

## VALORIZATION OF CENOSPHERES IN CERAMIC FOAM MANUFACTURING UTILIZING NATURAL SPONGES AS TEMPLATES

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### ABSTRACT

Recognizing the imperative of waste reduction and the transition to a sustainable circular economic model, we repurpose waste from the energy industrial sector into useful feedstock for the development of a novel material. Particularly, this study focuses on Cenospheres (CS), hollow microspheres primarily composed of silicate and alumina in a glass phase <sup>[1]</sup>, found in fly ash (FA), a byproduct of coal/lignite combustion <sup>[1]</sup>. Representing up to 3.8% of FA's weight <sup>[2]</sup>, CS is frequently considered as the most valuable component within FA <sup>[1, 3, 4]</sup> and is utilized in various applications. Herein, we aimed to fabricate ceramic foams starting from CS for potential bioscaffold usage.

For that purpose, a polymeric foam replication method was employed to produce the CS-based foams, utilizing natural sponges as templates for the replication. Four different types of natural marine sponges (Grass, Silk Fina, Hard and Honeycomb) that have been harvested in the Mediterranean Sea were used. Ceramic slurry was created using distilled water, PVA as a binder agent and CS, in which the templates were immersed. Subsequently, the specimens were dried and then sintered at 1200°C to produce ceramic foams. The internal microstructure of the foams obtained was examined using Scanning Electron Microscopy (SEM), and their elemental composition was estimated through Energy Dispersive Spectroscopy (EDS). Results indicated that Silk Fina was the most effective template, yielding CS foams with a similar morphology to the materials before sintering, followed by Hard and Honeycomb templates in efficiency, while Grass was the less effective one. EDS analysis confirmed the anticipated composition, with Silicon (Si), Aluminum (Al) and certainly Oxygen (O) being the predominant elements due to ceramic oxides presence.

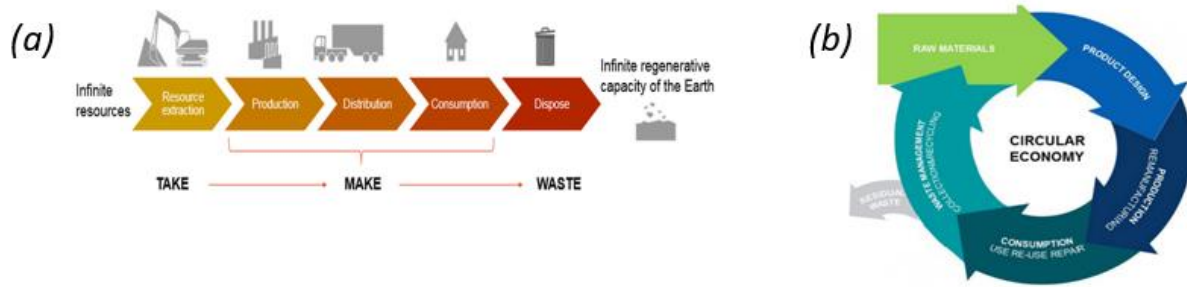
**KEYWORDS:** Fly Ash, Cenospheres, Ceramic Foam, Bioscaffold, Circular Economy

### INTRODUCTION

It is evident that the current economic system, characterized by a linear model as depicted in Figure 1a, is exacerbating the climate crisis through the unsustainable extraction and utilization of natural resources <sup>[5]</sup>. This model, predicated on resource extraction, product transformation, and eventual disposal, has resulted in severe environmental degradation <sup>[5]</sup>. The production processes associated with this model not only deplete natural resources but also generate substantial waste, contributing significantly to pollution <sup>[6, 7]</sup>. Experts widely acknowledge the unsustainability of this linear economic model <sup>[5]</sup>. In response, there is growing advocacy for transitioning to a circular economy (CE) model, which offers a more sustainable alternative.

