PARAMETER OPTIMIZATION OF CHEMICALLY ACTIVATED MORTARS CONTAINING HIGH VOLUMES OF POZZOLAN BY STATISTICAL DESIGN AND ANALYSIS OF EXPERIMENTS

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ABSTRACT

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This thesis illustrates parameter optimization of early and late compressive strengths of chemically activated mortars containing high volumes of pozzolan by statistical design and analysis of experiments. Four dominant parameters in chemical activation of natural pozzolans are chosen for the research, which are natural pozzolan replacement, amount of pozzolan passing 45 μm sieve, activator dosage and activator type. Response surface methodology has been employed in statistical design and analysis of experiments. Based on various second-order response surface designs; experimental data has been collected, best regression models have been chosen and optimized. In addition to the optimization of early and late strength responses separately, simultaneous optimization of compressive strength with several other responses such as cost, and standard deviation estimate has also been performed. Research highlight is the uniqueness of the statistical optimization approach to chemical activation of natural pozzolans.

Keywords: Response surface methodology, chemical activation of natural pozzolan, parameter optimization, dual response surface optimization, multiresponse optimization, qualitative factors in response surface methodology

ÖZ

YÜKSEK HACİMDE PUZOLAN İÇEREN KIMYASAL OLARAK AKTİFLEŞTİRİLMİŞ HARÇLARIN İSTATİSTİKSEL DENEY TASARIMI VE ÇÖZÜMLEME YÖNTEMLERİYLE PARAMETRE OPTİMİZASYONU

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Bu tez çalışması yüksek hacimde puzolan içeren kimyasal olarak aktifleştirilmiş harçların erken ve geç basınç dayanımlarının istatistiksel deney tasarımı ve çözümlenmesi yöntemleriyle parametre optimizasyonunu anlatmaktadır. Doğal puzolanların kimyasal olarak aktifleştirilmesinde baskın parametreler olan çimento ile ağırlıkça yer değiştiren puzolan miktarı, 45 μm eleğinden geçen puzolan miktarı, aktivatör dozajı ve aktivatör tipi araştırma parametreleri olarak seçilmiştir. İstatistiksel deney tasarımı ve çözümlenmesinde cevap yüzeyi metodolojisi kullanılmıştır. İkinci-dereceden çeşitli cevap yüzeyi tasarımları esas alınarak deney verisi toplanmış, en iyi regresyon modelleri seçilmiş ve optimize edilmiştir. Erken ve geç basınç dayanımları hem tek başlarına hem de fiyat ve standart sapma gibi bazı başka cevaplarla da beraber aynı anda optimize edilmiştir. Araştırmanın ilgi çeken özelliği uyguladığı istatistiksel optimizasyon yaklaşımının bu özel problem için tek olmasıdır.

Anahtar kelimeler: Cevap Yüzeyi Metodolojisi, Doğal Puzolanların Kimyasal Olarak Aktifleştirilmesi, Yöntem Parametre Optimizasyonu, Dual Cevap Yüzeyi Optimizasyonu, Çokcevaplı Optimizasyon, Cevap Yüzeyi Metodolojisinde Nitel Değişkenler

To my dear family

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CHAPTER 1

INTRODUCTION

The aim of this study is to use statistical design and analysis techniques for maximizing early and late compressive strengths of chemically activated mortars containing high volumes of natural pozzolan. Response surface methodology is used in experimental design and analysis in this research. Experimentation and analysis are based on a face-centered central composite design formed by three quantitative factors repeated for each level of the qualitative factor. Alternative economical designs specific to response surface designs including qualitative factors are also used in regression analysis and optimization of early and late compressive strengths of mortars. Six replicates for each experimental run were performed to reduce the effect of noise factors on mean compressive strength measurements. Best regression model for each response and each set of observations are chosen by regression analysis. Individual responses early and late compressive strengths are optimized alone and together with several other response variables of research interest. As an alternative to Taguchi’s robust parameter optimization dual response surface optimization has been used. Standard deviation estimate has been modeled and joint optimization of both standard deviation estimate and mean compressive strength has been done.

Concrete which is the most widely used construction material throughout the world leads to an enormous cement production. Cement production however is harmful on environment due to its significant contribution to man-made carbon dioxide production. Reducing cement production for sustainable development has been an important issue from construction materials perspective. Replacing Portland cement with high volumes of natural pozzolans has been reported as a good alternative.

Pozzolan is a siliceous or alumino-siliceous material that, in finely divided form and in the presence of moisture, chemically reacts at ordinary room temperatures with calcium hydroxide released by the hydration of Portland cement to form compounds possessing cementitious properties (Canadian Standards Association, 2000). Pozzolanic materials when used in concrete improve durability which is the ability of concrete to resist weathering action, chemical attack and abrasion. Pozzolanic materials bring in also other technical advantages such as low heat of hydration and high ultimate strength. Major disadvantages of concrete systems with pozzolans are high initial setting time and low early strength development. Early strength is a critic measure in concrete industry since it determines the speed of construction. Therefore, low early strength development is an obstacle in promoting pozzolan usage as Portland cement replacement.

In order to overcome low early strength development in pozzolanic materials, methods have been proposed in literature. Among them, chemical activation of pozzolans is popular since it is both effective and feasible.

Works on chemical activation of reactivity of natural pozzolans have mainly utilized one factor at a time approach as habitual in concrete literature. No study investigating the parameter effects together with interaction effects of parameters on pozzolanic reactivity has been seen.

Natural pozzolan replacement, amount of pozzolan passing 45 µm sieve, activator dosage and activator type have been selected as the most important parameters that affect compressive strength of mortars containing high volumes of pozzolan. As second-order parameter effects are research interests, a second-order response surface design is used for experimentation. Because activator type is a qualitative variable and applications in response surface methodology with qualitative factors is not common; alternative design approaches have been compared according to regression results. Best regression models for both early and high compressive strengths are fit and optimized. Due to multiobjective nature of the problem simultaneous optimization of several variables for different sets of responses have been done. Dual response surface optimization of mean compressive strength and standard deviation estimate has been included as an attempt for robust optimization.

The study shows that design space where the data collected and shaped by design of experiments has significant effect on the regression models and hence optimum response value. Maximization of early and late compressive strength led to the same parameter level conditions as optimum settings. When several responses are considered for optimization optimal settings changed in cases and optimal setting alternatives are found instead of a unique solution. Having the system of responses defined preferences of the decision maker guides optimization.

CHAPTER 2

BACKGROUND INFORMATION

2.1. Pozzolanic Activity

2.1.1. Pozzolan in Concrete

Concrete is a versatile construction material, and probably, the most widely used one throughout the world because of its low cost, availability of raw materials, strength, and durability. It is estimated that more than one ton of concrete is produced every year for each person on the planet (Neuwald, 2005). This figure leads to an annual cement production of 1.6 billion metric tons and making cement produces nearly equal amount of carbon dioxide (CO_2). Globally, the cement industry produces about 5% of man-made CO_2: half of this number is from the chemical process of clinker production and 40% from burning fuel. The remaining 10% is split between electricity use and transportation (CSI Progress Report, 2005). It is obvious that minimization of Portland cement clinker production would greatly help to reduce the CO_2 emission produced by the cement industry. One wise solution is to promote the usage of pozzolanic materials in concrete production. The research has proven that it is possible to replace Portland cement up to 70% by using certain pozzolanic materials such as fly ash. Use of pozzolanic materials in concrete is not only environmentally wise but also technically beneficial since it provides more durable product.

2.1.2. What is Pozzolan?

Pozzolan is defined as a siliceous or alumino-siliceous material that, in finely divided form and in the presence of moisture, chemically reacts at ordinary room temperatures with calcium hydroxide released by the hydration of

Portland cement to form compounds possessing cementitious properties (Canadian Standards Association, 2000).

The word “pozzolan” was actually derived from a large deposit of Mt. Vesuvius volcanic ash located near the town of Pozzuoli, Italy. Pozzolanic materials can be used either as an addition to the cement in the manufacturing process or as a replacement for a portion of the cement in the concrete production.

The pozzolans can be grouped into two categories – industrial by-products such as fly ash, silica fume and raw or processed natural materials such as volcanic ash, diatomaceous earth, rice husk ash, meta-kaolin, calcined shale.

2.1.3. Natural Pozzolan

In a review, natural pozzolans are classified into four categories on the basis of their principal lime-reactive constituents: unaltered volcanic glass; volcanic tuff; calcined clay or shale; and, raw or calcined opaline silica. Most natural pozzolan deposits contain more than one lime reactive constituent, and that their composition and properties vary widely. Volcanic glasses such as rhyolitic pumicites, pumice and obsidian; derive their lime-reactivity mainly from their very high composition of unaltered aluminosilicate glass. Volcanic tuffs, such as zeolitic minerals, consist of volcanic glass altered under hydrothermic conditions, and derive their lime-reactivity from a base exchange reaction between calcium (lime) and alkalis in the tuff. Natural clays or shales containing substantial proportions of kaolinite-type or montmorillonite-type clay minerals, or combinations thereof, require calcination at temperatures in the range of 540^{o}C to 980^{o}C to induce optimum pozzolanic activity. During calcination, which may occur naturally or may need to be carried out as part of a processing operation, the clay minerals decompose to form an amorphous or disordered aluminosilicate structure that reacts readily with lime at ordinary temperatures. Opaline materials, including diatomaceous earths and silica gel, are very reactive to lime, but typically have a very large surface area which may result in a very high water demand or requirement when these materials are used in

Portland cement concrete mixtures. It is also often necessary to calcine these materials (CMP Technologies Ltd., 2003).

