Application of response surface methodology and central composite design for the optimization of talc filler and retention aid in papermaking

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Cationic polyacrylamide (CPAM) has been used as a retention aid with talc (hydrous magnesium silicate) filler to get the variation of ash in paper using response surface methodology based central composite design. The need of CPAM for varying dosage of talc filler is calculated statistically through the data of first pass ash retention (FPAR) using analysis of variance. The design is employed by selecting the dosages of talc filler and CPAM as model factors to get the variation of ash in paper. The dosages of talc and CPAM range from 250 g/t to 750 g/t and from 50 g/t to 400 g/t pulp respectively. The results of first order factorial design show that both independent variables have significant effect on increasing the ash in paper. At any particular filler addition level, the increase in CPAM addition enhances the ash and FPAR. Optimum conditions to get around 55% FPAR and 15% ash in paper are found to be 382 kg/t talc and 230 g/t CPAM. The linear equations obtained from the designed experiments can be used to predict the dosage of inputs (talc and CPAM) on the basis of desired outputs (ash content and FPAR).

Keywords: Ash, Cationic polyacrylamide, Central composite design, First pass ash retention, Response surface methodology, Talc

Simply adding the filler to papermaking stock is not sufficient to increase the mineral content of the finished sheet. Since wood fibres and most of the fillers have a negative surface charge, there is no mutual attraction between fibres and the small mineral particles. Being lower in particle size (1-10 microns), the mineral filler particles pass through the forming wire and are lost from the sheet. Even though fibres have a negative surface charge in water, their lengths are about 3-7 mm for softwood fibres and about 0.8-1.5 mm for hardwood fibres. Therefore, fibres are easily retained on the screen which has around 70 micron wire opening. Fillers can be attached to fibres, despite negative charges, with the use of polymers through retention mechanisms²,6. The retention aid polymers are used to flocculate the filler particles, fibre fines, and make their agglomerates so that they could be retained within the fibre matrix during papermaking. The nature and dosage of retention aid chemicals primarily depend on the characteristics of mineral fillers, viz. charge density, particle size, particle shape and their addition level in paper⁶,8.

A full factorial design which includes all possible factor combinations in each of the factors is a powerful tool for understanding complex processes,
the detailed mechanism of which are not known, and for describing factor interactions in multifactor systems.

Response surface methodology (RSM) is a collection of mathematical and statistical techniques 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. The response of interest is influenced by several variables and the aim is to optimize this response. RSM is a widely practiced approach for the production and optimization of various industrially important products such as chemicals and enzymes. Recently, the authors have used the similar approach for the optimization of dosage of dispersed talc filler and the retention aid chemical in papermaking.

Based on the principal of design of experiments, the methodology encompasses the use of various types of experimental designs, generation of polynomial equations and mapping of the response over the experimental domain to determine the optimum product. The technique requires minimum experimentation and time, thus proving to be far more effective than the conventional methods of developing such products.

The most popular RSM design is the central composite design (CCD). A CCD has three groups of design points, namely (i) two-level factorial or fractional factorial design points; (ii) axial points (sometimes called ‘star’ or ‘alpha’ points); and (iii) center points. CCD is used to estimate the coefficients of a quadratic model. All point descriptions are in terms of coded values of the factors.

### Factorial points

The two-level factorial part of the design consists of all possible combinations of the +1 and -1 levels of the factors. For the two-factor case, there are following four design points:

\[(-1, -1) (+1, -1) (-1, +1) (+1, +1)\]

### Axial, star or alpha points

The star points have all of the factors set to 0, the midpoint, except one factor which has the value ±a. For a two-factor problem, the star points are:

\[(-a, 0) (+a, 0) (0, - a) (0, + a)\]

The value for \(a\) is calculated in each design for both rotatability and orthogonality of blocks. The default value is set to the rotatable value. Another position for the star points is at the face of the cube portion on the design. This is commonly referred to as a face-centered central composite design.

### Center points

Center points, as implied by the name, are points with all levels set to coded level 0; and the midpoint of each factor range (0, 0). Center points are usually repeated 4-6 times to get a good estimate of experimental error (pure error). For example, with two factors the design will be created with five center points by default.

