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# Notes on the occurrence of char plerospheres in fly ashes derived from Bokaro and Jharia coals (Jharkhand, India) and the influence of the combustion conditions on their genesis

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ABSTRACT

Plerospheres play a positive role in reducing particulate matter emissions, Br and U to the atmosphere, may assist in the synthesis of fly ash-based zeolites, and serve as a substrate to produce industrial grade multiwalled carbon nanotubes.

Optical and electron microscopy and laser granulometry have been used to evaluate the nature and origin of char plerospheres in two pulverized fuel (p.f.) fly ashes and one fluidized bed fly ash derived from Bokaro and Jharia coals (Jharkhand, India). The influence of plerospheres on the particle size distribution of the fly ashes was also assessed, including the potential for fragmentation of the char shell during ultrasonic dispersion associated with laser granulometry.

Char plerospheres were found to be common in one of the p.f. fly ashes (Chandrapura). Microscopic study shows that these are post-combustion morphotypes resulting from the infilling of the open-hollow-porous char particles by glassy morphotypes, and in this case should be classified as char pseudoplerospheres. Their formation is also related to the coal composition and the combustion conditions; the coal must contain vitrinite and low-reflectance semifusinite macerals that are able to produce open-hollow-porous char morphotypes, and the feed must be pulverized and heated in such a way that small glassy spheres are formed.

Experiments using ultrasonic dispersion resulted in a shift from trimodal to bimodal particle size distribution for the Chandrapura ash, due to the fragmentation of the char plerospheres and release of the glassy spheres contained within them. It may therefore be expected that some particle size-related utilization-friendly properties of fly ashes containing char pseudoplerospheres could change during handling and with time.

## 1. Introduction

Char cenospheres (from the Greek "*kenos*" for hollow and "*sphaira*" for sphere) resulting from coal carbonization were first identified in the 1920s (Newall and Sinnatt, 1924; Sinnatt et al., 1927). Forty years later, Erik Raask published the first study of the origin and formation of inorganic cenospheres (Raask, 1968), which provided a basis for explaining the formation of cenospheres and spheres encapsulated within spheres (plerospheres) in terms of surface-tension forces, the non-wetting properties of fused slag when in contact with coal or coke surfaces, and chemical reactions that produce gas bubbles inside slagged ash globules (Raask, 1985). Basically, Raask (1985) concluded that, for the formation of plerospheres, both coal substance and mineral matter should be intimately dispersed inside burning coke particles, so that the carbon could prevent coalescence of the encapsulated ash particles. Significant quantities of plerospheres are therefore likely to be produced from coal under pulverized fuel conditions.

Fisher et al. (1976) proposed the term "*plerosphere*" (plero — from the Greek *plérés*, full) to describe hollow spheres in fly ash that were packed with spheres, and these have since been reported by other authors (e.g., Boycheca et al., 2015; Carpenter et al., 1980; Chancey et al., 2010; Fisher et al., 1976, 1978; Furuya et al., 1987; Georgakopoulos et al., 1994; Ghosal and Self, 1995; Goodarzi, 2006a, 2006b; Goodarzi and Sanei, 2009; Michalíková et al., 2014; Mollah et al., 1999; Moreno et al., 2005; Shibaoka and Paulson, 1986; Vassilev, 1992; Zhai et al., 1996). Fisher et al. (1976) also proposed a hypothesis that plerospheres are due to the formation of an annular gas space between the molten shell and the core, combined with heating of the core through a connecting bridge of mineral matter to the liquid shell, and the formation of additional gas that causes the core to boil away from the interior surface. However, the transmitted light photomicrographs and scanning electron