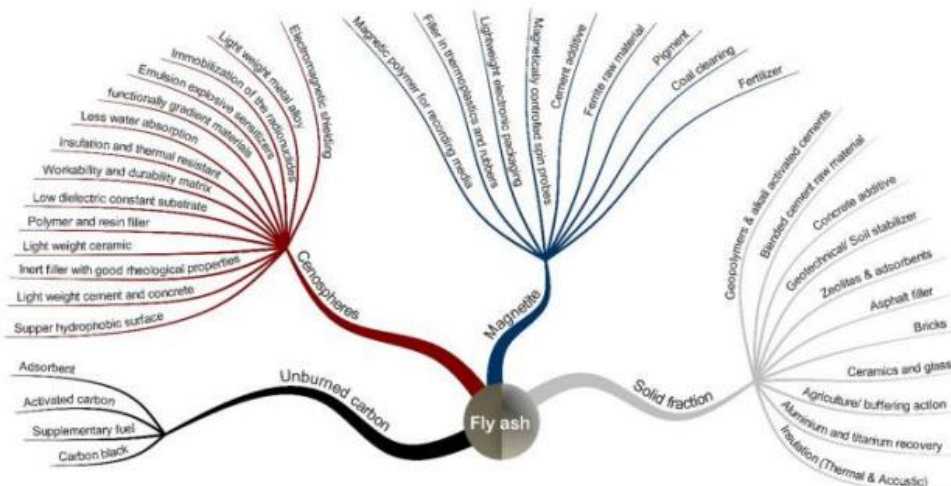
As its name suggests, CE relies on a circular system, the produced wastes are reused as feedstock for other processes, thus diminishing or even eliminating them <sup>[8]</sup>. The circularity of CE is depicted

in Figure 1b. What we actually see and conclude by comparing Figure 1a and 1b is that CE's goal is to close the loop of the material life cycle [7].



**Figure 1.** a) Linear economic model and b) Circular economic model.

For many years, the energy production has been accomplished using fossil fuels. One of the most common fossil fuel is coal, due to its abundance [1, 9]. However, coal combustion results in the production of ash, which comprises two categories: Bottom Ash and Fly Ash (FA) [1]. FA is a byproduct that contributes to the environmental crisis [1]. Further classification distinguishes FA into two types: Class F FA and Class C FA, primarily based on their calcium composition [1]. Notably, Class F FA exhibits lower calcium content compared to Class C FA [1]. The composition of FA typically includes unburned carbon, Cenospheres (CS), magnetite, and solid fractions [2, 3]. Figure 2 illustrates the variety of potential applications for FA composites after their separation. The global production of fly ash amounts to approximately 750 million tonnes annually [2, 3]. However, the demand for energy increases, and since there are no other equally efficient, economic, and safe ways to produce energy compared to coal combustion, it is estimated that its use will increase its contribution to global electricity production by 3%, from the current 41% to 44% by 2030 [3]. This leads to another problem; the waste management of such a large quantity of FA. Current practices involve the utilization of vast expanses of land for landfill sites and agricultural dumping, including oceans, ponds, and lagoons [2, 10]. Agriculture lands are employed for the disposal of wet form of FA, where FA is mixed with water for slurry creation, while the landfills serve for the storage of the dry form of FA [10, 11]. These practices not only pose a threat to the ecological balance and biodiversity but also have implications for human health [2]. A paradigm shift towards circularity and the reutilization of FA presents the most viable solution.



**Figure 2.** Fly ash composites and their potential applications for reuse [3].

Cenospheres (CS) is considered as the most valuable waste within FA [1, 3, 4] and its content can reach 3.8% [2,3]. Its unique properties, like high hardness, the resistance to heat transfer and electricity, their light-weight and their inertness in chemical reactions make it an intriguing material [1,4]. Regarding their optical properties, they are spherical, hollow inside, with thin wall thickness, while their size is at micro scale [12]. Chemically, they mainly consist of aluminosilicates in high ratios, approximately 90% in the glass phase of different forms of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , like cristobalite, quartz, and mullite [1]. The remaining 10% consists of other oxides observed in traces, like  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$  [1]. Figure 2 depicts the variation of pathways that CS can be reutilized.

