Determination of the mineral constituents of recycled paper mill sludge

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ABSTRACT: Innovative uses for recycled paper mill sludge are required to improve the industry's sustainability. While purified fractions of sludge may prove to be of greater value for targeted applications, rapid and accurate characterization of these heterogeneous waste materials is becoming essential. We examined three methodologies for determining the mineral composition of recycled paper mill sludge. We found thermogravimetric analysis (TGA) to be a fast and precise method for determining calcium carbonate based on its thermal decomposition temperature. Total ash content of recycled paper mill sludge determined at 700°C had a strong correlation to the traditional TAPPI ash. We evaluated fractionation methodologies using TGA and found that fiber-rich and inorganic rich-portions could be produced by dry screening recycled paper mill sludge.

Application: A rapid method for characterizing the industrial residue generated by the recycled paper manufacturing process can help to increase the industry's sustainability.

Recovered fiber is a mainstay of the global pulp and paper industry. The North American pulp and paper industry uses 48 million tons of recovered fiber each year [1, 2], while the combined consumptions of Japan and China represent 45 million tons per year [3, 4]. The industry is actively seeking strategies to use the vast quantities of waste solids generated by the recycling paper manufacturing process. Methods permitting fast, economical, and accurate characterization of this industrial by-product are essential to developing and implementing such strategies.

Recycled paper sludge is known to be composed of various amounts of lignocellulosics fiber, inorganic fillers, and ink components. However, every mill's sludge has a unique composition depending on the raw materials used and the deinking process. Standard methods for quantifying the total inorganic component, or ash, in wood and pulp [5] as well in paper and paperboard [6] are provided by pulp and paper technical associations. These methods do not attach any compositional meaning to the term "ash" but suggest that understanding the composition of the sample's ash must be known before choosing a procedure that will give meaningful results. The methods are time consuming and require an electric muffle furnace suitable for maintaining a temperature of 525°C and 900°C. In addition, errors in weight due to moisture absorption by the ash or loss of material due to unintentional flaming can result in inaccurate quantification.

We evaluated thermal gravimetric analysis (TGA) as a rapid method for characterizing the inorganic components of the waste by-product generated through the recycling paper process. We then applied the method to characterize the sludge from three recycling paper mills.

EXPERIMENTAL

Raw materials

Sludges were provided by three paper recycling mills in North America. One sludge was collected from a mill producing only newsprint (NP), one from a mill whose production consists of 85% newsprint and 15% tissue products (NP_TM), and one from a mill producing only tissue products (TM). We collected two sets of samples from each mill. The first set of samples (NP, NP_TM, TM) were collected at the final dewatering stage in the effluent treatment plant, stored in polyethylene bags, and frozen until analysis. The second set (NP KDS, NP_TM KDS, TM KDS) were collected after processing the sludge through a specifically designed vertical-shaft impact mill (KDS Micronex™), which dried the sludge to a solids content between 91%–97% [7]. All samples were stored at -4°C immediately after collection.

In addition to the six sludge samples described above, we also used fractions of the NP_TM KDS and NP KDS in the investigation. A laboratory-scale process was devised to expedite recovery of a fiber-rich fraction. A brief (20-s) agitation of the material in a Wiley Laboratory Mill equipped with a 2-mm-holed screen was sufficient to loosen the fine material from the dry fibrous agglomerates. The fine fraction readily passed through the screen while the long-fiber portion was retained in the Wiley Mill (NP_TM KDS fiber). The fine fraction was sieved on a 40-mesh screen to yield two additional fractions (NP_TM KDS fines 40+ and a NP_TM KDS fines 40-). In addition, the NP_TM KDS and NP KDS samples were sieved on a 40 mesh Endecotte test sieve, yielding 40+ and 40- fractions. Preparation of fractions had been previously documented by Krigstin and Sain [7].

