Economical and Efficient Use of Fly Ash for Newsprint Paper Quality Improvement

Anuj K. Verma,[a] S. Suresh,[a,*] and D. Mohta [b]

This research focused on the production of a novel calcium silicate pigment made from pulverized coal fly ash and its application as a coating pigment in a size press for fiber replacement. Improved specific base paper properties of the newsprint was investigated. This novel coated fly ash based calcium silicate (FACS) pigment and conventional precipitated calcium carbonate (PCC) pigment was applied using a cylindrical laboratory coater. When a 4.3 gsm coat weight of FACS was used during the size press application, the brightness increased 10 points, whereas, when the coat weight of FACS was increased to 7.8 gsm, the brightness increased to 21 points as compared to base newsprint sheet; however, FACS brightness was lower than the PCC coated newsprint sheet. Also, there was a significant gain in other newsprint specific base properties when fly ash based pigment was used. This indicated that it is feasible to utilize a novel fly ash based pigment in the size press coating application to replace fiber in order to reduce production cost, improve specific base properties, and reduce environmental pollution. To the authors' knowledge, this is the first study reporting the application of fly ash as a coating pigment for quality enhancement of newsprint.

Keywords: Pigment; Newsprint; Calcium silicate; Fly ash; Coating; Whiteness; Newsprint Properties

Contact information: a: Biomass/Waste-based Material Science and Technology Research Laboratory, Department of Chemical Engineering, MANIT Bhopal-462 003, India; b: Present Address: Business Development Manager at Amazon Papyrus Chemicals Ltd, Singapore;
** Corresponding author: sureshpecchem@gmail.com*

INTRODUCTION

The growth of any country depends on an effective conversion technology to turn industrial waste materials, such as fly ash, into valuable products. The lack of suitable utilization strategies causes global environmental problems. Mining and other mineral exploration processes are increasing the demand for natural resources and destabilizing ecosystems (Sinha *et al.* 2010). Because there is not 100% utilization of fly ash in India and the majority of other countries, some of the fly ash is disposed of in nearby places, such as power plants, causing pollution by mixing with air, water, and soil (Tiwari *et al.* 2016). Normally, silica, alumina, and iron oxides are the major components of fly ash. In thermal power plants, fly ash is a byproduct after burning coal, and electrostatic separators are used to collect it (Bayat 1998).

In the paper industry, finely divided white mineral pigment as a coating material provides special properties to paper such as surface gloss, weight, and reduced ink absorbency (Andersson 2008) The pigment fills the voids between the fibers and coating itself and thus, it improves the properties of the sheet (Chinga and Helle 2003). The most common papermaking pigments are kaolin clay (typical composition of 39% Al_2O_3, 46% SiO_2, and 13% H_2O), calcium carbonate (98 to 100% $CaCO_3$), titanium dioxide (98 to 100% TiO_2), and hydrated silica (consists of 78% SiO_2, 5% CaO, and 17% H_2O). Kaolin clays are commonly used pigment materials in papermaking, but the cost is high. Paper printability and appearance can be increased with the help of mineral coating on any grade of paper (Laufmann *et al*. 2000). Various properties of end product depend upon pigment, binders, and their amounts in a coating formulation. When two different types of pigment are used for the same coating weight, paper properties depend upon pigment shape, size, its distribution, and aggregation. Since pigment is a major component, it must be analyzed in an effort to achieve better optical, surface, and printing properties (Preston *et al*. 2001). It has been stated that "seven S factors" play vital roles in coating; these include size, shape, spacing, surface, spread, stirring, and structure (Patton 1979). Cost is another factor that motivates substitution of expensive fiber by coating, as pigment is a major component in coating formulations (Kettle *et al*. 2010). Fly ash has the same enhancement opportunities available as these common pigments (Song *et al.* 2012), but there has been limited research on the application of fly ash as a coating pigment in papermaking.

Consumption and Utilization of Fly Ash in India and World

In 1996, the generation of fly ash in India was 68.88 million tons, whereas the consumption was 9.63%. In 2016, the generation of fly ash increased to 107.10 million tons, while the consumption also jumped to 63.28%. This amounts to 33% of fly ash still being unused and causing many environmental problems (Singh 2015). In an effort to utilize 100% of the fly ash generated from power plants and various other sources, the Government of India has been continuously providing short term training and projects to increase the usage of fly ash in various sectors, such as cement, agricultural, bricks and tiles, mine filling, and concrete, but such efforts have not yet achieved full utilization of fly ash in India (Nawaz 2013). Table 1 shows the consumption of fly ash in various sectors in India. Coal has been a dominant player in energy generation worldwide. Fly ash generation and utilization is highest in China, consuming almost half of the global coal supply. India shows the largest growth in consumption, overtaking the US to become the world's second bigger consumer of coal (Sarkar *et al.* 2005).

