

Effect of thermal treatment on the structure of PCC particles

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ABSTRACT: The controlled combustion of paper is normally used to determine the filler content of paper. It can also be a valuable tool to isolate the mineral particles for extra characterization or additional applications. However, the ashing temperature greatly affects the filler particles. The main goal of this study was to analyze the effects of paper calcinations on the intrinsic properties of precipitated calcium carbonate filler (PCC) at distinct temperatures, from 400°C up to 1000°C. We characterized the size, density, surface area, porosity, chemical composition, color, and electrostatic charge of the original PCC particles and the ash. The experimental results revealed that for a calcination temperature of 400°C, the size, specific surface area, and porosity of the ash are similar to those of the PCC filler before being incorporated in paper. Other important filler properties, such as color and electrical charge, are much different. To overcome this disadvantage, higher ashing temperatures need to be used. This study has demonstrated that 600°C is the optimum temperature for isolating the paper fillers, without the collapse of the PCC structure, so that their physical, chemical, optical, and electrical characteristics are adequately balanced and not too different from those of the original particles.

Application: This study demonstrates the effects of thermal treatment on the structure of PCC particles and evaluates the potential of the ashing method to isolate these particles from filled papers.

At present, mineral fillers are extensively used in the production of many distinct paper grades. On the one hand, process costs may be reduced, since fillers are frequently cheaper than fibers. On the other hand, some paper properties, such as opacity, light scattering, brightness, smoothness, gloss, bulk and printability are improved by the intrinsic characteristics of the mineral particles. Additionally, fillers affect the papermaking process, particularly process waters, retention, dewatering and abrasion [1-4].

Depending on the paper grade and on the required final properties, different minerals may be used, namely ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), clay, talc, titanium dioxide, or muscovite. PCC is nowadays the most common mineral used in fine papers because of its high purity and brightness, and also due to the greater light scattering and bulk that it imparts to paper when compared to GCC [5-6].

Considering the high amount of fillers commonly used (mineral contents of 25%-30% are found in many printing and writing papers), reliable testing methods for the quantification of fillers in paper are needed [6]. The standard ash methods (e.g., Tappi T 211 om-93 and Tappi T 413 om-93) are based on paper combustion, using ashing temperatures from 525°C up to 925°C. However, at these temperatures

most of the fillers decompose or dehydrate, including PCC. Kocman and Bruno [5], who studied the thermal stability of some paper fillers, concluded that an ashing temperature of 400°C was sufficient to oxidize all the organic matter of the paper without disturbing the mineral filler. They also found a close agreement between the total filler level of the paper and the ash content, when using 400°C during at least 16 h for the paper combustion.

Nevertheless, the ash content of paper may include not only the mineral fillers but also mineral matter present in the pulp (0.1%-0.3%) and residues from chemicals used in the filler production and in the papermaking process (sizing, retention, brightening, and strength additives, among others). Therefore, the ashing temperature affects the decomposition of the filler particles themselves, plus their surface chemical composition, electrostatic charge, and color, because the chemical residues are expected to be adsorbed at their surfaces [1].

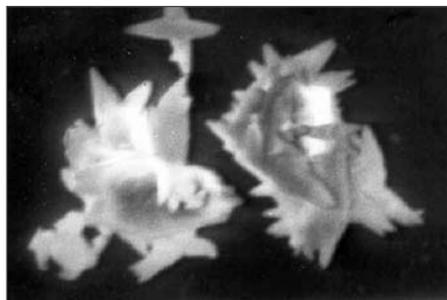
Most of the fillers used in fine papers are structured fillers, like PCC, with particles grouped in clusters having a specific shape and porosity, and particle average size, size distribution, and shape monitored according to the requirements of the papermakers [7-8]. These morphological properties also may be modified by the paper combustion process.

It is, therefore, of utmost importance to evaluate the effect of the ashing temperature on the intrinsic characteristics of the fillers. The paper ashing methods may be used not only to determine the amount of ash in the paper, but also to isolate the mineral particles, either to compare fillers from different commercial papers or for further applications.

