Statistical Approach for Optimizing Dosage of Dispersed Talc and CPAM for Target Ash and FPAR in Paper

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ABSTRACT

Retention of filler depends upon its particle size and shape, and colloidal chemistry during papermaking. The light scattering primarily depends upon solid-air interface; with increase in surface area, the light scattering increases. The dispersion of filler particles plays an important role in its retention, distribution and light scattering in paper. The talc filler was dispersed in deionized water along with non-ionic triblock polymeric wetting agent and anionic dispersant (sodium salt of polyacrylic acid). Controlling charge density of papermaking slurry with cationic polyacrylamide (CPAM) based retention aid polymer helped in protecting the retention of talc in paper without affecting the light scattering properties of both filler and paper. In the present paper the statistical approach was followed to optimize the dosage of both CPAM and talc filler using response surface methodology based central composite design to cut short the manual approach. The design was employed by selecting the dosage of talc and CPAM as model factors to get the variation of ash in paper. The need of CPAM for varying dosage of talc filler was calculated statistically through the data of first pass ash retention (FPAR) using Analysis of Variance. The results of first order factorial design showed that both independent variables had significant effect on increasing the ash in paper. At any particular filler addition level, increase in CPAM addition enhanced the ash and FPAR. The linear equations obtained from the designed experiments could be used to predict the dosage of inputs i.e. talc and CPAM on the basis of desired outputs i.e. ash content and FPAR.

Keywords: *Ash; CPAM; Dispersion; Experimental design; FPAR; Statistics; Talc*

Introduction

Mineral fillers are, now-a-days, an important additive used at the wet-end of papermaking process. Fillers are highly desirable in printing papers for increasing the opacity and raising brightness, and improving printing properties. Fillers also decrease the energy demand in pulp and papermaking process due to lesser usage of fibrous mass for constant production of paper [1,2].

In India, talc is one of the most commonly used fillers in papermaking applications. It is a layered magnesium silicate mineral ($Mg_3Si_4O_{10}$-$(OH)_2$) which usually occurs in foliated, granular, or fibrous form. It is characteristically hydrophobic, generally inert and softest mineral on earth. The light scattering coefficient of paper primarily depends upon the particle size and shape of filler. For the particles of same shape, the higher the particle size the lower is the scattering coefficient. Good dispersion of filler may increase the light scattering of filler and paper. The filler/pigment used in paper coating is dispersed well with suitable dispersing agent prior to the application on paper surface. Now-a-days calcium carbonate filler (GCC and PCC) are manufactured in-situ and available in the pre-dispersed slurry form. They are mixed with some amount of dispersant to avoid the agglomeration of particles. This practice is not in vogue for talc fillers. This may be because of comparatively higher particle size of talc fillers which is less favorable to particle agglomeration than calcium carbonate fillers having lower particle size. Being hydrophobic in nature, proper dispersion of talc might be required before its addition in papermaking slurry [3].

The cellulosic fiber and most of the fillers are anionic in nature; they do not have a mutual attraction. Being lower in particle size (1 to 10 microns) and higher density as compared to cellulose fibres, the mineral filler particles pass through the forming wire and are lost from the sheet. Despite having negative charge fillers can be attached to fibers with the use of appropriate retention aid chemical which acts by flocculating the filler particles and fiber fines, and retain within the fiber matrix during papermaking. The nature and dosage of retention aid chemical primarily depend on the characteristics of mineral fillers viz. charge density, particle size and shape, and their addition level in paper [4-6]. The extent of addition of a retention aid chemical for the retention of filler is an important task in papermaking. The optimum dosage of both the components may be developed based upon target ash, first pass ash retention (FPAR) and drainage rate through an effective experimental design procedure.

Response surface methodology (RSM) is a collection of mathematical and statistical technique for design of experiments, building models, evaluating the effects of factors and searching for the optimum conditions that are useful for the modeling and analysis of problems [7]. RSM is a widely practiced approach for the production and optimization of various

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industrially important products such as chemicals and enzymes [8,9]. The technique requires minimum experimentation and time thus proving to be far more effective than the conventional methods of developing such products. Central composite design (CCD) is an important component of RSM. A CCD has three groups of design points:

i. two-level factorial or fractional factorial design points
ii. axial points (sometimes called "star" or "alpha" points)
iii. center points

Through CCD the coefficients of a linear model are estimated. All point descriptions are in terms of coded values of the factors.

