

Effects of pulverized coal fly-ash addition as a wet-end filler in papermaking

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ABSTRACT: This experimental study is based on the innovative idea of using pulverized coal fly ash as a wet-end filler in papermaking. This is the first evaluation of the possible use of fly ash in the paper industry. Coal-based thermal power plants throughout the world are generating fly ash as a solid waste product. The constituents of fly ash can be used effectively in papermaking. Fly ash has a wide variation in particle size, which ranges from a few micrometers to one hundred micrometers. Fly ash acts as an inert material in acidic, neutral, and alkaline papermaking processes. Its physical properties such as bulk density (800–980 kg/m³), porosity (45%–57%), and surface area (0.138–2.3076 m²/g) make it suitable for use as a paper filler. Fly ash obtained from thermal power plants using pulverized coal was fractionated by a vibratory-sieve stack. The fine fraction with a particle size below 38 micrometers was used to study its effect on the important mechanical-strength and optical properties of paper. The effects of fly-ash addition on these properties were compared with those of kaolin clay. Paper opacity was found to be much higher with fly ash as a filler, whereas brightness decreased as the filler percentage increased. Mechanical strength properties of the paper samples with fly ash as filler were superior to those with kaolin clay.

Application: Fly ash can be a very good filler for laminate-grade colored base papers (dark grey, slate grey, bluish grey, violet base, teak base, gold rust, and other dark brown colors), colored magazines, and poster papers where very high opacity is sought but where whiteness is not important. Use of fly ash is expected to decrease paper production cost by approximately 40–60 U.S. dollars per ton of paper.

Fly ash is a major by-product of thermal power plants. It is carried by the stack gases and is collected in electrostatic precipitators or a baghouse before it exits the stack. It can be defined as a residual material resulting from the combustion of ground or powdered coal. Fly ash obtained from the burning of pulverized coal has a very fine particle size. Large amounts of fly ash are dumped close to power plants, causing environmental pollution by mixing with air, water, and soil over several hectares of land. Fly ash causes serious environmental pollution because of its fineness. It contains 35%–70% SiO₂, 15%–30% Al₂O₃, 1%–10% MgO, 1%–10% CaO, 5%–10% Fe₂O₃, and 1%–2% TiO₂, depending on the various types of coal used and the process conditions during burning. The principal contents of fly ash are normally silica, alumina, and iron oxide. Only a small quantity of the total fly ash generated by thermal power plants is used in brickmaking, concrete manufacture, soil stabilization treatment, the cement industry, and other applications.

Sustainability of industrial growth depends on the effective and environmentally friendly use of industrial waste materials. On the one hand, society is facing problems of solid-waste management because of the difficulty of finding suitable uses for these by-products, while on the other hand, mining and other mineral exploration processes are putting severe pressure on the natural resources of planet Earth. The common papermaking fillers are kaolin clay (typical composition 39% Al₂O₃, 46% SiO₂, and 13% H₂O), calcium carbonate (98%–100% CaCO₃), titanium dioxide (98%–100% TiO₂), hy-

drated silica (78% SiO₂, 5% CaO, and 17% H₂O), aluminum trihydrate (65% Al₂O₃ and 34% H₂O), and talc (magnesium silicate). Clay is still one of the most commonly used filler materials in papermaking [1]. Fly ash has physical and chemical characteristics very similar to those of the commercial fillers used in the pulp and paper industries.

Approximately 90 million tonnes of fly ash are being generated annually in India, and 65,000 acres of land are presently occupied by ash ponds. The high ash content (30%–50%) of Indian coals is contributing to these large volumes of fly ash [2]. Typical Indian fly-ash composition is shown in **Table 1**. Approximately 73% of India's total installed power-generation capacity is based on thermal power plants, of which 90 percent are using coal as fuel. These plants use either bituminous or sub-bituminous coal and produce large volumes of fly ash.

1. Chemical composition of fly ash.

Constituents	Percentage (Range)
Silica (SiO ₂)	49–67
Alumina (Al ₂ O ₃)	16–29
Iron oxide (Fe ₂ O ₃)	4–10
Calcium oxide (CaO)	1–4
Magnesium oxide (MgO)	0.2–2

Fly ash is siliceous or aluminous with an alkaline nature and has an average specific surface area of 1.45 m²/g.

