COMPOSITION AND MORPHOLOGY OF ORGANIC AND MINERAL MATTER
IN FLY ASH DERIVED FROM BITUMINOUS COAL COMBUSTED
IN THE BĘDZIN POWER STATION (POLAND)

Danuta SMOLKA-DANIELOWSKA¹, Magdalena MISZ¹

A b s t r a c t. Fly ash particles formed during coal combustion are composed entirely of organic or/and mineral matter. The proportions of the two components depends on combustion conditions and the presence of minerals in feed coal particles. The aims of this paper are the classification of char morphologies, the quantification of the inert- and semiinert components, and the characterisation of the morphologies and compositions of mineral particles in fly ash from Będzin Power Station, Poland. Various char morphologies are presented and their distribution in individual pulverised fuel boilers is discussed as are the morphologies of mineral particles and the distribution of major and minor elements in different size fractions of fly ash.

K e y w o r d s: coal, pulverised fuel combustion, fly ash, chars, mineral matter.

INTRODUCTION

Coal is a complex rock containing organic and mineral matter. During the combustion process both organic and mineral matter undergo severe changes. The solid products of this process are fly ash and slag. In this paper, the interrelations between transformed organic and mineral matter in fly ash are described.

The aims of the investigations were:
— the identification of the morphological forms of unburned organic matter, and their classification,
— the evaluation of the total inert- and semiinert-inertinite contents,
— the characterisation of the morphology and mineral composition of both isolated particles and their aggregates resulting from coal combustion in Będzin Power Station (Poland).

Coal combustion is a multistage process. Before coal particles enter the combustion chamber of a pulverised-fuel boiler, they are ground to less than 100 μm in size. Crushed coal is delivered to the combustion chamber together with exhaust gases. During delivery, they are heated to a temperature of up to 350°C and moisture is evaporated. At higher temperatures, ranging from 350–600°C, the coal particles undergo a process of softening. Further increase of temperature up to 700°C causes their devolatilisation and swelling (Solomon et al., 1993). The product of these processes is char containing carbon and varying proportions of transformed mineral matter (Kordylewski ed., 1993). Volatiles undergo ignition during their release (Jarosiński, 1996) or afterwards (Lau, Niksa, 1992). Burnout of released volatiles in the vicinity of char causes an increase in its temperature. After exceeding a critical temperature, partly transformed coal particles undergo ignition (Chomiak, 1977) and soot may be formed (Solomon et al., 1993). This process takes place in the temperature range 500–1800°C (op. cit.). The next stage is char combustion which involves 90% of the duration of the process (Kordylewski ed., 1993). It takes place in the temperature range 900–1800°C (Solomon et al., 1993). The last stage of the process involves the disintegration of char particles and the formation of fly ash (op. cit.).

Pulverised fuel boilers are characterised by the highest temperatures of combustion, ranging from 1200–1500°C, and the shortest time of combustion. It is assumed that plasticised coal particles do not agglomerate (Shampine et al., 1995).

The processes described above are influenced by such factors as the physico-chemical properties of the coal, its maceral composition and rank on the one hand and, on the other, by temperature, rate and time of combustion. In addition, the quantity and composition of mineral matter is important. All of these factors influence the amount of unburned organic matter

¹ University of Silesia, Department of Earth Sciences, Będzińska 60, 41-200 Sosnowiec, Poland
in fly ash (Walsh et al., 1994) as well as the mass distribution of ash (Morrison, 1986).

Coal is a heterogeneous organic rock. It contains micro-lithotypes and associated minerals. Individual coal particles may be formed exclusively of one maceral or associations of macerals. Their composition affects their behaviour during combustion. They may be divided into three groups.

**Reactive macerals** devolatilise and soften during combustion, e.g., vitrinite and liptinite (Falcon, Snyman, 1986), and the reactive portions of inertinite macerals, e.g., reactive semimacerals, low reflective funginite, secretinite, micrinite, macrinite and inertodetrinite (Kruszewska, 1990).

**Inert macerals** such as fusinite (pyrofusinite) and semimacerals (pyrosemifusinite) do not undergo changes during combustion (op. cit.).

**Semiinert macerals** exhibit properties intermediate between reactive- and inert macerals during combustion.

Though some coal particles may consist entirely of organic or mineral matter, most involve different proportions of these two constituents. The most common mineral groups occurring in coal are clay minerals, sulphides, carbonates and silica (Stach et al., 1982). Mineral matter can occur in syn- and epigenetic forms. In many cases, mineral matter co-exists with macerals as carbominerites. It can be dispersed within macerals as single particles a few microns in size or as aggregations of such particles. The shape of these aggregates can be spherical, oval or lenticular. Mineral matter can also fill intercellular spaces.