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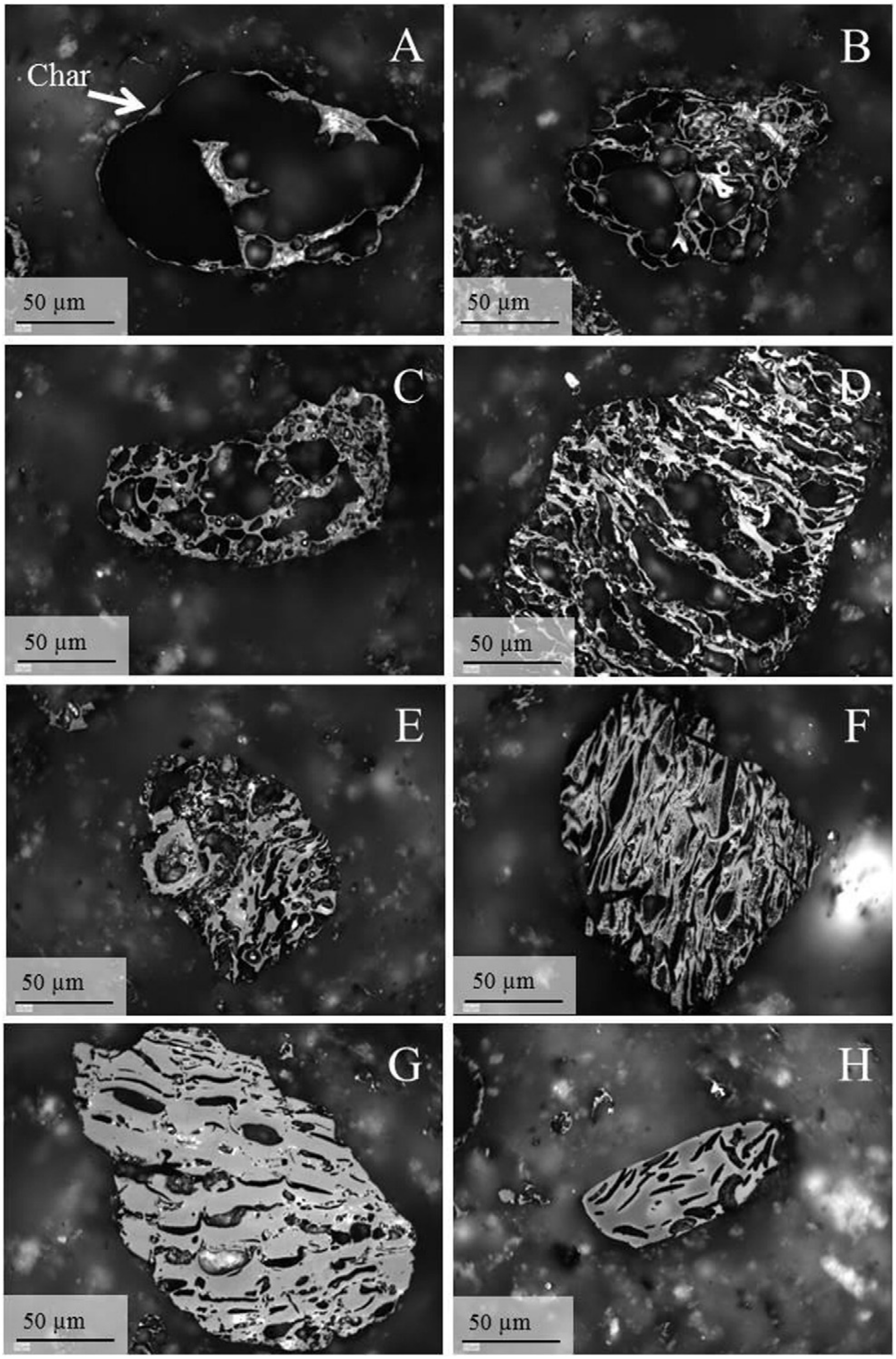

**Fig. 1.** Char morphotypes in Chandrapura fly ash sample (optical microscopy reflected white light; polished blocks): A) tenuisphere; B) tenuinetwork; C) crassinetwork; D) mixed-porous; E) mixed-dense; F) inertoid; G) solid fusinoid; H) solid (secretinoid).

microscopy (SEM) images provided by Fisher et al. (1976, 1978) do not corroborate this hypothesis, since they resemble infillings that developed after the aluminosilicate cenospheres were formed.

Attempts by Carpenter et al. (1980) to identify plerospheres by crushing the spheres in-situ under the optical microscope also did not corroborate this hypothesis. In no cases, filled spheres were observed, suggesting that, despite the conclusions of Fisher et al. (1976, 1978), plerospheres are not a common structure in fly ash.

The hypothesis of Fisher et al. (1976, 1978) was further refuted by Shibaoka and Paulson (1986), who argued that: (i) the model could only be sustained if particular conditions occur inside the pulverized fuel boilers and if plerospheres are common, (ii) no transitional forms from ash to plerospheres have been found, and (iii) the model does not explain how fully melted ash cenospheres, i.e. cenospheres of inorganic origin, could be formed inside partially unburnt char particles.

Shibaoka and Paulson (1986) were also the first to note, from examining polished-section samples using optical microscopy and SEM, that the char in some fly ash morphotypes could be filled by the sample preparation resin that entered the central cavities of the char through holes or cracks in the walls. They concluded that open inorganic cenospheres and char cenospheres could be filled in the same way by smaller spheres, for example when still suspended in the turbulent