FLY ASH

The total amount of fly ash produced in the United States from coal combustion is approximately 57 million tonnes per year. Only about one-third of the trapped fly ash (31% by weight in the United States) is used as a secondary raw material, while the rest is directly disposed of in surface impoundments and landfills [3]. Samples of fly ash taken from coal-fired power plants in various countries have been shown to have very similar chemical and physical properties, which are comparable with that of kaolin clay. The chemical and physical properties of fly ash from various coal-based power plants in the United States, Turkey, Israel, Greece, Spain, the Netherlands, and Italy have been reported in Fuel (Elsevier) and in other journals [3–8]. All these research papers have reported the important characteristics of various fly ashes, and it can therefore be verified that these properties are similar to those of conventional fillers.

Coal-fired power plants generate about 23% of the total electricity consumed worldwide [9]. The particle size range of the resulting fly ash is 0.2–90 micrometers for high-combustion-efficiency super-thermal power plants [10]. Significant variations in bulk density, porosity, and surface area were recorded in studies of fly ashes from different power plants [11]. Coal fly-ash elemental analysis on a dry basis shows Si (29.39%), Al (13.40%), Ti (1.01%), Fe (1.58%), Ca (1.71%), Mg (0.77%), and O₂ (50.43%) to be the major elements present [12]. The addition of filler affects the pore structure, and its interaction with paper properties has been found to be important. The particle content of the sheet must be high to produce effective filler-paper interaction [13].

EXPERIMENTAL PROCEDURE

Materials: Bleached rice-straw pulp and long-fiber southern pine pulp were used in an 80:20 ratio to make paper sheets. The rice-straw pulp was manufactured in a paper technology laboratory using acetic-acid pulping and a CEHP bleaching sequence. Acetic-acid pulping was done at atmospheric pressure in the presence of H₂SO₄ as a cata-

II. Fractionation of fly ash based on particle size.

Fraction	Screen opening size (10 ⁻⁶ m)	Mass retained (g)	Mass fraction	Average particle size (μm)
A	425	0.07	0.000708	425
B	250	0.37	0.003746	337.5
C	180	2.48	0.025108	215
D	106	11.26	0.114002	143
E	53	54.88	0.555634	79.5
F	38	14.01	0.141844	45.5
G	0	15.70	0.158955	19

A = fraction retained by sieve no. 36 B.S. (+425 μm); B = fraction retained by sieve no. 60 and passing through sieve no. 36 B.S. (-425 μm to +250 μm); C = fraction retained by sieve no. 85 and passing through sieve no. 60 B.S. (-250 μm to +180 μm); D = fraction retained by sieve no. 150 and passing through sieve no. 85 B.S. (-180 μm to +106 μm); E = fraction retained by sieve no. 300 and passing through sieve no. 150 B.S. (-106 μm to +53 μm); F = fraction retained by sieve no. 400 and passing through sieve no. 300 B.S. (-53 μm to +38 μm); G = Pan.

III. Properties of fly ash.

Fly-ash properties	Average value
Mean particle size, μm	30
Bulk density, kg/m ³	0.897
Brightness, % ISO	28.5
pH	8.5
Specific surface area, m ² /g	1.45
Refractive index	1.7
Color	Grey-brown

lyst. The long-fiber southern pine pulp was obtained from a nearby pulp mill. The rice-straw and pine pulps had brightness of 72.2% and 89% ISO, respectively. Coal fly-ash samples were collected from a thermal power plant in Bathinda, Punjab (India). Kaolin clay of commercial grade was used in paper-making for comparison purposes.

Methodology

Fractionation of fly ash based on particle size: A fly-ash sample was sieved for 30 minutes in a sieve shaker using sieves no. 36, 60, 85, 150, 300, and 400 (B S 410 1986). Fly ash was classified into seven fractions identified as A, B, C, D, E, F, and G. Mass fraction and average particle size of the fly ash for all seven classifications were calculated. The finest fraction, G, with an average particle size of 19 micrometers, was used as a filler in papermaking.

Paper handsheet preparation:

Dilute slurries (1% solids) of kaolin clay as well as of fly ash (G fraction) were prepared for better mixing with a pulp slurry. Preparation of paper handsheets was done using 200 grams of oven-dry (O.D.) pulp. The pulp was processed in a disintegrator and then diluted to 2% consistency for beating to 40° SR in a laboratory Valley beater. Fillers were added to the pulp slurry at 0, 10, 20, 30, and 40 wt% ratios based on the oven-dry pulp amount. The pulp slurry was diluted to 0.8% consistency, and paper handsheets of 100 g/m² basis weight were made on a laboratory sheet former with different weight percentages of fillers. The wet papers were pressed in a laboratory sheet press and then air-dried for 24 h. The air-dried papers were sealed in polythene bags for analysis of their important properties.

