**Characterization of coccoliths from *Emiliania huxleyi* cultivations**

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**Highlights**

* Characterization of biogenic particles.
* Wetting properties of coccoliths.
* Size estimations of oblate particles.

**1. Introduction**

The marine alga *Emiliania huxleyi*, one of the many species of the Coccolithophorida family was cultivated in this study with the intention to produce coccolith particles [1]. Coccolithophores are an extend group of calcifying unicellular algae found in the photic zone of oceans, best known for their ability to produce micron-sized calcareous platelets called coccoliths. Assumed to be responsible for half the existing global amount of calcium carbonate [2] their role in stabilizing the carbonate cycle is considered important as are also the data that have been retrieved from fossil particles for past climate conditions. Depending upon environmental availability, the algae are known to embed various elements in the particles’ structure resulting to slight different chemical compositions which enables reconstruction of past temperatures [3]. Coccoliths are composed of radially oriented calcite crystals and organic matter and are the focus of this study. As they are biologically produced it is impossible to reconstruct them synthetically and remain therefore a unique structure of calcium carbonate. The particles are here characterized and efforts are being made to cover a literature gap surrounding their properties.

**2. Methods**

After recovering intact coccoliths from fresh cultivations the material was characterized chemically (ICP-OES), while particular attention was placed on its surface chemistry (Zeta Potential, FTIR). The above results aided a better understanding of the material’s wetting behavior, estimated with the liquid penetration method and the Owens Wendt Rabel Kaelble (OWRK) model [4]. The surface free energy of the material was compared with synthetically CaCO3, chalk and comminuted oyster shells, three broadly used calcium carbonate sources. Further the particular form of coccoliths, resembling that of an oblate disc, helped compare commonly used particle size estimation techniques and evaluate their applicability for non-spherical particle systems.

**3. Results and discussion**

The surface free energy (SFE) of coccoliths was found to be similar to that of the comminuted oyster shells, with values of 27.6 and 26.03 mN·m-1 respectively. The highest SFE was noted for the synthetically produced CaCO3 at 34.7 mN·m-1 while chalk showed the lowest value at 16.4 mN·m-1. Based on the OWRK model, coccoliths showed the highest polar part of their SFE. In contrast to that the synthetically produced CaCO3 showed the lowest polar part. These findings are particular valuable in all processes where the material comes into contact with a fluid.

In the second part of this study the influence of oblate shaped particles on size measuring techniques was reviewed. By comparing results obtained from an analytical (LUMsizer) and a differential (DCS) centrifuge and a laser diffraction spectrometer (LDS) with microscopic image size evaluations (LM), it was found that LDS results at better representing the true size of the particles.

 

**Figure 1.** Particle size distribution (Q3) measured by different techniques for coccoliths.

Figure 1 shows four cumulative distributions measured for coccoliths. The particles are depicted finer with the analytical centrifuge (x50,LUM = 0.79 μm; LumiSizer). The median of the LDS (Helos KR; Sympatec) and LM (Axiotech 100 HD camera; Zeiss) methods was estimated at 1.92 μm and 1.9 μm respectively. As seen from the figure above, the two curves seem to deviate mostly in the finer region with LDS depicting particles finer than they probably are. Continuing with the differential centrifugal sedimentation (CPS) the media was estimated at x50,CPS = 11.87 μm.

**4. Conclusions**

Through the liquid penetration method, the surface free energy of four calcium carbonate materials could be estimated. The differences in the polar components can be attributed to the presence of organic materials, confirmed also through FTIR analysis, that can stabilize the surface by neutralizing the surface charge.

Considering the particular shape of coccoliths and observing the results presented in **Figure 1** it was concluded that laser diffraction analysis best suited the requirements of the system and represented the distribution of the particles. By comparing the four methods for different shaped particles it could be eliminated that the measuring deviations displayed a measuring inaccuracy.

**References**

1. N. Krumov, Green biosynthesis of Nanoparticles: Mechanisms and Applications, Berforts Information Press Ltd., UK, 2013
2. C. de Vargas, Evolution of primary producers in the sea, first ed., Elsevier Inc., China, 2007
3. H. M. Stoll, Geochemistry, Geophysics, Geosystems, Tech. Brief, Volume 2, (2001)
4. U. Teipel, I. Mikonsaari, Part. Part. Syst. Charact. 21 (2004) pp. 255–260