This study analyzes the influence of the ashing temperature on the physical and chemical modifications of PCC particles isolated from printing and writing uncoated papers. To do that, we measured size, density, surface area, porosity, chemical composition, color, and electrostatic charge of PCC particles isolated from papers at burning temperatures of 400°C, 600°C, 800°C, and 1000°C.

EXPERIMENTAL

A commercial printing and writing paper (P&W) from a eucalyptus kraft-based pulp was used. According to the supplier, this paper contains 19.3% weight-to-weight (w/w) of a commercial PCC, the only filler added in the papermaking process. A sample of this PCC was provided and analyzed to compare the properties of the paper ash with those of the original filler. Particles from the original filler have mainly the scalenohedral habit (Fig. 1).



1. Scanning electron microscope photograph of the original PCC filler (magnification x 10,000).

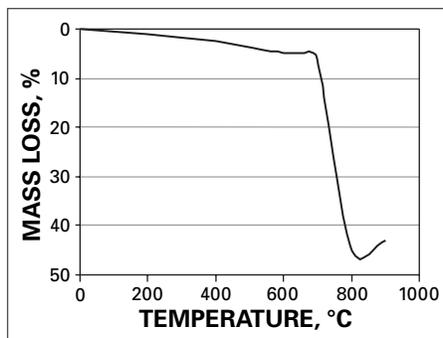
Small test pieces (1 cm²) of the P&W paper were oven-dried at 105±2°C and ignited in a muffle furnace, following the ashing procedure proposed by Kocman and Bruno [5] and using four distinct temperatures: 400°C, 600°C, 800°C, and 1000 °C. For each temperature, the ashing lasted for at least 16 h in covered porcelain crucibles, until no weight changes of the mineral residues were detected (±0.0001 g). The effects of temperature on the decomposition of the isolated original filler were evaluated by thermogravimetry (Linseis Thermobalance L81/1550).

For the ash content determinations, the test specimens and the corresponding ash were weighed in an analytical balance to the nearest 0.1 mg, after cooling to room temperature in a desiccator.

We characterized the original PCC particles and the ash obtained by the paper combustion (five different samples, as shown in **Table I**) in terms of the properties that most influence the paper performance, namely the morphological and the optical properties [1-3, 9], and also in terms of the mineralogical and chemical composition and particle electrostatic charge.

Particle size analysis (average size and size distribution) was performed by laser diffraction (Coulter LS130-Coulter Electronics) using water as the suspending medium. The particle shape and the presence of aggregates were visualized by scanning electron microscopy (SEM) (JSM 5310-JEOL).

The particle surface area was determined through nitrogen adsorption using the Brunauer, Emmett, Teller (1938) theory (ASAP 2000-Micromeritics); the true density (i.e., excluding voids) was measured by helium pycnometry (Accupyc 1330-Micromeritics). To determine pore structure characteristics, we used mercury intrusion porosimetry



2. Thermogravimetric curve of the original PCC particles.

(Poresizer 9320-Micromeritics). We also measured total intrusion volume (mL/g), total porosity (%), and the average pore diameter (mm) with the aid of equipment software.

We used other chemical characterization techniques to identify and quantify the inorganic constituents. Hydrogen, carbon, nitrogen, and sulfur were assessed by elemental analysis (EA 1108 elemental analyzer, Fisons Instruments). Sodium, magnesium, silicon, potassium, and calcium were quantified by atomic absorption spectrophotometry (3300 Spectrometer, Perkin Elmer). Chlorine (Cl⁻) and sulfate (SO₄²⁻) ions were identified by ionic chromatography using a conductivity detector (Waters 431, Millipore). We evaluated the surface charge by measuring the zeta potential at different pH values in a laser-based multiangle electrophoresis analyzer (Coulter DELSA 440, Coulter Electronics).

As for the optical properties, we measured the mean reflectance factors R_x, R_y, and R_z to compute the corresponding CIELAB color scales (L, a, and b) according to the SCAN-P 49:83 standard (Elrepho 2000, Datacolor). The mineralogical analysis was performed with an x-ray diffractometer (PW 3040/00 X-Pert MPD, Philips).

For the dispersion of the mineral suspensions, ultrasound treatment and dispersing ammonium polycarbonate (Targon 1128, BK Ladenburg, Germany) were used.

