone coal. Cenospheres are hollow bodies with desirable engineering properties, such as hardness, low bulk density and complete chemical inertness, thanks to which they can be used in biomedical engineering. The following review presents data on obtaining and processing the material, as well as potential biomedical applications.

Keywords: Cenosphere; Composites; Biomedical Applications

1 Introduction

Currently, stone coal is still the most widely used energy source in the world. About 41% of the world’s electricity is obtained from the combustion of stone coal in combined heat and power plants [1]. At the same time, there is a noticeable trend to move away from atomic energy toward both green renewable energy and increased use of stone coal, to a forecasted 44% in 2030 [1–3]. It is easy to observe that burning fossil fuels such as coal causes a significant amount of solid waste to be generated, including fly ashes, the unburnt parts of the raw material that are deposited with a negative effect on the transformation of the landscape, surface waters and animals. The management of this waste material remains a serious technological and environmental challenge [4, 5]. Ranjbar and Kuenzel state that the re-use of coal wastes is at 68 wt% in China, 47 wt% in Europe, 15 wt% in Russia and 25 wt% in general worldwide [1]. It can be stated that about 75 wt% remains unused, meaning that there are ashes and fleets in settling tanks and the lightest parts in the ‘lagoons’. The waste mainly comprises residues of magnetic ashes, alumina-silicates in a diversified spatial form, and most especially, the cenospheres – the alumina-silicates in the spherical form. The use of these residues mainly concerns the production of general building materials, road aggregates and materials for filling in inactive mines [6–8]. Of all the wastes, cenospheres are the most valuable part, at the same time forming the lowest proportion of the ashes. The estimated content is approx. 1.5 wt%, which for an annual world production of ash from coal of 750 million tons per year, means about 10 million tons are cenospheres [1, 9]. Due to its unusual properties, i.e. very low heat transfer coefficient, low specific density, high hardness, lack of electrical conductivity, and complete chemical inertness, cenospheres are a very good choice as fillers for polymer-ceramic composites, catalyst supports as well as heat-insulating and chemically resistant layers. Due to the range of potential applications in biomedical engineering, the perspectives for using this valuable raw material in preparing biomaterials will be described in this review paper.

2 Cenospheres, general information, formation

The word cenosphere is derived from Greek, combining kenos (hollow) and sphaira (sphere) [1]. The Ranjbar and Kuenzel [1] review publication presents the most sophisticated and comprehensive study so far on the acquisition and characterization of cenospheres. In other publications, especially authors from developing countries like China, India, Russia and Poland, whose energy is based mainly on hard and brown coal, detailed quantitative and qualitative data is available on the production and characteristics of cenospheres [10–13]. The development of cenospheres and the remains of the fly ashes from the combustion of coal is an important challenge, and, accord-

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Table 1: Properties of cenospheres and grain analysis [1, 10–23].

| Physical properties (PP)                      | (PP)value | Sieve Analysis (SA) | (SA)value |
|-----------------------------------------------|-----------|---------------------|-----------|
| Real particle density, kg·m⁻³                 | 750-800   | 30 µm               | n.d.*     |
| Bulk density, kg·m⁻³                          | 400-450   | 60 µm               | n.d.      |
| Hardness (Mohs Scale), MOH                    | 5-6       | 100 µm              | n.d.      |
| Compressive Strength, kg·m⁻³                  | 180-280   | 120 µm              | n.d.      |
| Packing Factor, %                             | 60-65     | 150 µm              | 0-10%     |
| Melting Point, °C                            | 1200-1300 | 240 µm              | 70-95%    |
| pH in Water, -                                | 6-7       |                     |           |
| Moisture, %                                   | 0.5 max.  | >240 µm             | 0-30%     |
| Loss on Ignition, %                           | 2 max.    |                     |           |
| Sinkers, %                                    | 5 max.    |                     |           |
| Oil Absorption, g                             | 16-19/100 |                     |           |