Table 1. Modes of Fly Ash Utilization in Various Industries*

S. No.	Mode of Utilization	Million-Tons	Percentage (%)
1	Cement	405,869	23.98
2	Mine filling	117,827	6.96
3	Brick and tiles	149,110	8.81
4	Reclamation of low lying area	11.0392	6.52
5	Ash dyke raising	11.8888	7.02
6	Roads &flyovers	6.1942	3.66
7	Agriculture	1.9243	1.14
8	Concrete	0.7647	0.45
9	Hydro power sector	0.0197	0.01
10	Others	7.984	4.72
11	Unutilized fly ash	62.1577	36.72
	Total	169.2534	100

*Source: Government of India Report (Singh 2015)

Scope for Use of Fly Ash as Coating Pigment in Newsprint Industry

The chemical and physical properties of various types of fly ash obtained from different courtiers show similar properties, which are comparable with the chemical and physical properties of kaolin clay, precipitated calcium carbonate (PCC), and other pigments used in the paper industry. This is evident as reported in the literature for several countries, *i.e.*, U.S.A., Turkey, Israel, Greece, the Netherlands, Italy, and Spain (Brownfield *et al.* 1999; Nathan *et al.* 1999; Bayat 2002). The particle size of Indian fly ash varies from 0.2 to 90 μm with a significant variation in surface area (0.138 to 2.31 m^2/g), porosity (45 to 57%), and bulk density (800 to 980 kg/m^3) (Zhang *et al.* 2013). The percentage of silica in coal fly ash is 29.4% on a dry basis. This high percentage makes fly ash suitable to be used as a pigment for coating in newsprint or other paper grades.

Scanning electron microscopy (SEM) analysis has shown that fly ash particles have irregular shapes with hollow spherical pores (Shreya *et al.* 2014). Energy dispersive x-ray analysis (EDAX) has revealed the presence of a high amount of silicate and mineral oxides with amorphous nature (Shreya *et al.* 2014). The major constituents are mullite and quartz. Lime, magnetite, hematite, gypsum, and rutile were the other minerals present in minor amounts (Smichowski *et al.* 2008). The addition of fly ash based calcium silicate pigment for coating to the newsprint base sheet changes its pore structure and enhances its properties, such as brightness, stiffness, breaking length, tear index, *etc.* The fly ash addition to the newsprint base sheet increases the opacity of the paper remarkably and better than kaolin clay (Sinha 2008). However, the application of fly ash as a pigment for coating application in the newsprint industry has not yet reported.

Purpose of Coating

Paper coating improves properties such as roughness, surface quality, opacity, and printability. Coating varies from 3 to 40 g/m^2 per side depending on the paper grade (Stoneburner *et al.* 2015). A formulation for coating depends upon the sizing application and end use of the paper. Color coating contains pigment, additives, and binders for coating applications in the size press to achieve enhanced paper properties and fiber substitution in newsprint. Synthetic and natural binders are used depending on the coating method. Surface and optical properties of newsprint can be improved with the help of various pigments. For various reasons, online coating has been preferred over offline applications (Greinecker and Stern 1983).

Newsprint Production in India and World

There are 1,023 newsprint mills in India, which are controlled by the Newsprint Control Order 2004. At present, as per the reported data, 2.5 million tons of newsprint is produced per annum from 64 mills; however, 23 mills are closed, and 36 mills stopped newsprint production. Thus, there was a sharp drop in the domestic newsprint production from 1.44 million tons to 1.02 million tons from the years 2014 through 2015 to 2015 through 2016. Therefore, India is importing half of its newsprint demand from other countries, and these imports significantly increased from 1.33 million tons to 1.5 million tons from the years 2014/2015 to 2015/2016 (Jain *et al*. 2017). There is increasing demand for improved newsprint properties because advertising is switching from the more expensive paper grades to newsprint without losing quality. The export of newsprint from India is negligible, so there is an urgent need for cheap pigment as a coating material.

This research is focused on using the solid waste material, fly ash, for manufacturing a valuable product, such as pigment for coating application in newsprint or other grade of papers. Since fly ash has a porous structure, it can provide better bulk and porosity as compared to conventional pigment such as PCC, GCC, kaolin clay, TiO_2, and talc (Sinha 2008). Using a calcium silicate pigment made from fly ash in a high-pressure carbonation method on the size press to achieve fiber substitution and other surface properties in newsprint manufacturing is a suitable utilization technique to increase the consumption of fly ash. The critical need for the newsprint paper industry can be summarized as to reduce cost of manufacturing, water, power, and energy consumption per unit weight of paper by improving the profitability through value added products such as fly ash based calcium silicate. There is also an urgent need to reduce the environmental issues due to fly ash generated from power plants, as nearly 35% of this material is unused. Paper makers must consider alternative material and method to achieve better newsprint quality at low cost.