Thermo gravimetric analysis

Thermo gravimetric analysis, which was carried out on a Q-500 TGA manufactured by TA Instruments, measures the weight change and rate of weight change in a material as a function of increasing temperature. The TG measurements were carried out using 5–20 mg of material and a heating rate

of 20°C/min to 800°C in air (flow rate of 60.0 mL/min). Calcium carbonate ($CaCO_3$) content of the samples and calcium oxide (CaO) content of the combusted residues were calculated from the molar weight loss of carbon dioxide (CO_2) over the temperature range of 600–709°C. Total ash was calculated as the weight of material remaining in the sample pan at the completion of the analysis. Kaolin content was calculated based on the assumption that the combustion residue contained only dehydroxylated kaolin ($Al_2O_3 \cdot 2SiO_2$) and CaO.

Ash measurement

Ash testing was done using a modified TAPPI procedure T413 pm-95 [6, 8]. The samples were charred at 250°C for 2 h to prevent flaming, and then heated at 525°C for 4 h. Samples were desiccated and weighed and then reheated to 900°C for 1 h to determine calcium carbonate content based on mass loss of carbon dioxide.

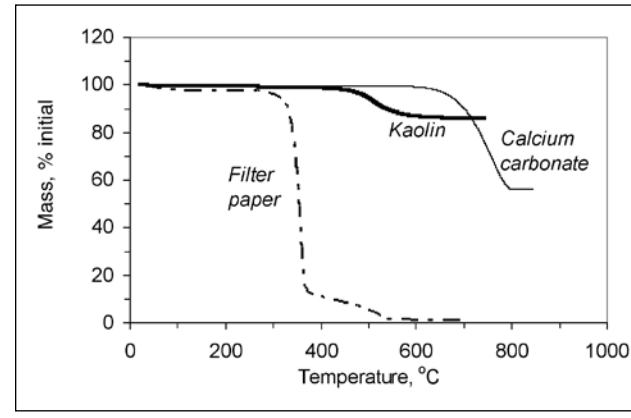
X-ray fluorescence measurements

X-ray fluorescence (XRF) spectrometry was used to determine the relative weights of inorganic oxides contained in the sludge using a Philips PW2404 system. In XRF spectrometry, atoms are irradiated with an x-ray that excites electrons to jump to higher bonding energy levels, creating vacancies in lower energy orbits and leaving the atom unstable. As the atom preferentially returns to its normal state, characteristic x-rays are emitted and analyzed by crystal diffraction patterns; these characteristic x-rays patterns correspond to specific elements [9]. The intensity of the x-rays is used to quantify the amount of each element present. Samples for XRF analysis were prepared by combusting all organic material in a muffle furnace set at 525°C for 4 h. Pressed pellets (5 tons/in^2) were formed combining the ash residue with an inert backing material (boric acid). Calcium carbonate content was calculated directly, assuming all calcium in the sludge was present as $CaCO_3$.

RESULTS AND DISCUSSION

Thermo gravimetric analysis

Constituent materials. The main constituents of recycled paper mill sludge are calcium carbonate, kaolin clay, and lignocellulosic fiber [10–12]. The thermal degradation behavior of each of the three main components was elucidated using TGA (**Fig. 1**). Thermal decomposition of kaolin clay takes place in one broad mass-loss step occurring over the temperature range of 405°C–694°C. This mass loss is a consequence of the dehydroxylation of the kaolinite crystal ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) to completely amorphous metakaolin ($Al_2O_3 \cdot 2SiO_2$) [11, 13, 14]. Two reactions are believed to be responsible for the loss of hydroxyl groups from the crystal structure. First, the dissociation of a hydroxyl group to a free proton and an oxygen ion (Eq. 1) followed by a second reaction that combines the proton with a second hydroxyl ion and forms a water molecule (Eq. 2). Various temperatures for this key thermal event have been previously reported. Shvarzman et al. [15] reported the decomposition over a narrower range of 450°C-600°C, with the exact interval depending on the crystallinity and particle size, while He et al. [13] observed the endothermic peak caused by the dehydroxylation reaction to occur at 565°C–570°C. A number of studies on kaolinite from different origins concluded that the maximum decomposition rate occurs at 550°C to 600°C [14].