*n.d.- no data

According to Hanif and Li [10], China alone produced more than 600 million tonnes of fly ashes in 2015. As mentioned earlier, the most valuable element of these ashes is the cenosphere. Their chemical composition as well as their physico-chemical properties are mainly dependent of the type of coal burned and the presence of impurities in the raw material, especially volatile oxides, and the type of combustion process [1, 11, 14]. The way in which a cenosphere is created is strongly dependent on the coal combustion process and on the type of compounds present in the coal, i.e. volatile organic compounds, crystalline and amorphous compounds. Depending on the viscosity of the melting compounds, different types of cenospheres can be created. Crystalline compounds rich in Fe ions form a fluid pathway of high density, which promotes the formation of relatively large-sized cenospheres, which also have a porous structure. In contrast, compounds with an amorphous nature containing Si ions favor the formation of systems with low viscosity, which result in the formation of spheres having a smaller diameter in comparison to cenospheres formed from crystalline compounds with Fe ions and high viscosity characteristics. In addition, the presence of amorphous compounds favors the formation of a solid shell and, as a consequence, cenospheres with smooth surfaces [1, 10, 11, 19]. The influence of Si and Fe ion content is discussed in more detail below, as part of the description of the effects of chemical and phase composition. The formation of cenospheres can be divided into two stages, essentially, both of which depend on the temperature: first to approx. 1000°C and the second between 1000 and 1200°C. In the first stage, large solid parts of fly ash are formed, including porous cenospheres based mainly on compounds with Fe ions. In the second stage, at an elevated temperature, compounds with Si ions prevail over the amorphous nature [1, 11]. Different authors, i.e. Ranjbar, Kenzel and Vassilev, suggest two possible mechanisms for the formation of a cenosphere during coal combustion [1, 20]:

1. the condensed gases formed after the thermal decomposition of sulfides, carbonates, nitrides, hydrosilicates and evaporated crystalline water are enclosed in the molten slag; these gases can penetrate the drop as it forms, giving a spherical shape of up to 500 µm in diameter;
2. within the high temperature boiler area, hot flue gas penetrates the melted slag, and then as the ash moves to the cooler part of the furnace, these gases are coated in a solid body.

The most likely formation mechanism is the first.

3 Cenosphere properties

The primary factor that makes the cenosphere an interesting material for prospective applications is their spherical, thin-walled structure and desirable chemical compositions. All these variables are dependent on the solid fuel combustion method and composition [10, 15–23]. The colour and sphericity of the cenospheres are also dependent on the type of coal [1, 24]. The key parameters affecting cenosphere usability are the size, the thickness of the shell and the presence of impurities. The latter increase the process costs due to the need to sterilize the material. The selected physical and chemical properties of the cenospheres (Table 1) include the chemical compositions (Ta-
### Table 2: Chemical composition of cenospheres [1, 10–23].

| \( \text{Al}_2\text{O}_3 \) | \( \text{CaO} \) | \( \text{SiO}_2 \) | \( \text{SO}_4 \) | \( \text{SO}_3 \) | \( \text{Na}_2\text{O} \) | \( \text{K}_2\text{O} \) | \( \text{TiO}_2 \) | \( \text{MnO} \) | \( \text{MgO} \) | \( \text{Fe}_2\text{O}_3 \) |
|---|---|---|---|---|---|---|---|---|---|---|
| 16.70-29.30 | 1.06-2.50 | 58.50-73.10 | 0.42 | 0.19-0.36 | 0.60-2.42 | 1.98-3.94 | 0.35-1.79 | 0.05 | 0.32-2.30 | 1.96-21.04 |