Material and Method

In this work, the lab experiment was performed on an uncoated base sheet of newsprint obtained from a local newsprint mill, whose raw material for the manufacturing of newsprint was 90% old newsprint (ONP). The base sheet obtained from the newsprint mill had a brightness of 50.2 ISO. The coal fly ash sample was obtained from a thermal power plant, Parichha (near Jhansi), Uttar Pradesh, India. The process flow chart to produce the calcium silicate from fly ash and its application in newsprint is shown in Fig. 1.

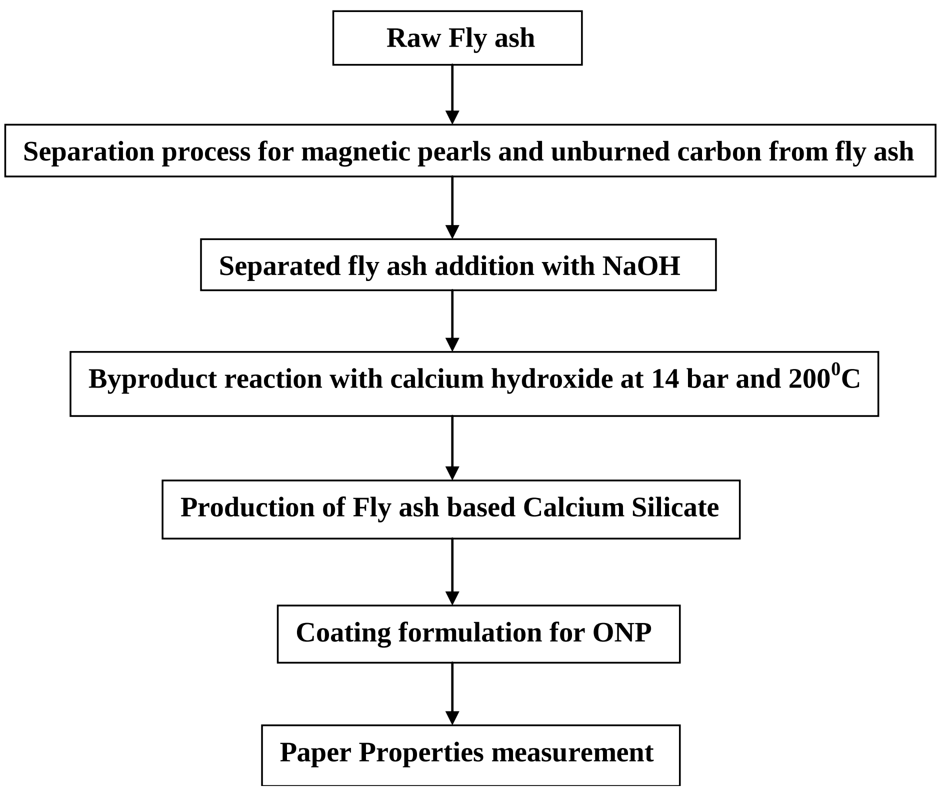

Fig. 1. Schematic flow diagram for modification fly ash

Grinding and Fractionation of Fly Ash Based on Particle Size

The fly ash sample was ground in a ball mill to achieve a uniform fine size, and then it was passed through stacks of sieves having mesh sizes of 200, 250, 300, 325, 400, 500, and 800. The sieving operation had a duration of 10 min, and after the shaking was completed, the material on each sieve was weighed. The particles in the size range from 21 to 39 µm were used as the pigment for papermaking.

Whiteness Improvement in Raw Fly Ash

Magnetic pearls, unburned carbon, and mullite content are the major influencers of the whiteness of the fly ash. Magnetic pearls are formed during the decomposition of coal minerals, such as magnetite arsenic, pyrites, and magnetite. During combustion, Fe_3O_4 and magnetic Fe_2O_3 form magnetic pearls, which are black in color and have strong magnetic properties. The average size of these pearls are 18 to 22 µm and a whiteness of only 9.1. These pearls present in fly ash have high influence on its whiteness. The non-magnetic fraction of fly ash was separated using magnets. Another component that affects the fly ash whiteness is unburned carbon particles. The content of unburned carbon particles in the present study was only 2.61%. Because the ultrafine unburned carbon particles are grey and black in color, they have a large effect on the whiteness of fly ash. A self-designed floatation separator was used for removing this unwanted material from the fly ash. The success of the flotation process depends on the collector dosages. In this experiment, the optimum collector dosages of 15 mL of kerosene per 1.5 kg of fly ash were taken. The coated fly ash based calcium silicate whiteness was measured using L&W Elrepho Code Number 070/071 (Kista, Sweden). After using a novel high-pressure carbonation process, the whiteness of the desired product improved to 71.7 ISO.