1. TGA curves of kaolin clay, $CaCO_3$, and ground filter paper (40 mesh) at a heating rate of 20°C/min in air atmosphere.

$$OH^- \leftrightarrow H^+ + O^{2-} \quad (1)$$

$$H^+ + OH^- \leftrightarrow H_2O \uparrow \quad (2)$$

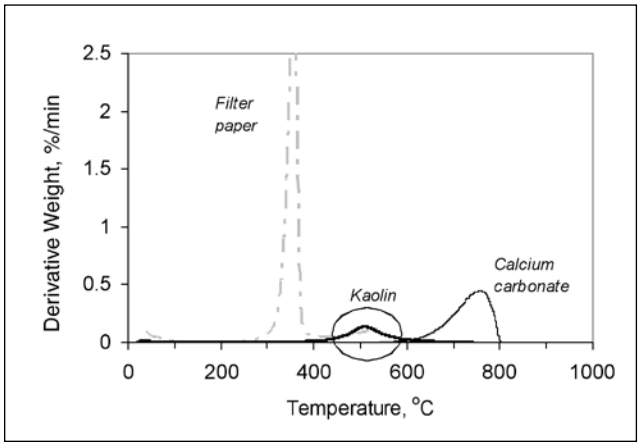
The theoretical mass loss associated with dehydroxylation of kaolin is 13.96% according to the chemical reaction given in Eq. 3. The mass loss measured by the TGA for the kaolin clay sample was 12.7%, which agrees closely with the mass loss of hydroxyl groups of 12.9% reported by He et al., [13]. Even though the difference in weight loss between theoretical and actual value is small (1.3%), it represents an error of about 9% on estimating the original weight of kaolin.

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \uparrow \quad (3)$$

Molecular Weights:

$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow$ 258.16 g/mole
$Al_2O_3 \cdot 2SiO_2 \rightarrow$ 222.13 g/mole
$2H_2O \rightarrow$ 36.03 g/mole

Similar to kaolin, calcium carbonate exhibits only one mass-loss step. In our analysis it occurred over the temperature range of 607°C–803°C (Fig. 1). Loss in mass on heating results from the calcination reaction in which CO_2 gas is released and a solid residue of CaO is produced. The temperature at which calcination takes place depends on the ambient pressure of CO_2 in the combustion environment. Paya et al. [16] showed that carbonate decomposition takes place over a temperature range of 750°C–850°C in an air environment. Frederick et al. [12] recorded the mass loss over a lower temperature range (500°C–630°C) in a nitrogen atmosphere. The theoretical mass loss of carbon dioxide from calcium carbonate on calcination is 44.0%. The actual mass loss of carbon dioxide from the calcium carbonate was measured as 43.5%,



2. DTG curves of kaolin clay, $CaCO_3$, and ground filter paper (40 mesh) at a heating rate of 20°C/min in air atmosphere, showing overlap in thermal degradation activities.

Temperature range (°C)	Possible reactions
275–380	Rapid decomposition of celluloses
380–545	Slow decomposition of char residue
405–695	Dehydroxylation of kaolin
607–803	Calcination of calcium carbonate

I. Explanation of mass-loss events during thermal decomposition of the components of recycled paper mill sludge.

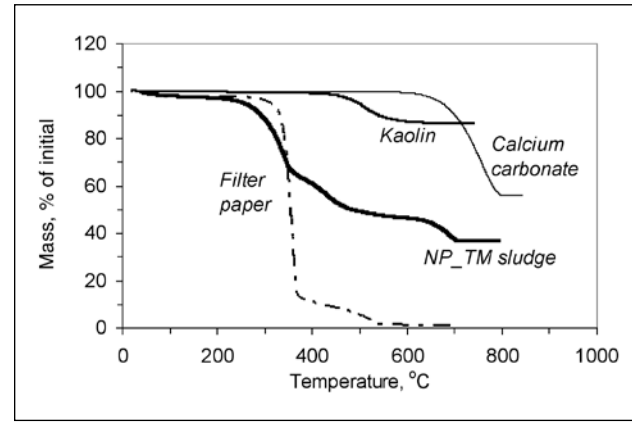
Temperature range (°C)	Possible thermal reactions of sludge
25–240	Evaporation of water
240–359	Rapid decomposition of lignocelluloses
359–600	Lignocelluloses char volatilization and dehydroxylation of kaolin
600–708	Calcination of calcium carbonate

II. Explanation of mass-loss events during thermal decomposition of recycled paper mill sludge.

leading to an error in the predicted weight of calcium carbonate of only about 1%.