2.1.4. Why do we Use Natural Pozzolan in Concrete?

The early known use of natural pozzolan dates back to ancient times. Lime-natural pozzolan mixtures were used in the masonry construction of aqueducts, bridges, retaining walls and buildings during roman times. These binders were strong and durable and had been used for centuries by different cultures all over the world. The invention of Portland cement in the 19th century resulted in a reduction in the use of lime-pozzolan binders. Portland cement has a shorter setting time and high early strength compared to lime-pozzolan mixtures. Today, pozzolans are used in combination with Portland cement due to their additional technical benefits.

When combined with water Portland cement clinker forms the glue material which bonds the aggregates. The reaction between water and cement is hydration. The hydration reaction produces calcium silicate hydrates (C-S-H) and calcium hydroxide (CH). C-S-H accounts for more than half the volume of the hydrated cement paste while CH accounts for about 25% of the paste volume. The remainder of hydrated Portland cement is predominantly composed of calcium sulfoaluminates (ettringite) and capillary pores. C-S-H is the main cementitious compound, or glue, that gives concrete its inherent strength. CH also contributes somewhat to concrete’s inherent strength because it will form large crystals inside voids, thereby reducing porosity. However, CH is a soluble compound, meaning it will move throughout the pore system in the presence of water and increases the concrete’s porosity thus making it less durable. The pozzolanic reaction converts the soluble CH to C-S-H which means enhanced ultimate strength and improved durability for concrete. The reduced porosity means limited water ingress and inhibited ionic mobility which in return, means increased chemical resistance (i.e. sulfate attack, alkali-aggregate reaction). The reduced Portland cement in the system leads to low heat evolution which is very important in mass concrete production such as dam body. Moreover, cost reduction is achieved since Portland cement is more expensive than most of the pozzolanic materials. On top of these, use of pozzolan in cementitious systems is an environmental friendly approach. It will greatly help the cement industry to push down its CO_2 emission resulted from the clinker manufacturing.

2.1.5. Activation of Natural Pozzolan

Addition of natural pozzolan has some major drawbacks particularly when speed is needed in the construction projects. It leads to prolonged setting times and lower early strength when compared to pure Portland cement. For a given binder content, early strength decreases with a retarded setting time as the quantity of pozzolan increases. This concept is vital when fast formwork removal in conventional building construction or early opening to traffic in concrete pavement production is needed. To overcome this problem and increase pozzolanic activity rate various methods have been proposed through extensive research. The following section is a brief summary of a review paper on the activation of reactivity of natural pozzolan (Shi, 2001).

Activation methods can be grouped in three headings – thermal activation, mechanical activation, and chemical activation.

Thermal activation is the heat treatment of pozzolanic material and can be classified into two categories – calcination of the raw material and elevated temperature curing of the product containing natural pozzolan. Some clay minerals possess pozzolanic property when treated with heat. A good example to the calcinations is metakaolin which is a very reactive pozzolan and marketed commercially. The raw material of the metakaolin is kaolin which exhibits no pozzolanic property in its natural form. By heat treatment, the crystal structure of the clay minerals is destroyed and an amorphous or disordered alumino silicate structure is formed leading to pozzolanicity. The effect of calcination on the pozzolanic reactivity of natural pozzolan is highly dependent on the material and varies with different pozzolans. The second thermal activation method is the curing of concrete with elevated temperatures. Based on the Arrhenius formula which describes the effect of temperature on reaction kinetics it was found that the hydration of lime-pozzolan mixtures is more susceptible to temperature than that of the

Portland cement. The research has indicated that the samples containing natural pozzolan show significant early strength increase when cured at elevated temperatures.

Mechanical activation refers to prolonged grinding of the parent material. For a chemical reaction between two materials, the reaction rate increases as the surface area available for the reaction increases. It is possible to attain a maximum pozzolanic reactivity with the extended grinding times since the surface area increases as the material gets finer. Although it is generally accepted that the pozzolanicity increases with the increased fineness there are also controversial results in the literature. It is again the nature of the pozzolanic material controlling the overall behavior. However it is generally accepted that the early strength is enhanced with the use of finer natural pozzolan.

The last method is the chemical activation. Either the pozzolanic material is treated with a chemical compound solution before it is added to the concrete or the chemical as a separate ingredient is directly put into the concrete containing natural pozzolan. The former involves the acid-treatment (i.e. hydrochloric acid) of pozzolans. Acid treatment greatly increases the reactivity at early ages. However, this method is only effective on low-Ca pozzolans. In addition, the method is not practical since it is too expensive and the application is too dangerous. The latter, addition of chemicals into cementititous mixture, has been found to be effective in increasing the reactivity of natural pozzolans. $CaCl_2$, and particularly, alkali bearing compounds such as Na_2SO_4 and NaOH were found to work well as activators. Use of chemical activators changes hydration products and accelerates pozzolanic reaction, which leads to faster strength developments and higher ultimate strength. In addition, chemical activators dramatically increase the pozzolanic reactivity when applied in combination with elevated temperature curing. Based on strength development and cost per unit of strength increase addition of chemical compounds is the most economical and effective activation method. It is also the most feasible one among the other methods due to its ease of application.

2.2. Response Surface Methodology

Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimizing processes (Myers and Montgomery, 1995). Methodology is also used in product development and improvement. Although related works in the field began with 1930s RSM was formally developed in 1951 and since then it has been successfully used and applied in many diverse fields such as chemical engineering, agricultural and biological research, food engineering, computer simulation and many others (Khuri and Cornell, 1987).

RSM is a high-potential method to explore relationships where a quality characteristic or performance measure, which is defined as a response in RSM terminology, is influenced by several input variables. Special experimental designs are developed for RSM so that the most useful data can be collected from the specified region of interest at minimum possible number of runs. Using collected data, regression analysis is used to fit some form of mathematical model (*f*) that empirically explains the relationship between the response (dependent variable) and input (independent) variables such as:

$y = f\ (x_1, x_2,\ldots,x_k) + \varepsilon$

where y is the response; $x_1, x_2,\ldots,x_k$ are independent variables and ε is the random error component. If the expected response is denoted by

$E(y) = f\ (x_1, x_2,\ldots,x_k) = \eta$, then the surface represented by

$\eta = f\ (x_1, x_2,\ldots,x_k)$ is called a response surface (Montgomery, 2001).

Regression analysis provides a better understanding of the characteristics of the response system under study and with this information at hand model testing procedures and optimization techniques are applied conveniently.

2.2.1. Design of Experiments

Most efficient experimental designs for fitting response surfaces are response surface designs. Type of the experimental design depends on the region of interest, experimental conditions and the type of regression model to be estimated. Since the second-order effects and interaction effects of the parameters are our research interests a second-order response surface design is chosen. Among alternatives such as spherical central composite design, Box-Behnken design or small composite design; a face-centered central composite design is chosen as the main design for this study. Face-centered central composite design is a useful variation of the central composite design. A central composite design consists of a 2^k factorial, with n_f runs, 2*k* axial or star runs and n_C center runs where k is the number of independent variables (Fig. 2.1). Two important parameters to be specified in the design are the distance α of the axial runs from the design center and number of center runs.

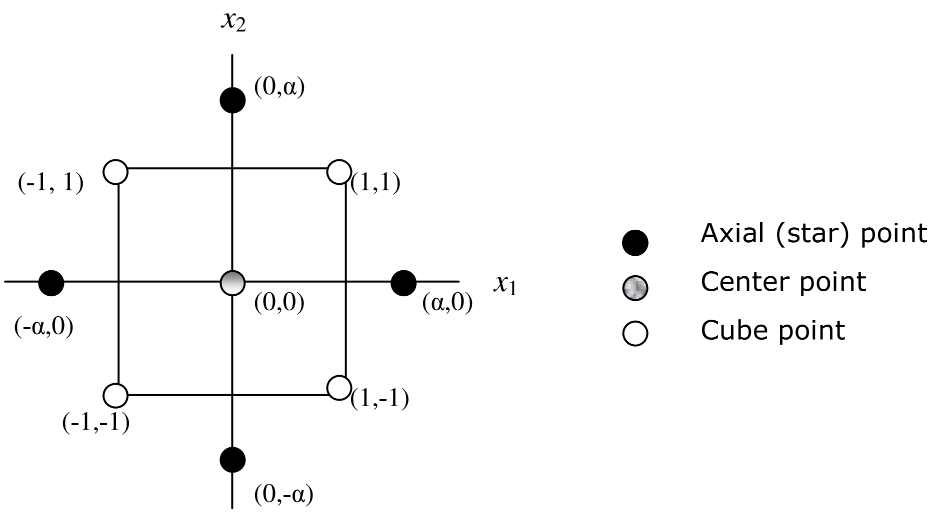

Figure 2.1 Central composite design for two independent variables

The main design used in this study is a face-centered central composite design that is composed of 40 runs. First a basic FCCD with 20 runs is formed by only quantitative factors as (2^3+2*3+6) where 2^3 (8) runs represent the cube points, 2*3 (6) runs represent star points and 6 runs represent the center points. By duplicating this design for each level of the qualitative factor the main design with 40 runs is obtained. 6 replications for each run is done for both responses; 6*40=240 observations for 7-day compressive strength, 6*40=240 observations for 28-day compressive strength, 480 observations in total.

Rotatability is an important concept for second-order response surface designs. For a rotatable design, variance of the predicted response $V[\tilde{y}(x)]$ is the same at all points x that are at the same distance from the design center. Preferably, choice of α is made so that the design is rotatable. However there are some situations where the region of interest is cuboidal rather than spherical and level of factors are difficult to change due to practical considerations such as laboratory conditions. In these cases face-centered central composite design (FCCD) is an efficient alternative with $\alpha=1$. The design is not rotatable; however as Myers and Montgomery state "rotatability or near-rotatability is not an important priority when the region of interest is clearly cuboidal" (Myers and Montgomery, 1995).