### Table 3: Phase composition of cenospheres [16].

| Phase | Phase Composition | Coal low temperature ash, wt.% | Coal ash samples, wt.% |
|---|---|---|---|
| | | Bokaro | Chandrapura | Jharia | Bokaro | Chandrapura | Jharia |
| Quartz | \( \text{SiO}_2 \) | 21.6 | 25.1 | 31.7 | 27.3 | 9.4 | 25.6 |
| Kaolinite | \( \text{Al}_2\text{Si}_3\text{O}_5(\text{OH})_4 \) | 34.9 | 34.1 | 40.7 | - | - | - |
| Illite | \( \text{K}_{1.5}\text{Al}_2(\text{Si}_{3.5}\text{Al}_{1.5})\text{O}_{20}(\text{OH})_4 \) | 13.5 | 8.4 | 7.6 | - | - | - |
| Mixed layer | Illite+(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_{4}\text{O}_{10}(\text{OH})_2 | 25.3 | 26.1 | 14.1 | - | - | - |
| Illite-smectite | Mullite | \( \text{Al}_6\text{Si}_2\text{O}_{13} \) | - | - | - | 26.8 | 31.1 | - |
| | Hematite | \( \text{Fe}_2\text{O}_3 \) | - | - | - | b.d. | 1.2 | - |
| | Magnetite | \( \text{Fe}_3\text{O}_4 \) | - | - | - | b.d. | 0.6 | - |
| | Dolomite | \( \text{CaMg(CO}_3\text{)}_2 \) | 0.2 | 1.6 | - | - | - | - |
| | Siderite | \( \text{FeCO}_3 \) | 1 | 1.6 | 4.6 | - | - | b.d. |
| | Calcite | \( \text{CaCO}_3 \) | - | - | - | - | - | b.d. |
| | Apatite | \( \text{Ca}_5\text{F(PO}_4\text{)}_3 \) | 1.3 | 2.3 | 1.2 | - | - | 0.7 |
| | Anatase | \( \text{TiO}_2 \) | 1.5 | 0.8 | - | - | - | 0.5 |
| | Rutile | \( \text{TiO}_2 \) | - | - | - | 0.3 | 0.4 | 0.6 |
| | Anhydrite | \( \text{CaSO}_4 \) | - | - | - | - | - | 0.3 |
| | Sylvite | \( \text{KCl} \) | 0.7 | - | - | - | - | - |
| | Amorphous (as metakaolin) | \( \text{Al}_2\text{O}_3\cdot2\text{SiO}_2 \) | - | - | 45.5 | 59.1 | 62.2 | |

b.d. – below detection limit of XRD/siroquant system
ble 2) and phase compositions (Table 3), and which are presented below in the tables. By comparing the table data with the chemical and phase composition, it is possible to evaluate the properties of a change in the country of origin of the coal [1, 10–24].

Given below, are selected properties of the cenospheres essential for the complementarity of this review. An exhaustive review of the properties was presented by Ranjbar and Kenzel [1] in their all-round cenosphere study.

### 3.1 Chemical composition

Taking into account the chemical composition investigations, cenospheres do not differ significantly from the composition of fly ash after coal combustion [1, 25, 26]. Based on the chemical composition (Table 2) it can be stated that even more than 90 wt.% of the cenospheres utilize SiO$_2$ and Al$_2$O$_3$ in different compositions. By analyzing the chemical composition diagram, it can be concluded that the cenospheres to which the fly ash belongs comprise six groups: calic, calsilic, ferrosialic, ferrocalsialic, ferrocalcic and sialic (Figure 1) [1]. The diagram correlates well with other experimental data from authors like Sokol et al. and confirms which minerals favour the creation of particular cenospheres [11]. In addition, according to Ranjbar and Kenzel et al., it can be stated that the chemical composition varies significantly, depending on the mineral impurities found in the coal as well as the additives used to improve combustion efficiency and minimize the amount of ash [1, 27, 28]. Based on the analysis of the chemical composition and combustion data, it was found that, despite its small share (0.35 – 1.79 wt.%), TiO$_2$ is indispensable in cenosphere formation [1]. This is probably due to the high surface energy of TiO$_2$, which in combination with the low viscosity of the slag during combustion, leads to the formation of spheres [1, 29, 30].

### 3.2 Phase composition

The phase composition, besides the chemical composition, is the main factor that makes cenospheres an interesting material. It can be considered that such microspheres consist of a crystalline skeleton and an amorphous shell that forms a smooth sphere [11, 31]. Due to the presence of iron and its crystalline compounds, cenospheres can be divided into magnetic and non-magnetic forms [1, 16, 32, 33]. Molecules containing mainly SiO$_2$ in their chemical composition are non-magnetic, while cenospheres typically from the ferrosialic group exhibit magnetic interactions [1, 11]. It can be concluded that a decrease in silicon in the content of minerals, decreases the percentage share in the ashes of cenospheres with smooth shells or cenospheres in general. The average phase compositions of the cenospheres are shown in Table 2, while Table 4 presents the
Table 4: The presence of crystalline phases and their effect on the magnetic properties of the cenospheres [1, 10, 11, 38].

