Alternative filler recovery from paper waste stream

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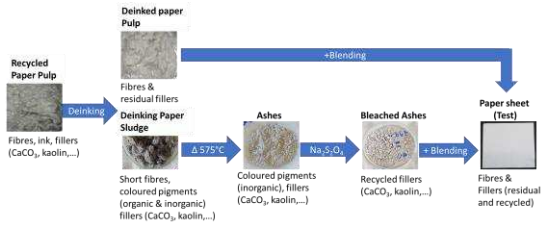
Abstract

The study is a first investigation of the feasibility to preserve recycled fillers (e.g. calcium carbonate, kaolin) from deinking paper sludge for newspaper production using an alternative approach respect to the actual methods. Deinking paper sludge was incinerated at 575°C. The thermal stability of the incinerated sludge (ash) was evaluated by infrared analysis. Subsequently, the resulting ash was bleached by sodium dithionite. The particle size of the ashes was analysed by laser diffraction. The effect of recycled fillers on recycled paper pulp, after blending, was evaluated by the analysis of the physical and optical properties of the obtained paper sheets. Analysis showed the conservation of the calcium carbonate and other fillers' molecular structure, both after incineration of the sludge and after bleaching. The dithionite treatment of the ashes resulted in ISO brightness levels of more than 70. The brightness was stable over one month. Paper sheets made by blending the bleached ashes with recycled paper showed an improvement of brightness and opacity but a decrease in terms of porosity and breaking length compared to paper sheets made without any filler. The proposed method still requires further studies to evaluate the economical application but offers an opportunity for the recycling of inorganic materials and valorisation of the sludge.

Keywords: deinking paper sludge, ashes, incineration, bleaching, dithionite, filler

Graphical abstract



Statement of novelty

In paper recycling, inorganic materials (ink and fillers) are removed by deinking the recycled paper, generating a waste stream of deinking paper sludge. The side stream could be valorised as raw material after incineration at 850-900°C [1,9], for road construction. The present study offers a new concept towards more valuable valorisation. Research shows the possibility to preserve the molecular structure of fillers by incineration of the waste stream at 575°C. By subsequently bleaching the resulting ashes, recycled fillers are obtained with sufficient brightness to make them suitable for newspaper production, increasing paper brightness and opacity compared to paper sheets made without any filler. This offers a potential improving the final process yield by avoiding the purchase of fresh fillers.

Introduction

Paper & Pulp Industry is one of the main manufacturing activities in the world, having a global revenue of around 564 billion U.S.D. [1]. Like in any other manufacturing activity, different waste streams are generated during paper production [2]. Those waste streams are recovered for economic, environmental and social reasons [3,4]. For example, the waste stream valorisation is one of the goals of the European Commission to reach climate neutrality by 2050 [5].

In the case of Paper & Pulp Industry, around 45 kg of sludge (dry) is generated in the production of 1 tonne of paper [2], 11 million tons of waste is produced only in Europe. The landfilling is the major option, in fact, around the 70-75 % of paper mill's solid waste was disposed of in a landfill. However, the disposal in landfill is facing prohibitive costs together with public and legislative opposition. The residual 25-30 % is recovered by the application in different fields, such as land application (composting) and incineration [2].

In this study, focus was on the deinking paper sludge, a waste stream originating from the deinking process of recycled paper for newspaper manufacturing. This waste is generated during the removal of the ink particles present in the recycled paper by flotation. The deinking paper sludge is composed of three components, water, organic matter, such as fibres, organic pigments and surfactant, and inorganic matter (insoluble pigments and soluble salts). It is estimated that magazine and newspaper products contain typically 1 to 2 % of ink (i.e. carbon black pigment, acrylic resin, metal complexes) and ash content around 14-20 % [2,6].

Focus is on the deinking paper sludge from newspaper production because it is averaging 68 % recycled paper content (the highest value if compared with other paper products such as cardboard) [7] and around 16-17 million tons are produced worldwide [8]. In literature, it has been reported that around 300 kg of dry sludge is produced for each dry ton of recycled paper [2]. These numbers make this waste an interesting case study. The deinking sludge is a source of short fibres. In literature, the recovery of fibres from deinking sludge by fractionation was reported [9]. The authors incorporated the recovered fibres in paper sheets mainly composed of mechanical fibres. A reduction in tensile strength was observed. However, the interest of this article was on the inorganic matter present in the sludge. The deinking paper sludge is a source of non-hazardous solid inorganic material [10-12]. In fact, it is composed of chemicals used for both colouration and filling. Therefore, this waste can be valorised having a relevant impact in the paper recycling industry. The principal components are fillers or coating agents, mainly consisting of kaolin and calcium carbonate but also other chemicals, such as talc, calcium sulphate and titanium oxide, are applied. Moreover, further inorganic materials are used for coating and colouration, such as zinc oxide, magnesium oxide and coloured complexes of iron, copper and chrome [13]. In literature, the use of deinking sludge as filler in polyethylene composites was studied [14,15]. It was possible to obtain a good balance in terms of physical properties adding Maleic-Anhydride Polypropylene to improve the interactions between sludge and plastic.

The actual valorisation of the inorganic components of the deinking sludge is found in the construction industry. After burning the sludge at temperatures up to 850 °C, the ashes are used in the production of concrete [2, 16]. Studies were performed to find alternative applications. Clay from deinking sludge ashes was functionalised for dye removal [17]. Another study focused on the use of ashes for geopolymer formation [18]. The application of fly ashes from a cogeneration plant for paper production has been reported. Hereto, the fly ashes were blended with starch and used as a surface sizing agent [19]. An increase of the rupture strength was observed; however, the dry strength is a result of the addition of starch, not from the ash.