RESULTS AND DISCUSSION

Figure 2 shows the thermogravimetric curve of the original PCC particles, which is coincident with the typical curve of the calcitic calcium carbonate [10]. A more detailed analysis of the curve reveals a loss of about 2.5% (w/w) of material between 400°C and 600°C and an additional loss of nearly 41.5%

Sample	Original PCC,	
1	Original PCC,	
2		400°C
3	Ash obtained	600°C
4	after paper	800°C
5	ashing at	1000°C

I. Samples identification.

Sample	Amount of ash%, w/w	Temp.
2	19.0	400°C
3	18.5	600°C
4	10.9	800°C
5	10.8	1000°C

II. Amount of ash obtained after paper controlled combustion (percentage relative to the initial paper weight) at different temperatures.

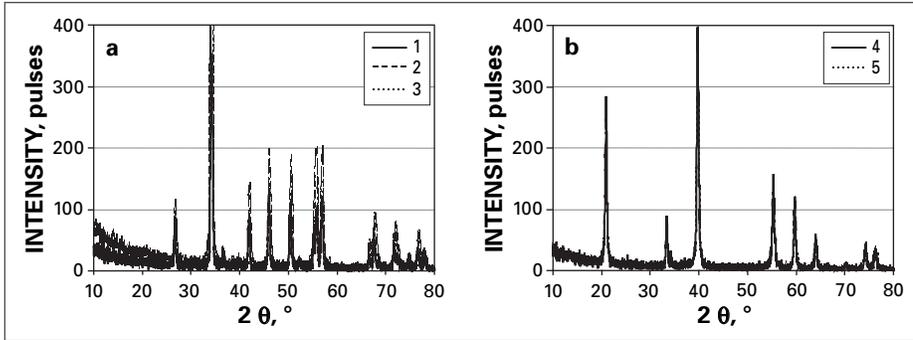
(w/w) between 600°C and 800°C. Up to 700°C the mass decrease corresponds to the loss of water, chemical additives added for the calcite synthesis, and stabilizing, retention, and sizing agents used in the papermaking process, all adsorbed at the mineral particles surface. It is only at 700°C that the calcite structure becomes unstable and starts to transform into lime and carbon dioxide, a process that causes an extensive reduction of mass and is finished at about 830°C.

Those values agree with those calculated from the data of **Table II**. This table also shows that the percentage of ash collected after paper combustion at 400°C (19%, w/w) is close to the filler content of the paper indicated by the supplier (19.3%, w/w). Therefore, it may be concluded that up to nearly 400°C the paper ashing process was adequately conducted, as far as the removal of filler is concerned.

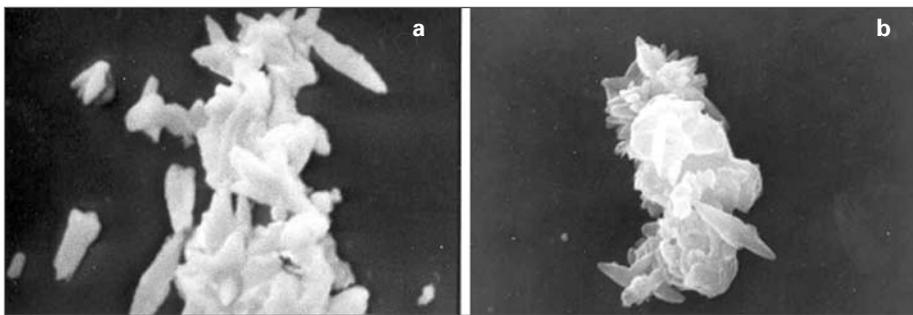
In addition, the x-ray diffraction (XRD) data from **Fig. 3-a** confirm that up to 600°C the ash calcite structure remains unchanged. The spectra for 400°C and 600°C are coincident with those of the original PCC particles. At higher temperatures (Fig. 3-b), calcite is no longer detected and the XRD profiles correspond only to lime structures [11].

Figure 4 shows the evolution of the ash particle sizes in terms of the cumulative undersize distribution curves obtained by laser diffraction and the corresponding median diameters (d₅₀). The calcium carbonate particles have a huge tendency to agglomerate.