The objective of the present work is to study the effect of wetting and dispersion of talc filler on retention and light scattering coefficient, and analyze the effect of the dosage of talc filler and cationic polyacrylamide (CPAM) on ash content and FPAR through statistical approach.

Materials And Methods

Materials

Bleached mixed hardwood kraft pulp was procured from an integrated pulp and paper mill in north India. The pulp furnish was a mixture of eucalyptus (50%), poplar (35%) and bamboo (15%). The dry powder of talc filler was procured from a talc manufacturer in north India. The non-ionic triblock polymer and sodium salt of polyacrylic acid (anionic) were used as wetting agent and dispersant, respectively. A commercially available medium to high molecular weight cationic polyacrylamide (CPAM) was used as a retention aid chemical.

Methods

The refining of the pulp was carried out in a PFI mill as per TAPPI method T248 sp-00 to attain 430 ml Canadian standard freeness (CSF) level. The pulp freeness was determined as per TAPPI method T227 om-09. The pH of filtrate of talc suspension (10% w/v) filtered through a 300 micrometer screen was measured with pH meter. The dry CPAM powder was dispersed in deionized water of ~40°C in a beaker and agitated at 300 rpm for 30 minutes to prepare 0.1% concentration (w/v) solution. The colloidal charge density or ionic behavior of both talc filler and CPAM was examined on Mutek particle charge detector (PCD 03) at 10% (w/v) and 0.1% (w/v) concentration, respectively. The talc and CPAM were titrated with cationic (Polydiallyldimethylammonium chloride) and anionic (sodium polyethylene sulfonate) polymers, respectively, to analyze the colloidal and dissolved charge in the form of streaming potential. The surface charge on talc filler was determined in the form of zeta potential on Mutek zeta potential meter (SZP 06). About 500 ml filler sample (10% w/v) was taken and mixed thoroughly before measurement. The viscosity of both talc and CPAM was measured with Brookfield viscometer. The particle size of talc filler was measured with Particle size distribution analyzer (model Horiba LA-950S2).

The paper hand sheets of 60 g/m^2 were prepared as per TAPPI method T205 sp-02. The ash in paper was determined at 525 ^{0}C as per TAPPI method T211 om-93. The ash and first pass ash retention (FPAR) were calculated with the following formula:

Ash in paper,

$$\% = \frac{\text{weight of ash in paper (g.o.d)}}{\text{weight of handsheet (g.o.d)}} \times 100$$

FPAR,

$$\% = \frac{\text{Ash in paper (\%)}}{\text{Filler added based on pulp and filler(\%)}} \times 100$$

Statistical approach for experiments design

A 2-fractional factorial design (FFD) was used to select the factors that influence the ash content and FPAR in paper significantly; insignificant ones were eliminated in order to obtain a smaller, more manageable set of factors. In developing the regression equation, the test variables were coded according to the following equation [10]:

$$X_j = (Z_j - Z_{0j}) / \Delta_j \quad (1)$$

where X_j was the coded value of the dependent variable, Z_j was the real value of the independent variable, Z_{0j} was the value of the independent variable on the centre point and Δ_j was the step change value. The linear model observed was expressed as follows:

$$Y = \beta_0 + \sum_{j=1}^{2} (\beta_j X_j) \quad (2)$$

where Y was the predicted response, β_0 was the intercept and β_j was the j^{th} linear coefficient. This linear model was used for the analysis of ash content and FPAR as response. Low and high factor settings were coded as -1 and 1, the midpoint coded as 0. The factor settings of trials that ran along axes drawn from the middle of the cube through the centers of each face of the cube were coded as -1.414 and +1.414 (-α and +α). The dosage of talc filler and CPAM were optimized statistically using CCD based RSM design. The CCD consisted of two input variables with two levels i.e. talc filler and CPAM. The target addition level of talc was 200 to 600 kg/t pulp and that of CPAM was 50 to 400 g/t pulp.