Modified Fly Ash Based Calcium Silicate Preparation

After separating the unwanted material from the fly ash, its whiteness increased to a high point value. However, this was not sufficient to be used as good quality pigment in newsprint. A novel method called high-pressure carbonation was then used to prepare the fly ash based calcium silicate (Mathur 2001).

In this method, the separated fly ash and NaOH were placed in the pressure vessel (Amar Equipment Pvt. Limited, Mumbai, India), heated to 200 °C and a pressure of14 bar for 1 hour, and then cooled to 90 °C using a heat exchanger. The byproduct obtained from the reaction was placed back into the reactor. The reaction of liquid byproduct in the form of silicate, $Ca(OH)_2$,and pure CO_2 (99.98%) were carried out under high pressure. Here the calcium hydroxide slurry react with silicon dioxide according the following reaction.

$$Ca(OH)_2 + SiO_2 \longrightarrow Ca_xSi_y(OH)_z.wH_2O$$

The slurry was stirred and again heated to 200 °C and a pressure of 14 bar. The higher pressure in the reactor resulted in an increased rate of the carbonation reaction. The closed carbonation reaction also prevented the CO_2 from escaping from the reactor into the atmosphere, contributing to pollution. This, in turn, increased the CO_2 utilization and caused a fast reaction. The reaction time for the hydro thermal reaction was approximately 2 to 2.5 h, which is faster than the open vessel reaction. The slurry was cooled by passing it through a heat exchanger, and it was piped directly into the collecting tank, allowing for the expansion of the silicate. Various properties of the modified fly ash based calcium silicate and marketed PCC is given in Table 2.

Table 2. Various Parameters of Calcium Silicate and PCC

Properties	FACS	PCC
Average particle size (µm)	15.8	1.75
BET area (m^2/gm)	83	11.2
Brightness (ISO)	91.2	96
Solid (%)	3.5	16
pH	8.1	9.2
Refractive index	1.64	1.57

Coating Formulation for ONP Size Press Coating

The coating formulation was made using a high shear mixer with a variable drive to provide high shear for dispersion of the pigments, but low shear for the addition of the latex and starch. The final coating formulation was then diluted with water to provide a coat range close to the target of 4.5 and 7.5 gsm on a coater having Brookfield viscosity of approximately 900 cp for both FACS and PCC. After the sheets were coated, they were immediately dried using a coated drum dryer, calendared, and then placed in a standard control room for testing. The coating formulation for the ONP on the size press is given in Table 3.

Table 3. Detail of Coating Formulation

Make-up parts	Parts (%)
Fly ash based calcium silicate pigment	100 Parts
Latex	5 Parts
Starch	7 Parts
Total	112 Parts

Characterization of Paper

The newsprint base sheet was conditioned for 3 h in an environmental chamber maintained at 25 °C and 52% relative humidity. Brightness (TAPPI T 452 om-98 1998), opacity (TAPPI T425 om-96 1996), breaking length (TAPPI T494 om-01 2001), tear index (TAPPI T414 om-98 1998), and Gurley stiffness (TAPPI T543 om-00 2000) were calculated using the given standard methods.

RESULTS AND DISCUSSION

Fly ash modification and substitution in newsprint or any grade of paper can be achieved based on a chemical and mechanical method and develop a correlation between pigment and fiber based on particle size, particle size distribution, specific surface area, brightness, refractive index, and dispersion model development.

Fly Ash Particle Size and Mess Screen

The biggest particle size was 76.1µm, while the smaller one was 18.4 µm. Particle sizes greater than 50 µm were judged not to be suitable for the use of pigment, and fly ash particles with a size of 18.4 µm were too small. To insure the consistency of particle size and increase the utilization rate of fly ash, 39 µm and 21 µm were selected for pigment manufacturing in this experiment. Chemical compositions of fly ash used in this experiment are given in Table 4.

Table 4. Chemical Composition of Fly Ash

Constituent	Fly Ash (%)
Silica(SiO_2)	61.7
Alumina(Al_2O_3)	31.3
Iron Oxide(Fe_2O_3)	3.5
Calcium Oxide(CaO)	1.1
Magnesium Oxide(MgO)	1.3

Whiteness of a Modified Fly Ash

The whiteness of unmodified fly ash was 27.7 ISO, as shown in Table 5. After removing magnetic pearls and unburned carbon, the whiteness was 37.3 ISO, while that of using high-pressure carbonation whiteness increased the most and was 71.7 ISO.