| Effect      | Cristalline phase                                                                 |
|-------------|-----------------------------------------------------------------------------------|
| Magnetic    | Melnikovite FeS$_2$+(As,Fe,H$_2$O)                                                |
|             | Mispickel FeS$_2$·FeAs$_2$                                                        |
|             | Coquimbite Fe$_2$(SO$_4$)$_2$·9H$_2$O                                             |
|             | Jarosite K$_2$SO$_4$·xFe$_2$(SO$_4$)$_3$                                           |
|             | Melanerite FeSO$_4$·7H$_2$O                                                       |
|             | Rozenite FeSO$_4$·4H$_2$O                                                         |
|             | Halotrichite FeAl$_2$(SO$_4$)$_6$·22H$_2$O                                        |
|             | Illite K$_{1.5}$Al$_{6.5}$Si$_{6.5}$Al$_{1.5}$O$_{20}$(OH)$_x$                    |
|             | Chlorite (MgFeAl)$_6$(AlSi)$_4$O$_{10}$(OH)$_8$                                    |
|             | Siderite FeCO$_3$                                                                 |
|             | Ankerite CaCO$_3$·FeCO$_3$                                                        |
|             | Magnetite Fe$_3$O$_4$                                                             |
|             | Hematite Fe$_2$O$_3$                                                              |
|             | Limonite Fe$_2$O$_2$·H$_2$O                                                       |
| Non-magnetic| Portlandite Ca(OH)$_2$                                                            |
|             | Calcite CaCO$_3$                                                                  |
|             | Dolomite CaMg(CO$_3$)$_2$                                                         |
|             | Magnesite MgCO$_3$                                                                |
|             | Quarz SiO$_2$                                                                     |
|             | Cristobalite SiO$_2$                                                              |
|             | Brucite Mg(OH)$_2$                                                                |
|             | Mullite Al$_6$Si$_3$O$_3$                                                         |
|             | Alumina Al$_2$O$_3$                                                               |

The presence of crystalline phases and their effect on the magnetic properties of the cenospheres. The data is primarily sourced from publications describing the effect of chemical composition of the polluted coal and the ashes generated during combustion [34–37]. The presence of some minerals in the composition of ashes and the cenospheres themselves, i.e. dolomite, does not appear similar, while their origin is associated with the method of storage and separation of cenospheres in settling tanks and lagoons [1, 11, 16].

3.3 Particle size and morphology

There is a lot of data concerning the potential sizes of cenospheres [1, 10, 11, 17, 19]. However, it can be stated that their sizes lie in the range 1-600 µm, with a dominating range of 200-400 µm [1, 10, 11, 17, 19]. The cenosphere size is essentially dependent on the chemical composition. It has been proved that an increase in SiO$_2$ content influences the diameter of the cenospheres, reducing it. Along with the increase in the mass share of Fe$_2$O$_3$ and the increase in the Al$_2$O$_3$/SiO$_2$ ratio, the diameter of the cenospheres increases. These observations seem to be confirmed by studies conducted by Sokol et al. [1, 11]. At the same time, the authors note that, besides the chemical composition, the batch is also important, from which it can be concluded that the combustion method, furnace condition and temperature influence on ash formation also have significant influence on cenosphere formation [11]. There is a similar situation with the thickness of the cenosphere shell. The thickness of the shell is significantly diversified, and ranges from 1 to 160 µm [1, 19]. An interesting fact is that the amorphous shell is not homogeneous, because it contains pores (Figure 2), from which it can be concluded that if properly etched it may form a good retention site for other materials, i.e. polymers in the creation of polymer-ceramic composites [1, 39].

4 Possibilities for cenosphere applications in biomedical engineering

The use of cenospheres in biomedical engineering may involve both the production of composite materials and stan-
Figure 3: Selected polymers used, among others in biomedical engineering, economic statement, possibilities of forming and shaping properties [5].

dalone applications. In the first case, it can be used in the field of dental prosthetics and epilation, because a composite material combining, for example, the advantages of ceramics and polymers would meet the expectations of the clinical environment regarding materials with high mechanical strength and at the same time being easy to use during the treatment. Currently, the use of zirconium oxide is, due to its phase uncertainty, a controversial material often discussed in dentistry [40–45]. Another possible application is to modify carbon fibers with cenospheres in order to obtain ceramic-carbon materials for medical applications [46]. Other issues in which the use of cenospheres may add a new perspective involve metal-ceramic composites for lower weight orthopaedic implants, as well as additional enrichment with drugs that reduce the risk of inflammation and postoperative complications [47–49]. These and other possible applications will be discussed below.