The Statease Design Expert software, version 8.0.5.1 was used for the experimental design, and regression and graphical analysis of the data obtained from the experiments. The statistical analysis of the model was performed in the form of Analysis of Variance (ANOVA).

Results And Discussion

Properties of talc filler and CPAM

Talc is anionic in nature; the cationic charge demand to neutralize the charge was 31.7 μeq/g. The zeta potential of the filler was -455 mV. The filler slurry was slightly alkaline in nature. The median particle size of talc (D50) was 6.0 μm. The Brookfield viscosity of talc of 50% solids (w/v) at room temperature was 24 cP. The anionic charge demand of the cationic polyacrylamide (CPAM) was 1134 μeq/g. The pH of CPAM was acidic and Brookfield viscosity of 0.1% solids (w/v) was 48 cP (Table 1).

Effect of dispersion of talc filler

The dispersion of filler might loosen the agglomerates, free the individual particles and increase the light scattering of the filler particles. Talc filler slurry of 50% solids (w/v) was prepared in deionized water by agitating the slurry in an agitator for 30 minutes at 2000 rpm. The wetting agent and dispersant were added separately to the talc slurry with continuous agitation and viscosity was measured after agitating the slurry for 5 minutes each time. The viscosity of talc filler dispersed in water was 234 cP which initially increased and subsequently decreased on increasing dosage of wetting agent. The initial increase was due possibly to (i) the higher viscosity of the wetting agent and (ii) inadequacy

Table 1: Properties of talc filler and CPAM

Particular	Talc	CPAM
Colloidal charge, mV	-326	+655
Charge demand, µeq/g	+31.7	-1134.5
Zeta potential, mV	-454.9	--
pH	9.31	4.91
Median particle size (laser), µm	6.03	--
Brookfield viscosity (25°C, 100 rpm), cP	24.2*	48.5**

** at 50% solids (w/v)*
*** at 0.1% solids (w/v)*
■ *not measured*

of its dosage resulting in less wetting. In contrast, the dispersing agent reduced the viscosity from the initial stage of dosing and attained constant level. The lowest viscosity was achieved with dosage of 7 kg/t wetting agent (56 cP) and 3 kg/t dispersant (40 cP) (Fig. 1a&b).

The combined effect of wetting and dispersing agent in the optimized dosage was also determined. The wetting agent was first added in the talc slurry at a dosage of 7 kg/t on talc and agitated for 5 minutes. The dispersant was subsequently added at three dosage levels (3, 6 and 10 kg/t on talc). It was observed that the combination of 7 kg/t of wetting agent and 3 kg/t of dispersant could synergistically act and decrease the viscosity to its lowest level i.e. 24 cP (Fig. 1c).

The wetting and dispersion of mineral particles are desirous to avoid the agglomeration of particles. It was observed that the particles size of talc filler wetted/dispersed in different manners was comparable due to the similar principle followed during particle size measurement by the instrumental technique. The median particle size of talc filler dispersed in water alone, and along with wetting agent, dispersant, and combination of wetting agent and dispersant was similar (6.0 µm). This was further confirmed from the results of light scattering coefficient of both talc and paper which was not affected by the addition of either wetting agent, dispersant or both. The scattering coefficient of talc and paper was around 123 and 50 m^2/kg, respectively (Table 2).

It was observed that the anionicity of talc increased on addition of either wetting agent or dispersant. The cationic colloidal charge demand of talc filler dispersed in deionized water was 2.0 which increased to 3.3 µeq/g upon addition of wetting agent. The anionicity of talc filler increased substantially to 24.2 µeq/g with the addition of dispersant. When both wetting agent and dispersant were added in talc slurry the cationic demand further increased to 28.9 µeq/g. These results indicated that the anionicity of the talc filler increased on the addition of dispersant which would have an effect on filler retention in paper. In order to understand the retention behavior of the dispersed filler, handsheets were prepared with the target ash of 15%. The dosage of talc was adjusted accordingly. It was observed that on wetting and dispersion of talc, its retention in paper was decreased. The FPAR of talc was 41.1% when it was dispersed in water alone and decreased to 38.8, 25.0 and 23.4% when dispersed with wetting agent,