For this study four parameters that affect the main response of interest are selected as independent variables. Information on the basis of selection is provided in section 3.1. In RSM applications, independent variables are assumed to be quantitative and continuous in nature, in general. However, there are cases where one (or more) of the independent variables is qualitative. The case is valid for this study as well where one of the four parameters is a qualitative one at two levels. Due to this specific property of designed problem standard designs are not suitable.

"Developing flexible families of designs for use when there are a number of factors with quantitative levels (response surface) combined with some factors with qualitative levels" is one of the several open problems outlined by Cox (1984). Three main approaches in the literature are encountered on response surface design and analysis including qualitative variables. Box (1954) believes that there is no way of finding the absolute optimum other than carrying out separate investigations for each qualitative factor combination unless some very specialized prior assumptions can be made about the qualitative factors. He further discusses that the experimenter would know whether the response surfaces for different levels of the qualitative factor are similar or different and encourages separate investigations for each level of the qualitative factor. This approach restricts the experimenter in finding out possible interaction effects of the qualitative factors with quantitative ones since qualitative factors are not defined as parameters of the experiment. Another approach is employing a basic response surface design for the quantitative factors and repeating this basic design for each level of the qualitative factors where qualitative factors are presented by dummy variables. By this approach, qualitative factor is included in regression analysis and the experimenter can find out whether qualitative factor interacts with quantitative factors and changes response surface (Tunalı and Batmaz, 2003). In a third approach smaller response surface designs with respect to the design in second approach by eliminating some of the runs under specific considerations are proposed (Draper and John, 1988; Wu and Ding, 1998).

For this study, as previously stated, the main design is an FCCD with three quantitative variables and 6 center runs. This main design is repeated for each level of the qualitative factor during experimentation. Analyses are first done for this design with 40 runs where qualitative factor is also an independent variable of the regression model. Then analyses are done for FCCD of each qualitative level separately to explore the difference of the same design with different analysis approaches. Finally, the analyses are done for two economical design alternatives chosen from the works of Draper and John (1988) and Wu and Ding (1998).

After first regression analyses are completed and the best regression model for the main design with 40 runs and 240 observations is found; a series of F tests proposed by Tunalı and Batmaz (2003) are applied to the data to check whether qualitative factor levels have identical response surfaces or not. 3 types of general regression models 1,2 and 3 are presented and definitions necessary for the F tests and calculation of F statistics in the paper are given below. These models are built sequentially by adding new terms to the first quadratic metamodel (1) which contains only k quantitative factors (x). The second metamodel (2) is built by adding the main effect terms (γ) for the q qualitative variables to the first equation. The third metamodel (3) is obtained by adding the interactions between the quantitative and the levels of the qualitative factors. $\beta, \gamma, \delta, \ell$ and η are regression coefficients of related regression parameters.

$$y = \sum_{i=1}^{k} \beta_i x_i + \sum_{i \le j} \beta_i x_i x_j + \varepsilon \tag{1}$$

$$y = \sum_{i=1}^{k} \beta_i x_i + \sum_{i \le j} \beta_i x_i x_j + \sum_{i}^{q} \gamma_i z_i + \varepsilon \tag{2}$$

$$y = \sum_{i=1}^{k} \beta_i x_i + \sum_{i \le j} \beta_i x_i x_j + \sum_{i}^{q} \gamma_i z_i + \sum_{i}\sum_{j} \delta_{ij} x_i z_j + \sum_{l}\sum_{i<j} \ell_{ijl} x_i x_j z_l + \sum_{l}\sum_{i} \eta_{il} x_i^2 z_l + \varepsilon \tag{3}$$

- SSE(1), SSE(2) and SSE(3) are the sum of squares for errors for (1)-(3) respectively.
- $p_1 = [2k + k(k-1)/2 + 1]$, $p_2 = [2k + k(k-1)/2 + q + 1]$ and $p_3 = \{(q+1)[2k + k(k-1)/2] + q + 1\}$ is the number of parameters of the same equations respectively.
- *N* is the total number of simulation experiments.

Test of homogeneity of response curves:

$H_0 : \gamma_i = 0 \quad (i = 1,..., q)$ and

$\delta_{ij} = 0 \quad (i = 1,..., k;\ j = 1,..., q)$ and

$\ell_{ijl} = 0 \quad (i, j = 1,..., k; i < j; l = 1,..., q)$ and

$\eta_{il} = 0 \quad (i = 1,..., k; l = 1,...q)$

H_A : not all of the parameters tested in the null hypothesis are zero.

$F^* = [(SSE(1) - SSE(3))/v_1]/[SSE(3)/v_2]$

Where $v_1 = p_3 - p_1$ and $v_2 = N - p_3$

Test of homogeneity for interactions

At this step the interaction parameters of equation (3) are tested for zero after having decided that each qualitative level has different models.

$H_0 : \delta_{ij} = 0 \quad (i = 1,...,k;\ j = 1,...,q)$ and

$\ell_{ijl} = 0 \ (i, j = 1,...,k; i < j; l = 1,...,q)$ and

$\eta_{il} = 0 \quad (i = 1,...,k; l = 1,...q)$

H_A : not all of the parameters tested in the null hypothesis are zero.

$F^* = [(SSE(2) - SSE(3)) / v_1] / [SSE(3) / v_2]$

Where $v_1 = p_3 - p_2$ and $v_2 = N - p_3$

If calculated *F** value is greater than the tabular critical value of F statistic (at selected level of significance with numerator and denominator degrees of freedoms, v1 and v2 respectively) then the hypothesis that all the parameters tested are equal to zero is rejected.

Test of homogeneity of intercepts

Having decided that the levels have a common response surface, the parameters added to (1) to obtain (2) are tested for significance.

$H_0 : \quad \forall \gamma_i = 0 \quad (i = 1,...,q)$

H_A : not all γ_i's in the null hypothesis are zero.

$F^* = [(SSE(1) - SSE(2)) / v_1] / [SSE(2) / v_2]$

Where $v_1 = q$ and $v_2 = N - p_2$

Tests for the differences among the levels of the qualitative factor

This test is applied after having decided that response surfaces are different for some levels of the qualitative factors or they have similar shapes but different intercepts.

Testing parameters of the qualitative factors individually

$H_0: \quad \gamma_i = 0$ versus $H_A: \quad \gamma_i \neq 0 \quad (i = 1,...,q)$

The test statistic is $t^* = \hat{\gamma}_i / s\{\hat{\gamma}_i\}$.

If H_0 holds , t^* will have a t distribution with $N - p_3$ degrees of freedom.

Testing the difference between the parameters of the qualitative factors

$H_0: \quad \gamma_i - \gamma_j = 0$ versus $H_A: \quad \gamma_i - \gamma_j \neq 0$

$(\forall i, j = 1,..., q$ *and* $i \neq j)$

The test statistic is $t^* = \hat{\gamma}_i - \hat{\gamma}_j / s\{\hat{\gamma}_i - \hat{\gamma}_j\}$

The first important attempt in constructing response surface designs for qualitative and quantitative factors of economical size was by Draper and John (1988). They discussed alternative designs and provided guidelines. Using a second-order response surface design for each level of the qualitative factor can take large number of runs and may be impractical (Wu and Ding, 1998). Wu and Ding further worked on these guidelines and came up with the below criteria:

- The overall design should be an efficient second-order design in quantitative factors, should have main effects of qualitative factors and two way interactions of quantitative factors with qualitative factors.
- At each combination of the qualitative factors or each level of a qualitative factor, it should be an efficient first order design in quantitative factors.
- Overall design consists of two parts: the first part is a first-order design for both quantitative and qualitative factors and the second part is a sequential addition to the first part so that the expanded design is second-order.
- When collapsed over the levels of qualitative factors it is an efficient second-order design for quantitative factors.

Wu and Ding (1998) developed a method that starts with an efficient design for the quantitative factors and then partitions the design points into groups corresponding to different level combinations of the qualitative factors. By this method, good designs are picked based on D-optimality from possible alternatives. D-optimality minimizes the variance in the regression coefficients of the fitted model. A design is said to be D-optimal if $|(X`X)^{-1}|$ is minimized (Montgomery, 2001).

2.2.2. Regression Analysis

After collecting the data according to previously discussed designs, to come up with an empirical mathematical model between the response and independent variables, the method of least squares is applied. By this method, the estimated model

$$\hat{y} = \hat{\beta}_0 + \hat{\beta}_1 x_1 + ... + \hat{\beta}_k x_k$$

is chosen so that it minimizes

$$SSE = \sum (y_i - \hat{y}_i)^2$$

SSE is the sum of squares of the errors. Error $(y_i - \hat{y}_i)$ is the difference between the predicted and observed values of y. A second-order regression model is preferred for the study. Model building and regression assumptions are explained in section 4.1.2. Validity of regression assumptions is essential in order to make hypothesis tests about regression parameters.

The variance of σ^2 of the random error ε is estimated by s^2 (MSE, mean square for error) and s^2 is calculated as:

$$s^2 = MSE = \frac{SSE}{n - (k+1)}$$

Here, n is the number of observations and k is the number of predictors in the regression. Root MSE, standard deviation s, is the frequently used measure of variability.

Regression analyses in this study are summarized by two tables. One is for parameter estimates where estimated predictor coefficients are tabulated with standard error, t and p values. T values are the test statistics where the hypothesis that a particular parameter coefficient is zero tested. P values in the table are corresponding values for this statistic. If a p-value for a parameter is smaller than pre-selected level of significance (α value which is usually 0.05 in practice) then the hypothesis is rejected and it is concluded that the association between the response and predictor is statistically significant.

