

Laminar Calcite Aggregate Formation In The Light Fly Ash Fraction

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ABSTRACT

The fly ash collected from the Economizer of a Portuguese power plant was characterized using different techniques. Two subsamples were obtained using the density separation method (1 g/cm³ distilled water; 22°C; 10 minutes of mechanical agitation; 24 h settling; vacuum filtration through a 1.2-µm membrane filter; oven drying at 80°C), but in the end around 2% of the sample was lost. Since carefully work was performed in order to save as much fine size fly ash as possible, this was considered an important and unexpected loss of particulate material. However, an explanation to this lost of sample may not be the loss of fine particulate but the dissolution of more easily mobilized elements such as calcium. In fact during this process, a thin inorganic coat floating on the top the light fraction was formed, and this layer was the target of a SEM/EDX study for components identification and chemical composition. The SEM results revealed a layer composed by rhombohedral microcrystals, and the EDX analysis a chemical composition made of calcium, carbon and oxygen which indicates that these layers are composed of calcite. Final remarks - some calcium carbonate precipitated in the light fraction as a layer composed of micro-calcite, and eventually the remaining dissolute material was lost after the filtration process contributing to the ≈2% lost of initial sample.

1. INTRODUCTION

Ceramic cenospheres can be easily separated from the bulk fly ash by sink-float method using just distilled water. This is possible since this fly ash fraction is composed by hollow glassy particles named “cenospheres” by Raask (1968), which are lighter than water.

They are molten droplets of melts having relatively high viscosities (Lauf, 1981; Sokol et al., 2000) that are inflated by gases, but the supply of calcite (and hence CO₂) do

not limit the production of these spheres, since calcium concentration and cenosphere production do not correlate (Lauf, 1981).

Although almost all Portuguese fly ash is sold for cement production, the Economizer fly ash is still disposed on a landfill. For that reason, that specific fly ash has been characterized in detail, and sub-sampling by sink-float method using distilled water was conducted.

However, in the final around 2% of the sample was lost and a thin inorganic layer of calcite was formed and was floating on the top the light fraction.

This posed the question: how does a 2.71 g/cm³ density mineral float on water? Our hypothesis is that part of the lime in fly ash reacts with atmospheric CO₂ and a rapid carbonation reaction occurs, producing calcite aggregates.

2. MATERIAL AND PROCEDURES

For three days the fly ash was collected from the hoppers of the economizer and blended to obtain an individual sample.

The coals burned during the fly ash sampling period were El Cerrejon coal from Colombia and Kangra coal from South Africa (Table 1).

Before and after any procedure all samples were weighed using high precision (up to 0.0001 g) Mettler model AE 240 balance and the sink-float process was performed using distilled water to obtain a light fraction (<1 g/cm³) and a heavy fraction (>1 g/cm³).

The initial fly ash sample used (Table 2) was suspended in distilled water with a solid/liquid weight proportion of 1:10. To avoid the agglomeration of the fly ash components the fly ash/water mixture was shaken for 10 minutes with a Heidolph apparatus, and settled for 24 hours at room temperature (22°C). After settling, the sample was decanted and vacuum filtered through a 1.2-µm membrane filter, and both fractions [light (<1 g/cm³), and heavy (>1 g/cm³)] were dried on an oven at ≈80°C.

Commercial lime (Quicklime) was purchased, added to distilled water in a solid/liquid weigh proportion of 1:10, manually agitated for two minutes, and settled for 24 hours. The characterization of the fly ash fractions and the experiment products was performed by scanning electron microscopy (SEM) and Energy dispersive X-ray

analysis (EDS) at the Centro de Materiais da Universidade do Porto: i) SEM/EDS equipment JEOL JSM-6301F/OXFORD INCA ENERGY 350, with thin window for carbon and oxygen detection; ii) ESEM/EDS equipment FEI Quanta 400FEG/EDAX Genesis X4M.

Table 1. Coal characterization.