Thermal decomposition of ashless filter paper (over 95% alpha cellulose) shows two distinct weight loss regions. From 272°C–378°C there is a rapid weight loss indicative of the decomposition of cellulose in an oxidative environment [17]. Decomposition of cellulose generates volatile gases; predominantly water, carbon monoxide, and carbon dioxide, as well as a solid char residue [17]. In the second weight loss region (378°C–545°C), which is very minor in magnitude compared with the first region, a gradual but complete decomposition of the char residue takes place leaving no residual ash.

Differential thermal gravimetric (DTG) analyses of the three individual components clearly shows an overlap of thermal activities over the temperature range of 400°C–550°C



3. TGA curves of kaolin clay, $CaCO_3$, filter paper (40 mesh), and NP_TM sludge at a heating rate of 20°C/min in air atmosphere.

(**Fig. 2**). Over this temperature range, the kaolin dehydroxylation reaction is commencing while the char decomposition of the cellulose is concluding. Thermal activity of the calcium carbonate occurs at a distinctly different temperature than that of the kaolin or the filter paper (**Table I**).

Sludge material. Specific thermal events that correspond to the characteristic mass loss zones in the TGA of recycled paper mill sludge have been identified by various researchers [11, 12]. The first of four mass-loss regions in the thermal degradation of the NP_TM sludge (**Table II**) occurs below 120°C and represents the mass loss from evaporation of water. The second region of mass loss occurs over the temperature range of 240°C–360°C and represents the loss of volatile organic compounds or pyrolysis products, produced from the thermal breakdown of organic matter contained in the woody fiber. The third region (359°C–600°C) corresponds to at least two independent thermal events; the dehydroxylation of kaolin clay from $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ to metakaolin ($Al_2Si_2O_7$) and the final combustion of the organic char residue. The final mass loss zone (600°C–710°C) corresponds to the loss of CO_2 on the calcination of $CaCO_3$. The dehydroxylation of talc occurs at a higher temperature (900°C–1000°C) and is not seen in the thermograph [18].

Figure 3 illustrates the differences between the thermal degradation of the NP_TM sludge to that of the individual components. First, the onset of thermal decomposition of the NP_TM sludge occurs at a lower temperature than that of the filter paper. This may be due to the presence of low and high molecular weight organic compounds that are commonly associated with deinking sludges [19, 20]. Such compounds could include water-insoluble chemicals such as resins, fatty acids, polyvinyl acetate, polyvinyl chloride, waxes and synthetic sizing agents. The initial, rapid decomposition of the sludge is similar to that of the filter paper with the transition to the slower rate of decomposition occurring at 370°C–380°C. The mass loss of the sludge over the char combustion stage is greater than that of the filter paper as demonstrated by the TGA (Fig. 3). This may be due to the greater proportion of lignin in the sludge than in the filter paper and hence a

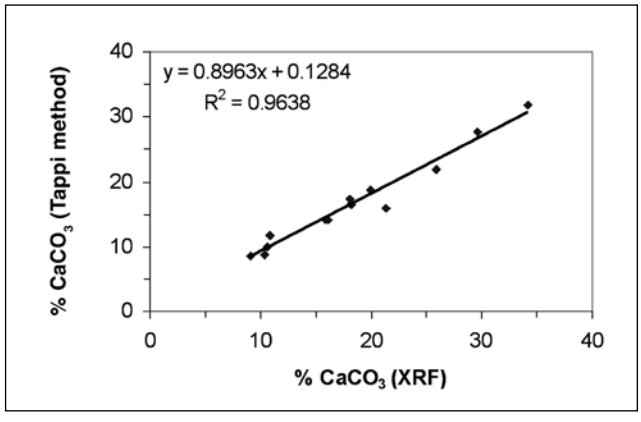
larger char component formed in the sludge. The mass loss due to dehydroxylation of the kaolin in the NP_TM sludge curve is difficult to distinguish. The theoretical weight loss on dehydroxylation is relatively small (14% of the original weight) and may be obscured by the ongoing char volatilization. The calcination temperature of the $CaCO_3$ in the sludge closely corresponds to that of the pure $CaCO_3$ (Table II).

