CELLULOSE CHEMISTRY AND TECHNOLOGY

IN-SITU CELLULOSE FIBRES LOADING WITH CALCIUM CARBONATE PRECIPITATED BY DIFFERENT METHODS

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In-situ loading of cellulose fibres is meant at maximizing filler retention, which is one of the most difficult problems in the production of printing papers with high filler content. Three methods for *in-situ* precipitation of calcium carbonate [$CaCO_3$] into the lumen and in the wall of the cellulose fibres were investigated (IS-PCC): a) calcium hydroxide [$Ca(OH)_2$] formation by the reaction of calcium chloride [$CaCl_2$] and sodium hydroxide [NaOH] in a fibre suspension, followed by $CaCO_3$ precipitation with carbon dioxide [CO_2] – carbonation; b) $CaCO_3$ precipitation by a double-exchange reaction between $CaCl_2$ and sodium carbonate [Na_2CO_3] in a fibre suspension; c) $CaCO_3$ precipitation through cellulose fibre saturation with a $Ca(OH)_2$ solution, followed by a carbonation reaction. The effectiveness of the *in-situ* precipitation methods was evaluated on pulp filter pads and paper handsheets, obtained on a standard lab former, by various analyses and investigations: calcium carbonate content, X-ray diffraction, SEM images, optical and mechanical properties of the paper sheets. The analyses proved that, whichever *in-situ* precipitation method was used, calcium carbonate precipitated both into the lumen and wall pores of fibres, particulates presenting a typical calcite diffraction pattern. However, significant differences were noticed among the *in-situ* precipitation methods concerning the yield of calcium carbonate precipitated into the fibre structure and particle sizes, and their distribution in the fibre wall and lumen, which influence the optical and mechanical properties of paper.

Keywords: papermaking, *in-situ* fibre loading, fibre wall and lumen, X-ray diffraction, SEM image, calcite

INTRODUCTION

Nowadays, a large range of paper filling materials, characterized by different chemical structures and morphologies, are available for paper industry, at competitive prices. Although the basic requirements for filling materials are the same, extensive research and development should to be mentioned in this domain, aiming at optimizing the balance between the *pros* and *cons* of mineral pigment (filler) application in paper and board production.

The fillers are selected to serve different papermaking objectives, mainly to enhance the optical and printing properties of paper and, sometimes, to reduce the production costs by partial substitution of fibrous materials. Consequently, fillers play an important role in producing quality printing paper, and also in the economic efficiency of the papermaking system. Due to the shifting trend from a conventional acid to a neutral/alkaline papermaking medium, the use of calcium carbonate as a filler is a reality in the production of writing and printing papers, representing over 90% of filler consumption for these paper grades.[1,2] The fillers are applied mainly to enhance paper properties, such as opacity, brightness, smoothness, porosity, printability and dimensional stability. Moreover, fillers with a high brightness degree allow papermakers to use fibre pulps with lower brightness, which leads to economical bonuses due to the lower price, as well as to a lower ecological impact, by reducing the consumption of chemicals during pulp bleaching.[3]

Generally, at increased paper loading levels, the influence of the filler increases, as both to its desired and undesired effects, so that the maximum filler content of the paper should consider an optimal compromise of such influences. In terms of filler loading, the limits are set primarily by an accompanying reduction of paper stiffness and insufficient strength properties (tensile strength, tear resistance, internal bond and surface strength). That is why, the filler content is limited in the case of paper grades with low basis weight or with high mechanical pulp content, due to an unacceptable decrease of the mechanical resistance indices.[4-6]

The effectiveness of the paper loading process depends on filler properties (chemical composition, particle morphology, particle size and particle size distribution, brightness, refractive index, specific surface, particle charge and abrasiveness), of great importance being also the potential interactions of the fillers with the wet-end furnish components. Actually, the wet-end interactions are strongly influenced when using retention chemicals, aimed at producing aggregation of filler particles and at improving retention by their entrapment into the network voids. As a function of the aggregation mechanism, the filler particles could be retained into the wet web as small or large aggregates of various structures. Small aggregates with porous structure lead to a higher optical heterogeneity and higher improvements in brightness and opacity, respectively. At the same time, at an equivalent filler content in paper, small aggregates and well-dispersed mineral particles produce a higher reduction of the fibre-fibre bonding potential, resulting in a higher decrease of the strength properties.[7,8]

At present, researchers are looking for new paper loading methods, which could lead to higher filler retention and a better relationship between the optical and strength characteristics. One of the solutions proposed is related to *in-situ* fibre loading. Some researchers in this area[9,10] evidenced the improvement in both optical and strength properties of paper as benefits of the *in-situ* loading method, besides a very high retention yield. Others[11,12] reported contradictory results on the increase in the mechanical resistance of paper through *in-situ* loading.