Coal	Moisture	Ash	VM	Elemental analysis (d.b., wt%)						
	(a.r., wt%)	(d.b., wt%)	(d.b., wt%)	C	H	N	S			
Kangra	8.5	13.8	25.0	72.4	4.1	2.0	0.9			
El Cerrejon	5.4	11.6	26.6	70.1	5.5	4.3	0.9			
	Vitrinite reflectance			Maceral composition (vol.%)				Net calorific value		
	R _r	σ	V	L	I	MM		(MJ/kg)		
Kangra	0.7	0.06	24	6	64	7		28.55		
El Cerrejon	0.6	0.06	74	3	15	8		29.01		
	High temperature (815°C) coal ash major oxides (wt%, dry basis)									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Ti ₂ O	CaO	MgO	MnO	K ₂ O	Na ₂ O	P ₂ O ₅
Kangra	45.6	23.4	9.18	1.27	10.39	0.58	0.05	0.58	1.06	0.71
El Cerrejon	68.50	17.30	8.73	1.46	3.86	0.41	0.08	1.96	n.d.	n.d.
	Low temperature (200°C) coal ash X-ray diffraction mineralogy (%)									
	Kaolinite	Quartz	Gypsum	Pyrite	K-felds	Na-felds	Calcite	Ankerite	Clorite	Mica
Kangra	66	9	11	3	4	QL	4	1	QL	2
El Cerrejon	49	26	7	4	QL	5	QL	QL	3	6

a.r. – as received; d.b. – dry basis; σ - standard deviation; V - vitrinite; L - liptinite; I - inertinite; MM - mineral matter.

n.d.: not determined; Q.L.: Below Quantification Limit; K-felds: K-feldspar; Na-felds: Na-feldspar.

Table 2. Economizer fly ash characterization.

Moisture	C _t	S _t	C _{graph}	C _{org}	C _{inorg}	LOI (1000°C)					
(a.r., wt%)	%										
0.4	9.24	0.12	1.23	7.73	1.02	10.5					
HTA (815°C) Major oxides (wt%, daf)											
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	CaO	MgO	MnO	Ti ₂ O	P ₂ O ₅	SO ₃	
43.6	25.1	13.1	1.2	1.2	10.1	2.8	0.1	1.3	0.9	0.2	
Fly ash X-ray diffraction mineralogy (crystalline phases %)											
Quartz	Mullite	Magnetite	K-feldspar	Hematite	Spinel	Portlandite					
50	15	24	1	7	2	1					

Total carbon, total sulphur, carbon species, inorganic carbon and LOI (1000°C) were conducted at ACME Analytical Laboratories LTD.

3. RESULTS AND DISCUSSION

After density separation, the two fly ash fractions were weighed, and the results are presented in Table 3. The weight difference shows that around 2% of the initial sample was lost during the density separation process. However, careful washing of

the recipient was done to avoid the loss of fine particles, and the fineness of the membrane filter used during vacuum pumping was 1.2- μm meaning that fines could not be lost that way, but most probable many elements (Ca, Cl, Na, S, Al, Cs, K, Mg, P, Si, Sn, and Ti) were leached by the water during the sink-float process (Vassilev et al., 2004).

Table 3 – Fly ash weigh results after density separation.

Fractions	Weight (g)	%
Light (<1 g/cm ³)	1.3652	1.95
Heavy (>1 g/cm ³)	66.9962	95.71
Total	68.3614	97.66

When compared to the Sokol et al. (2000) fly ash results, our Economizer fly ash light fraction mass is quite low (Table 3), since those authors reported a light fraction in fly ash up to 2/3 of the fly ash volume, but our values are similar to the ones reported by Vassilev et al. (2004). Ultimately, this is associated with the feed coal composition and the combustion conditions, since Lauf (1981) stated that not all power plants produce cenospheres in large quantities, and some produce them intermittently.

Visual observation of the light fraction still in water also revealed that the water was covered by a thin layer, instead of just ceramic cenospheres and some char.

In fact, the results of the SEM/EDS analysis show that the fly ash light fraction (<1 g/cm³) is composed by ceramic cenospheres, char, and Ca-rich flattened particles (Figures 1 and 2). However, the bulk Economizer fly ash sample is mainly composed of aluminosilicate glassy spheres, char, quartz relics, and aluminosilicate agglomerates. Other less common particles are ferri- and ferrospheres, Ca-rich phases, and others. But no flattened particles were found (Figure 3).