Based on the need to reduce the waste during the production of recycled paper, the present study investigates the scientific feasibility of the recovery of inorganic material from deinking paper sludge, preserving the kaolin and calcium carbonate structure and having an ISO brightness of more than 55 because it is the threshold for newsprint [20]. The final purpose is to use these inorganic compounds as recycled fillers for newspapers. Fillers are used for improving paper properties such as brightness and opacity. Papermakers tend to use only one type of filler, instead, recycled fillers are a mixture of components. However, newsprint is a cheap product and does not require high physical properties, so, the *in-situ* production of recycled fillers for the deinking paper sludge becomes useful to increase the yield of the entire process and be a partial replacement of fresh fillers. The main problem is that in the current process the ashes are burned at temperatures up to 850°C to produce energy. In terms of chemistry, the calcium oxide is made from calcium carbonate by the release of carbon anhydride. Calcium oxide is a valuable material for the concrete industry if separated from the other inorganics but not useful as paper filler. The reasons are its morphology (particle size, particle size distribution, surface area, particle shape and surface chemistry) and its chemical instability. When calcium oxide is added to wet paper pulp, calcium hydroxide is formed by the reaction between calcium oxide and water. Moreover, calcium hydroxide absorbs the carbon anhydride present in the air. For that reason, its structure changes by the time. Therefore, before being useful as a filler, it is necessary to re-synthesize the calcium carbonate by the addition of water and carbon anhydride to calcium oxide [21-23]. CalciTech Synthetic Minerals Ltd have patented a process were calcium derivates from paper sludge ashes are solubilised using a “promotor” (ex. sorbitol) and separated from the impurities. Afterwards, calcium derivates react with carbon dioxide to form calcium carbonate [24]. However, also this method requires to re-synthesise the calcium carbonate. Wet Air Oxidation under high temperature and pressure was proposed as an alternative technique to recover the fillers. The deinking sludge went first through a stage of hydrothermal hydrolysis in alkali conditions to remove fibres and stickies. In the second stage, the residual solid was subjected to hydrothermal oxidation to remove the ink. The result was a mixture of fillers and coating materials [25]. However, the necessity to work under pressure requires high installation costs, i.e. around 15 million U.S.D. for 10000 gallons per day unit [26]. Moreover, a cost of 38 U.S.D./ton of sludge was estimated [2].

This study aimed to evaluate if the recovery of inorganic components (e.g. calcium carbonate, kaolin) from the deinking paper sludge was scientifically possible using the actual technologies, preserving their molecular structure and leaving them suitable to be used as fillers in newspaper production.

The alternative approach consists of two steps, i.e. controlled incineration of organic components followed by bleaching of the solids. In the first step, two incineration temperatures, 525 and 575 °C were evaluated instead of the 850-900°C that is currently applied in the construction industry. This process at a temperature above 500 °C permits to remove by combustion the organic matter (short fibres and ink from organic sources) present in the sludge that can be also absorbed to the inorganic materials [27, 28]. Carbon black from black ink is combusted at temperatures around 500 and 550 °C [29, 30]. The incineration at 575°C avoids the decomposition of the fillers. Kaolin, talc and calcium sulphate are stable

up to 900°C [31, 32]. Instead, calcium carbonate is sensible to decomposition at lower temperatures (600 °C) [33]. The second step is the bleaching using sodium dithionite because coloured metal oxides (i.e. iron oxides) can still be present after this incineration step [2]. Dithionite is a reducing agent used in the purification of raw kaolin clay and precipitated calcium carbonate [34-36] because it solubilises undesired coloured inorganics such as iron oxides. At the end of these treatments, the bleached ashes consist of a mixture of calcium carbonate, kaolin and other fillers such as talc, for this study case. In the final part of our study, bleached ashes and recycled paper pulp were blended and paper sheets were made. The impact of the bleached ashes was evaluated by the measurement of the physical properties of the paper sheets.

Experimental part

Materials and Chemicals

The starting materials were provided from paper industry in Belgium: DeInked paper Pulp (DIP, ash 575 °C: 15.7 %; Consistency (K): 5.1 %) and Deinking Paper Sludge from a deinked paper pulp (DPS). All other chemicals and materials were purchased from Acros Organics.

Incineration

The incineration was done for 1 h at atmospheric pressure and in presence of air using a furnace ("Nabertherm 30-3000°C", Nabertherm, Germany, temperature accuracy ± 3 °C). 0.5 g DPS was burned at 525°C in a crucible and collected ashes were designated Ash525. The same amount was incinerated at 575°C which provided ashes that were called Ash575. 0.5 g of the latter was burned at 850°C which resulted in Ash850. A total amount of 50 g of Ash575 was prepared by burning 75 g of ashes for 3 hours divided into 15 crucibles. The level of accuracy was of ±0.005 g. A list of the samples is reported in Table 1.

Ashes bleaching

1g of Ash575 was suspended in 50 ml of water. The mixture was heated to 50 °C and 33 mg of sodium dithionite was added. The reaction ran for 1 h. The mixture was centrifuged (1 h, 20 °C, 4223 Relative centrifugal force, RCF) and the solid was washed with 50 ml of water and centrifuged again. As a final step, the bleached ashes (Ash575_Bleached) were dried overnight at 50 °C and stored under atmospheric conditions. A list of the samples is reported in Table 1.