Our previous investigations[13] have shown that cellulose fibres loaded by *in-situ* precipitation of calcium carbonate give lower paper strength, comparatively with conventional loaded paper with the same filler content. However, a study on the recycling potential of *in-situ* loaded paper[14] evidenced an improved recycling behaviour, comparatively with the conventional loaded paper. A part of *in-situ* precipitated calcium carbonate is strongly fixed into the fibre wall and retained in paper even after six recycling cycles, until the calcium carbonate retained by retention additives in conventional loading is totally lost after the second paper recycling. It was also found out that, at the same calcium carbonate content, the optical properties of *in-situ* loaded paper are consistently higher than those of the paper obtained by conventional loading. Considering these aspects, the present study aims at analyzing the effectiveness of different methods for *in-situ* precipitation of calcium carbonate, and at evaluating their potential applications in papermaking.

EXPERIMENTAL

Materials

The following materials were used in the study: softwood bleached kraft pulp, refined in a Valley Hollander at 30 °SR; calcium chloride p.a.; sodium hydroxide p.a.; sodium carbonate p.a.; calcium hydroxide, and carbon dioxide (compressed CO_2 cylinder) as chemicals for *in-situ* generation of precipitated calcium carbonate.

Methods

In-situ precipitation of calcium carbonate (IS-PCC) was performed by the three methods presented in Figure 1:

A. Direct generation of calcium hydroxide in the pulp suspension and carbonation with carbon dioxide under pressure, based on the following reactions:

$CaCl_2 + NaOH \rightarrow Ca(OH)_2$

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3$ (*IS-PCC$_A$*)

B. Double-exchange reaction between calcium chloride and calcium carbonate:

$CaCl_2 + Na_2CO_3 \rightarrow 2NaCl + CaCO_3$ (*IS-PCC$_B$*)

C. Saturation of cellulose fibres with calcium hydroxide and carbonation with carbon dioxide under pressure:

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3$ (*IS-PCC$_c$*)

The paper handsheets were obtained on a Rapid-Köthen apparatus, at a standard basis weight of 70 g/m^2; two series of handsheets were prepared for each type of *in-situ* loaded pulp, namely – *before washing* (pulp resulted after calcium carbonate precipitation) and *after washing* (pulp washed in several steps for complete removal of the free calcium carbonate particles).

Analyses

The paper handsheets were characterized by:

- C*alcium carbonate content*, according to Tappi Standard T413;[15] the calcium carbonate content was also measured for *in-situ* pulp pads (obtained on the filter paper).
- *X-ray diffraction patterns* of calcium carbonate particulates were obtained on a D8 ADVANCE, Bruker-AXS apparatus, equipped with a transmission type goniometer, using nickel-filtered, CuKα radiation (λ = 1.5418Å) at 36 kV; the goniometer was scanned stepwise every 0.10° from 10 to 60° in the 2θ range; X-ray diffraction was performed only for paper sheets obtained from washed pulps.
- *SEM – Scanning electron microscopy* images were obtained on an EGA/TESCAN instrument, to identify the localization of calcium carbonate crystals into the cellulose fibre structure (lumen and fibre wall pores).
- *Optical and mechanical properties*: the tensile strength of paper sheets, expressed as breaking length, was measured on a tensile tester instrument, according to ISO 1924; the opacity of paper sheets was measured on a L&W Elrepho 2000 spectrophotometer, according to ISO 2471. To better evaluate the effects of the *in-situ* loading methods on optical and mechanical paper, a reference paper sample was obtained by conventional loading (introduction of precipitated calcium carbonate into a fibre suspension at a dosage tested for giving about the same $CaCO_3$ content as for the handsheets from *in-situ* loaded pulps).