4.1 Polymer-ceramic composites

In general, polymers and polymer-based composites are used as a matrix or degrading carrier in the human body, or as a construction material. The first application relates to polymers and composites as carriers of drugs to be released at the inflammation site or as a dedicated treatment, i.e. encapsulation, tissue scaffolding or as a material for degradable regeneration structures [50–53]. For these composite and polymer applications, the following requirements are posed: no toxicity for the human body, no harmful interaction with the drug, no metabolic polymer transformation products excreted beyond the body, and beneficial mechanical properties if possible, to allow the transfer of the resulting stresses to the implant before the tissue recovers [50, 54, 55]. In the second case, composites find a structural application, i.e. they can be designed in such a way as to transfer physiological loads without trauma to the damaged tissues. Structural composites are mainly used in artificial joint elements, such as bone wedges and bone scaffolds, or as nails and bolts fixing damaged tissue structures [56–58]. Particular attention should be paid to 3D printed composites, currently considered almost a separate group, which is slowly revolutionizing the use of implants and medical structural materials [57]. Polymer-ceramic composites using mainly oxide ceramics, i.e. ZrO₂, SiO₂, and Al₂O₃, in comparison to polymeric materials have better mechanical properties, less abrasion and less water absorption. However, they are characterized by lower brittleness and weight, which increases their spectrum of applications. Table 5 presents a comparison of selected polymeric and ceramic materials used in biomedical engineering. Figure 3 shows the polymer groups used in medical applications and their economic interdependence.
Table 5: Comparison of selected polymeric and ceramic materials commonly used in biomedical engineering.

| Material   | Characteristic                                                                 | Major Drawbacks                                                                                                                                                                                                 | Ref   |
|------------|-------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
| Zirconia, ZrO₂ | Zirconia's properties are strongly dependent on oxide dopants stabilizing metastable phases; hence the zirconia properties closely related to the polymorphism of its crystal structure. The main effect is noticeable on the mechanical properties and i.e. it is enough to compare the properties of the full stabilized ZrO₂ with yttrium oxide (YSZ) and partially stabilized with magnesium oxide (PSZ). | The main disadvantage of zirconia is the so-called low-temperature degradation, susceptibility to loss of properties at the temperature range to 400°C. The issue is also related to the phase stability of metastable phases; the phase transformation has a martensitic transformation mechanism, which he accompanies a grain volume increase of approx. 4%. | [66–68] |

| Property          | YT-ZP | Mg-PSZ |
|-------------------|-------|--------|
| Density, g/cm³    | 6     | 5.5    |
| Grain size, µm    | 0.3–0.5 | 40–70 |
| Fracture toughness, MPa·m⁰.⁵ | 7.9 | 8-11 |
| Flexural strength, MPa | 900–1200 | 400–650 |

Alumina, Al₂O₃ | Alumina is the most commonly used ceramic in medical applications. After the development of purification methods for natural powders from bauxite, and the introduction of the first standard for alumina as a biomaterial alumina, is the most frequently chosen biomedical grade ceramic since 1970. | Strong covalent bonds in the crystalline lattice between Al³⁺ and O²⁻ directly affect the two main disadvantages of aluminum ceramics: the first is extremely high hardness (20–30 GPa on the Mohs scale) which makes machining difficult and costly. The second disadvantage is susceptibility to the impact of a moist environment as alumina are immersed in water or exposed to ambient air (which usually has at least 15% relative humidity), their surfaces react with water to produce surface hydroxyl groups. | [66, 69] |

| Property          | Alumina | Alumina-HIP (hot isostatic press) |
|-------------------|---------|----------------------------------|
| Density, g/cm³    | 3.90–3.95 | 3.97                             |
| Grain size, µm    | ≤4.5 | 1.75                             |
| Flexural strength, MPa | >300 | 650                              |
| Young Modulus, GPa | 380 | 400                              |
| Fracture toughness, MPa·m⁰.⁵ | 3.5 | 4.5                             |
| Hardness, GPa     | 18     | 20–21                            |
Table 5: ... continued