Analytical instruments and analysis

Brightness analysis

The brightness of ashes and DPS was measured following the standard procedure ISO 2470.

Infrared analysis

The infrared analysis of dry calcium carbonate, the different ashes and DPS was done using an infrared spectrometer (FTIR Microscope Lumos, Bruker, Belgium). Each sample was analyzed doing 64 scans in the wavenumber range between 4000 and 600 cm^{-1}.

X-ray analysis

X-ray fluorescence (XRF) was used for qualitative analysis to detect possible hazardous materials. The instrument used was QuanX EC from Thermo Electron Corporation. Around 1 g of Ash575 was placed in the cuvette and analysed at two

different acquisition rates (low and medium).

Brightness stability

Around 0.2 g of Ash575_Bleached was left on a petri dish under the exposure of air and light. An amount around 0.2 g of Ash575_Bleached, was placed in a polyethylene bag and in a black pack to avoid the lights. For a period of four weeks, the ISO brightness of the samples was measured once a week.

Paper sheet analysis of recycled paper with recycled ashes as filler

Bleaching

50 g of Ash575 were added to 2200 g of water and heated to 50 °C under stirring. 1.5 g of sodium dithionite was added. After 1 h of reaction, the mixture was washed twice (2 x 2 L) while separating the ashes by centrifugation (1 h, 20 °C, 4223 RCF). The obtained solid (Ash575_Bleached) (49 g dry weight) was left in 500 g of water. A sample of 1 g of the wet mixture was dried, and the brightness was measured. Half of the mixture of 500 g was de-agglomerated in a ball mill, Pulverisette 5 (Fritsch, Belgium), and passed through a filter of 0.16 mm slots. The differences in particle size of the ashes before and after de-agglomeration were measured by laser diffraction using a Spraytec (Malvern Panalytical, United Kingdom). A list of the samples is reported in Table 1.

Blending

Ash575_Bleached and DIP (K: 5.1 %) were blended for 1 h using a Blender N50CE (Hobart, United States). The pulp was recovered and stored in a closed pot and left in a fridge. Three different pulps were prepared.

Pulp 1: 1025 g of DIP (52.28 g of solid of which 8.21 g of ashes) was blended without the addition of the ashes.

Pulp 2: 1030 g of DIP (52.53 g of solid of which 8.25 g of ashes) was mixed with Ash575_Bleached without de-agglomeration (5.15 g of dry mass) Final composition, 57.68 g of solid (13.40 g of ashes, 23.2%).

Pulp 3: 1025 g of DIP (52.28 g of solid of which 8.21 g of ashes) was mixed with Ash575_Bleached after de-agglomeration (5.13 g of dry mass). Final composition, 57,41 g of solid (13.34 g of ashes, 23.2%). A list of the samples is reported in Table 1.

Paper sheets analysis

Paper sheets were made from the pulps 1, 2 and 3 following the procedure ISO 5269-1 and the mechanical/physical properties were measured by the following standard procedures: Brightness ISO 2470, Opacity ISO 2471, Porosity ISO 5636-3, Breaking Length ISO 1924-2, Tearing power ISO 1974, Ash content ISO 1762.

Results and Discussion

DPS was incinerated at two different temperatures, 525 and 575°C giving corresponding ashes Ash525 and Ash575. In the paper industry, the ash content is determined at 525°C (method TAPPI T 211 om-02). For this reason, the first temperature to test for ash recycling was selected at 525°C. However, in order to be sure that all carbon black was combusted, a higher temperature was selected as a second testing point. Since it is known in the literature that calcium carbonate starts to decompose at temperatures higher than 600°C (≈1% weight loss at 600°C) [33], the second temperature was selected to be 575°C. This higher temperature could lead to a better compromise between molecular structure preservation and brightness of the ashes.

The mass loss between Ash525 and Ash575 differs only 2% (Table 2) and the brightness of the sample Ash575 is higher

and guarantees to pass the threshold of 55 % ISO Brightness. For these reasons, the ashes obtained at 575°C were used for further experiments on bleaching and after this step for blending with DIP for papermaking and the following testing.

Comparison of ashes at different temperatures

Pictures of DPS, Ash525, Ash575 and Ash850 are shown in Figure 1. Mass loss and brightness values of the samples are reported in Table 2.

In the DPS (Figure 1A), it is possible to observe brown and white fibres together with ink and white fillers. The images show an increase in the brightness of DPS after incineration at 525°C (Figure 1A and 1B). This increase is caused by the combustion of coloured material such as brown fibres and organic inks. This is confirmed by the incineration results in Table 2 and the absence of fibres in Figure 1B. Also, higher brightness is observed for ashes incinerated at 575°C compared to 525°C (Figure 1B and 1C). The ISO values between Ash525 and Ash575 (Table 2) are close. In fact, both samples differ 4 points in terms of brightness. The incineration at 850°C resulted in a high brightness level of 78. It is possible to suppose that such an increase is caused by a change in the molecular structure of the inorganic components and consequently a variation in terms of the crystal structure and refractive index.

The Ashes575 were also analysed by XRF to detect possible hazardous materials. The element observed were: Calcium, Aluminium, Silicon, Iron, Manganese, Titanium, Copper, Zinc. The resulting spectra are reported in Figure 2. Calcium is the main component detected.