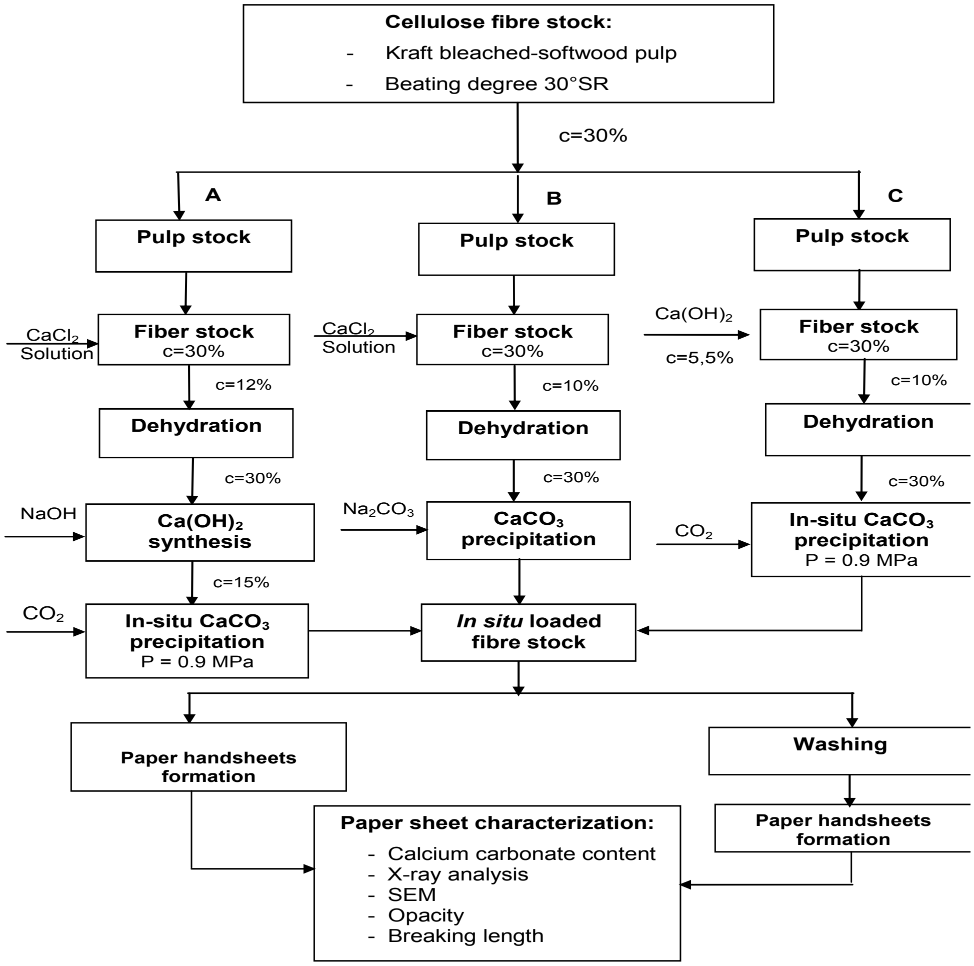


Figure 1: Experimental program for *in-situ* loaded fibres by different methods

RESULTS AND DISCUSSION

Calcium carbonate content of pulp filter pads and paper sheets

The calcium carbonate content of filter pads obtained from *in-situ* loaded pulps, before and after washing (for removing the free calcium carbonate particles), is presented in Figure 2. The calcium carbonate content is calculated from the ash content and incineration loss of the precipitated calcium carbonate, obtained by the same methods, but in the absence of fibre suspension. The double-exchange reaction – IS-PCC(B) – gives the highest precipitation yield of calcium carbonate into the cellulose fibre structure (lumen and fibre wall), namely 73% of the total precipitated $CaCO_3$ remains in the pulp after washing. The other two methods based on carbonation lead to much lower yields, 33% for IS-PCC(A) and 31% for IS-PCC(C), respectively. The difference in the yield of calcium carbonate precipitated into the fibre structure is mainly due to the more heterogeneous reaction conditions (three-phase system) in the case of carbonation (methods A and B), comparatively with the double-exchange reaction (two-phase system).

The calcium carbonate content of the handsheets obtained from both unwashed and washed pulps does not significantly differ from that of filter pads (Fig. 3). Practically, the formation of handsheets by water drainage from a diluted suspension (0.3 g/L) on forming wire has a similar effect as the washing process. However, method B gives the highest retention of calcium carbonate in paper, about 75%, while methods A and C result in only 27 and 35%, respectively, indicating that calcium carbonate is mainly precipitated at the fibre surface, from where it is easily removed by washing.