Mineral composition

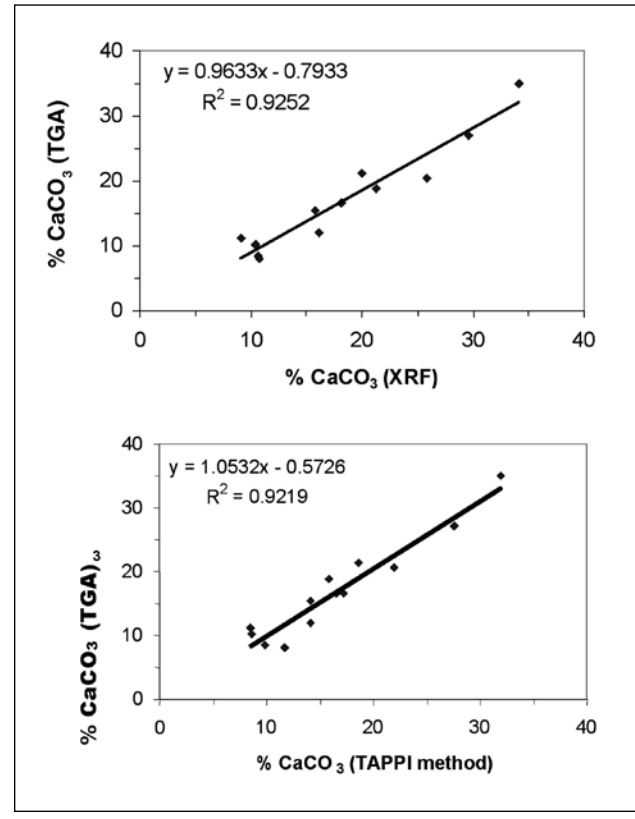
Table III shows the calcium carbonate content of 13 samples of paper mill sludge, determined by XRF analysis, TGA, and a modified TAPPI method. The XRF data and the data generated from the modified TAPPI method had the highest correlation among the data sets (**Fig. 4**). The calcium carbonate contents derived from the TGA showed a good correlation to both the XRF data and the data from the modified TAPPI method (**Fig. 5**). The TAPPI method was expected to give an overestimation of calcium carbonate content, because some of the mass loss measured over the temperature range was due to loss of H_20 from kaolin dehydroxylation and not only from loss of CO_2.

Sample	% $CaCO_3$		
	XRF	TAPPI	TGA
NP	15.8	14.1	15.4
NP KDS	16.1	12.0	12.0
NP KDS 40+	10.8	11.7	8.0
NP KDS 40-	18.1	16.5	16.6
NP_TM	25.8	21.9	20.5
NP_TM KDS	18.1	16.9	16.6
NP_TM KDS 40 +	9.1	8.5	11.2
NP_TM KDS 40 -	20.0	18.6	21.3
NP_TM KDS fiber	10.6	9.9	8.5
NP_TM KDS fines 40 +	10.4	8.7	10.1
NP_TM KDS fines 40 -	21.3	15.9	18.8
TM	34.1	31.9	35.0
TM KDS	29.6	27.6	27.1

III. Comparison of three methods for determining calcium carbonate content (% of o.d. weight) of recycled mill sludge.



4. Correlation of calcium carbonate content as determined by a modified TAPPI method and XRF. Correlation coefficient 0.9817 and standard error 1.404.