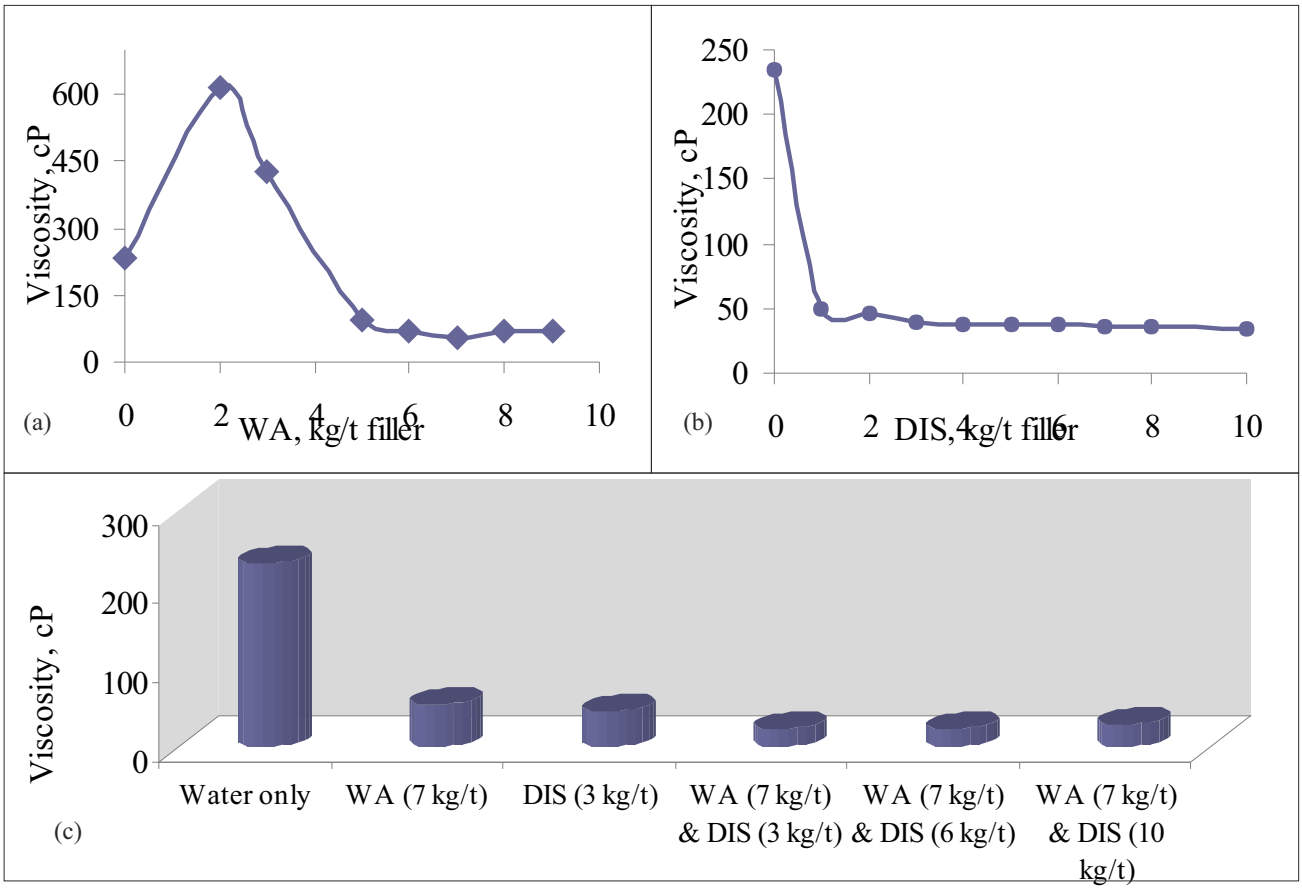

Fig. 1. Effect of wetting agent (WA) and dispersant (DIS) on viscosity of talc filler

dispersant, and both wetting agent and dispersant, respectively (Table 2). These results indicated that the dosage of wetted and dispersed talc needed to be increased for getting the same ash in paper. For getting 15.1±0.2% ash in paper, the dosage of talc dispersed in water alone and with wetting agent, dispersant, and both wetting agent and dispersant were 58, 65, 150 and 180%, respectively.