In this research was used CS as main material to create a ceramic foam for biomedical use as bioscaffold. Polymeric foam replication method was utilized to fabricate the foams, while natural sponges from the Mediterranean Sea were employed as replication templates. The sponge-CS material was then sintered at 1200 °C for 1 hour to obtain the final material, consisted of compacted CS in the sponges' shape and size. After manufacturing this material, characterization tests were conducted, including SEM and EDS.

## MATERIALS AND METHODS

In order to fabricate a foam of CS, powder from the Netherlands was obtained, with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  compositions of 58.67% and 34.55% respectively, with trace amounts of other oxides (<2% each one of them), including a small percentage of unburned carbon (Loss On Ignition – LOI 0.53-1.2%) (Plomp Mineral Services, PMS). The CS powder exhibited a bulk density of 0.40  $\text{g/cm}^3$ , a specific density of 0.86  $\text{g/cm}^3$  and an average grain size of 170  $\mu\text{m}$ . Natural sponges originating from the Mediterranean Sea, specifically from the island of Kalymnos, were procured. Four types of natural sponges were acquired: Grass type, Silk Fina, Hard type, and Honeycomb. The sponges were procured in their natural brown color, except Hard sponge, which was bleached and as a result had a yellow shade. Furthermore, PVA powder with an average molecular weight (MB) of 30000-70000  $\text{gr/mol}$  (Sigma-Aldrich) served as the binder agent.

To fabricate the ceramic foams, the ceramic slurry was produced first, mixing distilled water with PVA and CS. Three slurries were created composed of 100ml of distilled water, 2% wt PVA, while

the mixing ratio of PVA to CS was  $\frac{1}{2}$ , 1 and 2 and the slurries denoted as CS/PVA.1/2, CS/PVA.1 and CS/PVA.2 respectively. Prior to the introduction of CS, the distilled water-PVA solution underwent magnetic stirring at 90°C until complete dissolution of PVA. After the dissolution of PVA and the temperature's drop to the room's one, the CS was added and the mixing lasted for 1 hour. The sponges were cut into cubes and were immersed in the slurry, except Honeycomb sponge, which due to its unique structure could not be cut in the desired size, so it was formed into pastille. The Honeycomb templates underwent uniaxial pressing with the applying weight of 5 tones. Then, they were let to physically dry in room temperature for one day. The next day, they were immersed again in the slurries. Both first and second immersion lasted 10 minutes for each sponge, under magnetic stirring. After both immersions the templates were squeezed for the removal of the excess slurry so not to obstruct the pores of the sponge. After the second immersion, the next step was to dry the sponges in a furnace at 100°C for 4 hours. The final step entailed sintering at 1200°C for one hour, with an intermediate soaking at 400°C for one hour. The heating rate during sintering was set at 2°C/min.

The samples underwent SEM and EDS analysis. SEM provided information about their microstructure, porosity and interconnectivity of the created pores, while EDS provided information about the elements and phases existing after the sintering.