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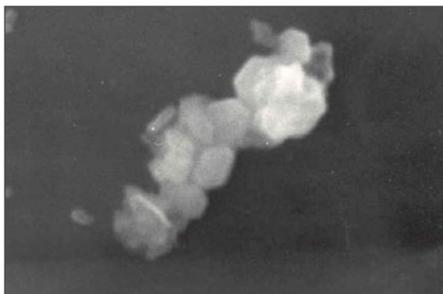
3. Results of x-ray diffraction analysis: (a) original fillers (1) and ash obtained after paper ashing at 400°C (2) and at 600°C (3); (b) ash obtained after paper ashing at 800°C (4) and at 1000°C (5).



5. Scanning electron microscope photographs of the ash obtained after paper ashing at 400°C (a) and at 600°C (b) (magnification x 10,000).

Sample	True density, g/cm ³	Specific surface area, m ² /g	Total porosity, %	Temperature
1	2.64	5.12	76.43	Original filler
2	2.64	4.69	70.45	400°C
3	2.66	3.73	60.36	600°C
4	2.28	13.75	77.23	800°C
5	2.28	14.13	—	1000°C

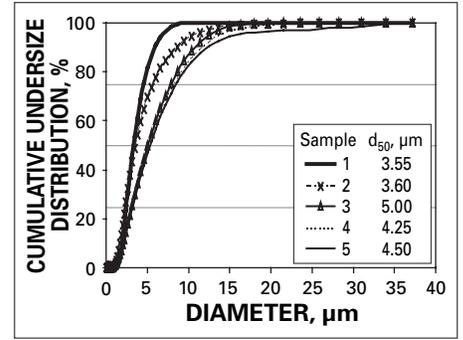
III. True density, specific surface area and porosity of the original fillers and of the paper ash obtained at different temperatures.



6. Scanning electron microscope photograph of the ash obtained after paper ashing at 800°C (magnification x 20,000).

Even with a careful dispersing procedure, the results of size analysis should be interpreted with some caution because they may reflect the existence of both individual particles and porous aggregates.

Although the ash obtained at 400°C possesses the same average size as the original PCC particles, a slightly broader size distribution is found, probably due to the presence of more isolated particles and, essentially, of some larger aggregates. This fact can be confirmed by comparing the images of Fig. 1 and Fig. 5-a, obtained by SEM and corresponding respectively to the original PCC and to the ash collected at 400°C. With the increase of the ashing temperature up to 600°C and the subsequent loss of the surface adsorbed chemicals, the tendency of the particle clusters to agglomerate into larger structures also increases (Fig. 5-b). These findings explain the substantial shift of the cumulative curve in Fig. 4 to the right and the significant increment of the median diameter.



4. Particle size data for the original PCC particles (1) and for the paper ash obtained at different temperatures (2: 400°C; 3: 600°C; 4: 800°C; 5: 1000°C).

As previously mentioned, at 800°C the calcite structure has already collapsed and new particles of lime have been formed. Figure 6 reveals that these particles are smaller than those of calcium carbonate (the magnification is double those of Fig. 5); they also have a great tendency to aggregate in larger clusters. Therefore, though having a median diameter moderately smaller than that of the ash obtained at 600°C, the corresponding cumulative curve in Fig. 4 presents a slight deviation to the right. Considering the results relative to the ash obtained at 1000°C, Fig. 4 demonstrates that the size distribution and the median diameter are quite close to those corresponding to 800°C. The percentage of coarser aggregates is somewhat larger, however, most certainly as a consequence of some additional sintering promoted by the high temperature.

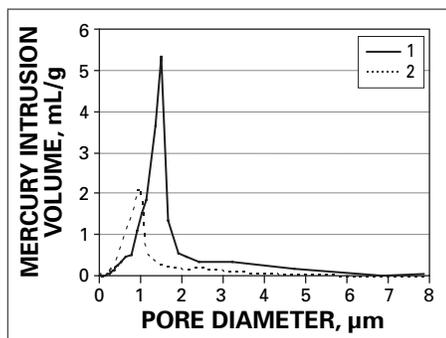
Table III shows the results of the true density, specific surface area, and porosity measurements. The true density values confirm that two clearly distinct materials were obtained by paper ashing: calcium carbonate particles with the same density of the original PCC particles ($\approx 2.65 \text{ g/cm}^3$) and lime particles with a somewhat lower density ($\approx 2.28 \text{ g/cm}^3$).