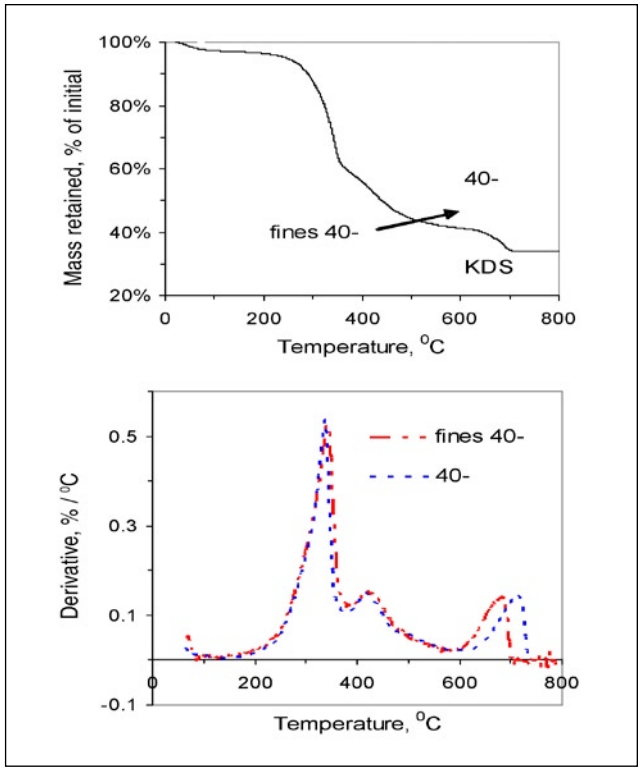
5. Correlation of calcium carbonate content as determined by thermogravimetric method and XRF (correlation coefficient 0.9619 and standard error 2.2144) and correlation of calcium carbonate content as determined by thermogravimetric method and a modified TAPPI method (correlation coefficient 0.9602 and standard error 2.2631).

A good correlation was found between the percentage of ash remaining after the TG run and the percentage of ash (at 900°C) determined by the modified TAPPI method (900°C). The correlation coefficient between the two sets of data was 0.8951, with a standard error of estimate of 3%, which is within the repeatability specified in TAPPI T413 procedure.

The TGA is not a suitable method for determining the kaolin content of recycled paper mill sludge. The overlap in the thermal degradation of the kaolin with the char combustion of the lignocellulosics materials, hinders the determination of mass loss for the dehydroxylation reaction alone. An estimate of the amount of kaolin could be derived from the TGA under the assumption that the ash residue remaining at the conclusion of the run is made up of only calcium oxide and metakaolin ($Al_2Si_2O_7$). However, such an assumption is invalid because small amounts of inorganic compounds such as titanium dioxide and talc are likely to be in the residue and would result in an overestimate of the amount of metakaolin. Researchers found a more precise measure of kaolin content by using the results of the XRF analysis and adding the amounts of Al_2O_3 and SiO_2 present in the ash after correcting for the SiO_2 present in e talc (**Table IV**). The kaolin content determined by the two methods had a 0.8291 correlation coefficient and a standard error of estimate of 2.4%.

Sample	% $Al_2O_3 \cdot SiO_2$	
	XRF	TGA
NP	18.4	23.1
NP KDS	18.1	15.1
NP KDS 40+	13.4	13.2
NP KDS 40-	20.5	24.7
NP_TM	26.5	26.0
NP_TM KDS	23.5	24.7
NP_TM KDS 40+	13.2	20.7
NP_TM KDS 40-	25.7	31.2
NP_TM KDS fiber	14.9	16.1
NP_TM KDS fines 40+	14.9	16.2
NP_TM KDS fines 40-	27.1	28.8
TM	20.2	28.1
TM KDS	18.3	21.9

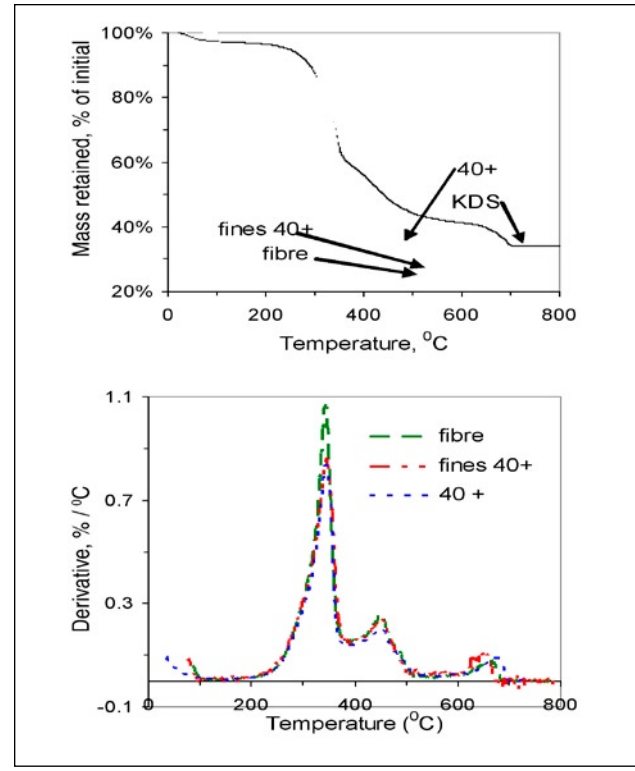
IV. Metakaolin content of sludge samples as determined by XRF and TGA.