A more detailed analysis of the fly ash light fraction revealed that flattened particles are made of aggregates of calcite (CaCO₃; Figure 4) rhombohedra crystals, which have a density of 2.71 g/cm³.

The heavy fraction (>1 g/cm³) composition is similar to the bulk fly ash sample, and no precipitation of calcite was detected, at least in amounts similar to the ones found in the light fraction.

Apart from the low amount of ceramic cenospheres found in the Economizer fly ash, it was surprising to find the formation of a layer made of calcite aggregates in the light fraction, since calcite is much denser than water, and no calcite was found in the heavy fraction (Figure 5).

A closer look at Figure 1 reveals that ceramic cenospheres are covered by calcite aggregates, suggesting that ceramic cenospheres may have simultaneously played a nucleation and a floater role for calcite formation and floatation. Figure 1 also shows that char did not participate in the calcite-formation process, since its surface is calcite free. However, char could be responsible for catalytic fixation of CO₂ in the water.

Once calcium in fly ashes may be found in calcite minerals, glass, anhydrite, etc., but mainly in CaO, a simple experiment was conducted to prove that CaO in water forms laminar calcite aggregates that float on water, very similar to those obtained with fly ash.

Since Quicklime is produced according to the following reaction (Equation 1)



it is basically the same process that leads to the formation of CaO in fly ashes.

Therefore, by mixing Quicklime with water we expected to obtain a similar result as the one observed in the fly ash light fraction

Since Quicklime can be hydrated, i.e., combined with water, and hydrated lime is produced according to the reaction (Equation 2):



After carbonatation occurs, i.e., a chemical reaction where calcium hydroxide reacts with carbon dioxide from the air and forms insoluble calcium carbonate (Equation 3)



and laminar calcite aggregates are formed, and the water surface tension is not disrupted, resulting in a floating layer (Figure 6). The major difference observed is the

habit of the calcite crystals: rhombohedra for CaO in fly ash and scalenohedra for Quicklime.

Contrary to the very slow carbonatation process in concrete, where carbonatation of the lime in cement causes a lower pH, and may lead to corrosion of the steel reinforcing rods and damage to the construction, the carbonatation of fly ash lime forming calcite aggregates must be a very rapid reaction rate, otherwise instead of calcite microcrystals aggregation, larger crystals would be formed and sink in the water to join the heavy fraction. But that was not the case since the heavy-fraction large calcite crystals were not observed (Figure 5).

4. CONCLUSIONS

Since the aim of the experimentation was just to prove that calcite crystals may form and float on water, we may conclude that some CaO in fly ash may also behave the same way and may be responsible for undesirable contamination of ceramic fly ashes by calcium carbonate.

Eventually, the collection of ceramic cenospheres by the sink float method using water must be conducted in few minutes to avoid the formation of calcite.