The reduction of the specific surface area for temperatures up to 600°C is in agreement with the tendency of the scalenohedral particles to join into larger aggregates at smaller ashing temperatures. It also agrees with the tendency of these aggregates to be less porous, as confirmed by the porosity values in Table III. The increase of the specific surface area between 600°C and 800°C is, however, much larger than would be expected considering the small decrease of the

Sample	C %, w/w	Na mg/g	Mg mg/g	Si mg/g	K mg/g	Ca mg/g	Cl ⁻ mg/g*	SO ₄ ²⁻ mg/g*	Temperature
1	11.143	0.075	2.066	0.177	0.047	624.925	0.0396	0.1862	Original filler
2	11.199	5.966	2.351	< 0.048	0.220	603.548	0.3280	0.8985	400°C
3	10.852	3.651	3.637	0.024	0.167	572.314	0.1790	0.1110	600°C
4	0.705	0.154	4.819	0.186	0.114	741.840	n.d.	n.d.	800°C
5	0.571	0.030	4.815	0.342	0.095	741.268	n.d.	n.d.	1000°C

* mg/g of soluble residue; n.d. = not detected

IV. Chemical composition of the original PCC particles and of the paper ash obtained at different temperatures.



7. Pore size distribution curves of the original PCC clusters (1) and of the ash obtained after paper ashing at 400°C (2).

median diameter. At first sight, this is contrary to the presence of the clusters that lead to a shift of the cumulative curve of Fig. 4 to the right. This increase results because at 800°C the aggregates are formed by small particles which, accordingly, have a higher specific surface area. In addition, their porosity is superior to that of the PCC ash obtained at 400°C and at 600°C. Consequently, the surface area available for nitrogen adsorption is also superior. The difference between the surface areas of the ash for 800°C and 1000°C is not relevant. Both the surface area and the porosity correspond to the aggregates and not to the individual scalenohedral particles.

The pore size distribution curves displayed in Fig. 7 correspond to the original PCC clusters and to the ash removed from paper at 400°C (which is less damaged by the ashing temperature). From these we see that, at this moderate temperature, the paper ashing process not only reduces the filler total porosity (expressed by the mercury intrusion volume), but also decreases the size of the corresponding pores.

The results of the chemical characterization listed in Table IV show that, in spite of being primarily composed of calcium, carbon, and oxygen (not included in the analysis), the original filler and the ash contain minor quantities of other

Sample	L	a	b	Temp.
1	98.78	-5.42	6.90	O.F.*
2	83.65	-3.57	10.95	400°C
3	88.56	-4.66	9.29	600°C
4	96.13	-5.49	7.57	800°C
5	98.27	-5.57	7.60	1000°C

* Original filler.

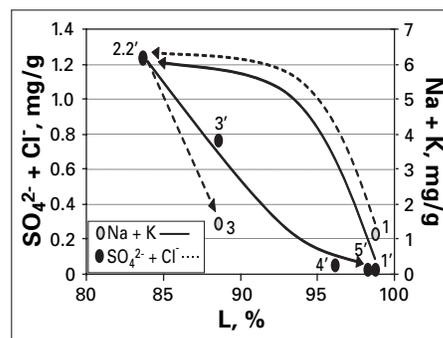
V. CIELAB color scales (L, a, and b) of the original PCC particles and of the paper ash obtained at different temperatures.

elements. These appear due to the calcite synthesis or to the papermaking process, as already noted. The increase of the calcium content and the outstanding decrease of the carbon content between 600°C and 800°C confirm the breakdown of the calcium carbonate structure and the emergence of lime. At the same time, considerable increments of potassium, sodium, and also SO₄²⁻ and Cl⁻ ions, are detected when comparing the original filler and the ash obtained at 400°C. These are “contaminants” resulting from the chemicals used in the paper machine. They are retention and sizing agents that remain adsorbed at the particles surface and that are progressively eliminated with the thermal treatment, especially above 600°C. Ionic chromatography was unable to detect the SO₄²⁻ and Cl⁻ ions, which were eventually present in the ash obtained at 800°C and 1000°C. Table IV shows that magnesium and silicon are thermo-resistant up to 1000°C, and are thus not removed (the corresponding percentages increase with temperature). The amounts of hydrogen, nitrogen, and sulfur in all samples were always less than 100 ppm.