Testing of paper samples: The paper handsheet samples were placed in an environmental chamber, which was maintained at a temperature of

25°C and 52% relative humidity for three hours. Important properties like brightness (ISO), opacity (ISO), burst strength, tear strength, tensile strength, Gurley porosity, and Bendtsen roughness were measured as per TAPPI Test Methods.

Experimental design: Experiments were planned to obtain approximately 0%, 5%, 10%, 15%, and 20% ash levels in the paper handsheets. The following experiments were conducted:

1. Five handsheets of 100 g/m² were prepared without adding any filler (kaolin clay or fly ash).
2. Kaolin clay was added to the pulp slurry to obtain weight percentages of 10%, 20%, 30%, and 40% in the pulp slurry on an oven-dry basis. Five handsheets with each clay percentage were made on a semiautomated laboratory sheet former.
3. In a similar manner, fly ash was added at different percentages on a trial basis, in such a way that the retained fly-ash percentage was the same as that of the kaolin clay. The sample handsheets (five for each composition) loaded with fly ash were made and stored.

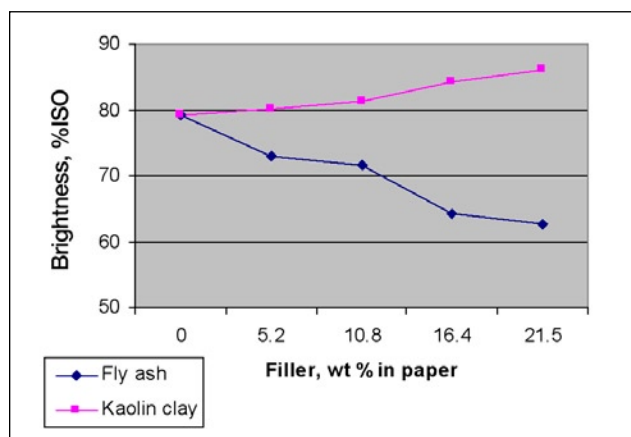
RESULTS AND DISCUSSION

The addition of filler as an inert material has an adverse effect on most mechanical strength properties by interfering directly with interfiber bonding. Particle size and shape play key roles in determining the severity of this effect for a given pigment. Addition of fly ash causes a lesser decrease in mechanical strength properties because of its larger particle size and irregular shape compared with kaolin clay. The major constituents of both fly ash and kaolin clay are silica (SiO₂) and alumina (Al₂O₃). However, fly ash also contains other oxides such as titanium dioxide, magnesium dioxide, calcium oxide, and iron oxide, which provide higher opacity and lower brightness in paper.

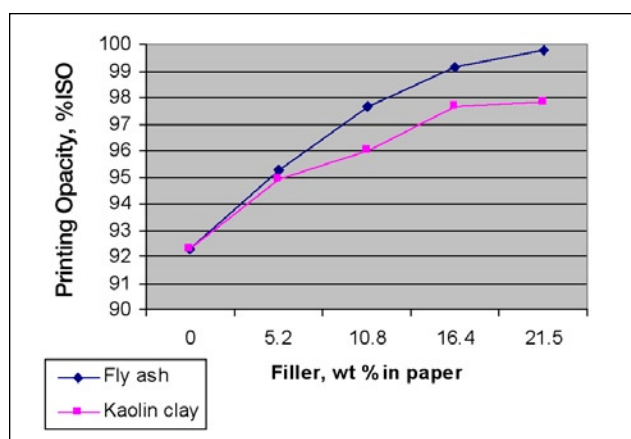
The fractionation of fly ash based on different sizes (as retained on sieves) is shown in **Table II**. Approximately 55.5% of fly ash sample was retained on screen with 53-μm openings. This fraction has an average particle size of 79.5 μm. The finest fraction, G, with an average particle size of 19 μm, which made up 15.89% of the total mass of fly ash collected, was used as a filler in papermaking.