X-ray analysis

X-ray diffraction remains the main method for the identification of atom arrangement in minerals. In this study, X-ray analysis was applied to determine the polymorphic form of calcium carbonate particles retained in paper sheets obtained from *in-situ* loaded fibre pulps. Figure 4 compares the X-ray diffraction patterns of the paper samples filled by *in-situ* precipitation of calcium carbonate performed by different methods.

Precipitated calcium carbonate has been reported to occur usually in three basic polymorphic forms: calcite, vaterite and aragonite, the calcite being the most thermodynamically stable and vaterite the least, under ambient conditions. The patterns of Figure 4 show obviously that, whichever precipitation method was used, the calcium carbonate particulates present the same polymorphic form. X-ray diffraction of the $CaCO_3$ crystals precipitated in the wall and/or lumen of the fibres revealed a typical calcite diffraction pattern. As reported in literature,[16] calcite (I) is trigonal-rhombohedral in shape, *R*3*c*, with trigonal axes a = 4.99Å and c = 17.06Å. The structure has Ca atoms at the origin and in layers, every $c/6$ along c. The planar CO_3 groups are oriented perpendicularly to c.

The diffractograms in Figure 4 clearly demonstrate a strong reflection of calcite at $2\theta = 29.3°$, corresponding to the (104) plane, and at $2\theta = 39.4°$, corresponding to the $(11\bar{3})$ plane. In addition to the characteristic peaks of calcite, the X-ray diffractograms present no other characteristic peaks, typical of vaterite or aragonite.

Besides polymorphic form identification, the X-ray diffraction analysis was used to prove the presence of calcium carbonate in the lumen of fibres. In this respect, the *in-situ* loaded fibres were washed with an acid solution to remove the particles from the surface pores, the absence of which was evidenced by SEM micrographs. However, X-ray diffraction evidenced a characteristic reflection peak of calcite at 29.3^0(104), which demonstrates the presence of calcium carbonate into the fibre lumen.

Starting from the above experiment, aimed at localizing the calcium carbonate particles into the fibre lumen, a non-destructive method for evaluating calcium carbonate content of *in-situ* loading pulp or paper was developed. In this respect, the relationship between the calcium carbonate content and the ratio of the peak heights at 29.3° (104), specific to calcite, and of the peak heights at 22.5° (002), specific to cellulose, was established. Experimental data were obtained by repetitive acid washings of an *in-situ* loading pulp sample (washed for removing free $CaCO_3$ particles).

The calcium carbonate from the fibre surface pores was completely removed in a single acid washing step, as shown by the SEM images. Further on, two acid washing steps led to complete dissolution of calcium carbonate from the fibre structure. The graph plotted in Figure 5 (ash content *versus* X-ray diffraction intensity ratio) shows a very good correlation, that could be used to estimate the calcium carbonate content, based on diffraction intensity ratio measurements (ratio zero corresponding to the ash of the cellulose fibres).

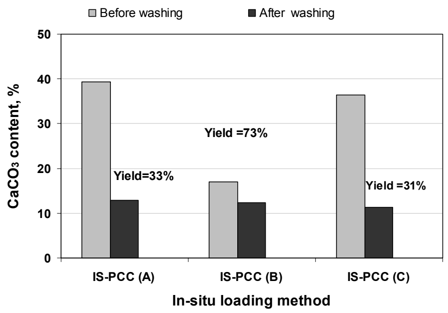


Figure 2: Calcium carbonate content of filter pads obtained from *in-situ* loaded pulps: IS-PCC(A) – $CaCl_2/NaOH/CO_2$; IS-PCC(B) – $CaCl_2/Na_2CO_3$; IS-PCC(C) – $Ca(OH)_2/CO_2$)

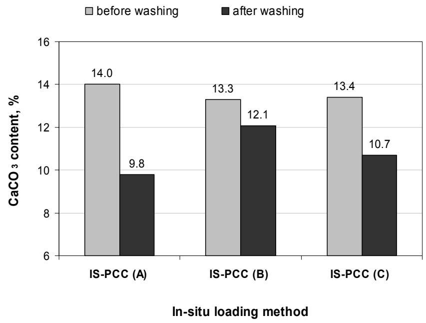


Figure 3: Calcium carbonate content of paper samples obtained by different *in-situ* loading methods: IS-PCC(A) – $CaCl_2/NaOH/CO_2$; IS-PCC(B) – $CaCl_2/Na_2CO_3$; IS-PCC(C) – $Ca(OH)_2/CO_2$