Acknowledgments

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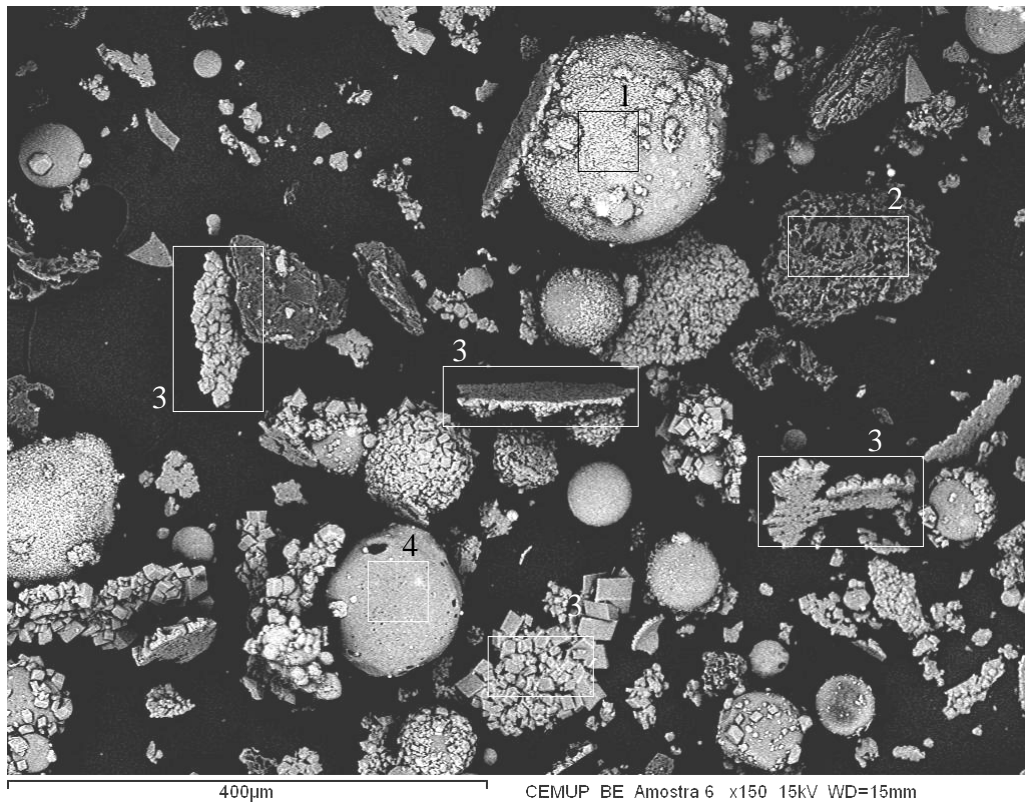


Figure 1. Economizer fly ash light fraction (backscattered electron signal; $\times 150$): 1) aluminosilicate glassy cenosphere with calcite crystallization at surface; 2) char particle; 3) flattened particles 4) aluminosilicate glassy cenosphere.