The presence of aluminium, silicon, in Figure 2A confirms the presence of Kaolin. Calcium, titanium (in traces) and zinc (in traces) in Figure 2B established the presence of calcium carbonate, titanium dioxide and zinc salts used as fillers. [2]. Iron is present in wood, also in the fresh process water and it is a component of coloured pigments. Manganese is present in wood and in fresh process water. Copper is a wood component, and in coloured inorganic pigments [13].

Analysis by infrared (Figure 3) shows in DPS the presence of cellulosic fibres by a peak at 1029 cm^{-1} that correspond to the vibrations of the ether bonds of cellulose. Also, the hydroxyl vibration at 3305 cm^{-1} is indicative for the presence of cellulose [37]. The peak at 2899 cm^{-1} is correlated to the stretching vibration of aliphatic groups of biopolymers (cellulose, hemicellulose and lignin) [9]. The peak at around 1644 cm^{-1} can be correlated to the carbonyl groups of lignin. The peaks at 1410 cm^{-1}, 872 cm^{-1} and 711 cm^{-1} are typical for calcium carbonate. A small peak at 1792 cm^{-1} can be correlated to the presence of magnesium in the carbonate structure [15]. At 3691 cm^{-1}, the hydroxyl stretching of kaolin (Al_2O_3 $2SiO_2$ $2H_2O$) and/or talc ($Mg_3SiO_4O_{10}(OH)$) is observed.

In Figure 4, which depicts the ashes obtained at different temperatures, the fibres are no more present in the ashes, indicated by the absence of the hydroxyl groups at around 3300 cm^{-1}. The peak at 3691 cm^{-1} is also no more present which shows the dehydration of kaolin and talc by incineration. In the same graph, it is also possible to observe carbonate peaks (CO_3^{2-}) at 1409 cm^{-1} (asymmetric stretching), 873 cm^{-1} (in-plane deformation vibrations) and 712 cm^{-1} (out of plane deformation vibrations) [38]. Moreover, the small peak at around 1796 cm^{-1} is still observed. The infrared spectrum of the ashes obtained by the incineration at 525 and 575°C was compared with the spectrum of calcium carbonate (Figure 4). After incineration at 525 and 575°C, the molecular structure of calcium carbonate was not influenced by incineration. Also, there is no difference between the two incineration temperatures. Furthermore, it is possible to reveal the peak of Si-O stretching at 1017 cm^{-1} originating from silicate fillers such as kaolin and talc [38]. A peak at 671 cm^{-1} was observed and correlated to the symmetrical bending of Si-O from kaolin and talc. These peaks were previously overlapped by the

cellulosic matter. Instead, the incineration at 850°C changes the structure of the inorganic material, as reported in the literature [31, 32]. The carbonate peaks are strongly reduced with the formation of one main peak at 903 cm^{-1}. The significant difference between the infrared of the Ash850 compared to the other is a confirmation of the relevant structural changed of the inorganic materials.

Estimation of calcium carbonate amount

The experimental data in Table 2 allow to estimate the calcium carbonate content in the sample Ash575. The absence of peaks of hydroxyl (-O-H) stretching at around 3600 cm^{-1} (see Figure 4) permits to conclude for the complete dehydration of the silicates (kaolin and talc) at 575°C [35, 38]. As reported in the literature, carbon black is almost 100 % decomposed [31] and the metals such as iron are present in traces in their oxide form [2]. For these reasons, it can be hypothesized that the mass loss observed for the incineration of the ashes from 575 to 850 °C is caused by the decomposition of calcium carbonate to calcium oxide. Based on these assumptions, the calcium carbonate amount can be calculated for 0.5 g of Ash575 incinerated at 850°C.

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \quad (1)$$

The data are reported in Table 3 and the calculation shows that calcium carbonate is expected to be present at around 66 % in the ashes at 575 °C. It also indicates that the preservation of this compound must be taken into account.

The results permit to provide an estimation of the composition of the deinking sludge and Ash575. About the DPS, the incineration at 575 °C caused a mass loss of 32 %. It is possible to consider that the DPS is composed of 32 % of organic matter and 68 % of inorganic matter. Instead, the Ash575 is composed of 66 % of calcium carbonate and the remaining 44 % is a mixture of silicates such as kaolin and talc.

Bleaching

Ash575_Bleached is shown in Figure 1E. The values of brightness and mass loss caused by the bleaching step are reported in Table 2.

The Ash575_Bleached is brighter than Ash575 and brightness is similar to Ash850 (Figure 1, Table 2). The Ash575_Bleached has a suitable brightness for application in magazine production. Bleaching with sodium dithionite permitted to reach brightness values over 70 with a mass loss of 2 %. This value is close to the brightness level of the fresh fillers that are 70 ISO or higher [39]. The chemical explanation for the increase of brightness is that the organic components (cellulose fibres, organic pigments, etc...) are removed by combustion during the incineration at 575°C. The further treatment using dithionite permits to solubilize and remove by filtration coloured materials comprising oxides of iron and manganese [34-36]. An example of a bleaching reaction using sodium dithionite is the reduction of ferric oxide to the ferrous state, following the equation reported below [40]:

$$S_2O_4^{2-} + 2Fe^{3+} \rightarrow 2SO_2 + 2Fe^{2+} \quad (2)$$

The spectra of Ash575 and Ash575_Bleached were compared (Figure 5A and Figure 5B).

The bleaching treatment did not modify the structure of calcium carbonate and other fillers. For that reason, the reaction using sodium dithionite is a suitable method to improve the brightness of recycled fillers because their molecular structure is not altered by the process. It has also a major advantage to processes cited in the literature because pH adjustment at around 2-3 [34,35] is not required to remove the contaminants, moreover, the addition of other chemicals to form again

the calcium carbonate [36] is not necessary.