As the FPAR of talc filler in paper was reduced on addition of wetting agent and dispersant, the cationic polyacrylamide (CPAM) retention aid (200 g/t pulp) was added in pulp stock. As described earlier, when no retention aid was used the FPAR of talc filler dispersed in water alone, and with wetting and dispersing agent was 41.1 and 23.4%, respectively which

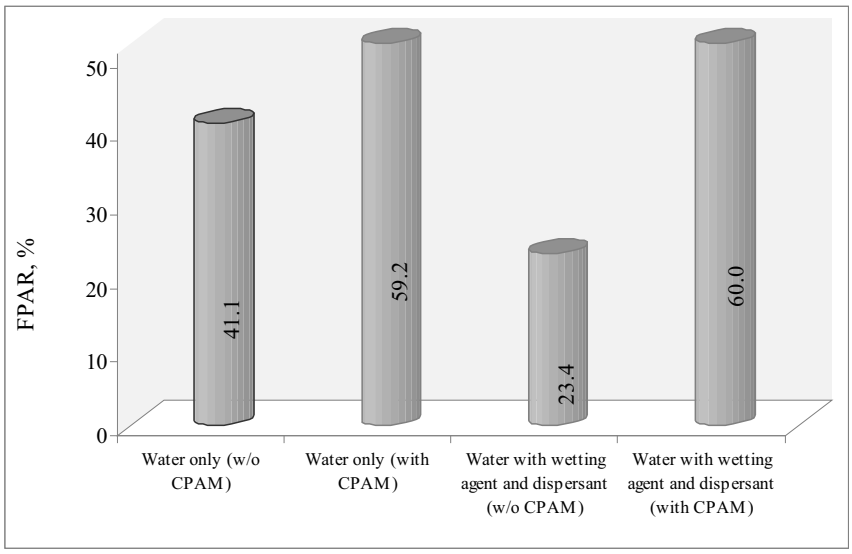

Fig. 2. Effect of wetting and dispersion of talc filler on its retention in paper when used without and with retention aid chemical

Table 2: Effect of mode of dispersion of talc filler on colloidal charge, FPAR and light scattering coefficient

Dispersion mechanism	Cationic charge demand, μeq/g	FPAR, %	Light scattering coefficient of talc, m^2/kg	Light scattering coefficient of paper, m^2/kg
With water only	2.0	41.1	122.9	49.2
With wetting agent*	3.3	28.8	123.8	49.7
With dispersant**	24.2	25.0	123.6	49.3
With wetting agent* and dispersant**	28.9	23.4	122.9	50.0

** Wetting agent = 7 kg/t on filler*
*** Dispersant = 3 kg/t on filler*

increased to 59.2 and 60.0%, respectively with the addition of same amount of retention aid in both the cases. In latter two cases the dosage of talc was substantially reduced (33% only). In all the cases target ash in paper was 15±0.2%. The high cationicity and molecular weight of CPAM helped in maintaining the charge chemistry of the papermaking slurry which, in turn, increased the FPAR values. Moreover, it was observed that the dispersion technique was not having any negative effect on FPAR when CPAM was used. CPAM changed the colloidal charge chemistry and helped in filler retention through its flocculation mechanism (Fig. 2). The study revealed that wetting and dispersing agents only help in particle separation while affecting the retention of the talc filler in the paper sheet due to higher anionicity in the resultant pulp slurry. The latter is adequately compensated with the addition of cationic polyacrylamide as flocculating and retention aid.