Table 5. Whiteness Enhanced during Various Process

Sample	Process	Whiteness (ISO)	Code of the Sample
Raw fly ash	-	29.1	A
Fly ash after removing magnetic pearls	Separation	34.2	B
Fly ash after removing unburned carbon	Separation	37.3	C
Fly ash based calcium silicate	High Pressure	71.7	D

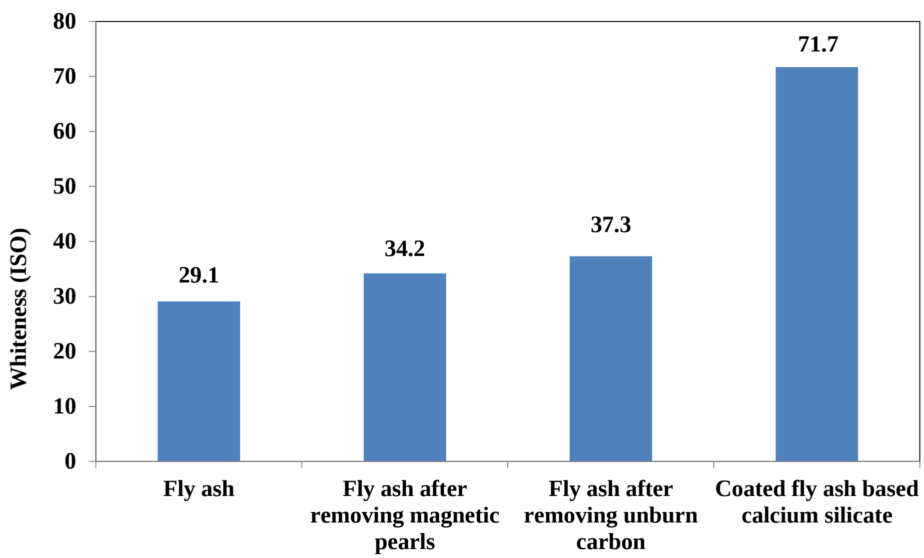

Fig. 2. Effect of Whiteness after various processes

Figure 2 shows that the color of the modified fly ash changed from dark brown to near white. A visual picture of whiteness improvement of the fly ash after separation and high-pressure carbonation pressure (HPC) is shown in Fig. 3.

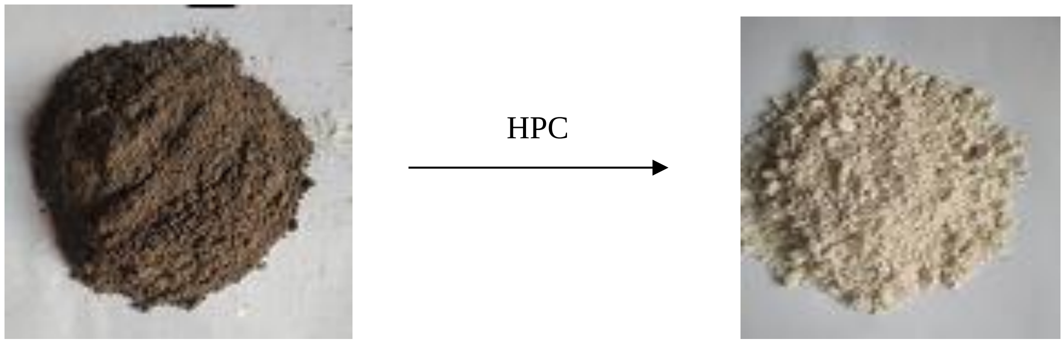

Fig. 3. Fly ash color conversion and modified calcium silicate

Effect of Modified Fly Ash Based Calcium Silicate on Newsprint Properties

The final coat weight for this experiment was 4.3gsm and 7.7 gsm (±0.5 gsm). Four coating pigment formulation were prepared: FACS-4.3 gsm (F1), FACS-7.8 gsm (F2), PCC-4.2 gsm (P1), and PCC-7.6 gsm (P2) are shown in Table 6.

Table 6. Newsprint Various Properties Before and After Coating (significant differences at $p < 0.06$)

Types of Paper	Brightness (ISO)	Opacity (ISO)	Gurley Stiffness (mg)	Tear Index (mN.m^2/g)	Breaking Length (km)	Smoothness (su)
Newsprint sheet as such	50.2±1.2	98.1±3.2	25.9±4.2	5.1±0.5	5.2±0.8	226±12
F1	63.4±2.3	99.2±4.3	28.8±3.2	5.9±0.8	6.8±0.1	248±10
F2	73.2±1.7	99.6±2.1	35.8±1.2	5.6±0.3	6.9±0.4	295±16
P1	67.4±2.1	99.5±2.7	26.8±3.4	5.3±0.4	5.9±0.6	284±13
P2	79.8±1.8	99.8±3.0	29.4±2.3	5.5±0.2	6.3±0.2	327±18