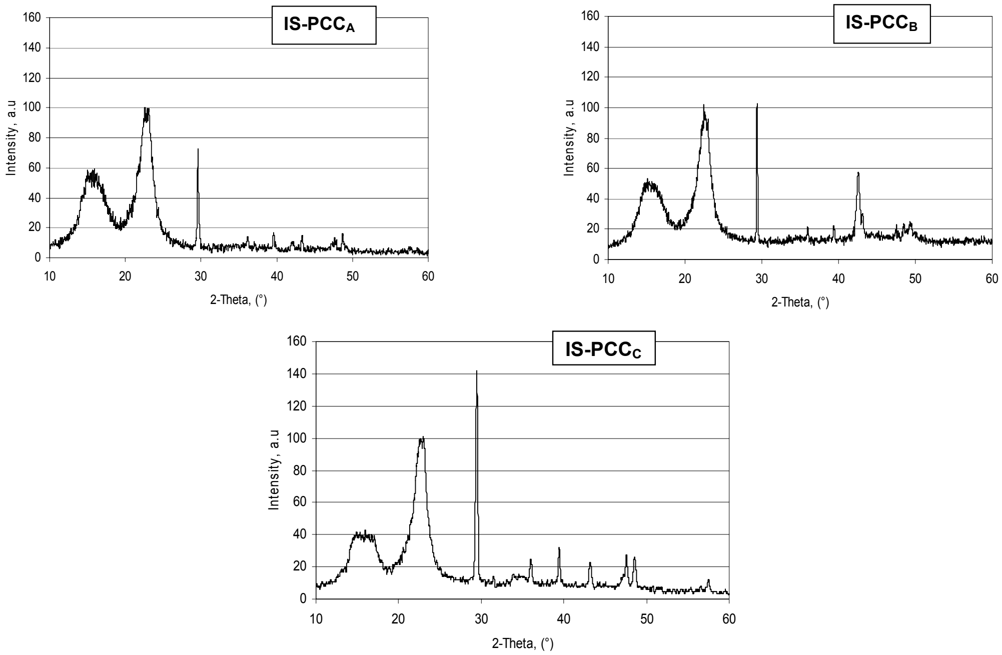


Figure 4: X-ray diffraction patterns of paper samples obtained by different *in-situ* loading methods: IS-PCC(A) – $CaCl_2/NaOH/CO_2$; IS-PCC(B) – $CaCl_2/Na_2CO_3$; IS-PCC(C) – $Ca(OH)_2/CO_2$

Scanning electron microscopic images

The examination of the SEM images (Figs. 6, 7) evidenced the presence of calcium carbonate crystals within both lumen and fibre wall pores. The results also indicated that the crystallization of $CaCO_3$ occurs with the formation of calcite micro-crystals of specific shape. SEM micrographs show that, at about the same content of calcium carbonate, the highest number of visible surface crystals of precipitated calcium carbonate appears for method B (double-exchange reaction – $CaCl_2/Na_2CO_3$), the lowest occurring in the case of method C (fibre saturation with $Ca(OH)_2$, followed by reaction with CO_2). In the last case, calcium carbonate particles have a smaller size and a slight presence within fibre surface pores, indicating that precipitation occurs mainly within fibre lumen.

Physical-mechanical properties of paper samples

It is well-known that the size, shape and distribution of pigment particles into the paper structure influence strongly and in opposite directions the optical and, respectively, the mechanical resistance of paper. X-ray and SEM analyses showed differences among the *in-situ* precipitation methods with regard to particle size and distribution within the fibre cell wall and lumen, as reflected by the levels of the opacity and tensile strength of paper sheets (Figs. 8 and 9). The results are presented comparatively with a reference paper sample obtained by conventional loading with precipitated calcium carbonate.

The graphs from Figure 8 show the highest levels of paper opacity in the case of unwashed *in-situ* loaded fibres. The effect is explained by the presence of well-dispersed pigment particles at the fibre surface, as well as within the fibre wall pores. By washing, the free calcium carbonate particles are removed and, consequently, opacity slightly decreases.

The *in-situ* loaded paper obtained by fibre saturation with calcium hydroxide and carbonation (method C) presents the highest opacity level after washing, although the $CaCO_3$ content is slightly lower than in case of the other two *in-situ* precipitation methods. These differences could be explained by the smaller $CaCO_3$ particle size, as shown by the SEM micrographs. At a calcium carbonate content close to that of the washed *in-situ* loaded samples, the opacity of the conventional loaded paper (reference) is significantly lower than that of the *in-situ* loaded samples. The lower opacity of the reference sample is due to the less uniform distribution of the PCC particles into the paper structure (mainly the large particles are retained through filtration). Thus, one can conclude that *in-situ* loading, especially by methods B and C, is more efficient with regard to the optical properties of the paper sheets.