Though it is a source of air pollution, inorganic matter in coal does confer some advantages — and disadvantages — during the combustion process. Coal particles containing mineral matter are characterised by a higher specific heat capacity. They need more time to be combusted. Mineral matter may also act as catalysts (Wigley et al., 1997). Chars containing greater amounts of calcium and magnesium impurities are more reactive due, probably, to the catalytic activity of these elements during coal oxidation (Walker et al., 1968 in Jenkins et al., 1973). Coal demineralisation may either cause a decrease in coal reactivity or an increase. Any increased reactivity is probably the result of an increase in porosity enhancing oxygen migration into the combusting coal particles (Jenkins et al., 1973). The combustion temperatures of demineralised coals are lower than those of mineralised coals (Crelling et al., 1992; Menéndez et al., 1994). Mineral matter may also influence fragmentation during combustion (Wigley et al., 1997).

Whether the various minerals and their phases undergo changes during combustion is reflected in the composition of the solid waste products. The composition of the mineral matter in coal and the high burnout temperatures achieved during combustion in conventional power stations influence the composition and mineralogy of fly ash, e.g., the occurrence of amorphous aluminosilicate glass and of high-temperature crystalline phases such as mullite, quartz and magnetite (Querol et al., 1996). These products are the result of various processes such as decomposition, oxidation, reduction, dehydration, hydration, carbonatization and sulphatization, melting and solution. In addition, pre-existing and newly-formed compounds also react with one another.

These processes result in the formation of fly ash particles that provide a matrix for the interactions of a great variety of substances formed during coal combustion and the emission process. The size of the fly ash particles depends on several factors, e.g., initial coal particle diameters, mineral content and its distribution within coal particles, degree of coalescence of fused mineral matter and number and size of fragments produced during combustion (Morrison, 1986).

Fly ash particles can be classified with regard to chemical composition and origin into coal particles, combustion particles and condensation particles (Querol et al., 1995). The latter form in the high temperatures of the combustion chamber when the largest mineral particles fuse and condense as cenospheres (Karr, 1979). It is likely that the spherical form reflects the action of surface tension (Wadge et al., 1986).

Five pulverised-fuel boilers are installed in Będzin Power Station. Two steam boilers of OP-120 type (K-6 and K-7), one is a water boiler of WP-70 type (K-5) and two are water boilers of WP-120 type (K-8 and K-9) (Materials, 1995). The thermal efficiency of the boilers ranges from 88–90% (E. Piotrowska, oral inf.). The exhaust gases are carried away through electrofilters to a single chimney. Every year, 279.1 thousand tons of coal are combusted in these boilers (Materials, 1995). The heating value of the feed coal is 21.2 MJ/kg, the ash content ranges up to 20% and sulphur content up to 0.8%.

**SAMPLE COLLECTION AND ANALYSIS**

Samples of fly ash were collected once a week during the period November 6, 1996–June 26, 1997. In total, 77 fly ash samples were collected from five pulverised fuel boilers — 5 samples from WP-70 (K-5), 27 from OP-140 (K-6), 26 from OP-140 (K-7), 9 from WP-120 (K-8), and 10 from WP-120 (K-9). As the OP-140 boilers were in use during most of the sampling time, most of the samples were collected from these. Fly ash samples were collected at the bottom of the electrofilters.

The following analyses were carried out:

- analysis of unburned organic matter contents,
- determination of char morphological forms at 500 points for each sample,
- evaluation of the total-, inert- and semiinert inertinite contents,
- X-ray diffraction analysis,
- scanning electron microscope analysis (SEMA),
- electron microprobe analysis (EPMA).
Morphologies of unburned organic matter in fly ash

During the period of sample collection, no pattern was observed in the measured unburned organic matter contents. Except for one sample with 18.40% unburned organic matter, all of the other samples comprise between 1.33% and 12.07% of this matter.

The classification of char forms is based on porosity, wall thickness, presence/absence of anisotropy and the degree of alteration. That used here is a modified classification based on classifications given by Jones et al. (1985), Tsai, Saroni (1987), Oka et al. (1987), Bailey et al. (1990), Bend et al. (1992), Rosenberg et al. (1996), ICCP (2001).