Brightness

Brightness of various coating pigments used in newsprint base sheet are shown in Table 6. The brightness of coated sheet increased with an increase in coating. This improvement can be attributed to the excellent coverage of the darker base layer at higher coating weight using different pigment (Juuti *et al.* 2009). On comparing brightness of different pigment coated newsprint sheet, the PCC-coated sheet showed higher brightness in both 4.3 and 7.8 gsm coated sheet as compared to FACS coated and base newsprint sheet due to the high light scattering characteristics. FACS coated sheet brightness is also comparable and increases base newsprint to a desirable point, which overcomes the drawback of low brightness of fly ash used in various literature (Sinha 2008; Fan and Qian 2012). The results obtained from FACS pigment coating to base newsprint are encouraging and can be used for production of any grade of paper. Brightness of newspaper can be increased to a very high level depending upon the pigment used and coating process. Thus, newspaper can be used for various other applications where brightness plays an important role.

Opacity

Opacity of FACS-coated sheets was excellent as compared to base newsprint sheet, but opacity was lower than PCC-coated newsprint sheet in both 4.3 and 7.8 gsm coated sheet (Table 6). Narrow span and smaller size result in an excellent light scattering coefficient (McLain and Ingle 2009). The average particle size of FACS pigment and PCC were different but the distribution was similar. This light scattering affect, by changing the number of pigment particles in the coating application, resulted in higher opacity of the PCC coated sheet. So, from Table 6 it is clear that there was no need to add further coating of FACS to newsprint base sheet as 4.3 gsm fly ash based pigment coating is sufficient to provide the enhancement needed in the opacity due to its porous structure.

Stiffness

The rigidity of any paper sample is determined by stiffness measurements. It is essential for the sheet stiffness of a paper to provide rigidity as required for various grade of coating paper such as printed travel tickets, business cards, and folding cartons. In order to achieve proper rigidity, the pigment, binders, and method of coating plays an important role (Mathur 2004). The base newsprint sheet stiffness was 25.9 mg, but when the 4.3 gsm coating of FACS pigment was applied to the newsprint base sheet the rigidity increased 2.9 points, whereas the stiffness increases 0.3 points using PCC as a coating pigment. The highest stiffness was obtained in FACS coated sheet due to high bulk and strong bonding. For a higher stiffness, a 7.7 gsm coating of FACS and PCC pigment was applied to the sheet, which caused an increase of 10 points and 6.6 points compared with the base sheet. Overall, the stiffness values of FACS are better than PCC and base newsprint because of its high bulk, particle shape, size, and aggregation property (Seo 2002). Table 6 shows a comparison of different pigment coating of FACS, PCC, and base newsprint.

Tear Index

Tear strength depends on fiber length, fiber, and pigment bonding (Chauhan *et al.* 2013). The base newsprint sheet also plays an important role when coated with any pigment. The tear index of the FACS-coated sheet was better than the PCC-coated sheet and base newsprint sheet for both 4.3 and 7.8 gsm due to the porous structure of fly ash based pigment, which increases friction between base sheet and pigment coating, resulting in higher tear strength. Thus, surface roughness also plays an important role in tear index (Chauhan *et al.* 2013). The coated sheet strength increased by 10% to 20% using FACS compared with the uncoated ONP newsprint sheet and PCC, which indicates that coated newsprint using FACS can stand in modern high speed folders and automatic press feeders (Kumar 2009). Various values of tear index using different types of coating pigment are shown in Table 6.

Breaking length

Breaking length depends upon formation of base newsprint sheet, which relies on the binder, pigment, and coating process (Kumar 2009). The breaking length of the newsprint base sheet was 5.2 km. When the 4.3 gsm coating of FACS and PCC pigment coating was applied compared to the base newsprint sheet, the breaking length increased from 5.2 to 6.8 km and 5.2 to 5.9 m. Thus, when a suitable pigment is used in coating applications, the breaking length can be increased to a significant degree, as pigment plays an important role in coating formulation and paper properties (Santos and Velho 2004). Increase in the breaking length by 35% compared with the base sheet and 10% with other pigment using FACS also indicates better fiber to pigment bonding result and good inherent strength of newsprint. Hence, it can be stated that the fly ash based pigment is a good substitute for coating pigment in newsprint due to its particle size, shape, and aggregation as compared to PCC and uncoated base sheet of newsprint. A comparison of various properties of breaking length is shown in Table 6.