To summarize, CCD requires 5 levels of each factor, namely -a, -1, 0, 1 and +a. One of the major attributes of the CCD is that its structure lends itself to sequential experimentation.

The optimization of dosage level of a retention aid chemical for the retention of filler is an important task in papermaking. The optimum dosage level of both the components may be developed based upon target ash, FPAR and drainage rate through an effective experimental design procedure. The objective of the present work is to apply CCD based RSM to analyze the effect of the dosage of talc filler and CPAM on ash content in paper, FPAR of talc filler and the drainage rate, and to search for the optimal values for attaining the target values. The RSM may prove to be more productive and beneficial than the conventional technique by virtue of investigation of the effect of all the parameters simultaneously.

### Experimental Procedure

#### Materials

A dry powder of talc filler with median particle size of 5.4 µm was procured from the Golcha Group, Jaipur, India. Bleached mixed hardwood kraft pulp was collected from an integrated pulp and paper mill in north India. The pulp (w/w) was composed of eucalyptus (50%), poplar (35%) and bamboo (15%). A medium to high molecular weight cationic polyacrylamide (CPAM) was obtained from BASF India Ltd. and used as a retardation aid chemical.

#### Methods

The pulp was refined in PFI mill to 430 mL Canadian standard freeness (CSF) level. Talc suspension (10% w/v) was filtered through a 300 micrometer screen and the pH of the filtrate was measured with the help of pH meter. The dry CPAM powder was mixed with deionized water.
of ~40°C in a beaker and agitated at 300 rpm for 30 min to prepare 0.1% concentration (w/v) of the CPAM solution. The colloidal charge density or ionic behavior of 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 or p-DADMAC) and anionic (sodium polyethylene sulfonate or PES-Na) polymers respectively to neutralize the colloidal and dissolved charge. The PCD 03 analyzed 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 system zeta potential meter (SZP 06). About 500 mL filler sample (10% w/v) was taken and mixed thoroughly before measurement. The viscosity of CPAM was measured using Brookfield viscometer.

The particle size distribution of talc filler was measured using particle size distribution analyzer (model Horiba LA-950S2). The LA-950S2 laser diffraction instrument consists of two light sources, a sample handling system to control the interaction of particles and incident light, and an array of high quality photodiodes to detect the scattered light over a wide range of angles. The scattered light collected on the detectors was used to calculate the particle size distribution of the sample analyzed using Mie theory.

The paper hand sheets of 60 g/m² were prepared as per Tappi test method T205 sp-02. The ash content in paper hand sheet was determined at 525°C as per TAPPI test method T211 om-93. The first pass ash retention (FPAR) was calculated using the following formula:

\[
\text{FPAR, \%} = \left(\frac{\text{Ash in paper (%)}}{\text{Filler added based on pulp & filler (\%)}}\right) \times 100
\]  

\[
\ldots (1)
\]

The drainage time of the pulp slurry was measured on modified SR tester using Litchfield method. The equivalent amount of 2 g (oven dry) pulp from the pulp slurry was taken and made-up to 1 L using cold filtered water to maintain the final temperature of pulp stock at around 20 °C. The back (vertical) orifice of the tester was closed using a rubber stopper and the pulp slurry was taken in the jar of the tester. The time required to drain the water from pulp slurry for collection of 900 mL filtrate from the front orifice was measured and reported as the drainage time in seconds.

### Experiments design

Central composite design (CCD, rotatable) and response surface methodology (RSM) were used to optimize the dosage level of talc and CPAM. The CCD consisted of two factors with two levels i.e. talc filler addition (323 and 677 kg/t pulp) and CPAM addition (102 and 349 g/t pulp). The target addition level of talc was from 250 – 750 kg/t pulp and that of CPAM was 50–400 g/t pulp (Table 1).