Statistical analysis

Though mechanical entrapment plays an important role in holding the talc filler in paper sheet, the ash and FPAR depend, mostly, upon the filler and CPAM addition for satisfying the electrostatic charge. The dosage of talc and CPAM were taken as the most significant input factors in the experimental design and represented as 'A' and 'B', respectively. The output variables were also two i.e. ash and FPAR. The range and levels of the variables, coded values of factors, design and results of experiments investigated in this study are given in Table 3. The statistical significance of the regression model was tested using the ANOVA and the probability "p value".

ANOVA for Ash

The combined effect of dosage of talc and CPAM on ash content is shown in the 3D surface graph in Fig. 3. As expected, the ash in paper was increased with increasing addition of talc filler at constant CPAM level. Similarly, increase in dosage of CPAM at constant filler addition also increased the ash in paper. It was due to the increased flocculation of filler with increase in dosage of CPAM. The high charge density and molecular weight of CPAM was responsible for the better flocculation of talc filler.

F-test is a statistical test in which the test statistic has an F-distribution under the null hypothesis. The "Model F-value" of 291.8 in case of ash content implied that the model was significant.

Table 3: Statistically designed experiments through central composite design using response surface model showing the coded and uncoded variables

Exp. no.	Coded variables		Uncoded variables			
	A	B	Talc addition, kg/t pulp	CPAM addition, g/t pulp	Ash content, %	FPAR, %
1	-1	-1	259	102	12.3	57.5
2	1	-1	542	102	20.0	53.7
3	-1	1	259	349	14.5	66.0
4	1	1	542	349	22.1	62.2
5	+1.414	0	200	225	11.8	62.5
6	-1.414	0	601	225	24.6	65.6
7	0	+1.414	401	50	15.7	53.9
8	0	-1.414	401	400	18.7	65.8
9	0	0	401	225	17.4	60.9
10	0	0	401	225	17.2	60.2
11	0	0	401	225	17.4	60.9
12	0	0	401	225	17.2	60.2
13	0	0	401	225	17.4	60.9

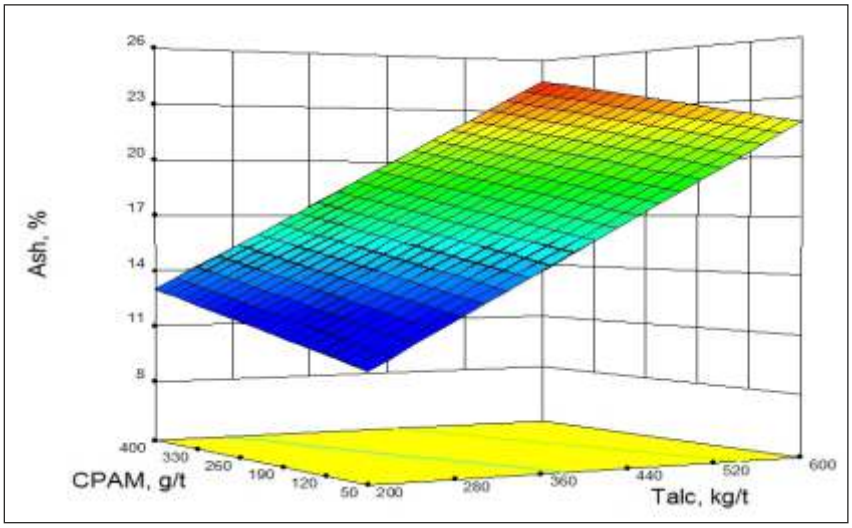

Fig. 3. 3D surface graph showing the combined effect of talc and CPAM on ash content in paper