Polymers, PU
- PU is obtained by polymerization of isocyanates, polyls, and various additives, and has been used for coatings, adhesives, and various applications due to its favorable biocompatibility and mechanical properties. PU combines a rigid hard segment with a soft segment to add variety in structure and mechanical properties. The hard segment is formed by expanding a low molecular weight diol or diamine to the end of di-isocyanate. Different methodologies can also be used for the synthesis of PU polymers. Structural diversity of diisocyanates, diols, and chain extenders offer numerous possibilities for designing PU with required microphase morphologies and thermo-mechanical properties.

| Property                          | PU                          | Major PU drawbacks:                          |
|-----------------------------------|-----------------------------|----------------------------------------------|
| Density, g·cm⁻³                  | 1.22–1.27                   | • poor thermal capability,                   |
| Tensile Modulus, GPa             | 0.01–2.03                   | • poor weatherability,                       |
| Tensile strength, MPa            | 4.84–6.96                   | • susceptible for most of the organic and non-organic solvents, |
| Flexural strength, MPa           | 39.98–111.70                | • problem with non-polymerized rest of toxic isocyanates,   |
| Compressive strength, MPa        | 33.03–85.50                 | • flammable.                                  |
| Hardness (Shore), GPa            | 45–88                       | The most crucial for biomedical engineering applications are issues related to the possibility of PU infiltration by body fluids. That is why the issues related to the application of barrier layers to the PU surface are crucial for all-around biomedical applications. |

Polyamide, PA
- Aliphatic polyamides are significant engineering materials that find wide industrial applications because of their outstanding properties such as high modulus, toughness, and abrasion resistance. Among these polyamides, several all-bio-based polyamides or partly bio-based polyamides were commercialized. Polyamide-11, an all-bio-based polyamide, was synthesized from 11-aminoundecanoic acid which is derived from castor oil after a multistep chemical treatment. The all-bio-based polyamide-10,10, polyamide-4, 10 and the partly bio-based polyamide-6, 10, polyamide-10, 12 with good engineering applications are synthesized by using one or two of the biobased monomers: sebacic acid (SA), 1, 10-decaminediamine (DD), and 1, 4-butanediamine (BD).

| Major PA drawbacks:                          |
|----------------------------------------------|
| • high moisture susceptibility connected with dimensional instability and degradation of mechanical and thermal properties, |
| • requires UV stabilization,                  |
| • high shrinkage during molding,              |
| • lack of resistance to oxidizing agents, strong acids and bases, |
| • high material notch sensitivity.            |
Table 5: ... continued

| Property                              | PA (nylon 12)    |
|---------------------------------------|------------------|
| Density, g·cm\(^{-3}\)                | 0.97–1.22        |
| Tensile Modulus, GPa                  | 0.434–1.94       |
| Tensile strength, MPa                 | 29.37–61.02      |
| Flexural strength, MPa                | 15.72–98.60      |
| Compressive strength, MPa             | n.d.             |
| Hardness (Shore), GPa                 | 74–78            |

Poly(methyl methacrylate) (PMMA) is another glassy polymer whose brittleness may hinder its use for some applications. Polymethylmethacrylate (PMMA) is generally used as denture base material due to its biocompatibility and aesthetic properties. However, it suffers from insufficient ductility and strength, which may result in brittle fracture or cracks of the bases during normal use or being accidentally dropped by patients. However PMMA is a polymer with the advantages high applications advantages like low cost, stable specification and excellent reproducibility of production.

| Property                              | PMMA             |
|---------------------------------------|------------------|
| Density, g·cm\(^{-3}\)                | 1.14–1.21        |
| Tensile Modulus, GPa                  | 1.31–3.74        |
| Tensile strength, MPa                 | 43.37–75.15      |
| Flexural strength, MPa                | 46.68–122.73     |
| Compressive strength, MPa             | 96.53–119.97     |
| Hardness (Shore), GPa                 | 67–105           |

Major PMMA drawbacks:
- poor solvent resistance
- susceptibility to stress cracking
- low continuous service temperature,
- flexible grades unavailable,
- Poor impact resistance

[78, 80–82]