The second table is the analysis of variance table for the regression. The results of the global test where the hypothesis that all regression parameters are equal to zero is tested are given in this table. If the test statistic F is greater than the F value for pre-selected level of significance then the hypothesis is rejected meaning that at least one of the parameter coefficients in the equation is not zero and hence the regression is statistically significant.

R^2 (R-sq, multiple coefficient of determination) and adjusted R^2 (R-sq(adj)) values represent the proportion of variation in the response data explained by the predictors. (R-Sq) describes the amount of variation in the observed response values that is explained by the predictor(s). Adjusted R is a modified R that has been adjusted for the number of terms in the model. If unnecessary terms are included, R can be artificially high. Therefore R-sq(adj) is taken into consideration while evaluating regression models.

Insignificant parameters may be discarded from the regression equation starting from the one with highest p-value. However, a lower-order term cannot be excluded as long as its higher order term is included in the model. This is called response surface hierarchy.

Lack of fit test is also done when possible to check whether the data fits the model well. This test is available only when repeated observations (such as center runs) on the response are available. If the F value is greater than the F value for chosen level of significance it is concluded that the current model does not fit the data well.

2.2.3 Response Surface Optimization

The eventual objective of RSM is to determine the optimum operating conditions for the system under discussion. Theoretically, optimization process starts with an initial estimate for optimum operating conditions and searches for points with better response values. The method of steepest ascent is a sequential procedure for moving along the direction of the maximum increase in the response. If minimization is desired the technique is called method of steepest descent. A presentation of the path is given in Fig. 2.2 (Montgomery, 2001). Iterations follow until no further increase in the response is observed.

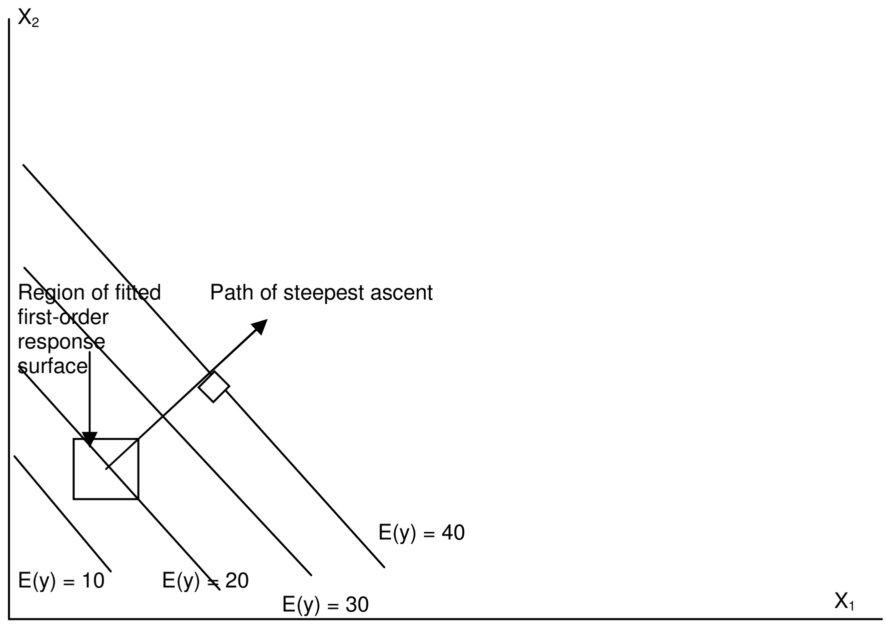

Figure 2.2 First-order response surface and path of steepest ascent (adapted from Montgomery, 2001)

Optimization modules in many software commercially available work with this logic. The experimenter guide the optimization process by defining response function(s); minimum and maximum or target values for the response(s); relative importance of the responses (if there are more than one).

In many RSM applications multiple responses are observed so multiple response techniques are developed to find optimum operating conditions that satisfy all responses under discussion. A common method is use of desirability function. Developed by Derringer and Suich (1980), the method uses a desirability function in which the researchers' priorities and desires are built into the optimization procedure. First desirability functions for individual responses are formed and then they are put into a single composite response which is the geometric mean of the individual desirabilities. Then, conditions that maximize composite desirability are searched.

Another multiple response technique that is employed in the case of two responses is the dual response approach. This term was introduced by Myers and Carter in 1973. Since then the approach has been extensively discussed and considered as an alternative to Taguchi's robust parameter design (Vining and Myers, 1990; Myers, Khuri and Vining, 1992). Taguchi's robust parameter design seeks for the optimum quality with minimum variance by signal to noise ratio concept. Noise factors are the external factors that cause undesirable variation and signal to noise ratio, in a sense, measures the sensitivity of the quality characteristic to noise factors. The aim is to achieve highest possible signal to noise ratio so that the signal is dominantly high with respect to noise factors and eventually robust.

Taguchi suggested three formulations based on mean squared deviation for three goals in parameter optimization as larger the better, smaller the better and target is the best. These goals are maximizing the response, minimizing the response and attaining a certain target value respectively. Since the 1980s the method has always been at the spotlight and had significant contribution to quality improvement, but on the other hand important general criticisms of robust parameter design are present. The method is criticized about the inefficiency of signal to noise ratio, lack of flexibility in designing variables, lack of economy in experimental design plan, preoccupation of optimization and no formal allowance for sequential experimentation (Myers, Khuri and Vining, 1992).

The dual response surface optimization procedures have been adapted in the spirit of Taguchi's RPD where one should simultaneously optimize mean and standard deviation but by considering both mean and standard deviation functions separately. Usually the works on dual response surface problems identify the mean as a primary response and standard deviation as a secondary response and aim to optimize the primary response with some restrictions on the secondary response. Restrictions on standard deviation are not favorable as the interest is on minimizing it as much as possible.

Vining and Myers (1990) formulated the problem as a minimization or maximization of primary response mean, subject to an equality constraint on standard deviation. For target is best case, standard deviation was defined as the primary response to be minimized subject to mean equals target constraint. Del Castillo and Montgomery (1993) further developed their approach by introducing flexibility in type of response functions and experimental designs.

Lin and Tu (1995) proposed a composite objective function based on the mean square error. They developed the formulation by removing the restriction on standard deviation. However, since the objective function is a composite one the problem becomes a single response problem rather than a multiresponse problem and causes undesirable information loss.

Copeland and Nelson (1996) loosened the restriction on standard deviation constraint as changing the equality to a smaller or equal to type for larger the better and smaller the better cases. On the other hand the put a restriction on how far mean may be from target value for target is best case.

Del Castillo, Fan and Sample (1997) and Fan (2000) introduced new computational methods for a unique global solution within a spherical region of interest and discussed that some other techniques such as general nonlinear programming methods may fail to find the global optimum.

Kim ad Cho (2002) and Tang and Xu (2002) came up with alternative formulations based on goal programming. Their formulations let the experimenter to consider meeting the targets for both the mean and the standard deviation.

Most recently, Koksoy and Doganaksoy (2003) proposed a more flexible formulation of the problem by considering secondary response as another primary response. The method generates more alternative solutions with respect to previous formulations and gives flexibility to decision-maker in exploring alternative solutions. How controllable variables affect both responses simultaneously can be examined by this method. Generated alternative solutions are Pareto optimal solutions. A solution can be considered Pareto optimal if there is no other solution that performs at least as well on every criteria and strictly better on at least one criteria (Hofstra University, 2006). That is, a Pareto-optimal solution cannot be improved upon without hurting at least one of the criteria. A solution is not Pareto-optimal if one criterion can be improved without degrading any others.

Formulation of Koksoy and Doganaksoy does not give a direct solution to target is best case but advises iterative solution. Two other cases are defined as:

The smaller the better: {Minimize $\hat{\mu}$, Minimize $\hat{\sigma}$}
Subject to x ϵ R;

The larger the better: {Maximize $\hat{\mu}$, Minimize $\hat{\sigma}$}
Subject to x ϵ R;

Where $\hat{\mu}$ and $\hat{\sigma}$ represent the fitted second-order response surface functions for the mean and standard deviation. Unless a constraint is defined in addition to above formulation many alternative Pareto optimal solutions can be found and the decision-maker can choose the optimal solution according to the case. For instance, if one is willing to increase the mean response, this is possible by sacrificing from standard deviation since a bigger mean value can be found but with a bigger standard deviation value as well, in a maximization problem.

Koksoy and Doganaksoy's approach is applied in dual response optimization of this study. The NIMBUS software is used for nonlinear multiobjective programming problem. The software can be accessed at WWW-NIMBUS webpage.

2.3. Literature Review

Literature on pozzolanic activity and chemical activation of natural pozzolans in specific are reviewed and referred in section 2.1 and chapter 3. This optimization study about chemical activation of pozzolan is unique with its multivariate characteristic and optimization approach. Statistical design and analysis are rarely used in construction materials field and one-factor-at-a-time approach is the general approach that can be found in the literature. One-factor-at-a-time experiments succeed each other as a series in which, at each step, a single factor is changed while other factors remain constant. Therefore this approach fails in detecting possible relationships between interaction factors and response variables. Few applications of statistical design and analysis found in the construction materials literature are included below.

Soudki et al. (2001) aimed to optimize a concrete mix design for hot climates by statistical design and analysis. A full factorial experiment with 432 samples of 48 mixes at three levels of temperature was used. The statistical relationships between the water/cement ratio, coarse aggregate/total aggregate ratio and total aggregate /cement ratio and temperature on compressive strength were estimated and analyzed using polynomial regression. A second-order regression model was developed for concrete strength as a function of temperature and mix proportion. Response surface optimization for three different temperatures was performed and recommendations were provided.