6. TGA of NP_TM fine fractions and corresponding DTA.

Fraction purity

Novel applications for recycled paper mill sludge may depend on generating high purity fractions from a normally heterogeneous process by-product. TGA was used for characterizing fractions of sludge derived by two fractionation methodologies. The first fractionation method produced three fractions from the NP_TM KDS material, a 'fiber' fraction and two fine fractions (fines 40+ and fines 40-). The second method produced two fractions by screening NP_TM KDS on a 40-mesh screen with the aid of a rubber-tipped spatula ('40+', '40-'). A comparison of the small particle fractions from the two methods showed very similar thermal behavior (**Fig. 6**). The calcium carbonate content calculated from the mass loss for the



7. TGA of NP_TM fibrous fractions and corresponding DTA.

NP_TM KDS 'fines 40-' was 18.8% and for the '40-' sample was 21.3%. Similarly the total ash content for the '40-' sample was slightly higher (43.13%) than for the NP_TM KDS 'fines 40-' sample (39.35%). Both fractions had higher inorganic contents than the original NP_TM KDS material (34.0%).

Figure 7 shows a comparison of the thermal behaviors of fractions derived from NP_TM KDS. The fractions all show lower total ash than the original material (NP_TM KDS). The 'fiber' fraction has the lowest inorganic contamination of the three fractions, containing only 20.9% total ash compared with 21.9% for the 'fines 40+' and 26.9% for the '40+'. The calcium carbonate contents of all three fractions are similar, ranging from 8.5%–11.2%. However, there is a significant reduction in the amount of calcium carbonate in the 'fiber' fraction (8.5%)compared with the original material (16.6%).

CONCLUSION

TGA has proved to be especially valuable in the analysis of minerals in recycled paper mill sludge because of the small sample size required and the short testing time (40 min). Calcium carbonate content of paper mill sludge can be accurately determined even though many different crystal forms and particle sizes of the mineral exist in paper mill sludge. However, kaolin content of the sludge cannot be precisely determined with this technique due to the overlapping of the dehydroxylation reaction with the final organic char combustion.

Novel applications of paper mill sludge will require fast, efficient ways to characterize the raw material. Applications

in corrugated material, molded pulp products, hardboard, asphalt, and insulation board will all require a high proportion of fiber and minimum inorganics. Other applications such as bricks, cement, and building blocks will benefit from a high proportion of inorganics and a low amount of organic contaminates. KDS-prepared paper mill sludge shows potential for fractionation to higher purity fractions by dry fractionation methods. **TJ**

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INSIGHTS FROM THE AUTHORS

If purified fractions of sludge are to be more highly valued for targeted applications within the recycled paper manufacturing industry, it is essential to be able to rapidly and accurately characterize these heterogeneous waste materials.

Paper mill sludge has been tested on TGA in earlier research as a qualitative evaluation tool, mostly for heat generating applications. We quantified the amount of calcium carbonate and kaolin clay and compared the results with those obtained using other methodologies.

The difficult part of our research was trying to isolate chemically purer fractions of sludge. The work we detailed provided a fast and accurate means of characterizing the fractions separated by various schemes. We discovered there are environmentally acceptable applications that are suitable for the entire sludge mass and others that are more suited to fractions of sludge that have more homogeneous characteristics.

As mills seek new environmentally friendly strategies for dealing with their waste by-products, especially when used as raw materials for other processes, they will need a method for conducting ongoing measurement of the materials' characteristics. Our next step will be to focus on economically and ecologically viable applications for the sludge material.

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