The graphs plotted in Figure 9 show that all *in-situ* loading methods lead to lower paper strength (expressed in Figure 8 as breaking length) as compared to conventional loading ones (reference sample). In the case of unwashed pulps, the low paper strength is due mainly to the higher content of calcium carbonate and to the presence of free particles on the fibre surface. By pulp washing, a part of the calcium carbonate from the fibre surface is removed and, consequently, tensile strength slightly increases. It is obvious that, at a comparable level of calcium carbonate content, *in-situ* loading gives a lower paper strength than conventional loading, which is an effect proved in some previous studies of ours.[13,14]

A better evaluation of the loading method effectiveness could be done by representing graphically a pair of strength and optical properties of the paper sheet. The levels of opacity and breaking length for each loading method are represented in Figure 10. The graphical representation evidences clearly that method C [$Ca(OH)_2/CO_2$] assures the best combination of the two paper properties, which are influenced in opposite directions by filler loading.

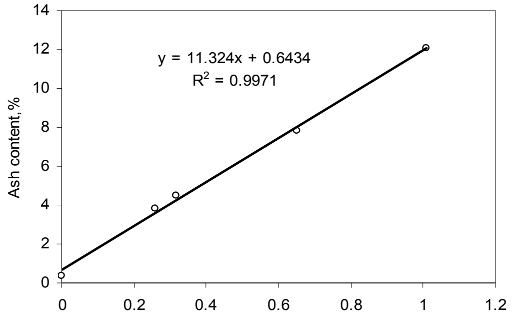
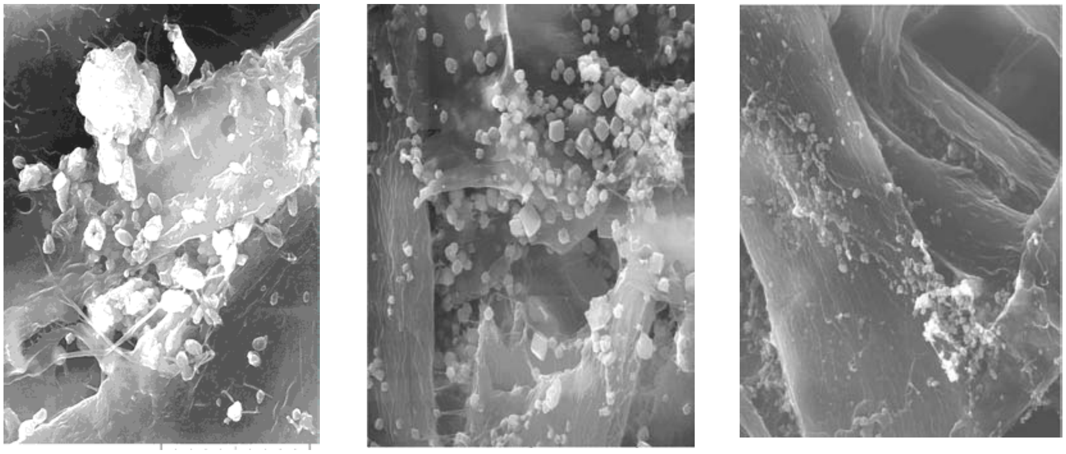


Figure 5: Correlation between ratio of I_{104} / I_{002} diffraction intensity and ash content of paper samples filled *in-situ* by method A ($CaCl_2/NaOH/CO_2$) and washed with an acid solution