Khan and Lyndsaleb (2002) worked on the optimization of a blended cementitious system for the development of high-performance concrete. Blended cementitious systems based on ordinary Portland cement (OPC), pulverised fuel ash (PFA) and silica fume (SF) were investigated. Binary and ternary PFA up to 40% was used, and to these blends, 0%, 5%, 10% and 15% SF were incorporated as partial cement replacements. Experimental design plan was not reported. Based on the experimentally obtained results, second-order prediction models were developed for compressive strength, tensile strength, oxygen permeability and carbonation of concrete where PFA content and FS content were the only two independent variables used in model building. Isoresponse contours showing the interaction between the various parameters were investigated. It was found that the incorporation of 8–12% SF as cement replacement yielded the optimum strength and permeability values.

Roy et al. (2003) statistically investigated the relationship between alkali-silica reaction (ASR) expansion and four Portland cement characteristics as fineness, silica content, C_3A content and SO_3 content. Response surface modeling has identified a negative trend of clinker SiO_2 and a direct trend of Na_2O_{eq} as significantly contributing to ASR expansion. The study could not detect any other significant relation between ASR expansion and cement characteristics.

Sonebi worked on an optimization for medium strength fresh self-compacting concrete (SCC). Compressive strength and several other response variables of filling and passing abilities and segregation were modeled by five key parameters as contents of cement and pulverized fuel ash (PFA), water-to-powder (cement + PFA) ratio (W/P), and dosage of superplasticizer. Second-order prediction models were fit to experimental data based on a central composite design. The results show that medium strength fresh self-compacting concrete can be achieved with a 28-day compressive strength of 30 to 35 MPa by using up to 210 kg/m^3 of PFA.

Lin et al. (2004) adopted Taguchi's approach with an L16 (2^{15}) orthogonal array to decide for an optimum mixture for concrete made with recycled aggregates that satisfy desired requirements. Five control factors (water/cement ratio, volume ratio of recycled coarse aggregate, replacement by river sand, content of crushed brick and cleanness of aggregate) and four responses (slump and compressive strengths at 7, 14, and 28 days) were used. Analysis of variance (ANOVA) and significance test with F statistic were used to check the existence of interaction and level of significance, and computed results of total contribution rate to select an optimal mixture of concrete qualifying the desired engineering properties.

In the study by Carrasco et al. (2005), the interaction between limestone filler (LF) and blast-furnace slag (BFS) on compressive and flexural strengths was analyzed in mortars in which Portland cement (PC) was replaced by up to 22% LF and BFS. A central composite response surface design was used to fit second-order regression models and to draw the isoresponse curves. BFS and LF content were two independent variables of the investigation. Results showed that compressive and flexural strength evaluated at 2, 7, 14, 28, 90 and 360 days are affected by the presence of mineral additions. At all ages, there is a ternary blend of LF, BFS and PC that present an optimum strength, better than binary LF or BFS cement and plain Portland cement. The isoresponse method highlighted the significance of the effect of the mineral addition and their interactions, and it permitted to obtain the optimum combination to make a composite cement that meet with the standard or the user requirement regarding the environmental regulations (energy saving and emission reducing).

CHAPTER 3

LABORATORY STUDIES

3.1. Process Parameter Selection

The use of natural pozzolans in cement or concrete systems improves several important properties of these systems such as low heat of hydration, high ultimate strength, low permeability, high sulfate resistance and low alkali-silica activity (ACI Committee, 1994). Furthermore, the use of pozzolanic materials with high volumes as cement replacement is promising for sustainable development of the cement and concrete industry (Mehta, 1998). Despite these advantages, broad usage of pozzolans in concrete is delayed due to a major drawback, low early strength. Eventually, the focus of this study is selected as optimization of low early strength development. Since achieving the highest possible ultimate strength has always been the concern in construction materials, it is selected as the second response of interest.

In order to overcome low early strength problem of pozzolans; thermal, mechanical and chemical activation methods are proposed. Among these three methods chemical activation is reported as the most effective and cheapest one and hence utilized for this study (Shi, 2001).

For a given binder content, early strength decreases with a retarded setting time as the quantity of pozzolan increases (Turanli et al., 2005). Therefore natural pozzolan replacement is selected as the first parameter for investigation. Activator dosage, activator type and fineness of the pozzolan are selected as other parameters. Chemical activation is possible by proper chemicals at specific amounts so the reason to select second and third parameters is obvious. Past research proved effect of particle size on pozzolanic activity and fineness of pozzolan is selected as a process parameter for this reason (Turanlı et al., 2005). Other factors that may effect compressive strength development kept constant to keep the number of experimental runs at a manageable level.

Selected parameters, their levels and coded values of these levels with center coding as -1, 0 and 1 are as follows:

Parameter P: Natural pozzolan replacement (% by weight)
    Levels: -1: 35% 0: 45% 1: 55%
Parameter F: Amount of pozzolan passing 45 μm sieve (% by weight, fineness parameter)
    Levels: -1: 70% 0: 80% 1: 90%
Parameter D: Activator dosage (% by weight of binder)
    Levels: -1: 0.5% 0: 1% 1: 1.5%
Parameter T: Activator type
    Levels: -1: NaOH (sodium hydroxide)
    1: Na_2SO_4 (sodium sulphate)

Levels of natural pozzolan replacement (P) indicate percentage of natural pozzolan by weight of blended cement. The levels are chosen in accordance with past research on blended cements containing high volumes of natural pozzolans. Amount of pozzolan passing 45 μm sieve (F) is preferred as fineness parameter. Na_2SO_4 and NaOH work well as chemical activators and they are included as parameter levels for activator type (T). Range for activator dosage is also decided based on past research.

3.2. Experimental Methods

Natural pozzolan used in the research is a volcanic tuff from Turkish deposits (Askale Region). The natural pozzolan was received in a bulk form and crushed into particles less than 16 mm before grinding. X-ray diffraction pattern identified phases of the pozzolan in its mineralogical composition and according to the X-ray diffraction data the pozzolan contains some crystalline minerals and a glassy phase indicated by a raised background of the pattern.

The pozzolan was ground by a laboratory mill which is 450 mm in length and 420 mm in diameter. A combination of 50 and 20 kg cylindrical steel balls were used as grinding media. 10 kg of raw ground pozzolan is fed into the mill at once. Grinding continued until required levels for fineness measured as amount of pozzolan passing 45 μm sieve was attained. Since there are three levels for fineness of pozzolan and three levels of natural pozzolan replacement; 9 different combinations of blended cements with respect to natural pozzolan replacement and fineness are present in the study. Chemical composition and physical properties of the Portland cement used in this study are given in Table 3.1.

Table 3.1 Chemical composition and physical properties of the Portland cement

	PC
SiO_2, %	19.94
Al_2O_3, %	5.34
Fe_2O_3, %	3.72
CaO, %	63.02
MgO, %	2.44
SO_3, %	2.95
Loss on ignition, %	1.02
Insoluble residue, %	0.51
Specific gravity	3.03
Blaine fineness, m^2/kg	313
Initial setting time, min	140
Final setting time, min	205
Compressive Strength, MPa	
3 days	26.8
7 days	33.5
28 days	51.1

The mortar mixtures were prepared by using 0.5 water to cement ratio and 2.75 sand-cement ratio. Mixing and curing of the specimens were carried out in accordance with ASTM C 109. Chemical activators were also added to mixing water with specified type and dosage of that particular experimental run. A sulfonated naphthalene formaldehyde condensate type superplasticizer in a dry powder form was used during mortar mixing to obtain adequate workability since fine pozzolan decreases workability of fresh mortars. Compressive strength is affected by the workability of fresh mortars therefore it is kept constant during laboratory study for each mortar mix. Consistency of fresh mortars was measured by flow table according to ASTM C 109 before casting. The flow was kept constant between 95 to 105% by arranging the amount of superplasticizer added to mixing water. Compressive strength of hardened mortars was measured at 7 and 28 days.
For both 7-day and 28-day compressive strength, 40 experimental runs with 6 replicates were done. In total 480 cube (50 mm*50 mm*50 mm) specimens were produced, cured and finally tested for compressive strength on the test day in accordance with ASTM C 39. A power operated hydraulic screw type testing machine is used in compressive strength determination. The load was applied to the cube specimen at a constant rate and the maximum load applied to the cube specimen was measured. The compressive strength of the specimen was calculated by dividing the maximum load applied to the specimen by cross-sectional are and reported in MPa as in equation 3.1.

$$\sigma_{comp} = \frac{P_{\max}}{A} \qquad (3.1)$$

Not to introduce any additional variance to the system or to keep it at the minimum, each type of job was done by the same person during all through the experimentation. Experimental runs are randomized during laboratory studies for the same purpose.

In addition to the 480 specimens above, control runs without chemical activators added for 9 different blended cement combinations were prepared and tested. These control runs were done to see whether chemical activation was effective in increasing early strength. 128 cube specimens were tested for control runs. Average of compressive strength for both control and activated runs at both ages are summarized in Table 3.1. Plots of averages are presented in Figures 3.1 and 3.2.