The following morphological forms of unburned organic matter were determined in the fly ash samples (Misz, 1999, 2002):

**Crassospheres** (Plate I, Fig. 1), one of the most frequent forms in fly ash, derive from vitrinite. Their contents in the analysed fly ash samples range from 0.6–37.0%. The highest average contents of crassospheres were observed in fly ash from the K-6, and K-7 boilers (20%). Lower average contents were observed in fly ash from the K-5 boiler (17.4 %) and the lowest average contents were measured from the K-9 (10%) and K-8 (12%) boilers (Table 1).

**Tenuispheres** (Plate I, Fig. 2) probably derive from clarite. Their contents (up to 5.0%) are always significantly lower than the crassosphere contents in the same sample of fly ash. The fly ash from all of the boilers reveal average tenuisphere contents of about 1.6%. Boiler K-5 (2.9%) is somewhat lower than the crassisphere contents in the same sample of fly ash. Contents range from 12.6–85.8% . The highest detritus content of slightly altered inertinite is found in fly ash from the K-5 boiler (17.4 %) and the lowest in fly ash from the K-8 and K-9 boilers.

**Isotropic networks** (Plate I, Fig. 3) are common in the fly ash examined (Table 1). They probably originate from cladrodurite and duroclarite or from some forms of vitriniterite. Their quantities in fly ash range from 4.0–44.2% and are lowest in fly ash from the K-6 and K-7 boilers. Fly ash from the smallest boiler (K-5) revealed the highest average contents (27.2%).

**Anisotropic networks** (Plate I, Fig. 4) possibly result from the combustion of vitrinertite or trimacerite. They are always lower in number than isotropic networks in the same sample – ranging up to 11.8% only (Table 1). As with isotropic networks, average contents of anisotropic networks are the lowest in fly ash from the steam boilers. The determined averages from the K-5 boiler are twice as high as in the K-8 and K-9 boilers.

**Tenuinet-works** are among the rarest forms (Table 1). These may originate from clarite with a liptinite content higher than that of vitrinite. In many samples, including all from the K-8 boiler, this form is absent. The highest quantities (1.2%) were seen in fly ash from the K-5 and K-6 boilers and the highest average content (0.3%) from the K-5 boiler.

**Honeycombs** (Plate I, Fig. 5), probably resulting from combustion of seminert inertinite, make up to 9.6% of all char forms in the fly ash. Fly ash from the K-6 and K-7 boilers contains the least amounts and fly ash from the K-5 boiler the greatest amounts (Table 1).

**Inertinite** (Plate I, Figs. 6, 7) forms from the most inert part of the feed–coal inertinite, particularly from pyrofusinite, pyrosemifusinite and in part from secretinite, funginite and the most inert part of inertodetrinite. Some fly ash inertinite is morphologically identical to that in the feed coal. The contents of this unaltered inertinite range up to 8.6% (Table 2). Fly ash from K-5, K-6 and K-7 boilers reveal similar average amounts (4%). Fly ash from the K-5 boiler has a higher average content of unaltered inertinite; boiler operation conditions are probably a key factor.

Slightly altered parts of inertinite in both slag and fly ash show small, round pores, irregular cracks and rounded edges. This morphological subgroup is less common than unaltered inertinite. As with unaltered inertinite, the highest average content of slightly altered inertinite is found in fly ash from the K-5 boiler (Table 2).

**Detritus** (Plate I, Fig. 8) is the dominant form of char in the fly ash. Contents range from 12.6–85.8%. The highest detritus contents, and the highest average contents, characterise the K-8