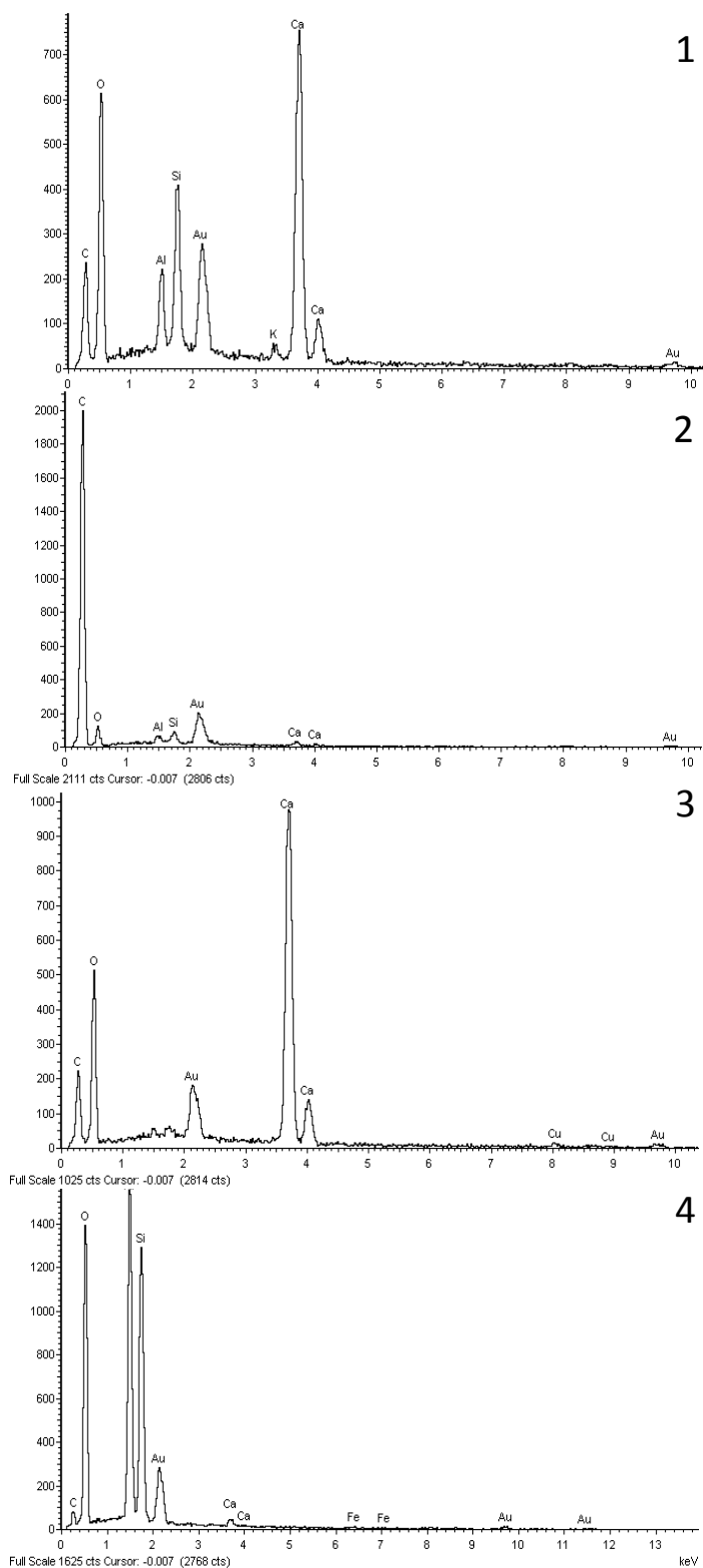


Figure 2. Economizer fly ash light fraction: EDS spectra of the square areas in Figure 1.