### Statistical analysis

A 2-fractional factorial design (FFD) was used to pick factors that influence the ash content in paper and drainage rate of pulp stock significantly. The insignificant ones were eliminated in order to obtain a smaller and more manageable set of factors. The statistical analysis was done based upon the process described by Muthuvelayudham & Viruthagiri. In developing the regression equation, the test variables were coded according to the following equation:

\[
X_j = (Z_j - Z_{0j}) / \Delta_j
\]  

\[
\ldots (2)
\]

where \(X_j\) is the coded value of the independent variable; \(Z_p\), the real value of the independent variable; \(Z_{0j}\), the value of the independent variable on the centre point; and \(\Delta_j\), the step change value. The linear model observed was expressed as follows:

\[
Y = \beta_0 + \sum \left( B_j X_j \right)
\]  

\[
\ldots (3)
\]

where \(Y\) is the predicted response; \(X_j\), the input variables which influence the response variable \(Y\); \(\beta_0\), the intercept; and \(B_j\), the \(j^{th}\) linear coefficient. This linear model was used for the analysis of ash content and FPAR as response.

Experiments were performed along the steepest ascent path until the response did not increase any more. This point would be near the optimal point and can be used as center point to optimize the medium parameters. After identifying the critical factors, the CCD was proceeded to obtain a quadratic model with drainage rate as response. For two-factors, the quadratic model obtained was expressed as follows:

\[
Z = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2
\]  

\[
\ldots (4)
\]

where \(Z\) is the measured response; \(\beta_0\), the intercept; \(\beta_1\) and \(\beta_2\), the linear coefficients; \(\beta_{11}\) and \(\beta_{22}\), the quadratic coefficients; and \(\beta_{12}\), the coded independent variables.
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 $+1.414$ ($-\alpha$ and $+\alpha$). The statease design expert software (version 8.0.5.1) was used for the experiments design, and regression and graphical analysis of the data were obtained from the experiments. The statistical analysis of the model was performed in the form of analysis of variance (ANOVA).

Validation of model

The mathematical model generated during RSM implementation was validated by conducting various check point studies. The experimentally obtained data were compared with the predicted one.

Results and Discussion

Properties of talc filler and CPAM

The talc filler is anionic in nature as indicated by the negative colloidal charge (-326 mV). The cationic charge demand to neutralize the anionic charge of talc is 2.1 µeq/g. The zeta potential of talc is -492 mV which also confirms the anionicity of the talc filler. The pH and median particle size (D50) of talc filler are 9.1 and 5.4 µm respectively. The colloidal charge of CPAM is +655 mV and the anionic charge demand is 1134 µeq/g which shows its high cationicity. The pH of CPAM is 4.9 and Brookfield viscosity of 0.1% solids (w/v) is 48.5 cP.

Statistical analysis

The range and levels of the variables, coded values of factors, design and results of experiments investigated in this study are given in Table 1. Two most significant factors ‘A’ representing talc and ‘B’ representing CPAM were selected to get the desired ash content in paper with a target FPAR. The statistical significance of the regression model was tested using the ANOVA and the probability ‘p value’. The ‘F value’ was the ratio of mean sum of square due to model variance by that due to error variance. The coded and uncoded variables based upon experimental results showing the input and output variables respectively are depicted in Table 1.

**ANOVA for ash content**

The 3D surface graph showing the combined effect of dosage of talc filler and CPAM on ash content in paper is shown in Fig. 1. The figure indicates that the increase in dosage of talc filler at constant CPAM level increases the ash in paper. This is simply the increase in output due to increasing input material.

<table>
<thead>
<tr>
<th>Exp no.</th>
<th>Coded variables</th>
<th>Uncoded variables</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>+1.414</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>-1.414</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>+1.414</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>-1.414</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Similarly, the increase in dosage of CPAM at constant filler addition level also increases the ash in paper. The high molecular weight of CPAM is responsible for the increase in ash content in paper. The flocculation of talc filler could have increased due to increasing dosage of CPAM and hence the ash content in paper is increased at constant filler addition levels.

Similar to the previously published data by the authors\textsuperscript{11}, in this case also the ‘Model F-value’ of 6310.3 implies that the model is significant. There is only a 0.01% chance that a ‘Model F-value’ occur due to noise. Values of ‘Prob > F’ less than 0.05 indicates that the model terms are significant. In this case, both ‘A (dosage of talc)’ and ‘B (dosage of CPAM)’ are significant model terms. Values greater than 0.10 indicate that the model terms are not significant. The ‘lack of fit F-value’ of 0.86 implies that it is not significant (Table 2). The following single order equation in terms of actual parameters got from the ANOVA can be used to calculate the ash content in paper at given dosage of talc filler and CPAM:

\[
\text{Ash, } \% = 3.35538 + 0.02786 \times A + 0.00424 \times B \quad \cdots (5)
\]

**ANOVA for FPAR**

The effect of increasing dosages of talc and CPAM on FPAR is shown in Fig. 2 which is not similar to the case of ash content. Increase in the dosage of either talc or CPAM helps in increasing the ash in paper, however in case of FPAR the increase in dosage of talc filler at constant CPAM level slightly decreases the FPAR. At constant talc addition level, the FPAR increases on increasing the dosage of CPAM.