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**Table 1**

<table>
<thead>
<tr>
<th></th>
<th>Crassospheres</th>
<th>Tenuispheres</th>
<th>Isotropic networks</th>
<th>Anisotropic networks</th>
<th>Tenuinetworks</th>
<th>Honeycombs</th>
<th>Inertinite</th>
<th>Detritus</th>
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<td>K-5</td>
<td>9.4</td>
<td>0.6</td>
<td>13.8</td>
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<td>1.0</td>
<td>7.4</td>
<td>15.2</td>
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<tr>
<td></td>
<td>23.6</td>
<td>4.8</td>
<td>37.4</td>
<td>11.8</td>
<td>1.2</td>
<td>9.6</td>
<td>12.8</td>
<td>56.2</td>
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<tr>
<td></td>
<td>17.4</td>
<td>2.9</td>
<td>27.2</td>
<td>5.0</td>
<td>0.3</td>
<td>3.4</td>
<td>9.6</td>
<td>34.2</td>
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<td>7.4</td>
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<td>0.0</td>
<td>1.2</td>
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<td>36.4</td>
<td>6.0</td>
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<td>5.0</td>
<td>14.6</td>
<td>76.6</td>
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<td>0.1</td>
<td>1.7</td>
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<td>9.4</td>
<td>0.0</td>
<td>4.0</td>
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<td>0.0</td>
<td>1.0</td>
<td>12.6</td>
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<tr>
<td></td>
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<td>37.4</td>
<td>5.2</td>
<td>0.4</td>
<td>5.0</td>
<td>12.2</td>
<td>82.6</td>
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<tr>
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<td>19.5</td>
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<td>17.8</td>
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<td>0.0</td>
<td>1.8</td>
<td>4.7</td>
<td>52.8</td>
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<tr>
<td>K-8</td>
<td>8.0</td>
<td>0.0</td>
<td>6.2</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
<td>2.2</td>
<td>35.6</td>
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<tr>
<td></td>
<td>14.6</td>
<td>4.0</td>
<td>35.4</td>
<td>6.2</td>
<td>0.0</td>
<td>5.8</td>
<td>8.4</td>
<td>78.8</td>
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<td></td>
<td>12.0</td>
<td>1.7</td>
<td>19.5</td>
<td>2.3</td>
<td>0.0</td>
<td>1.9</td>
<td>4.8</td>
<td>57.8</td>
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<td>K-9</td>
<td>0.6</td>
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<td>8.4</td>
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<td>0.2</td>
<td>1.4</td>
<td>29.0</td>
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<td></td>
<td>26.8</td>
<td>3.4</td>
<td>44.2</td>
<td>8.2</td>
<td>0.2</td>
<td>4.6</td>
<td>12.4</td>
<td>85.8</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>1.5</td>
<td>21.4</td>
<td>2.6</td>
<td>0.0</td>
<td>2.0</td>
<td>5.7</td>
<td>56.8</td>
</tr>
</tbody>
</table>

Composition and morphology of organic and mineral matter in fly ash...
and K-9 boilers. Lower average contents characterise fly ash from the K-6 and K-7 boilers and the lowest average contents of all were determined in samples collected from the K-5 boiler (Table 1).

**Transformed mineral matter in fly ash samples**

Inorganic mineral matter in the fly ash consists mainly of amorphous glass spheres and lesser amounts of various crystalline components. Major mineral phases would usually be quartz, mullite, Ca–Fe silicates, Ca–Na silicates, magnetite, hematite, wustite, feldspars, gypsum, bassanite, lime, sillimanite, and anhydrite. Minor phases (calcite, ferrite spinel, corundum, oxides of titanium) and accessory phases (iron, apatite) are also typical (Smo³ka, 1998).

Samples of fly ash collected from the electrostatic precipitators were separated into fractional sizes ranging from 20–200 μm. Most of the fly ash particles are smaller than 50 μm (Table 3).

Amorphous aluminosilicate glass makes up 30–80% of the fly ash. Amounts differ from sample to sample. The smaller the particle size, the greater the content of amorphous glass. Most (70–92%) of the fly ash particles are < 50 μm in size (Table 3). Glassy fly ash particles occur mainly as spherical forms and, rarely, as oval forms. Spheres in the Bêdzin fly ash have, in the main, diameters ranging from < 5–200 μm.

Alumina and silica are the major elements in fly ash. Following Smolka (1998), these glassy particles can be divided into two groups: smooth particles rich in aluminosilicate (Plate II, Fig. 1) and porous particles rich in aluminosilicate and other elements (Plate II, Fig. 2). Porous particles contain many pores filled with oxides of potassium, sodium, calcium, magnesium, iron, titanium, manganese, sulphur, phosphor and barium (Plate II, Fig. 3).

Cereda et al. (1995) classified aluminosilicate particles on the basis of two factors. The first is the most important. High and positive factor loadings for Al and Si and high negative factor loadings for all other elements confirm a connection between enriched concentrations of minor and trace elements in particles and lower concentrations of Al and Si and accounts for 69.9% of the variance. The second factor, accounting for 16.4% of the variance, is related to the variability in the distribution of Ca concentrations. The occurrence of different particle classes reflects the heterogeneous nature of the mineral matter in the parent coal and combustion-related, particle-formation mechanisms.

Coal combustion is one of the major sources of atmospheric pollution by toxic trace elements. Some fly ash particles adsorb elements or mineral phases on their surface. Trace elements are dissolved in the melts and inherited by the glass. Different elements may also be adsorbed on the surface of fly ash particles during crystallization. Trace elements are concentrated mainly in the smallest fly ash particles. Most elements (e.g., As, Ba, Co, Cr, Mn, Ni, Pb, Zn, Cu) are concentrated in the size class below 20 μm. Average trace element concentrations are given in Table 4.