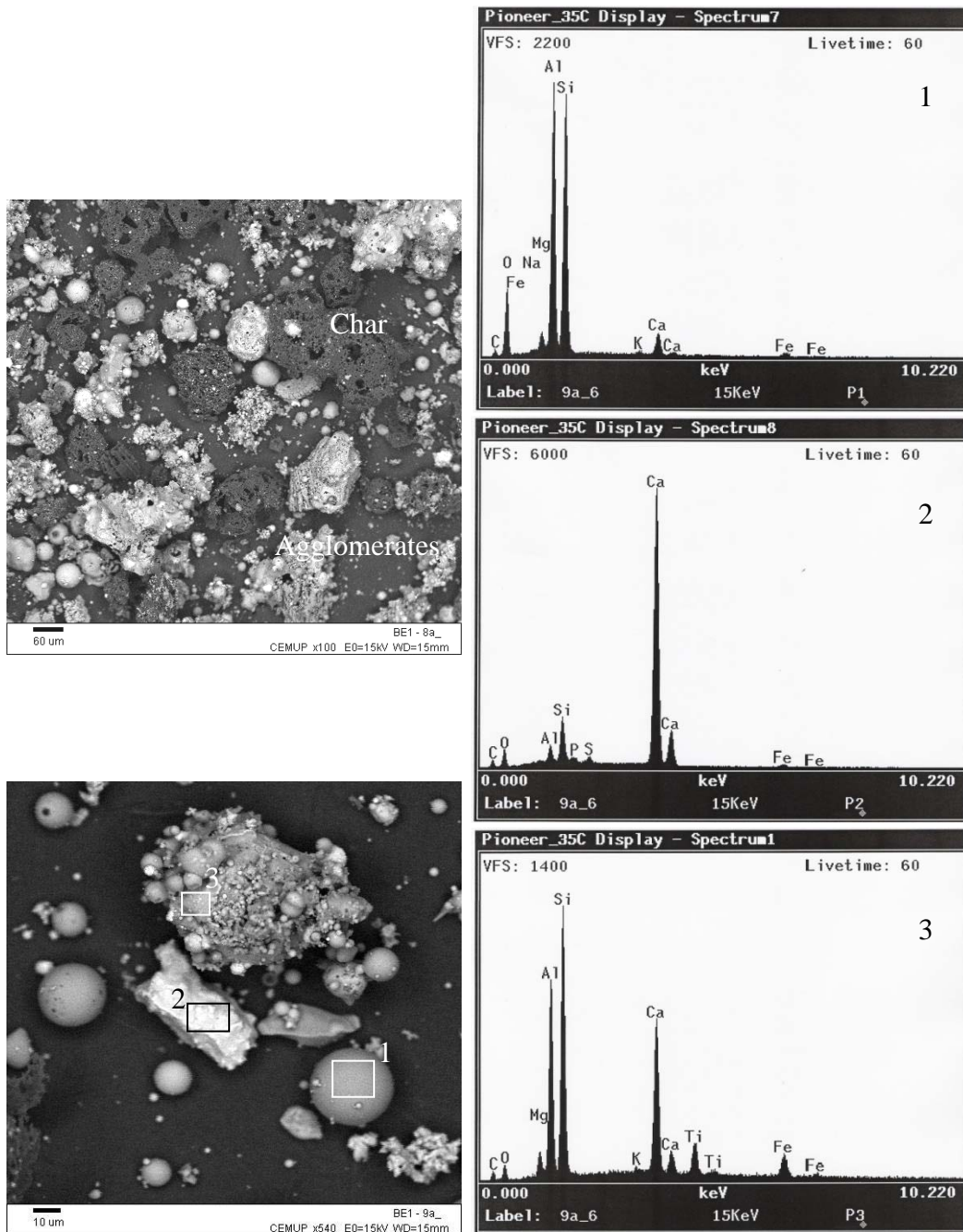


Figure 3. Left: Overview of the economizer fly ash (backscattered signal): a) Major components are char, agglomerates and glassy spheres (×100 magnification); b) EDS analysis area of: 1) glassy sphere , 2) Ca-rich particle, and 3) Al-Si-Ca agglomerate with Fe and Ti (×540 magnification).