Brightness stability

Atmospheric conditions such as light, temperature and presence of oxygen can cause a decrease in brightness. For that reason, the brightness of Ash575_Bleached was measured over a period of 4 weeks to evaluate the brightness stability. The data are reported in Figure 6. The ISO value is constant over time which means that, in terms of brightness, the bleached ashes are stable under exposure to air and solar light.

Paper sheet analysis of recycled paper with recycled ashes as filler

Milling and deagglomeration

The particle sizes of Ashes575_Bleached before and after deagglomeration are reported in Figure 7, and the data are reported in Table 4.

An effective de-agglomeration is observed upon milling as the biggest particles are reduced (Dv (90) from 314.40 to 44.88 µm). The fines are not too much reduced (from 3.00 µm to 2.56 µm). The use of the un-milled ashes as fillers looks prohibitive taking into account the typical paper sheet thickness (the nominal calliper of newsprint is 85 µm) [41]. Milling improves largely the usefulness of the recycled fillers.

Paper sheet characterisation

An example of a paper sheet is showed in Figure 8. The results from the paper sheets analysis are reported in Table 5.

The results show improvements in terms of brightness and opacity of the Pulps 2 and 3 compared to Pulp 1 that does not contain recycled fillers. For example, the brightness of Pulp 3 has a small but important increase of 2 ISO points towards the threshold of 55 ISO Brightness. Moreover, the opacity has an increase of 1.7 % and 3.3 % respectively in Pulp 2 and Pulp 3 compared to Pulp 1. The tearing power is not strongly influenced by the addition of recycled fillers. However, porosity and breaking length properties decreased in Pulp 2 and 3 in comparison to Pulp 1. The major decrease of breaking length is observed in Pulp 2. Instead, the porosity is higher in Pulp 3. The positive effect on brightness and opacity are correlated to the light scattering and absorption of the fillers. The detrimental effect of the fillers on these two mechanical properties (porosity and breaking length) is known in literature [42]. It is correlated to the lack of hydrogen bonds between fillers and cellulose fibres. Consequently, bigger filler particles cause more severe structural problems in the papermaking. Further work has to be done on the particle size optimisation because the bleached ashes are still too large (fresh filler agent has a particle size range of 0.1-10 µm [42]).

Mass recovery

The starting ashes content of the DIP is 15.7 % (see "**Materials and Chemicals**" and Table 5) of the total pulp mass. The ashes measured on the paper sheet are 13.0 %; it means that in the papermaking there is a systematic ash loss of around 2.7 %. It can also be observed that Pulp 2 has the same percentage of ashes as Pulp 3 (23.2 %). However, they have different values of ash content in the paper sheets (respectively 18.2 and 20.5 %). Taking into account the 2.7 % of systematic mass loss, it is possible to consider that the recycled ashes added in Pulp 3 are quantitatively present in the paper sheet. Therefore, Pulp 3 shows a better blending quality than Pulp 2. The difference is caused by the ash's particle sizes that are smaller in the case of Pulp 3.

The overall scheme of this study about filler recovery can be summarised as presented in Figure 9.

The process permits to recover a mixture of inorganic materials (calcium carbonate, kaolin and talc) with a brightness value that makes it suitable for use as a filler in newsprint production. Considering the data reported in the literature [2], it is possible to estimate that around 200 kg of recycled fillers is produced by the incineration at 575 °C and further bleaching of 300 kg of dry deinking sludge (66.6 % of the total mass) generated during the deinking of 1000 kg of recycled paper.

Future research

Further studies will enable to fine-tune the blending by improving de-agglomeration of the ashes to make particle sizes with a maximum of 10 µm. Furthermore, the microstructure of the particles should be investigated using different analytical techniques such as SEM (Scanning Electron Microscope) and XRD (X-ray diffraction). Moreover, the amount of recycled filler to be added to the paper pulp should be evaluated. The addition of a retention aid (i.e. bentonite and polyacrylamide) to reduce the loss of fine particles could optimise the blending conditions. In a further step, a comparison of recycled with fresh fillers and a full economic study, considering also the energy required and produced, will allow to evaluate a scale-up and possible implementation in the production of newsprints from recycled paper. Herein, the use or not of the bleaching step will have to be considered based on its contribution to the process cost. If the evaluation gives promising results, the study of different sludges from the paper industry can be considered to evaluate their implementation in other mills.

Conclusion

This study permitted to confirm that fillers can be recovered from deinking paper sludge, preserving their molecular structure if the incineration is performed at a lower temperature, in this study case, until 575 °C. A subsequent dithionite bleaching was proposed to increase the brightness of the recycled fillers. This step resulted in a loss of only 2 % of the mass and without changes in molecular structure. In this method, the recycled fillers are a mixture of inorganic compounds (calcium carbonate, kaolin and talc) having suitable brightness to be used for newspaper production. Moreover, the brightness of the bleached ashes is stable in time. Test paper sheet samples were prepared by blending of recycled paper pulp and recovered fillers. The analysis revealed an improvement in brightness and opacity but a reduction of breaking length and porosity, as expected by the addition of fillers.