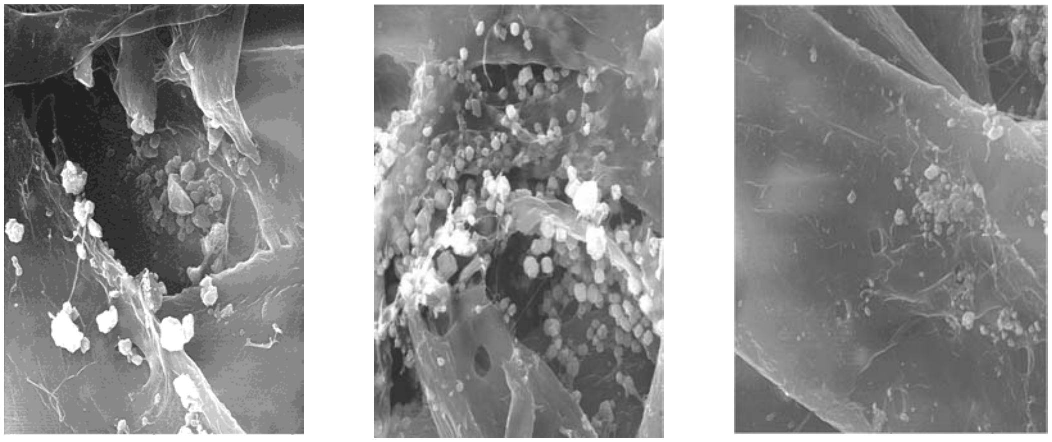


IS-PCC$_A$: $CaCl_2/NaOH/CO_2$
$CaCO_3$ content = 14%

IS-PCC$_B$: $CaCl_2/Na_2CO_3$
$CaCO_3$ content = 13.28%

IS-PCC$_C$: $Ca(OH)_2/CO_2$
$CaCO_3$ content = 13.41% $_3$

Figure 6: SEM images of paper samples, obtained from *in-situ* loading pulps, before washing



IS-PPC$_A$: $CaCl_2/NaOH/CO_2$
$CaCO_3$ content = 9.78%

IS-PCC$_B$: $CaCl_2/Na_2CO_3$
$CaCO_3$ content = 12.06%

IS-PCC$_C$: $Ca(OH)_2/CO_2$
$CaCO_3$ content =10.69%

Figure 7: SEM images of paper samples, obtained from *in-situ* loading pulps, after washing

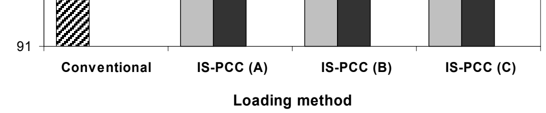


Figure 8: Opacity of paper samples obtained by different *in-situ* loading methods: IS-PCC(A) – $CaCl_2/NaOH/CO_2$; IS-PCC(B) – $CaCl_2/Na_2CO_3$; IS-PCC(C) – $Ca(OH)_2/CO_2$

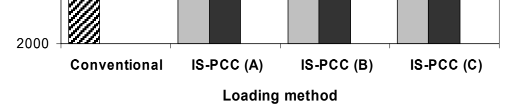


Figure 9: Breaking length of paper samples obtained by different loading methods: IS-PCC(A) – $CaCl_2/NaOH/CO_2$; IS-PCC(B) – $CaCl_2/Na_2CO_3$; IS-PCC(C) – $Ca(OH)_2/CO_2$

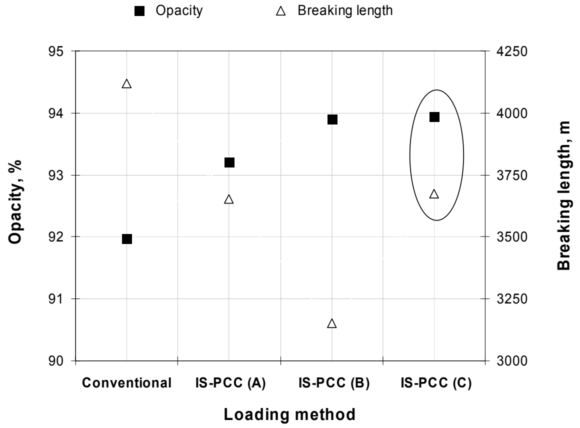


Figure 10: Opacity and breaking length of paper obtained by different loading methods: IS-PCC(A) – $CaCl_2/NaOH/CO_2$; IS-PCC(B) – $CaCl_2/Na_2CO_3$; IS-PCC(C) – $Ca(OH)_2/CO_2$

CONCLUSIONS

In-situ loading of cellulose fibres with calcium carbonate was performed by the following methods: IS-PCC(A) – the reaction of calcium chloride with sodium hydroxide, followed by carbonation with carbon dioxide; IS-PCC(B) – double-exchange reaction of calcium chloride with calcium carbonate; IS-PCC(C) – fibre saturation with calcium hydroxide, followed by carbonation with carbon dioxide. The analyses and investigations on *in-situ* loaded paper led to the conclusions below.