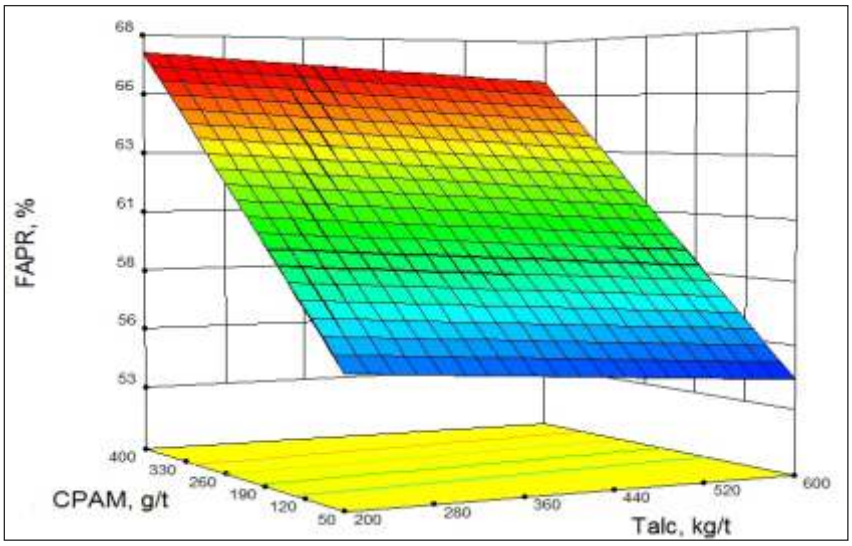

Fig. 4. 3D surface graph showing the combined effect of talc and CPAM on FPAR

Secondly, the values of "Prob > F" less than 0.05 indicated that the model terms were significant. In case of model for ash content, both 'A' and 'B' variables were significant model terms. The "Lack of Fit F-value" of 34.7 also implied that the model was significant (Table 4). A single order equation was achieved from the ANOVA which can be used to calculate the ash content in paper at given dosage of talc filler and CPAM.

Ash in paper,

$$\% = 3.646 + 0.030 * A + 0.009 * B \quad (3)$$

ANOVA for FPAR

The combined effect of dosage of talc and CPAM on FPAR, as shown in Fig. 4, was not similar to that on ash content. The increase in dosage of talc filler at constant CPAM dosage slightly decreased the FPAR which was different to the case with ash content in paper. However, the increase in dosage of CPAM at constant filler addition level increased the FPAR values to the great extent.

Table 4: Analysis of variance for response surface linear model for ash content and FPAR

Source	Parameter	Sum of squares	Mean square	F-value	p-value
Model	Ash	148.6	74.3	291.8	< 0.0001
	FPAR	144.3	72.2	16.0	0.0008
A	Ash	139.5	139.5	547.8	< 0.0001
	FPAR	1.3	1.3	0.3	0.6050
B	Ash	9.1	9.1	35.8	0.0001
	FPAR	143.1	143.1	31.6	0.0002
Lack of Fit	Ash	2.5	0.4	34.7	0.0021
	FPAR	44.7	7.4	50.6	0.0010

Note: A is dosage of talc filler in kg/t pulp and B is the dosage of CPAM in g/t pulp

In case of FPAR, the "Model F-value" of 16.0 implied that the model was significant. In this case, 'B' was significant model term. The "Lack of Fit F-value" of 50.6 also implied that the model was significant (Table 4). A single order equation in terms of actual parameters was achieved from the ANOVA which can be used to calculate the ash content in paper at given dosage of talc filler and CPAM.

FAPR,

$$\% = 54.233\ \ 0.003 * A + 0.034 * B \quad (4)$$

Prediction of output variables

Equations 3 & 4 were used to calculate the output parameters vis., ash content and FPAR using the input parameters vis., dosage of talc and CPAM. The calculated values were termed as the predicted values. Nine input values of dosage of talc and CPAM were put in the equations and nine values of output variables were predicted. It was observed that the experimental values of ash and FPAR closely matched with the predicted ones (Fig. 5&6).

From the study, it is obvious that increasing the dosage of either talc or CPAM increases the ash content in paper. The input values of dosage of talc and CPAM could easily be used to predict the output variables. The dosage of talc filler and CPAM were calculated using the equations targeting the FPAR of 55, 60 and 65% and varying ash content of 15, 18, 21 and 24% (Table 5). In order to get the higher FPAR, dosage of talc was decreased; however, that of CPAM was increased substantially. In order to get higher ash in paper, the dosage of talc needs to be increased; however, it also required slightly higher amount of CPAM to get the similar FPAR.