**Table 2**

<table>
<thead>
<tr>
<th>Inertinite</th>
<th>K-5</th>
<th>K-6</th>
<th>K-7</th>
<th>K-8</th>
<th>K-9</th>
</tr>
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<tbody>
<tr>
<td>Total</td>
<td>7.4</td>
<td>1.2</td>
<td>1.0</td>
<td>2.2</td>
<td>1.4</td>
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<tr>
<td>Unaltered</td>
<td>1.8</td>
<td>0.1</td>
<td>0.4</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Slightly altered</td>
<td>2.2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Table 3**

<table>
<thead>
<tr>
<th>Fraction [μm]</th>
<th>Lowest [%]</th>
<th>Highest [%]</th>
<th>Average [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>200–160</td>
<td>0.10</td>
<td>3.90</td>
<td>2.10</td>
</tr>
<tr>
<td>160–90</td>
<td>0.40</td>
<td>4.60</td>
<td>2.60</td>
</tr>
<tr>
<td>90–50</td>
<td>1.20</td>
<td>15.60</td>
<td>7.30</td>
</tr>
<tr>
<td>50–20</td>
<td>5.50</td>
<td>22.10</td>
<td>16.40</td>
</tr>
<tr>
<td>&lt; 20</td>
<td>55.80</td>
<td>91.20</td>
<td>71.60</td>
</tr>
</tbody>
</table>

Some of the aluminosilicate glassy particles are rich in iron. Those with a spherical shape but a porous structure may also be characterised by the presence of iron oxides, mainly magnetite and hematite (Plate II, Fig. 4) and, rarely, ferrite spinel and wustite. Pores occurring in the crystalline components of fly ash may be filled with calcium, aluminium, silica and magnesium oxides. Characteristic skeletal, dendritic and fan structures result (Plate II, Fig. 5). The dendritic forms of magnetite and ferrite spinel, ranging in size from 90–160 μm, are derived from iron-rich minerals.

Other forms of transformed inorganic matter (mainly magnetite) are represented by spherical forms, empty inside or with a gaseous bubble surrounded by a wall of inorganic matter. Magnetite, enriched in Ti, Mn and/or S, occurs as rounded crystals and hematite as platy and lamellar crystals. Hematite may result from the thermal transformation of, e.g., pyrite present in the feed coal. Larger fly ash particles tend to have lower hematite contents.

The incorporation of Fe into the glass phase suggests that the melt exceeded temperatures of 1300°C. This would be consistent with the temperature of the furnace. The abundance of magnetite, hematite and ferrite spinel indicates that the glass was formed under oxidizing conditions with excess air (Mukhopadhyay et al., 1996).
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CONCLUSIONS

Our observations outlined above show that, in Będzin Power Station, boilers of similar type and size produce similar average contents of given char morphological forms. The average quantity of tenuisphere, isotropic and anisotropic networks, honeycombs and inertinite is generally higher in the WP-70 boiler than in other boiler types. The lowest average contents of detritus and unburned organic matter also characterise this boiler type. This pattern of occurrence of the different char morphological forms is probably influenced by the fact that the WP-70 has the lowest boiler load demand, and the shortest operating times in hours per day.

Fly ash particles, released into the environment in exhaust gases as a result of coal combustion, provide a matrix for the interaction of a great variety of substances during the combustion and emission processes. The major elements involved are aluminium, silica, iron, calcium, sulphur, and titanium.

Small particles of fly ash may be transported long distances from the source of their emission. Fly ash particles inhaled and deposited in the lung can cause serious health problems. That is one reason why knowledge of fly-ash properties, trace element contents, and the chemical interactions that take place in boilers must continuously be improved in a world where coal will be used for a considerable time to come.

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PLATE I

Figures 1–8. Magnification 200x

Figure 1. Crassisphere
Figure 2. Tenuisphere
Figure 3. Isotropic network
Figure 4. Anisotropic network
Figure 5. Honeycomb
Figure 6. Inertinite
Figure 7. Inertinite
Figure 8. Detritus
Danuta SMOLKA-DANIELOWSKA, Magdalena MISZ — Composition and morphology of organic and mineral matter in fly ash derived from bituminous coal combusted in Będzin Power Station (Poland)
Figure 1. SEM. Smooth particle of aluminosilicate
Figure 2. SEM. Porous particle of aluminosilicate
Figure 3. SEM. Particle composed of Al, Si, Ba, P oxides
Figure 4. Magnetite particle. Magnification 600x
Figure 5. Dendritic structure of iron oxides