Table 3.2 Compressive strength averages for 9 blended cement combinations at 7 and 28 days

#	P	F	7-day Control (MPa)	7-day Activated (MPa)	28-day Control (MPa)	28-day Activated (MPa)
1	35%	70%	19.94	22.02	31.90	30.63
2	45%	70%	13.79	16.28	27.39	27.33
3	55%	70%	12.10	12.47	23.80	26.16
4	35%	80%	12.87	12.99	34.26	32.79
5	45%	80%	15.13	15.67	35.70	29.48
6	55%	80%	12.68	13.63	26.87	26.51
7	35%	90%	20.53	22.78	40.80	36.93
8	45%	90%	13.99	17.62	34.85	34.45
9	55%	90%	12.88	15.50	28.64	26.02

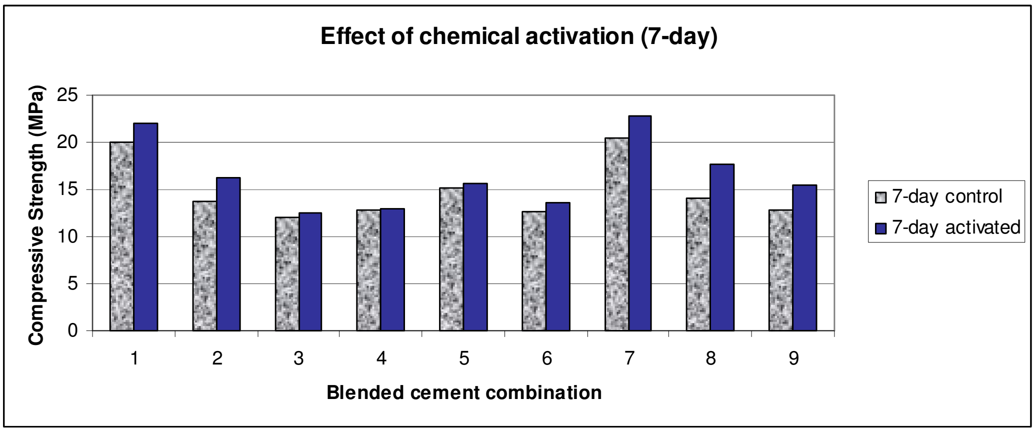

Figure 3.1 Effect of chemical activation plot for 7-day compressive strength

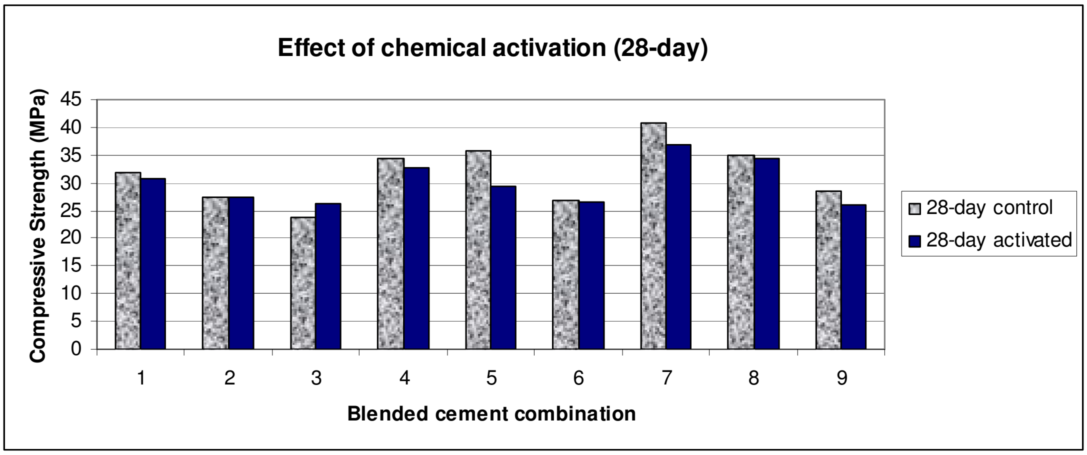

Figure 3.2 Effect of chemical activation plot for 28-day compressive strength

Average of compressive strength for both control and activated runs at both ages and figures 3.1 and 3.2 show that the chemical activation increased compressive strength for early strength values. On the other hand, 28-day compressive strength values were affected negatively, positively or not affected at all.

CHAPTER 4

EXPERIMENTAL DESIGN AND ANALYSIS WHEN THE RESPONSE IS 7-DAY COMPRESSIVE STRENGTH

The study focuses on the optimization of two main responses which are 7-day and 28-day compressive strengths. For consistency, the same experimental design approach is used for both responses. There are four main factors as explained in section 3.1 as natural pozzolan replacement, fineness of pozzolan (indicated as amount of pozzolan passing 45 μm sieve), activator dosage and activator type. While other three are quantitative variables, activator type is a qualitative variable. Since effects of these parameters, their two-way interactions and effect of their quadratic terms to the responses are research interests, an experimental design for fitting second-order response surface models is chosen. In Section 4.1, response surface methodology for mean 7-day compressive strength when face-centered central composite design (FCCD) is used for each level of the qualitative factor is explained. In section 4.2, response surface methodology for mean 7-day compressive strength with economical design alternatives proposed in the literature is given.

4.1. Response Surface Methodology when FCCD is Used for Each Level of the Qualitative Factor

4.1.1. Design of Experiments

Since the region of interest and the region of operability for the study is the same cubical region, the face-centered central composite design which is an effective second-order design is chosen for the study (Batmaz and Tunalı, 2002). The FCCD is constructed for three quantitative variables with 20 runs and this basic design is repeated for each level of the activator type due to the qualitative nature of the variable. Though levels of this qualitative factor have no quantitative meaning; they are presented as -1 and 1 using center coding. Main factors for the experiment and their levels are summarized as follows:

Parameter P: Natural pozzolan replacement (% by weight)

Levels: -1: 35% 0: 45% 1: 55%

Parameter F: Amount of pozzolan passing 45 μm sieve (% by weight)

Levels: -1: 70% 0: 80% 1: 90%

Parameter D: Activator dosage (% by weight of binder)

Levels: -1: 0.5% 0: 1% 1: 1.5%

Parameter T: Activator type

Levels: -1: NaOH (sodium hydroxide)

1: Na_2SO_4 (sodium sulphate)

For each experimental run (parameter level combination) 6 replicates are performed. Since there are 40 parameter level combinations (rows) in the specified design, 240 experiments were conducted for each response. Results of these experiments are presented in Appendix 4.1. Experimental runs are randomized according to a random string proposed by Design-Expert Software (Design-Expert, Version 7.0.0, Stat-Ease Inc.) and the sequence is also presented in Appendix 4.1. Experimentation and regression analyses in following sections are carried out in accordance with this random sequence in order to be able to calculate Durbin-Watson statistic and hence conclude about residual correlation.

4.1.2. Regression Analyses for Mean 7-day Compressive Strength

Mean compressive strength is modeled by general linear regression using the method of least squares in this study and MINITAB Software is used for the analysis (MINITAB® Release 14.12.0).

The general regression equation preferred involves main factor terms, two-way interaction terms and quadratic terms as presented below.

$$y = \beta_0 + \Sigma\, \beta_i X_i + \Sigma\, \beta_{ii} X_i^2 + \Sigma\beta_{ij} X_i X_j + \varepsilon \qquad (4.1)$$

In this equation:

y = the response (mean 7-day compressive strength, will be referred as CS7 henceforth)

x = regression parameters (predictors)

β = regression coefficients

ε = error term

Four basic assumptions about the general form of the probability distribution of the error term have been made and controlled for each regression model in this study as explained by Mendenhall and Sincich (2003):

1. The mean of the probability distribution of ε is zero.
2. The variance of the probability distribution of ε is constant for all settings of the independent variable x.
3. The probability distribution of ε is normal.
4. The errors associated with any two different observations are independent.

These assumptions enable developing measures of reliability for the least squares estimators and develop hypothesis tests for examining the utility of least squares line (Mendenhall and Sincich, 2003). Residual plots and test statistics allows checking validity of these four assumptions.

In order to write a regression equation containing all main factor effects, two-way interactions and quadratic terms when one of the factors is qualitative; three stages are followed (Mendenhall and Sincich, 2003) as explained below:

Stage 1: The second-order model for three quantitative variables is written.

$$CS_7 = \beta_0 + \beta_1 P + \beta_2 F + \beta_3 D + \beta_4 P^2 + \beta_5 F^2 + \beta_6 D^2 + \beta_7 PF + \beta_8 PD + \beta_9 FD$$

Stage 2: Main effect and interaction terms for the qualitative variables are added.

$+ \beta_{10} T$ (Only one qualitative variable hence no interaction terms)

Stage 3: Interaction terms between qualitative and quantitative variables are added.

$+ \beta_{11} PT + \beta_{12} FT + \beta_{13} DT + \beta_{14} P^2T + \beta_{15} F^2T + \beta_{16} D^2T + \beta_{17} PFT + \beta_{18} PDT + \beta_{19} FDT$

All of the above regression variables may be included in the model since the experimental design has 39 degrees of freedom that enables the estimation of all regression coefficients in the model.

Before applying the regression analysis for above regression equation that includes two way interaction and quadratic terms; a regression analysis for only first order main factors is employed. The regression equation is found as:

$$CS_7 = 16.8 - 3.80\ P + 0.892\ F + 1.43\ D + 0.601\ T \quad (4.2)$$

S = 2.09556   R-Sq = 70.0%   R-Sq(adj) = 66.6%

ANOVA for the significance of above regression equation is given in Table 4.1. The hypothesis that all β terms are equal to zero is rejected with a confidence level of (1-p)*100%, which is 100% for this model. This implies that at least one coefficient in the model is not zero.

Table 4.1 ANOVA for the significance of the regression model applied for 7-day mean compressive strength based on face-centered central composite design with only main factors

Source	DF	SS	MS	F	P
Regression	4	359.465	89.866	20.46	0.000
Residual Error	35	153.698	4.391		
Lack of Fit	25	143.986	5.759	5.93	0.003
Pure Error	10	9.712	0.971		
Total	39	513.163			

R-Sq(adj) value indicates that 66.6% of the sample variation in the mean 7-day compressive strength can be explained by the regression model (4.2) after adjusting for sample size and number of independent variables in the model.