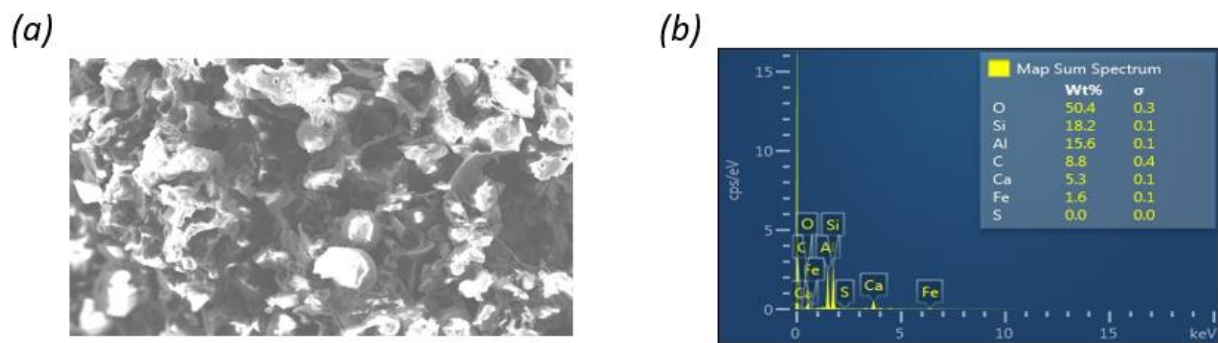
## RESULTS AND DISCUSSIONS

After sintering, ceramic foams derived from the Silk Fina template exhibited slight shrinkage as expected. While their geometry remained unchanged, they were characterized by brittleness. Ceramic foams derived from the Hard sponge template were more brittle than those from the Silk Fina template. In most cases, the foams retained their shape and geometry after sintering. Ceramic foams derived from the Honeycomb template had an amorphous shape. This occurred because, after immersion of the sponge in the slurry, the template could not maintain its pastille shape and reverted to its natural form. Brittleness was also observed in ceramic foams of this template. Finally, the Grass template proved to be inefficient. During sintering, the particles failed to aggregate to form a foam, resulting in a powdery substance. Figure 3 demonstrates the ceramic foams of Silk Fina, Hard and Honeycomb templates respectively.



**Figure 3.** a) Ceramic foam derived from Silk Fina template, b) Ceramic foam derived from Hard template and c) Ceramic foam derived from Honeycomb template.

SEM analysis indicated the existence of pores and their interconnectivity. However, it is observed that in some spheres the structure collapsed. It is believed that the binder agent played a key role in the failure of the material's microstructure. The PVA that was utilized could not perform as it should, resulting in ceramic slurries with not the ideal thixotropy and viscosity, which as a result led to brittle foams. On the other hand, EDS analysis yielded results largely as expected. In all specimens Oxygen (O) is the main element, due to the presence of oxides, followed by Silicon (Si) and Aluminum (Al). Furthermore, the presence of carbon was observed in all products, likely attributed to the incomplete combustion of residual carbon in the initial CS powder. Figure 4 depicts the SEM image and the EDS analysis of ceramic foam derived from Silk Fina.



**Figure 4.** a) Ceramic foam that used Silk Fina as a template and b) elemental graph of ceramic foam that used Silk Fina as a template.

## CONCLUSIONS

In light of the imperative to reduce waste and transition to a circular economic model, a novel approach has been undertaken wherein waste from the energy sector, particularly cenospheres derived from Fly Ash, is repurposed as feedstock for the creation of a new ceramic foam designed for biomedical use as a scaffold. The manufacturing process involves the utilization of CS, which primarily comprises  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , following the principles of the foam replication technique. For this purpose, natural sponges harvested from Kalymnos, Greece, have been procured to serve as replication templates. The process of creating these ceramic foams entails the production of a ceramic slurry using distilled water, CS powder, and PVA as a binder agent. The natural sponges were meticulously shaped and sized before being immersed in the slurry. Subsequent to the drying of the samples, they underwent sintering at  $1200^\circ\text{C}$  for a duration of 1 hour. Following this, the produced ceramic foams underwent through SEM and EDS tests to evaluate their microstructure and their elemental composition. The inadequate rheological properties of the produced ceramic slurries, resulting in the inability to fabricate stiff ceramic foams, highlight concerns regarding the suitability of the PVA binder agent employed.

Silk and Hard type exhibited great replication properties, while Honeycomb lost its shape due to its unique structure during the preparation of the samples. However, the use of PVA with proper binding properties during slurry preparation would yield to slurry with the ideal rheological properties, which would also affect the sponges' efficiency as replication templates. Thus, structurally stable ceramic foams with the desired shape would have produced.

In summary, the process of manufacturing ceramic foams from CS presents a promising avenue for the creation of bioscaffolds. Moreover, the favorable results obtained through the utilization of natural marine sponges as replication templates are encouraging. However, to further substantiate the potential of these CS foam bioscaffolds, optimizing the manufacturing technique is imperative. This should begin with the utilization of a more suitable PVA binder agent.

## ACKNOWLEDGEMENTS

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## Figures

Figure 1a, T.Wautelet, (2018), << Exploring the role of independent retailers in the circular economy: a case study approach>>, Luxembourg

Figure 1b, <https://urbact.eu/articles/circular-economy-another-buzzword-or-your-citys-future>