The pH of the fly ash also falls in the same range as that of commercial fillers (the pH values of calcium carbonate and of alumina-silicate filler are 9.5 and 5.0 respectively). The major differences are the lower brightness and higher particle size of fly ash in comparison to commercial fillers, as shown in **Table III**.

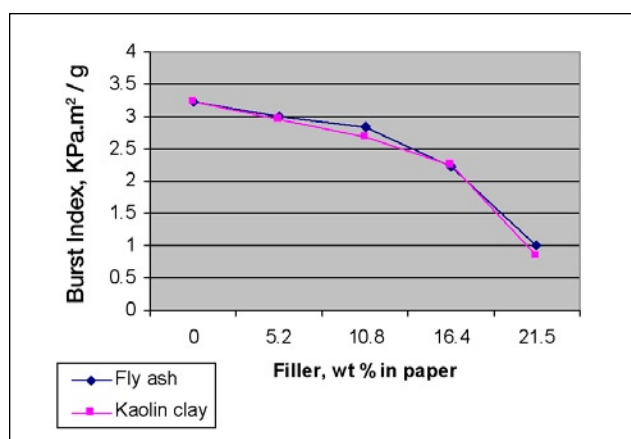
Effect of filler addition on optical properties: The brightness of paper with fly ash as filler decreases as the filler percentage increases, due to the lower brightness of fly ash compared with kaolin clay, as shown in **Fig. 1**. However, printing opacity is remarkably higher for fly-ash-loaded paper, and the difference increases with filler percentage, as shown in **Fig. 2**.



1. Effect of fillers on paper brightness.



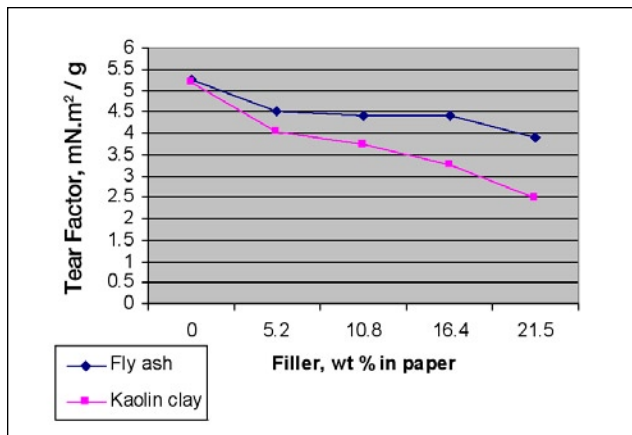
2. Effect of fillers on printing opacity of paper.



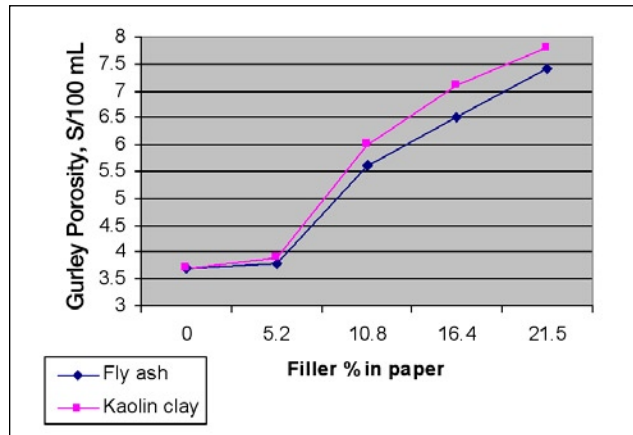
3. Effect of fillers on burst index of paper.

Effect of filler addition on mechanical strength properties: Burst strength index of paper loaded with fly ash is approximately equal to that of paper loaded with kaolin clay, as shown in **Fig. 3**. A comparison of the effect of filler addition on tear factor is shown in **Fig. 4**. The decrease in tear factor with increased filler percentage is less for paper loaded with fly ash than for paper loaded with kaolin clay. This means that fly-ash-loaded paper has a higher tear factor than