Another aspect that needs to be considered is the heterogenicity of the recycled paper streams that the different paper mills can use. However, the paper industry tends to use a restricted number of families of fillers and coating agents [43]. Globally, the 73 % of fillers is composed by carbonates (GCC and PCC, same molecular structure), 21 % by Clay (Kaolin), 5 % of Talc and 1 % of other materials. The infrared analysis permitted to observe calcium carbonate, kaolin and talc. It is possible to expect the same type of chemicals in the deinking sludge of other paper mills, from a qualitative point of view. Quantitatively, the composition can change but the thermal treatment at 575 °C permitted to maintain the chemical structure of recycled fillers. For that reason, the recycled fillers can fit in the production of newsprint to increase the yield and be a partial replacement of fresh fillers because this product does not require high physical properties in comparison of packaging products such as cardboard [44].

This approach is scientifically and technologically possible. Recycled fillers have the potential to be used in a “closed-loop” in the newspaper production. This work can be an interesting alternative to the actual methodologies considering that the world newspaper production, from recycled material, is around 16-17 million tons. However, it is also proof of the difficulties for a scale-up. In fact, further studies will be necessary to improve the de-agglomeration and reduce the

complexity of the process, for example by removing the bleaching step. Afterwards, the economic analysis will be crucial to evaluate the development at an industrial scale, as reported above in "Future research".

Acknowledgements

This study was supported by research funding from Flanders Innovation & Entrepreneurship (VLAIO, project number IWT.155050) and University of Antwerp.

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Table 1 List of the samples

Sample	Description
DIP	Deinked paper pulp, starting material
DPS	Deinking paper sludge, starting material
Ash525	Incinerated DPS at 525 °C
Ash575	Incinerated DPS at 575 °C
Ash850	Incinerated DPS at 850 °C
Ash575_Bleached	Ashe575 after bleaching
Pulp 1	DIP blended without addition of ashes
Pulp 2	DIP blended with not deagglomerated Ash575_Bleached
Pulp 3	DIP blended with deagglomerated Ash575_Bleached

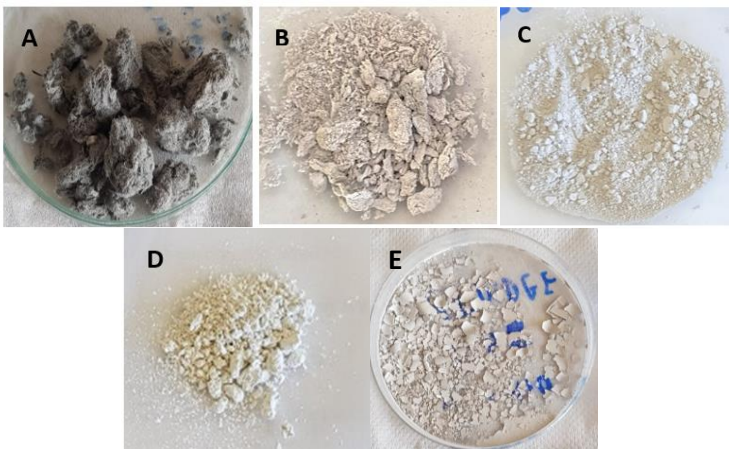

Fig. 1 Visual aspect A: DPS; B: Ash525; C: Ash575; D: Ash850; E: Ash575_Bleached

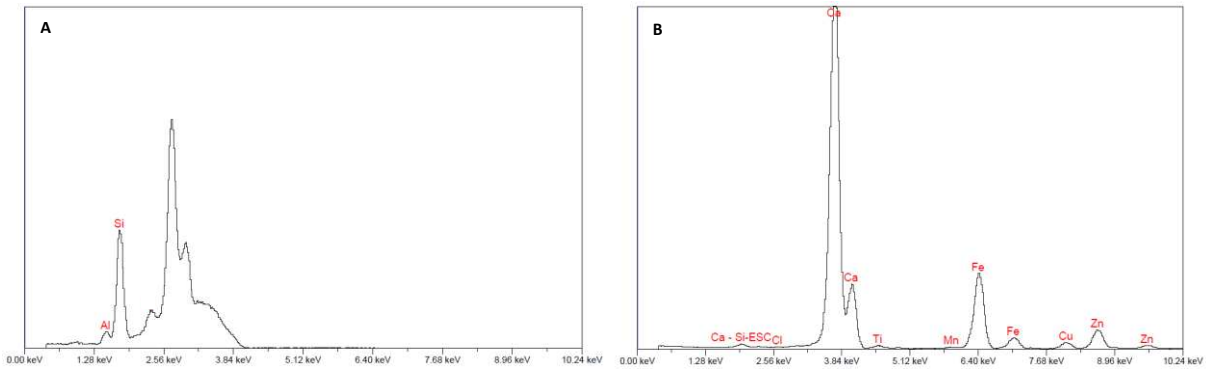

Fig.2 Qualitative analysis of Ash575 by XRF for the determination of metals. A: low energy spectra. B: medium energy spectra