The significance of β terms of the regression model is presented in Table 4.2. The normal probability plot of the residuals and the residual versus fitted values plot of this model are given in Fig. 4.1 and Fig. 4.2. These plots do not indicate any violation of the basic regression assumptions. The hypothesis that the residuals follow a normal distribution cannot be rejected since related p-value for normality test is 0.108 and this value is greater than pre-selected α-value, 0.05. As it can be seen in Appendix 4.2, lack of fit test results encourage considering higher order terms of existing predictors to get a better fit of the data. A p-value which is smaller than a pre-selected α-level indicates that the linear predictors are not sufficient to explain the variation in response. Overall lack of fit p-value (0.006) and individual lack of fit p-values (for P 0.022; for F 0.007 and for D 0.006) are smaller than pre-selected α-value, 0.05, for this model. Possible curvature in variables P (natural pozzolan replacement), F (amount of pozzolan passing 45 μm sieve) and D (activator dosage) is also indicated in lack of fit test result.

Table 4.2 Significance of β terms of the regression model based on face-centered central composite design and applied for mean 7-day compressive strength

Predictor	**Coef**	**SE Coef**	**T**	**P**
Constant	16.8184	0.3313	50.76	0.000
P	-3.7952	0.4686	-8.1	0.000
F	0.8924	0.4686	1.9	0.065
D	1.4318	0.4686	3.06	0.004

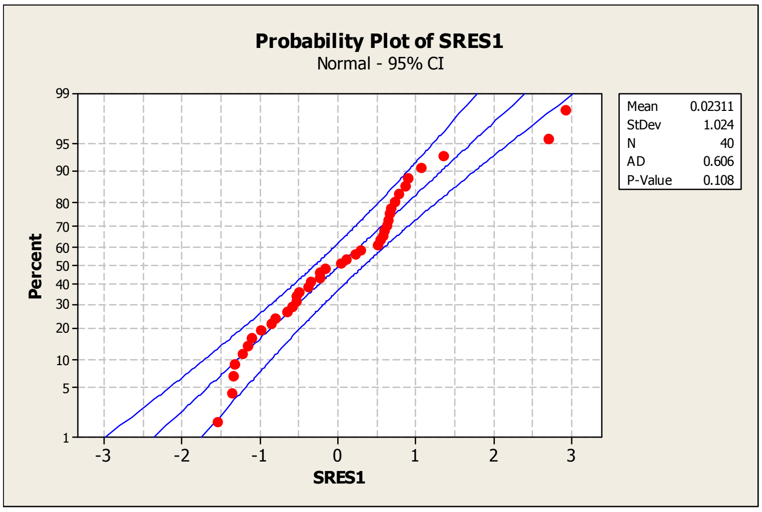

Figure 4.1 Normal probability plot of the residuals for the regression model based on face-centered central composite design and applied for CS7 with only main factors

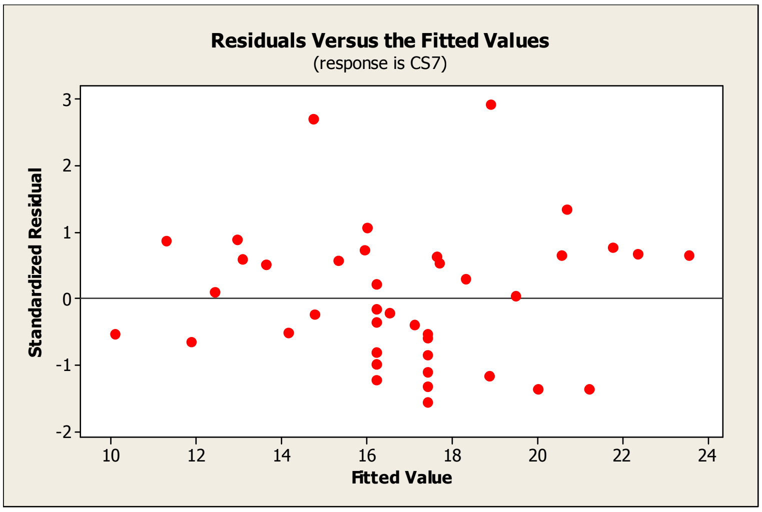

Figure 4.2 Residuals versus the fitted values plot of the regression model based on face-centered central composite design and applied for CS7 with only main factors

In Table 4.2 "Coef" refers to the value of β estimate for that particular predictor, "SE Coef" refers to the standard error of this estimate, T refers to the t-value of hypothesis test for the significance of the coefficient and P is the related p-value for the test. The table shows that except F (amount of pozzolan passing 45 μm sieve) the relationship between all main factors and the response is statistically significant at 0.05 α-level.

As also proposed in the lack of fit test results of the first regression model, a regression model that involves all two-way interaction and quadratic terms is employed as the second model. The regression equation is found as:

$$
\begin{aligned}
CS7 = {} & 15.4 - 3.80\ P + 0.892\ F + 1.43\ D + 0.215\ T + 0.162\ Psq + 1.34\ Fsq \\
& + 1.36\ Dsq + 0.564\ PF + 0.662\ PD - 0.382\ PT + 0.637\ FD - 0.036\ FT \\
& - 1.21\ DT + 0.492\ PsqT + 0.230\ FsqT + 0.051\ DsqT + 0.057\ PFT \\
& + 0.065\ FDT - 0.286\ PDT \qquad (4.3)
\end{aligned}
$$

where X represents the main effect of a parameter,
Xsq represents the quadratic term for a parameter
XY represents two-way interaction effect of parameters X and Y
and XYZ represents three-way interaction effect of parameters X,Y and Z

S = 1.28716   R-Sq = 93.5%   R-Sq(adj) = 87.4%
Durbin-Watson statistic = 1.82212

The regression is statistically significant at 100% confidence level. By this second regression model standard deviation of the error decreased from 2.09556 to 1.28716 and R-Sq(adj) value increased from 66.6% to 87.4%. There is a considerable improvement with this regression model and 87.4% of the sample variation in the 7-day compressive strength can be explained after adjusting for sample size and number of independent variables in the model. The Durbin-Watson statistic states that there is not any indication of the presence of residual correlation as statistic (1.82) is above the tabulated upper bound which is 1.52 with 4 independent variables and 40 observations at 0.01 significance level. Residuals versus the fitted values plot of the regression model (Fig. 4.3) and normal probability plot of the residuals (Fig. 4.4) do not indicate any violation of the basic regression assumptions. It can be said that the residuals are normally distributed and the error term has a constant variance and a mean of zero and hence basic regression assumptions are satisfied. Regression analysis can be found in Appendix 4.3.

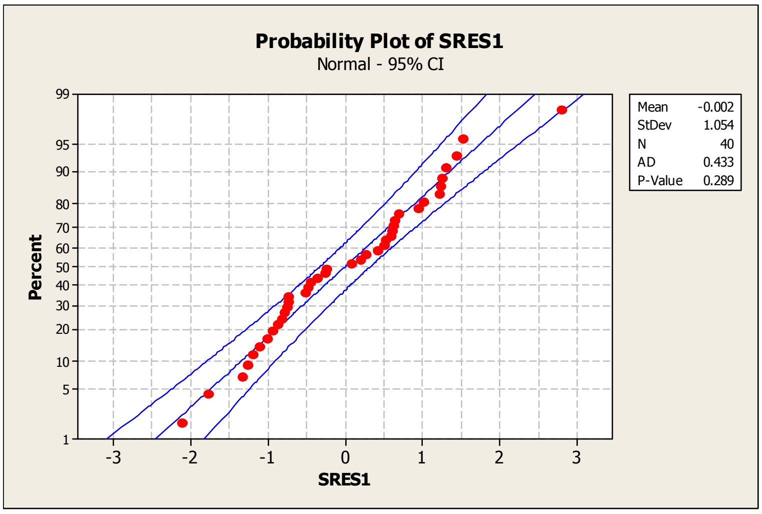

Figure 4.3 Normal probability plot of the residuals for the regression model based on face-centered central composite design and applied for CS7 involving all two-way interaction and quadratic terms

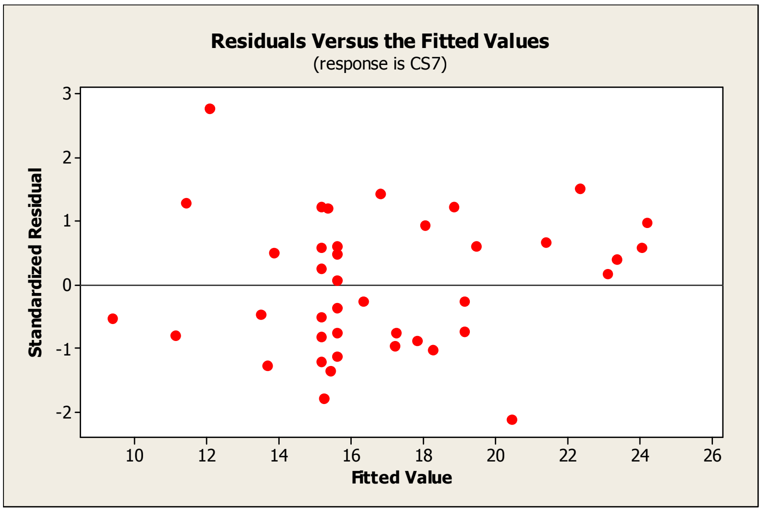

Figure 4.4 Residuals versus the fitted values plot of the regression model based on face-centered central composite design and applied for CS7 involving all two-way interaction and quadratic terms

In Table 4.3 ANOVA for the significance of the regression model (4.3) is given. The hypothesis that all β terms are equal to zero is rejected with a p-value of 0.00, which is smaller than pre-selected level of significance, 0.05.