Concluded
4.2 Metal-ceramic composites

The use of metal implants, such as in orthopaedics or prosthetic dentistry, is associated with their respective mechanical properties and the ease of forming shapes and geometrical forms. A problem arises when the implants are left in the bone permanently. It is not always possible to obtain a permanent connection to the bone, known as osseointegration, and there is a risk of rejection of the implant [59, 60]. In addition, all currently implanted metals and implantological alloys have higher mechanical properties than bone, which can cause its stiffening and negative consequences, i.e. secondary fractures of the bone or implant rejection [61, 62]. Therefore, it can be concluded that the use of porous alloys with ceramic fillers characterized by developed specific surface areas may significantly improve the applicability of implants in the environment of the human body. The application of aluminum-silicate cenospheres for the preparation of ‘syntactic foams’ shows promise due to the extensive application possibilities for alloys with different, programmable porosities, i.e. aluminum, magnesium and titanium [62–66]. This is particularly important, especially for magnesium degradable alloys and titanium implant alloys that can be used as bone scaffolds and implant screws through which the newly forming bone grows. Thanks to these types of alloy implants, with mechanical properties similar to human bone, bone stiffness and bone damage can be avoided. Particular attention in this type of application is given to titanium alloys with cenospheres, formed using powder metallurgy techniques. The compressive behavior of these is similar to that of human bone [65]. It is also worth noting that, thanks to the sintering temperature in powder metallurgy and the varied amounts of cenospheres, it is possible to influence the mechanical properties to modify implant behavior to the biomechanical pattern of human bone. Modal et al. note that it is possible to obtain the compressive strength of titanium alloys with cenospheres at the level of 40-116 MPa with porosity in the range of 45-70% [67]. Mondal et al. [64], in their very well planned studies, confirm the effectiveness of the use of cenospheres, and suggest that cenospheres could be used as space holders to make Ti-cenosphere syntactic foam and that a key element for obtaining valuable foams for implant applications is the rushing of cenospheres, porosity and the density of Ti-cenosphere. In addition, they state that broken cenospheres can cure the alloy, leading to a higher hardness of the Ti matrix. These observations correlate well with the studies of Braszczyńska-Malik and Kamieniak [64], Jha et al. [65], Vogiatzis et al. [66], Goel et al. [67]. However, all papers clearly show that it still not certain how to achieve the functionalization of cenospheres, or the optimal method for foam composite sintering. The Figure 4 shows random aluminum-cenosphere syntactic foam obtained by Mondal et al. [64].
4.3 Composite foams

The increase in the development of minimally invasive surgical techniques has caused a significant clinical demand for injectable microporous foams to improve tissue healing [68]. Currently, injectable biomaterials include: low porosity calcium phosphate cements [66], porous calcium phosphate cements [77], composites with calcium phosphates (CPC) [76], hydrogels [83], and porous polymer foams or polyurethane foams [84]. These biomaterials have pores on a nanoscale, which limit the migration rate and cellular proliferation. Microporosity is introduced in order to increase cellular infiltration and tissue healing, while the many methods that generate micropores require stringent processing conditions that exclude the use of injectable foams. Therefore, every compound in the foam must be biocompatible and demonstrate non-cytotoxicity at the concentrations used [66]. Achieving the required characteristics of an injectable foam system include a number of strategies based on different perspectives of design. The most important properties, processing technologies and applications in medicine of biomaterials are presented in Table 6. Injectable microporous foams are expected to have a great impact on improving patient treatment outcomes in many clinical procedures. All the above means that the cenospheres described in the review are suitable for injectable foams. Kumar et al. [84] presented multifunctional lightweight carbon composite foams, developed by impregnation of phenolic resin and cenospheres (0-40 wt%) into the substrate with polyurethane foam (PU). The impregnated foams were then transformed into composite foams with carbon-cenospheres via heat treatment at 1000°C. This allows the cenospheres to be used as a substrate for composite foam materials, in a variety of applications.