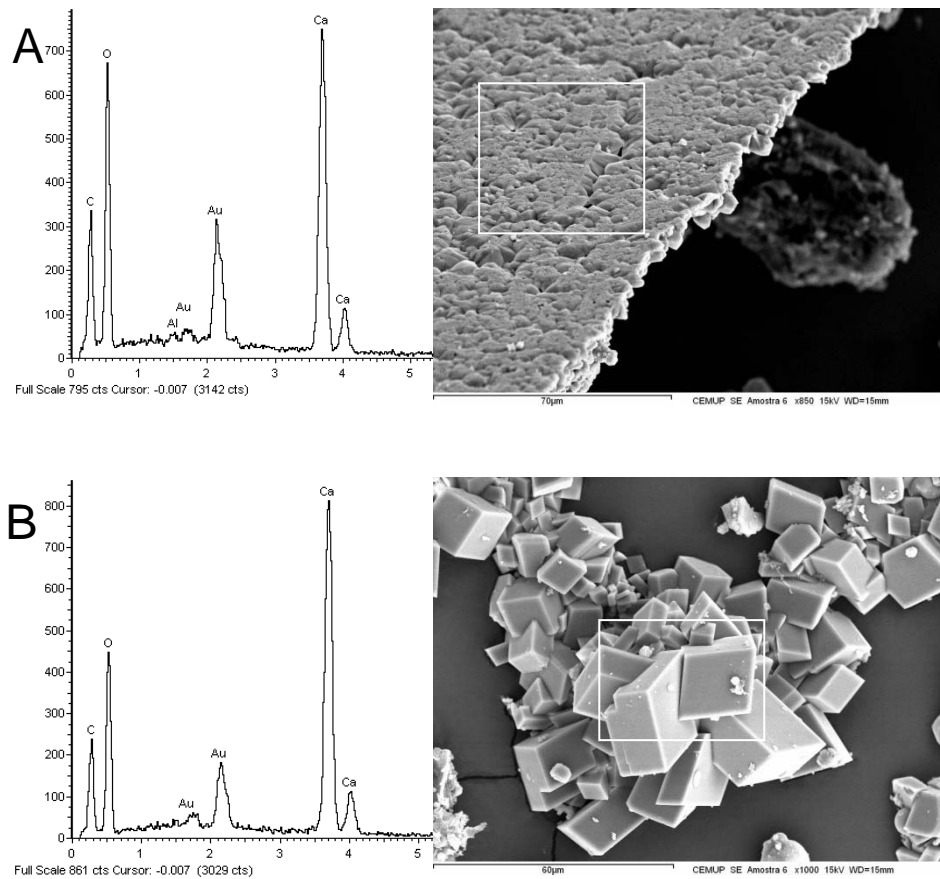


Figure 4. SEM/EDS analysis of the flattened particles in the Economizer fly ash light fraction (secondary electron signal): A) Flattened particle: left: EDS CaCO₃ spectrum; right: SEM micrograph of one side; B) The other side of a flattened particle: left: EDS CaCO₃ spectrum; right: SEM micrograph of calcite rhombohedra.

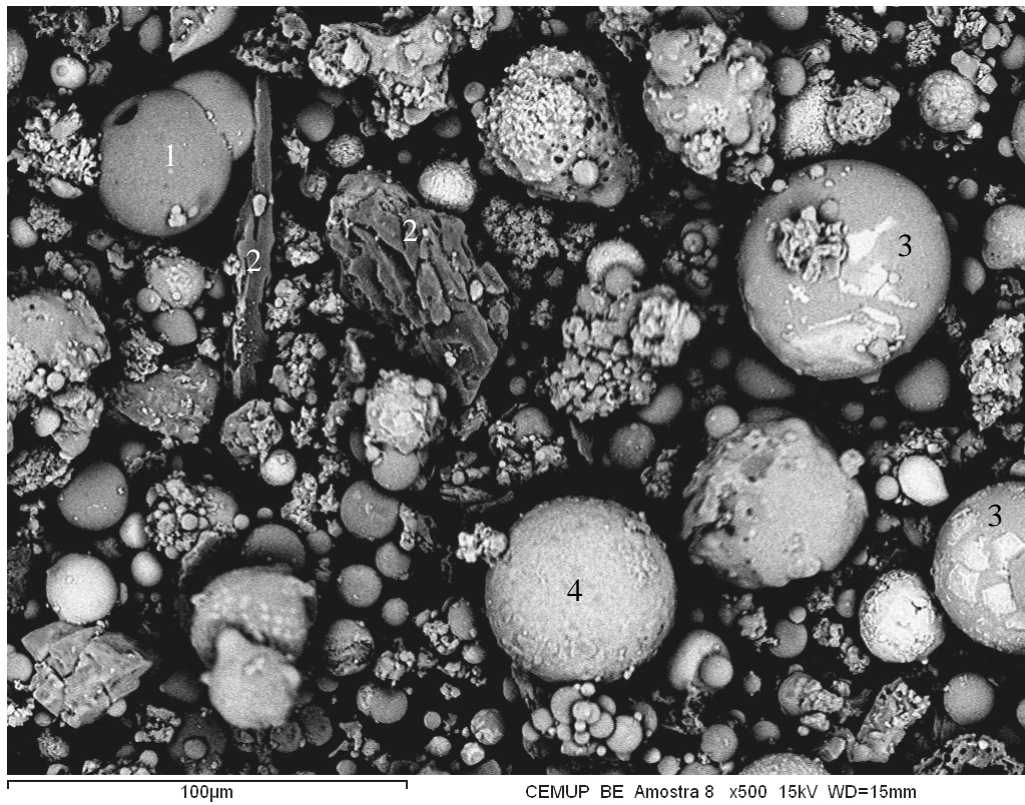


Figure 5. Economizer fly ash heavy fraction (backscattered electron signal; x500): 1) aluminosilicate glassy sphere; 2) char particle; 3) Ferrospheres; 4) Ca-Fe-rich sphere.