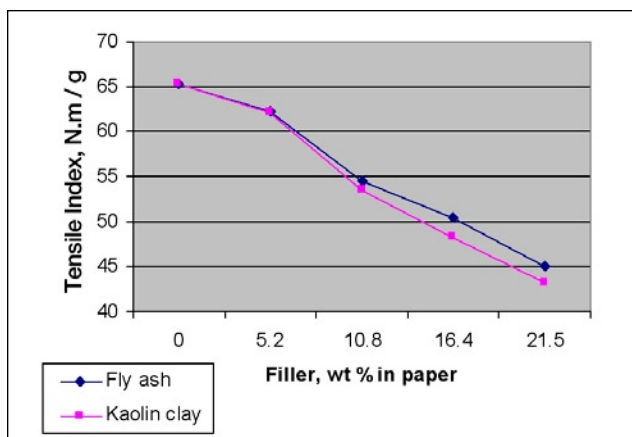
FLY ASH



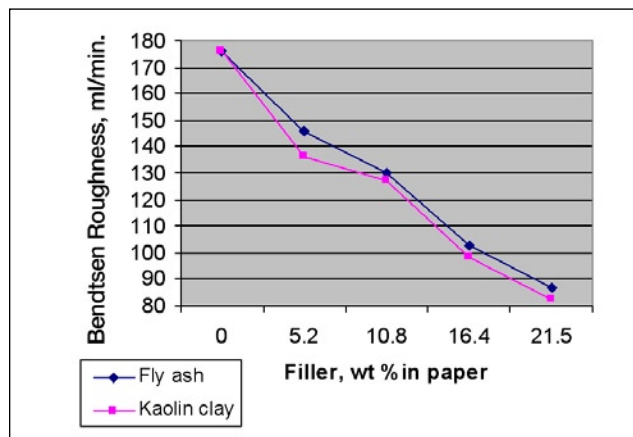
4. Effect of fillers on tear factor of paper.



6. Effect of fillers on paper porosity.



5. Effect of fillers on tensile index of paper.



7. Effect of fillers on top-side smoothness of paper.

kaolin-clay-loaded paper, especially at higher filler percentages. Both these fillers have similar effects on the tensile index of paper up to 10% filler loading. As shown in **Fig. 5**, paper with fly ash shows better tensile index at a higher percentage of filler addition.

Effect of filler addition on porosity and smoothness of paper: Porosity of paper (measured as Gurley porosity) with fly ash as filler is approximately equal to the porosity of paper with kaolin clay up to 5% filler content, as shown in **Fig. 6**. At higher filler content, fly-ash-containing paper shows lower values of porosity compared with clay-containing paper. A comparative study of the effect of filler addition on Bendtsen roughness (ml/min) for fly-ash- and kaolin-clay-containing papers is illustrated in **Figs. 7 and 8**. Fly-ash-containing paper has higher Bendtsen roughness than kaolin-clay-containing paper. Both these fillers exhibit similar trends of decreased paper roughness with increased filler loading.

Economics and benefits: Use of coal fly ash as a paper filler provides four important benefits. The first is the negligible cost of fly ash compared with other paper fillers, which is expected to reduce the cost of paper production by 3%–5%. Second, it provides higher paper opacity for a given filler percent-

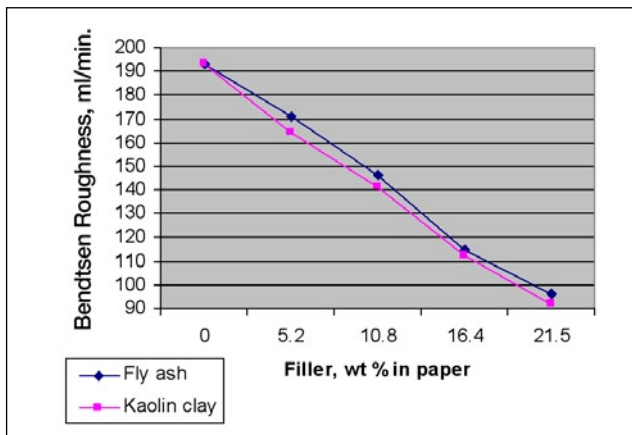
age. Third, mechanical strength properties are superior to those of kaolin-clay-containing paper. Finally, environmental degradation may be avoided by ensuring proper use of fly ash, which is a major solid waste product available in all parts of the world.