4.4 Silver coated cenospheres

Wound healing is a complex process, and the failure to complete it can lead to serious consequences. There are many situations in which the use of a dressing is indicated or obligatory, for which it is very important to use the most effective materials. Before choosing a material, we need to consider: protection of the wound against physical damage, elution of microorganisms from the wound, prevention of the transmission of microorganisms, blood and exudate from the wound edges, and improvement in patient comfort [88]. Controlled drug release materials show promising applications in medical dressings. The introduction of drugs and other therapeutic materials give bandages more universal applications. Cellulose fibres are natural polymers used to make dressings; therefore, the high performance of the natural fibre properties should be enhanced. There are several ways to functionalize natural fibres, such as by deposition or infiltration of functional polymeric materials on or into the surface of the fibres using nanotechnology still while maintaining the fibre properties [87–102]. Silver has for many years been used to treat various ailments or to prevent the transmission of infections [103]. It finds applications in burn and ulcer treatments, surgical incisions, blood infections, urinary tract infections, and vascular prostheses [104]. This use of silver is mainly due to its bactericidal action. The latest silver technology has focused on the use of nanoparticles as an antimicrobial. Nano-crystalline silver releases small, sub-critical particles of uncharged silver with a longer length, increasing the surface of the wound in contact with the silver particles and the duration of this contact. These particles react more slowly with chlorine ions, slowing the release of silver from the dressing [96]. Modern Technologies use silver nanoparticles, which are introduced into various types of dressing materials, including mesh, activated carbon and polymer matrices [106]. Example of silver-coated cenospheres are shown in Figure 5. Archan et al. prepared material for a chitosan dressing made of polyvinylpyrrolidone with silver oxide nanoparticles. Treated films have better thermal, morphological, mechanical and antibacterial properties than cotton dressings [107]. The use of coating technology to apply a layer of silver to cenospheres is known in electronic devices. However, this does not exclude the addition of plastics, composites, gums etc. The material may be a sprayed or injection moulded under suit-
Table 6: Formulations of injectable macroporous foams for regenerative medicine.

| Materials | Setting mechanism | Macroporous formation | Intended application | Ref. |
|-----------|-------------------|-----------------------|----------------------|------|
| CPC: CDHA/CSD | Reaction of α-TCP and CSH with water in an aqueous \( \text{Na}_2\text{HPO}_4 \) solution | CSD and CSH crystal dissolution | Bone void filler (CERAMENT™ spine and orthopaedic indications) | [85] |
| CPC: CDHA | Reaction of α-TCP with water in an aqueous \( \text{Na}_2\text{HPO}_4 \) solution | Air entrainment using SDS | Hard tissue scaffold | [86] |
| CPC with polymeric Porogens | Reaction of reactive calcium phosphate powders with water in an aqueous \( \text{Na}_2\text{HPO}_4 \) solution | Porogen (PLGA, poly(trimethyl carbonate, gelatin) leaching | Hard tissue scaffold | [87] |
| Hydrogel: Alginate/Fibrin Hydrogel: Methacrylated alginate/PEG Fumarate: Poly(propylene fumarate) Fumarate: Oligo(poly(ethylene glycol) fumarate) polyHIPE: PFDMA/PGPR 4125 polyHIPE: Dextran-b-polyNIPAAm Polyurethane: LDI | Ionic/Enzymatic crosslinking Free radical polymerization | Mixing fibrin with degradable alginate/fibrin microbeads Cryogelation | Cell encapsulation material, soft tissue scaffold | [88] |
| | | | Cell delivery, Soft tissue scaffold | [89] |
| | | | Soft or hard tissue scaffold | [90] |
| | | | Cell and drug delivery, Soft tissue scaffold | [91] |
| | | | Hard tissue scaffold | [92] |
| | | | Drug delivery, soft tissue scaffold | [93] |
| | | | Soft tissue scaffold, drug delivery | [94] |
able conditions [108]. The integration of cenosphere and silver may be a good solution for dressings that accelerate wound healing.

5 Conclusion

This paper focuses on presenting the possibilities of cenosphere use in biomedical engineering. Alumina-silicates in cenospheres are a very desirable component from fly ash originating from the combustion of predominantly stone coal, though it can also be obtained from brown coal. Thanks to properties such as low bulk density, low density, hardness and complete chemical inertness, the cenospheres are a desirable material for biomaterials. Especially noticeable application potential is found in the field of polymer-ceramic and metal-ceramic composites. On the basis of the scientific data review, it was found that the best cenospheres originate mainly from Kazakhstan and India pay the attention of researchers. Precise determination of the property, their comparison and applications is an open issue worth investigating. This fact is explained by the occurrence of appropriate stone coal types in these countries, and that their power supply system is based mainly on coal, hence creating abundant sources of cenospheres with diverse properties. Not without significance is the fact that the use of such a resource carries significant environmental benefits, not only in biomedical engineering.

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