The yield of calcium carbonate precipitation into the wall pores and fibre lumen depends strongly on the *in-situ* precipitation method. The double-exchange reaction – IS-PCC(B) gives the highest *in-situ* precipitation yield, respectively 78% of the total precipitated $CaCO_3$ remain in pulp after washing. The other two methods, based on carbonation processes, lead to lower yields [IS-PCC(A) – 35%, and IS-PCC(C) – 36%], as due to the more heterogeneous reaction conditions.

The analysis of the X-ray diffraction patterns and SEM images show that, regardless of the *in-situ* precipitation method applied, the calcium carbonate particulates present a typical calcite diffraction pattern, precipitation occurring in both the lumen and the wall pores of the cellulose fibres. However, these analyses evidenced significant differences among the *in-situ* precipitation methods as to particle sizes and their distribution into the fibre wall and lumen.

The optical and mechanical strength properties are strongly influenced by the loading method applied. At about the same level of calcium carbonate content, all paper samples with *in-situ* loading show higher opacity and lower tensile strength than the reference paper obtained by conventional loading. Among the *in-situ* loading methods, method C (fibre saturation with calcium hydroxide and carbonation with CO_2) provides the optimum combination of optical and strength properties.

However, the double-exchange reaction method (B) appears as the most effective one for *in-situ* loading of printing paper, for the following reasons: about 75% of $CaCO_3$ resulting by *in-situ* precipitation is finely retained in the paper sheet, comparatively with 27% – method A, and 35% – method C; paper opacity is about the same as that obtained by method C and much higher than that obtained by conventional loading; a lower tensile strength (about 18%) should not be a problem because printing papers request a relatively low strength level, which can be easily optimized by using a strength additive, whose cost is compensated by the high retention yield.

REFERENCES

[1] E. Bobu and V. I. Popa, in "Chemical-Colloidal Processes in Papermaking", (in Romanian), Cermi Press, Iasi, Romania, 1998, pp. 175-187.

[2] K. Beazley, in "Papermaking Fillers. A Literature Review", Pira International, Surrey, U.K., 1993, pp. 21-29.

[3] R. Subramanian and H. Paulapuro, *Procs. Symp. New Technologies in Non-Wood Fiber Pulping and Papermaking*, edited by Zhan Huaiyu, Chen Fangang and Fu Shiyu, South China University Press, 2006, pp. 270-276.

[4] L. Lin, X. Yin, E. Retulainen and M. M. Nazhad, *Appita J.*, **60**, 469 (2007).

[5] M. A. Hubbe and R. A. Gill, *Procs. Spring Tech. Conf.*, Tappi Press, Atlanta, 2004.

[6] L. Li, A. Collis and R. Pelton, *J. Pulp Pap. Sci.*, **28**, 267 (2002).

[7] J. H. Klugness, M. L. Strolka, M. S. Sykes, F. Tan, S. M. AbuBakr, W. Witek and O. U. Helse, *Procs. Tappi Joint Conference*, Tappi Press, Atlanta, 1999, pp. 1047-1053.

[8] R. Subramanian, T. Maloney, T. Kang and H. Paulapuro, *Pap. Technol.*, **47**, 27 (2005).

[9] J. H. Klugness, M. S. Sykes, E. Tan, S. Abubakr and J. D. Eisenwasser, *Tappi J.*, **79**, 267 (1996).

[10] K. Doelle, O. Heise, J. H. Klungness and S. M. AbuBakr, *Specialty & Technical Papers Europe Conference*, Berlin, Germany, 2000.

[11] P. Silenius, *Licentiate Thesis*, Lappeenranta University of Technology, Department of Chemical Technology, 1996, pp. 94-105.

[12] S. V. Chauhan, P. S. Singh and K. B. Pramod, *BioResources*, **2**, 560 (2007).

[13] M. Ciobanu and E. Bobu, *Environ. Eng. Manag. J.*, **8**, 307 (2009).

[14] E. Bobu and M. Ciobanu, *Celuloza si Hartie*, **56**, 12 (2007).

[15] *** T413 – Ash in Paper and Board, *Tappi Test Methods*, Tappi Press, Atlanta, USA, 1999.

[16] P. Obrocea, E. Bobu and D. Gavrilescu, “Paper Technology. Practical Applications”, vol. II, (in Romanian), Rotaprint I. P., Iasi, 1987, 67 pp.

[17] T. Menahem and Y. Mastai, *J. Cryst. Growth*, **310**, 3552 (2008).