CONCLUSIONS

Coal fly ash obtained from thermal power plants using pulverized coal as fuel is available in abundant quantities worldwide. Fly ash is a solid waste product available free of cost. The governments of numerous countries are providing incentives and other benefits to encourage the use of fly ash in various industries. The physical and chemical characteristics of fly ash are similar to those of kaolin clay. Comparative study of the effects of fly-ash and kaolin-clay fillers highlights the fact that printing opacity and tear factor are higher in the case of fly ash. Other properties such as burst index, tensile index, and smoothness are almost the same. The brightness of paper loaded with fly ash is significantly lower than that of paper loaded with kaolin clay at more than 10% filler loading. The grey color of fly ash, together with its low brightness, is a major impediment to the use of fly ash in white paper. However, fly ash is suitable for use in brown, grey, and other dark-colored papers and boards. Laminate base paper is the best example. Because fly ash provides better opacity and strength

LITERATURE CITED

1. Scott, W.E., Chapter 10 in *Principles of Wet End Chemistry*, TAPPI PRESS, Atlanta. 69(1996).
2. Kumar, V., Mathur, M., Kharia, P.S., *Fly Ash Management: Vision for the New Millennium 2000*, Technology Information, Forecasting and Assessment Council (TIFAC), New Delhi, 1.
3. Giere, R., Carleton, L.E., Lumpkin, G.R., *American Mineralogist* 88:853(2003).
4. Affolter, R.H., Brownfield, M.E., Cathcart, J.D., *International Ash Utilization Symposium 1998*, Center for Applied Energy Research, University of Kentucky, 50.
5. Bayat, O., *Fuel* 77(9):1059(1998).
6. Nathan, Y., Dvorachek, M., Pelly, I., et al., *Fuel* 8:205(1999).
7. Wigley, F. Williamson, J., *Prog. Energy Combust. Sci.* 24:337(1998).
8. Moreno, N., Querol, X., Andres, J. M., et al., *Fuel* 84:1351(2005).
9. Energy Information Administration (EIA), *2002 World Production of Primary Energy by Selected Country Groups (Btu)*, Energy Information Administration, U.S. Department of Energy.
10. Sarkar, A., Rano, R., Mishra, K.K., et al., *Fuel Processing Technology* 86(11):1221(2005).
11. Asokan, P., Saxena, M., Asokan, A., et al., *Waste Management & Research* 22(4):265(2004).
12. Turn, S.Q., Jenkins, B.M., Jakeway, L.A., et al., *Biomass & Bioenergy* 30:565(2006).
13. Kinoshita, N., Katsuzawa, H., Nakano, S., et al., *Canadian Journal of Chemical Engineering* 78:974(2000).
14. Huang, X., Hwang, J.Y., Gillis, J.Y., *Journal of Minerals & Materials Characterization & Engineering* 2(1):11(2003).



8. Effect of fillers on wire-side smoothness of paper.

properties, it may improve the quality of laminate base and other colored papers. This possibility may convert fly ash from an environmental pollutant to a resource material for the paper industry. It may even be possible to develop some new grades of paper, so much research work is required in this new area. **TJ**

Received: September 13, 2007

Accepted: November 28, 2007

ACKNOWLEDGEMENT

The author expresses his sincere thanks to Dr. Manohar Singh, professor (Chemical Technology) of Sant Longowal Institute of Engineering and Technology (SLIET) India, for his valuable advice and encouragement. The author would also like to thank Dr. Kamlesh Prasad, A.P. (Food Technology) of SLIET for his help in the setting of the text and figures.

INSIGHTS FROM THE AUTHORS

Fly ash is produced in huge quantities by fossil fuel (especially coal) combustion and has a very small particle size, presenting major challenges for its suitable and environmentally friendly management. To avoid having to landfill large amounts of fly ash, it is essential to find new uses for it in industry.

The major constituents of fly ash (silica, alumina, calcium oxide, magnesium oxide, and titanium oxide) are very much the same as those of wet-end fillers currently used in the paper industry, and therefore there seems to be an opportunity to convert this solid waste into a useful material for paper and other industries that use inert oxides as fillers.

This research examined the effects of fly ash on important paper properties after addition of different percentages of fly ash to pulp slurry. The papers prepared with fly ash were compared with similar papers prepared with a common commercial filler, kaolin clay, having similar chemical constituents. Paper opacity was found to be much higher with fly ash as a filler, but brightness decreased as the filler percent-

age increased. Mechanical strength properties of the paper samples with fly ash as filler were superior to those with kaolin clay. An additional attractive aspect of fly ash as a paper filler is that it is essentially free of cost.

The next step will be to find an industry partner to perform an industrial trial and then to develop methods to increase the brightness of papers made with fly ash.



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