Similar to the case of ash content, in case of FPAR too the model is significant which is confirmed from the ‘Model F-value’ of 27.70. There is only a 0.01% chance that a ‘Model F-value’ could occur due to noise. In this case, ‘B (dosage of CPAM)’ is significant model term. The ‘lack of fit F-value’ of 0.44 implies that it is significant. There is a 73.6% chance that it could occur due to noise (Table 3). Equation (7) obtained from the ANOVA cannot be used for the prediction of drainage time due to insignificant model terms, as shown below.

\[
\text{FAPR, } \% = 48.35124 + 0.00137 \times A + 0.03138 \times B \quad \cdots (6)
\]

**ANOVA for drainage rate**

Another important parameter such as drainage time is also plotted in 3D surface graph (Fig. 3). The figure of indifferent shape shows that increase or decrease in the dosage of either retention aid polymer (CPAM) or talc filler affects the drainage rate in a different way. The lowest drainage time is achieved at 18.9% ash in paper with the dosage of talc filler and CPAM of around 500 kg/t pulp and 400 g/t pulp respectively.

The ‘Model F-value’ of 0.25 shows that the model is not significant. There is a 92.71% chance that a ‘Model F-value’ could occur due to noise. In this case, there is no significant model term. The ‘lack of fit F-value’ of 0.44 implies that it is significant. There is a 73.6% chance that it could occur due to noise (Table 3).

<table>
<thead>
<tr>
<th>Source</th>
<th>Ash</th>
<th>FPAR</th>
<th>Mean square</th>
<th>F-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>196.7</td>
<td>120.6</td>
<td>98.36</td>
<td>6310.3</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>A</td>
<td>194.5</td>
<td>0.470</td>
<td>194.5</td>
<td>12479.7</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>B</td>
<td>2.196</td>
<td>120.2</td>
<td>2.196</td>
<td>140.9</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>0.088</td>
<td>20.33</td>
<td>0.015</td>
<td>0.856</td>
<td>0.5892</td>
</tr>
</tbody>
</table>

A – Dosage of talc filler in kg/t pulp; B – Dosage of CPAM in g/t pulp.

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**Table 2 – ANOVA for response surface linear model for ash content and FPAR**

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**Fig. 2 – 3D surface graph showing effect of talc filler and CPAM on FPAR**
Drainage time, s = 32.92483+0.05348*A-0.05131*B-6.86E-05*A^2+7.13E-05*B^2  ... (7)

Prediction of output variables

The output parameters (ash and FPAR) were calculated using the same input parameter (dosage of talc and CPAM) and the equations for the prediction of ash and FPAR. It is observed that the actual experimental values of ash and FPAR are almost comparable to those predicted from the equations. There is a little difference in values at higher dosage of talc with lower dosage of CPAM (Table 4).

It is known that increasing the dosage of either talc or CPAM increases the ash content in paper; however their effect on FPAR and drainage rate is difficult to be predicted well. The dosages of talc and CPAM are calculated based upon the ANOVA equations [Eqs (5) & (6)] achieved from the RSM-CCD experimental results, targeting the 55% FPAR (Table 5). It is observed that at lower addition level of talc, the requirement of CPAM is also lower, which increases on increasing the target ash in paper. The requirement of CPAM for getting 15% ash in paper with 55% FPAR is 230 g/t pulp. An increase in dosage of filler requires comparatively higher dosage of retention aid (CPAM) in order to get the similar FPAR. The dosages of CPAM calculated from the results are 230, 235, 240 and 245 g/t on pulp for the target ash content in paper of 15, 18, 21 and 24% respectively at ~55% FPAR. The dosages of talc and CPAM can be predicted depending upon the target ash content and FPAR.