Smoothness

In the paper industry, paper comes in a variety of finish specifications, which means it may be smooth or rough or in between. Generally, coated paper is smoother and the range of smoothness depends upon light scattering coefficient (Lourenço *et al.* 2013). In the present study, a PCC coated newsprint sheet exhibits high smoothness as compared to a FACS and base newsprint sheet for both 4.3 and 7.8 coat weight. This is because small particles of the PCC pigment scatter more light and fill the voids within the coating; this results in a smoother surface of the base newsprint sheet.

CONCLUSIONS

1. Low cost waste fly ash has been used as coating pigment in newsprint for quality improvement, which provides economic and environmental benefit.
2. The most significant increase was in brightness, which generates a potential for higher revenue in newsprint.
3. Newsprint made with a calcium silicate pigment coating can compete with the imported newsprint.
4. Fly ash generated from the power plant in a newsprint mill can be used as a potential coating pigment in the size press for energy savings during drying and result in higher opacity of newsprint and superior mechanical strength properties.
5. The production of modified fly ash based coating pigment using the high-pressure carbonation process shows excellent optical and strength properties when compared to PCC and base newsprint sheet.

ACKNOWLEDGMENTS

The authors are very thankful to Dr. Raj Kumar Arya, Associate Professor, Department of Chemical Engineering, Thapar Institute of Engineering & Technology, Patiala, for technical discussion.

REFERENCES CITED

Andersson, C. (2008), "New ways to enhance the functionality of paperboard by surface treatment–a review," *Packag. Technol. Sci.* 21(6), 339-373.

Bayat, B. (2002). "Comparative study of adsorption properties of Turkish fly ashes: I. The case of nickel (II), copper (II) and zinc (II)," *J. Hazard. Matr.* 95(3), 251-273. DOI: 10.1016/S0304-3894(02)00140-1

Bayat, O. (1998). "Characterisation of Turkish fly ashes," *Fuel* 77(9-10), 1059-1066. DOI: 10.1016/S0016-2361(97)00274-3

Brownfield, M. E., Affolter, R. H., Cathcart, J. D., Brownfield, I. K., Hower, J. C., and Stricker, G. D. (1999). "Dispersed volcanic ash in feed coal and its influence on coal combustion products," in: *International Ash Utilization Symposium*, Lexington, KY, USA, pp. 18-20.

Chauhan, V. S., Bhardwaj, N. K., and Chakrabarti, S. K. (2013). "Effect of particle size of magnesium silicate filler on physical properties of paper," *Can. J. Chem. Eng.* 91(5), 855-861. DOI: 10.1002/cjce.21708

Chinga, G., and Helle, T. (2003), "Relationships between the coating surface structural variation and print quality," *J. Pulp Pap. Sci.* 29(6), 179-184.

Fan, Y.-m., and Qian, X.-r. (2012). "Study on using fly ash as a papermaking filler," *China Pulp Pap.* 31(4), 22-26. DOI:10.102/ie3028813.

Greinecker, H., and Stern, G. (1983). "Filler for paper, card or board, a process for its manufacture, and paper, card or board containing the filler," U.S. Patent 4,405,744.

Jain, R. K., Eriksen, Ø., Isaksson, A., Ritin, K., Kumar, V., and Marwaha, A. (2017). "Development and adoption of appropriate technologies for enhancing productivity in the paper and pulp sector," in: *International Exhibition & Conference on Pulp, Paper & Allied Industries (PaperEx South India)*, Chennai, India.

Juuti, M., Koivunen, K., Silvennoinen, M., Paulapuro, H., and Peiponen, K. E. (2009). "Light scattering study from nanoparticle-coated pigments of paper," *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 352(1-3), 94-98.

Kettle, J., Lamminmäki, T., and Gane, P. (2010), "A review of modified surfaces for high speed inkjet coating," *Surf. Coat. Tech.* 204(12-13), 2103-2109.

Kumar, A. (2009). "The effect of pigment coating on various grades of base paper," Master thesis, IIT Roorkee, India

Laufmann, M., Forsblom, M., Strutz, M. D., and Yeakey, S. R. (2000). "GCC *vs.* PCC as the primary filler for uncoated and coated wood free paper," *Tappi J.* 83(5), 76-76.

Lourenço, A. F., Gamelas, Jaf., and Zscherneck, C. (2013). "Evaluation of silica-coated PCC as new modified filler for papermaking," *Ind. Eng. Chem. Res.* 52(14), 5095-5099. DOI**:** 10.1021/ie3035477

Mathur, V. K. (2001). "High speed manufacturing process for precipitated calcium carbonate employing sequential perssure carbonation," U.S. Patent 6,251,356.

Mathur, V. K. (2004). "Novel silicate "fibrous fillers" and their application in paper," Proc. TAPPI Spring Technical Conference.