The lightness of the filler particles, expressed by the L parameter, suffers a sharp reduction with paper ashing at 400°C, but practically recovers the initial value with the rise of the ashing temperature up to 1000°C (Table V). This behavior is consistent with the variation of the content of the papermaking residues that coat the calcite (or lime) particles,

Sample	Zeta potential, mV	Temp.
1	-18	Original filler
2	-40	400°C
3	-35	600°C
4	-18	800°C

VI. Zeta potential of the original PCC particles and of the paper ash obtained at different temperatures.



8. Relationship between the whiteness (L) and the Na + K content and the SO₄²⁻ + Cl⁻ content of the original filler (1 and 1') and of the paper ash obtained at different temperatures (400°C (2 and 2'); 600°C (3 and 3'); 800°C (4'); 1000°C (5')).

especially sodium and potassium, but also SO₄²⁻ and Cl⁻ ions (Fig. 8). These residues are also responsible for the changes of the CIELAB a and b color scales, which are opposite to the changes of the L parameter and confirm that the ash tends to lose its red and yellowish tone with the increase of the ashing temperature. This evidence confirms that higher temperatures are indicated to produce whiter ash.

One important issue in recovering fillers from paper is the influence of the ashing temperature on the particles electrostatic charge. This property considerably affects further uses of the PCC, namely in terms of choosing the retention agents. Table VI presents the results of the zeta potential analyses. Each value is the average of the measurement

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performed in the pH range between 7 and 14, where the zeta potential remains practically constant. Below pH 7, the particles charge increases and reaches positive values as the pH decreases. Nonetheless, it was impossible to determine the isoelectric point of each sample because calcite and lime are extremely unstable in acid conditions. Although all samples are negatively charged, the charge of the ash increases with temperature and approximates that of the original fillers. As expected, this trend matches the evolution of the SO_4^{2-} and Cl^- ions content—the higher the concentration of these anions the more negative is the charge of the particles.

CONCLUSIONS

From the results and the discussion carried out so far, we conclude that ashing temperatures greater than 700°C are not appropriate if the objective is to isolate the PCC present in paper sheets. In fact, they cause the decomposition of calcium carbonate in calcium oxide and carbon dioxide. To preserve the structure of the PCC aggregates in terms of size, specific surface area, and porosity, 400°C is the most suitable temperature for paper controlled combustion. However, in this situation, important filler properties,

such as color and electrical charge, are much disturbed by the chemical residues of the papermaking process, which have been adsorbed at the particles surface. These residues, containing compounds with sodium, potassium, sulfate, and chloride, are gradually removed with the rise of the ashing temperature. As a consequence, 600°C seems to be the best temperature for isolating the paper fillers in such a way that their physical, chemical, optical, and electrical characteristics are adequately balanced and not too different from those of the original particles. **TJ**

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INSIGHTS FROM THE AUTHORS

PCC is the most commonly used paper filler in the Portuguese paper mills. There is an increasing interest in developing procedures to isolate the mineral particles for extra characterization or additional applications.

This research work is part of a broader research project conducted by the authors concerning the influence of fillers on the properties of office papers. It differs from other previous research because it includes a deeper characterization of paper ashes obtained for a wider range of ashing temperatures.

The most difficult aspect was the development of a correct and reliable methodology for the separation of filler particles from paper.

This research showed that it is possible to isolate PCC particles from paper without the collapse of the PCC structure so that their physical, chemical, optical and electrical properties remain adequate for further applications.

The study showed in detail how paper ashing temperature affects the properties of the PCC

fillers, and this information can be of utmost importance not only for PCC manufacturers but also for paper mills, namely regarding the possibility of fillers recycling.

The next step is to blend the PCC particles separated from paper by paper ashing with other commercial PCC samples and to evaluate the potential of these mixtures either as fillers or pigments for paper coating.

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Ferreira



Velho



Figueiredo



Mendes