**Conclusion**

The effects of input variables i.e. dosage of talc and CPAM on the ash content in paper, FPAR and drainage rate have been investigated using the central composite rotatable design of response surface methodology. The model terms attained for ash content are found to be significant for both the input variables. Optimization of input variables is critical to get the target output variables in the desired range. The data indicate that the increase in dosage of either talc filler at constant CPAM level or vice versa will increase the ash content in paper. With respect to FPAR, the increase in dosage of talc filler at constant CPAM level will slightly decrease the FPAR, and an increase in dosage of CPAM at constant filler addition level will increase the FPAR values to the great extent. The model terms for drainage time are not significant and would not be able to predict the drainage time based upon the input variables.

---

**Table 3 – ANOVA for response surface linear model for drainage time**

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F-value</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>82.82</td>
<td>16.56</td>
<td>0.250</td>
<td>0.9271</td>
</tr>
<tr>
<td>A</td>
<td>0.0013</td>
<td>0.0013</td>
<td>1.9E-05</td>
<td>0.9966</td>
</tr>
<tr>
<td>B</td>
<td>28.02</td>
<td>28.02</td>
<td>0.422</td>
<td>0.5365</td>
</tr>
<tr>
<td>AB</td>
<td>9</td>
<td>9</td>
<td>0.136</td>
<td>0.7235</td>
</tr>
<tr>
<td>A^2</td>
<td>32.53</td>
<td>32.53</td>
<td>0.490</td>
<td>0.5064</td>
</tr>
<tr>
<td>B^2</td>
<td>8.227</td>
<td>8.227</td>
<td>0.124</td>
<td>0.7351</td>
</tr>
<tr>
<td>Lack of fit</td>
<td>115.6</td>
<td>38.54</td>
<td>0.442</td>
<td>0.7359</td>
</tr>
</tbody>
</table>

Drainage time, s = 32.92483+0.05348*A-0.05131*B-6.86E-05*A^2+7.13E-05*B^2  ...

**Table 4 – Validation of model through comparison of predicted and actual ash and FPAR values from original input parameters**

<table>
<thead>
<tr>
<th>Talc addition kg/t pulp</th>
<th>CPAM addition g/t pulp</th>
<th>Ash content, %</th>
<th>FPAR, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>102</td>
<td>12.6</td>
<td>51.6</td>
</tr>
<tr>
<td>677</td>
<td>102</td>
<td>22.5</td>
<td>52.1</td>
</tr>
<tr>
<td>323</td>
<td>349</td>
<td>13.9</td>
<td>60.8</td>
</tr>
<tr>
<td>677</td>
<td>349</td>
<td>23.6</td>
<td>59.8</td>
</tr>
<tr>
<td>250</td>
<td>225</td>
<td>11.3</td>
<td>56.6</td>
</tr>
<tr>
<td>750</td>
<td>225</td>
<td>25.3</td>
<td>59.0</td>
</tr>
<tr>
<td>500</td>
<td>50</td>
<td>17.6</td>
<td>52.8</td>
</tr>
<tr>
<td>500</td>
<td>400</td>
<td>18.9</td>
<td>62.1</td>
</tr>
<tr>
<td>500</td>
<td>225</td>
<td>18.2</td>
<td>56.0</td>
</tr>
</tbody>
</table>

**Table 5 – Calculated dosages of talc and CPAM from equations attained from ANOVA to get the target ash content in paper with ~55% FPAR**

<table>
<thead>
<tr>
<th>Talc addition kg/t pulp</th>
<th>CPAM addition g/t pulp</th>
<th>Ash content %</th>
<th>FPAR %</th>
</tr>
</thead>
<tbody>
<tr>
<td>382</td>
<td>230</td>
<td>15.0</td>
<td>55.0</td>
</tr>
<tr>
<td>490</td>
<td>235</td>
<td>18.0</td>
<td>55.1</td>
</tr>
<tr>
<td>596</td>
<td>240</td>
<td>21.0</td>
<td>55.1</td>
</tr>
<tr>
<td>705</td>
<td>245</td>
<td>24.0</td>
<td>55.1</td>
</tr>
</tbody>
</table>
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References