Conclusion

The proper dispersion of talc filler was achieved through its wetting and dispersion mechanism which was indicated through reduced viscosity of filler slurry. However, the particle size

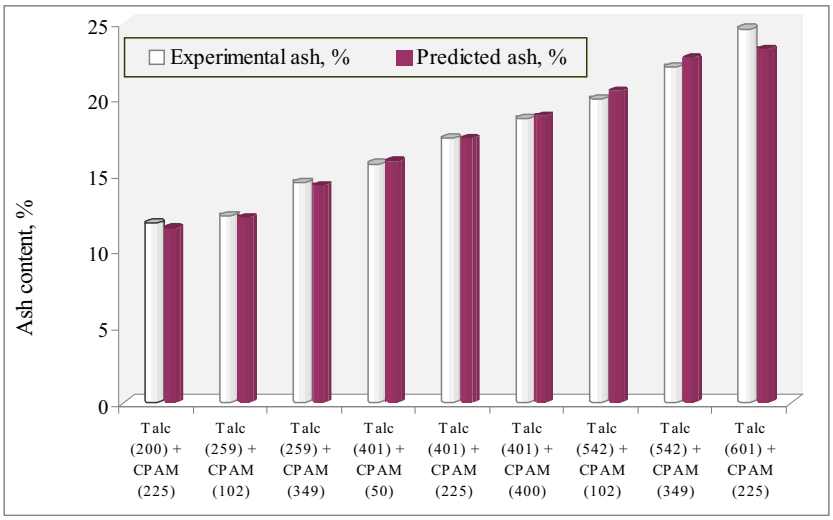

Fig. 5. Validation of model through comparison of predicted and experimental values of ash content

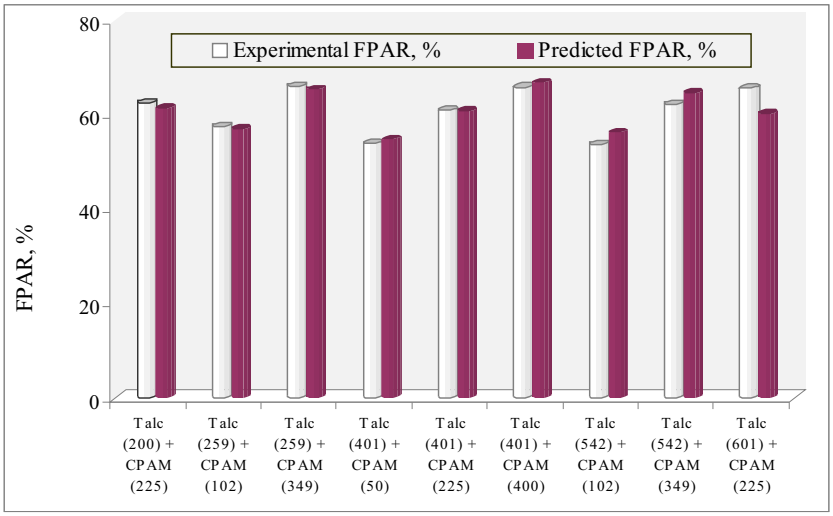

Fig. 6. Validation of model through comparison of predicted and experimental values of FPAR

of wetted and dispersed filler was not changed. Moreover, the wetting and dispersion changed the colloidal charge chemistry of the talc filler and made it more anionic which caused the reduction in filler retention in paper. The decreased FPAR could be compensated using CPAM. The statistical approach provided the single order mathematical linear equations for the prediction of ash and FPAR from the input parameters of dosage of talc and CPAM. The model terms attained for ash content were significant for both the input variables. The effect of increasing dosage of talc and CPAM on ash and FPAR was different. The statistical approach provided the equations which could be used to predict the outputs based upon input variables.

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Table 5: Calculated dosage of talc and CPAM from the model equations to get the target ash content in paper with 55, 60 and 65% FPAR

Ash, %	FPAR, %					
	55		60		65	
	Talc, kg/t	CPAM, g/t	Talc, kg/t	CPAM, g/t	Talc, kg/t	CPAM, g/t
15	370	52	326	196	285	340
18	470	62	425	205	386	348
21	566	70	526	212	485	355
24	665	79	625	222	584	365

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