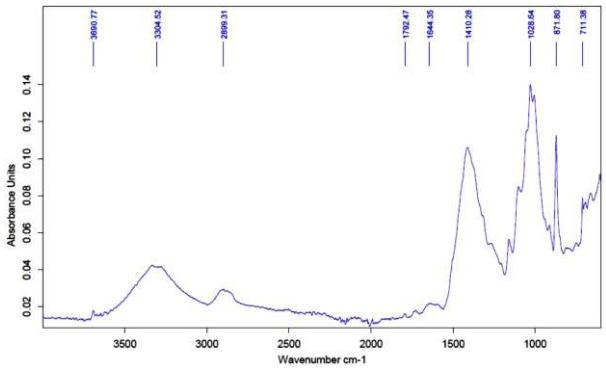

Fig. 3 DPS infrared spectrum

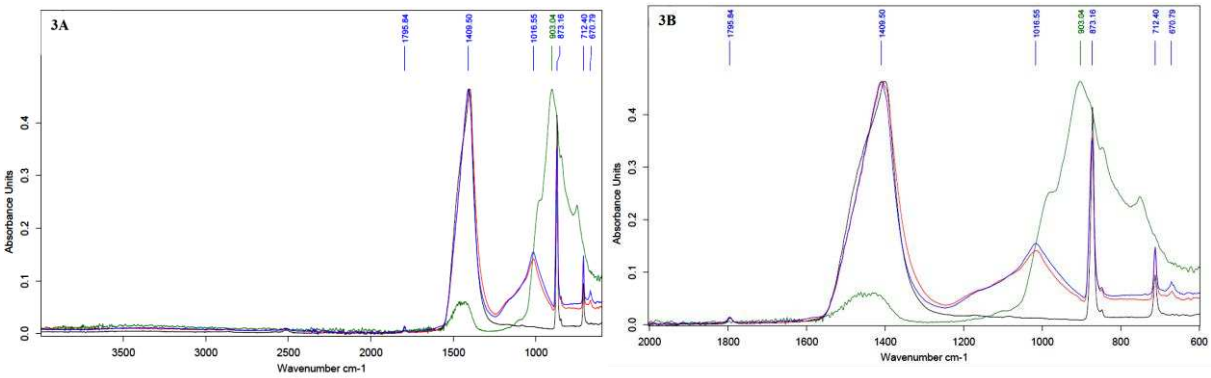

Fig. 4 A: Infrared spectra range 4000 and 600 cm^{-1} of (red) Ash525, (blue) Ash575, (black) Calcium carbonate, (green) Ash850; **B**: Infrared spectra range 2000 and 600 cm^{-1} of (red) Ash525, (blue) Ash575, (black) Calcium carbonate, (green) Ash850

Table 2 Brightness of DPS, Ash525, Ash575, Ash850

Sample	ISO brightness (%)	DEV.STD. (bright.)	Mass loss (%)*
DPS	28	5.0	-
Ash525	54	3.1	30
Ash575	58	2.8	32
Ash850	78	2.3	52 (29**)
Ash575_Bleached	73	5.2	2***

*Starting from DPS; **mass loss from Ash575 after incineration at 850°C; ***mass loss caused by bleaching

Table 3 Calcium carbonate amount in Ash575

Sample	$m_{850°C}$ (g)	m_{CO2} (g)	n_{CaCO3} (mol)	m_{CaCO3} (g)	$CaCO_3$ (%)
Ash575	0.355	0.145	0.0033	0.330	66

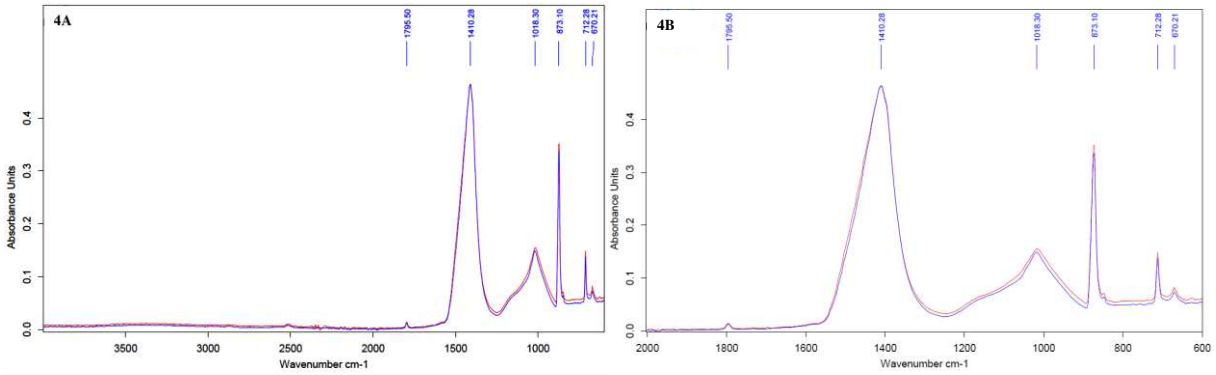

Fig. 5 A: Infrared spectra range 4000 and 600 cm^{-1} of (blue) Ash575_B; (red) Ash575_Bleached; **B**: Infrared spectra range 2000 and 600 cm^{-1} of (blue) Ash575_B; (red) Ash575_Bleached

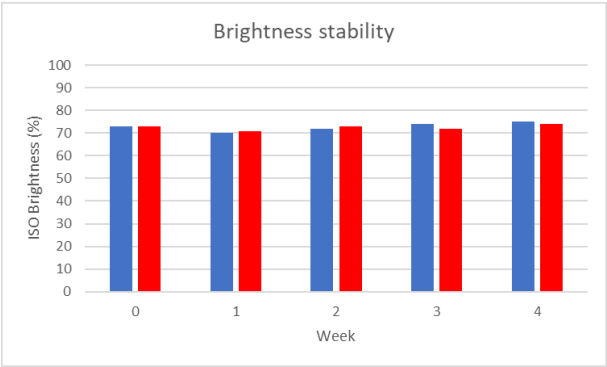

Fig. 6 Brightness variation by time: (Blue) Ash575_Bleached not exposed to air and light; (Red) Ash575_Bleached exposed to air and light