McLain, L., and Ingle, D. (2009). "Fillers," in *Applications of Wet-End Paper Chemistry*,

Springer, pp. 113-136.
Nathan, Y., Dvorachek, M., Pelly, I., and Mimran, U. (1999). "Characterization of coal fly ash from Israel," *Fuel* 78(2), 205-213. DOI: 10.1016/S0016-2361(98)00144-6
Nawaz, I. (2013). "Disposal and utilization of fly ash to protect the environment," *Int. J. Innov. Res. Sci. Eng. Technol.* 2(10), 5259-5266.
Preston, J., Nutbeem, C., Parsons, J., and Jones, A. (2001). "The printability of coated papers with controlled microstructure," *Pap. Technol.* 42(2), 33-41.
Patton, T. C. (1979). *Paint Flow and Pigment Dispersion: A Rheological Approach to Coating and Ink Technology*, Wiley.
Santos, N., and Velho, J. (2004). "Coating structure with calcium carbonate pigments and its influence on paper and print gloss," Annual meeting – Pulp and Paper Technical Association of Canada, Pulp and Paper Technical Association of Canada.
Sarkar, A., Rano, R., Mishra, K., and Sinha, I. (2005). "Particle size distribution profile of some Indian fly ash - A comparative study to assess their possible uses," *Fuel Process. Technol.* 86(11), 1221-1238. DOI: 10.1016/j.fuproc.2004.12.002
Seo, Y. B. (2002). "New concept of stiffness improvement in paper and board," *J. Korea Tech. Assoc. Pulp Paper Ind.* 34(5), 63-69.
Shreya, N., Paul, B., Ribeiro, J., Valentim, B., and Flores, D. (2014). "Fly ash characterization of Jharkhand (India) by lasergranulometry and SEM/EDS," *Comunicações Geológicas*101(Especial II), 851-854.
Singh, M. (2015). *Report on Fly Ash Generation at Coal/Lignite Based Thermal Power Stations and its Utilization in the Country for the Year 2014–15*, Central Electricity Board, New Delhi, India.
Sinha, A., Singh, M., and Singh, S. (2010). "Study on use of non-magnetic fraction of pulverized coal fly ash as filler in specialty paper manufacturing," *IPPTA J*. 22(2), 117-120.
Sinha, A. S. K. (2008). "Effects of pulverized coal fly-ash addition as a wet-end filler in papermaking," *Tappi J.* 7(9), 3-7.
Smichowski, P., Polla, G., Gómez, D., Espinosa, A. J. F., and López, A. C. (2008). "A three-step metal fractionation scheme for fly ashes collected in an Argentine thermal power plant," *Fuel* 87(7), 1249-1258. DOI: 10.1016/j.fuel.2007.07.011
Song, S., Zhang, M., He, Z., Li, J. Z., and Ni, Y. (2012). "Investigation on a novel fly ash based calcium silicate filler: Effect of particle size on paper properties," *Ind. Eng. Chem. Res.* 51(50), 16377-16384. DOI: 10.1021/ie3028813
Stoneburner, R., Joyce, M., Klass, C., and Mathur, V. (2015). "A novel silica-based nano pigment as a titanium dioxide replacement," in: *Paper Conference and Trade Show, PaperCon 2015*, Kalamazoo, MI, USA.
Tiwari, M. K., Bajpai, S., and Dewangan, U. K. (2016). "Fly ash utilization: A brief review in Indian context," *Int. Res. J. Eng. Technol.* 3(4), 949-956.
TAPPI T 414 om-98 (1998). "Internal tearing resistance of paper (Elmendorf-typemethod)," TAPPI Press, Atlanta, GA, USA.
TAPPI T 425 om-96 (1996). "Opacity of paper (15/d geometry, illuminant A/2°, 89% reflectance backing and paper backing)," TAPPI Press, Atlanta, GA, USA.
TAPPI T 452 om-98 (1998). "Brightness of pulp, paper, and paperboard (directional reflectance at 457nm)," TAPPI Press, Atlanta, GA, USA.

TAPPI T 494 om-01 (2001). "Tensile properties of paper and paperboard (using constant rate of elongation apparatus)," TAPPI Press, Atlanta, GA, USA.
TAPPI T 543 om-00(2000). "Bending resistance of paper (Gurley-type tester)," TAPPI Press, Atlanta, GA, USA.
Zhang, M., Song, S., Wang, J., Sun, J., Li, J. Z., Ni, Y., and Wei, X. (2013). "Using a novel fly ash based calcium silicate as a potential paper filler," *BioResources* 8(2), 2768-2779. DOI: 10.15376/biores.8.2.2768-2779

Article submitted: April 3, 2018; Peer review completed: May 13, 2018; Revised version received and accepted: May 25, 2018; Published: June 11, 2018.
DOI: 10.15376/biores.13.3.5765-5777