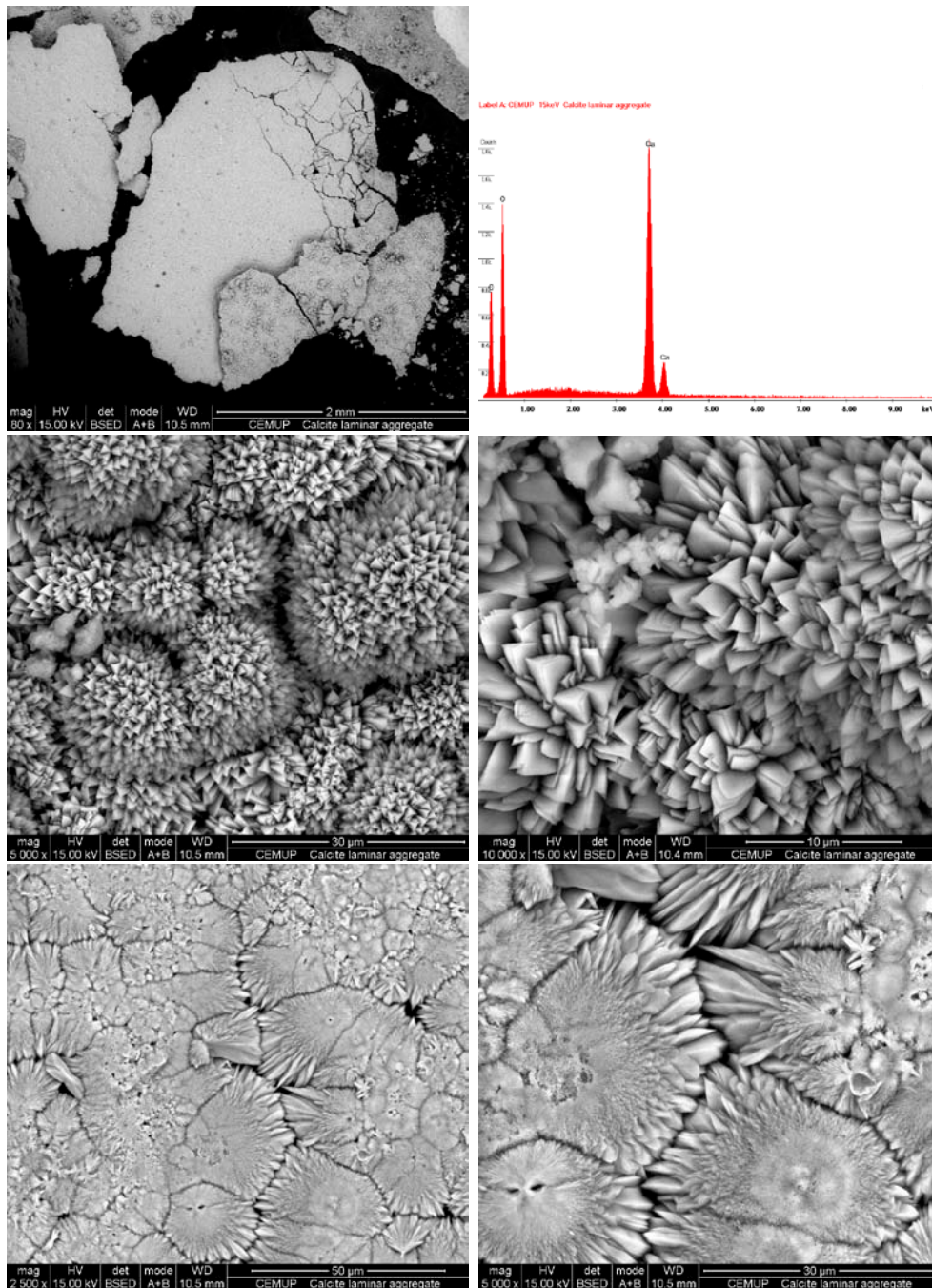


Figure 6. Calcite laminar aggregates formed from Quicklime (backscattered electron signal): Top left: Fragment of the floating sheet formed after mix Quicklime and water ($\times 80$); Top right: EDS CaCO_3 spectra of the previous image; Centre left and right: faced exposed to air: aggregate of calcite crystals with scalenohedra habit; Bottom left and right: water contact face: Each aggregate started from a single nucleation point, and after joined together and formed a floating layer.