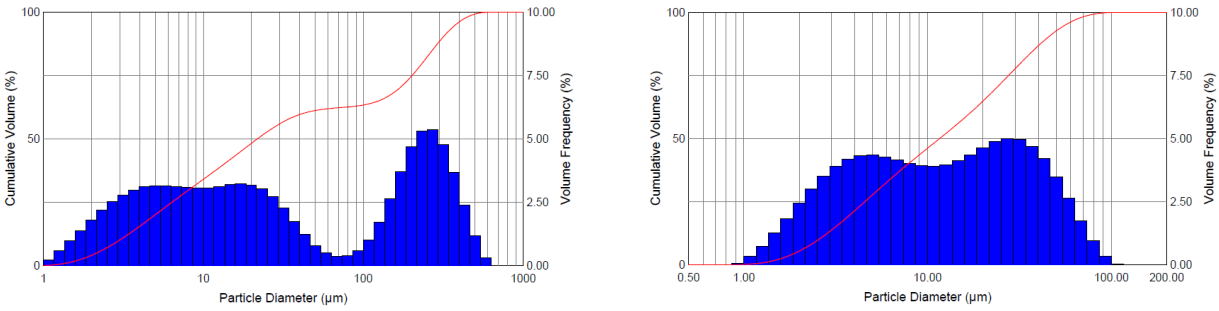

Fig. 7 Left: particle size before de-agglomeration; Right: particle size after deagglomeration

Table 4 Particle size data before and after de-agglomeration process by milling of Ash575_Bleached

Sample	Dv(10) µm	Dv(50) µm	Dv(90) µm	D[3][2] µm	D[4][3] µm	Span
Before milling	3.00	21.80	314.4	8.85	105.20	14.28
After milling	2.56	11.62	44.88	6.45	18.48	3.64

Fig. 8 Example of paper sheet (DIP2 pulp) used for the mechanical and physical analysis

Table 5 Mechanical and physical data from paper sheets

Sample	Brightness (% ISO)	Opacity (% ISO)	Porosity (ml/min)	Breaking Length (m)	Tearing power (Nm)	Ashes in the pulp (%)	Ashes in the paper (%)
Pulp 1	53	90.3	1001	3429	408	15.7	13.0
Pulp 2	54	92.0	1263	3173	400	23.2	18.2
Pulp 3	55	93.6	1476	3253	408	23.2	20.5

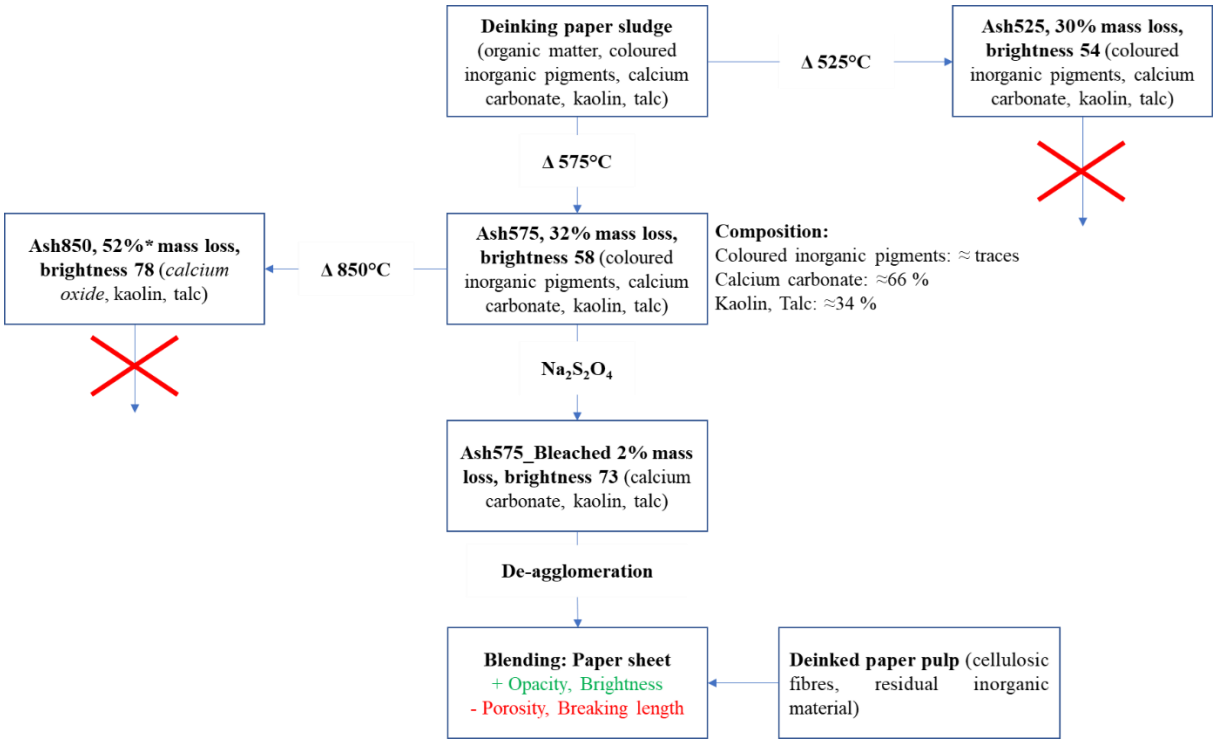

Fig. 9 Full scheme of the filler recovery from DPS to paper sheet comprising the incineration at 850°C. *mass loss measured starting from DPS