Table 4.3 ANOVA for the significance of the regression model applied for 7-day mean compressive strength based on the face-centered central composite design involving all two-way interaction and quadratic terms

Source	**DF**	**SS**	**MS**	**F**	**P**
Regression	19	480.028	25.265	15.25	0.000
Residual Error	20	33.135	1.657		
Lack of Fit	10	23.423	2.342	2.41	0.091
Pure Error	10	9.712	0.971		
Total	39	513.163			

In Table 4.4, β estimates and their standard errors are tabulated with related p-values.

Table 4.4 Significance of β terms of the regression model based on face-centered central composite design and applied for mean 7-day compressive strength

Predictor	**Coef**	**SE Coef**	**T**	**P**
Constant	15.3905	0.3129	49.19	0.000
P	-3.7952	0.2878	-13.19	0.000
F	0.8924	0.2878	3.1	0.006
D	1.4318	0.2878	4.97	0.000
T	0.2151	0.3129	0.69	*0.500*
Psq	0.162	0.5488	0.3	*0.771*
Fsq	1.3388	0.5488	2.44	0.024
Dsq	1.3551	0.5488	2.47	0.023
PF	0.5639	0.3218	1.75	*0.095*
PD	0.6619	0.3218	2.06	*0.053*
PT	-0.3825	0.2878	-1.33	*0.199*
FD	0.6374	0.3218	1.98	0.062
FT	-0.036	0.2878	-0.12	*0.902*
DT	-1.2095	0.2878	-4.2	0.000
PsqT	0.4918	0.5488	0.9	*0.381*
FsqT	0.2303	0.5488	0.42	*0.679*
DsqT	0.0505	0.5488	0.09	*0.928*
PFT	0.0572	0.3218	0.18	*0.861*
FDT	0.0654	0.3218	0.2	*0.841*
PDT	-0.286	0.3218	-0.89	*0.385*

From Table 4.4, it is seen that 12 of the 19 predictors have p-values greater than pre-selected α-value 0.05. The relationship between the response and these 12 predictors is not statistically significant. Therefore, the model can be improved by discarding insignificant terms from the regression model

(Ayan, 2004). The first factor to discard from the regression equation is the one having the largest p-value. After eliminating this factor a new regression equation is fit with remaining factors. For the new regression analysis basic regression assumptions are checked and the second factor to discard from this new equation is chosen according to the p-values of the significance of β terms. Excluding a lower-order term affects the response surface hierarchy. To include a higher-order term in the model, the lower-order term must also be included. The procedure follows this sequence until no significant improvement in multiple coefficient of determination (R-sq(adj)) and estimate of standard deviation (S) is achieved. The best model in accordance with this procedure is achieved by pooling DsqT, FT, PFT, FDT, Psq, FsqT, PDT and PsqT terms to the error term.

The regression equation for the best model chosen results as:

$$CS7 = 15.4 - 3.80\,P + 0.892\,F + 1.43\,D + 0.601\,T + 1.40\,Fsq + 1.42\,Dsq + 0.564\,PF + 0.662\,PD - 0.382\,PT + 0.637\,FD - 1.21\,DT \quad (4.4)$$

S = 1.18784   R-Sq = 92.3%   R-Sq(adj) = 89.3%
Durbin-Watson statistic = 1.67847

Residuals versus fitted values plot of the regression model (Fig. 4.5) and normal probability plot of the residuals (Fig. 4.6) do not indicate any violation of the basic regression assumptions. There is not any indication of the presence of residual correlation as Durbin-Watson statistic (1.68) is above the tabulated upper bound which is 1.52 with 4 independent variables and 40 observations at 0.01 significance level.

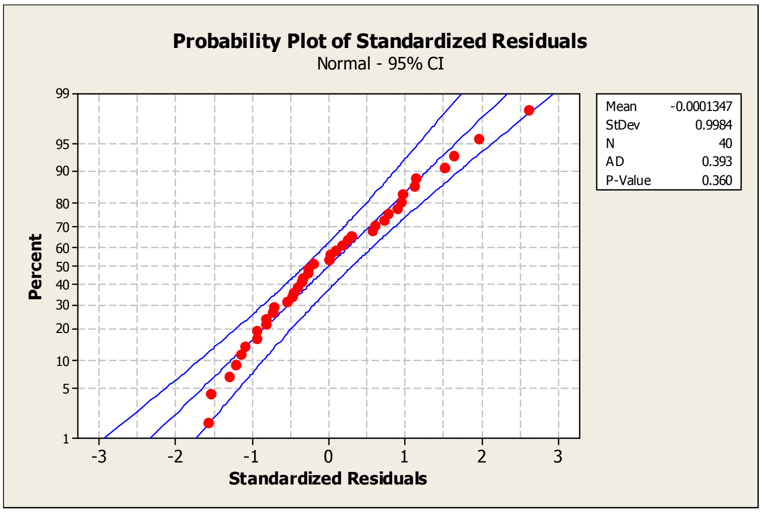

Figure 4.5 Normal probability plot of the residuals for the regression model based on face-centered central composite design and applied for mean 7-day compressive strength after elimination of insignificant terms

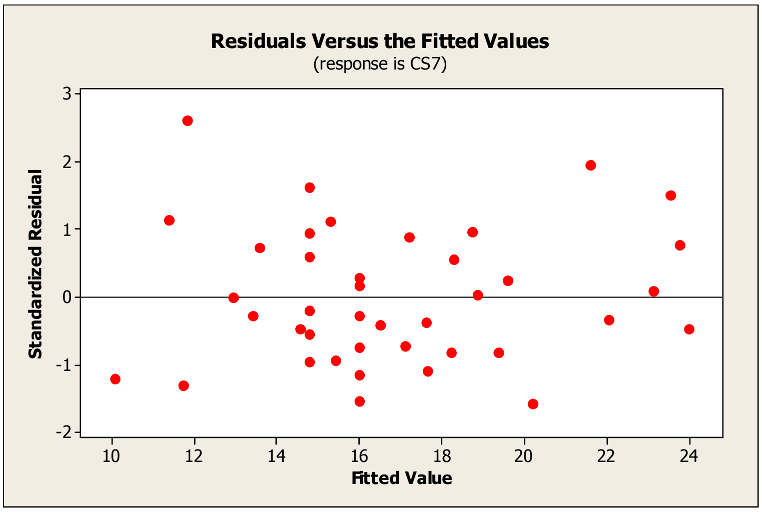

Figure 4.6 Residuals versus the fitted values plot of the regression model based on face-centered central composite design and applied for mean 7-day compressive strength after elimination of insignificant terms

In Tables 4.5 and 4.6 ANOVA results for the significance of the regression model and significance of β terms are tabulated. The regression is significant with a p-value of 0.00 and there is no evidence of lack of fit since p-value of lack of fit test (0.196) is greater than pre-selected α-value of 0.1 (Appendix 4.4). The adjusted multiple coefficient of determination shows that 89.3% of the sample variation in the mean 7-day compressive strength can be explained by this model. This value is 87.4% for the model including all possible predictors. Standard deviation for current model is 1.19 while it is 1.28 for the previous model. Improvement in explained variation and standard deviation are achieved by the final model.

Table 4.5 ANOVA for the significance of the regression model applied for 7-day mean compressive strength based on the face-centered central composite design after elimination of insignificant terms

Source	DF	SS	MS	F	P
Regression	11	473.656	43.06	30.52	0.000
Residual Error	28	39.507	1.411		
Lack of Fit	18	29.795	1.655	1.700	0.196
Pure Error	10	9.712	0.971		
Total	39	513.163			

Table 4.6 Significance of β terms of the regression model based on face-centered central composite design and applied for mean 7-day compressive strength after elimination of insignificant terms

Predictor	Coef	SE Coef	T	P
Constant	15.4107	0.2817	54.7	0.000
P	-3.7952	0.2656	-14.29	0.000
F	0.8924	0.2656	3.36	0.002
D	1.4318	0.2656	5.39	0.000
T	0.6015	0.1878	3.2	0.003
Fsq	1.3995	0.4695	2.98	0.006
Dsq	1.4158	0.4695	3.02	0.005
PF	0.5639	0.297	1.9	0.068
PD	0.6619	0.297	2.23	0.034
PT	-0.3825	0.2656	-1.44	0.161
FD	0.6374	0.297	2.15	0.041
DT	-1.2095	0.2656	-4.55	0.000

As it is indicated in Table 4.6, activator type and its two-way interactions with natural pozzolan replacement and activator dosage are significant in the final regression equation.

Tunalı and Batmaz (2003) propose a series of homogeneity tests "to check whether the effects of quantitative factors remain the same across the levels of the qualitative factor". F-tests are performed to check the significance of the interaction between levels of the qualitative factor and quantitative factors. If such an interaction does not exist, it is concluded that the regression model has identical response surfaces for the levels of the qualitative factor. Below, these homogeneity tests are performed for mean 7-day compressive strength. For the calculation of necessary sum of squares of errors (SSE) for three regression metamodels, regression analyses are performed. Results are presented in Appendix 4.5. Explanations on these tests can be found in section 2.2.1.

Test of homogeneity of response curves:

$F^* = [(SSE(1) - SSE(3)) / v_1] / [SSE(3) / v_2] \quad \{v_1 = p_3 - p_1 \;\; v_2 = N - p_3\}$

$= [(86.016-33.135) / 10] / [33.135 / 20]$

$= 5.288 / 1.66 = 3.19$

Since $F^* = 3.19 > F_{0.05,10,20} = 2.35$, it is concluded that at least one of the coefficients of a regression parameter involving the qualitative factor T (T, x_iT, X_iX_jT, X_i^2T etc. where x represents a quantitative factor) is different from zero. Therefore, the second-order model for only quantitative factors is not sufficient to explain the relation between quantitative factors and the response at each level of the qualitative factor.

Test of homogeneity for interactions:

$F^* = [(SSE(2) - SSE(3)) / v_1] / [SSE(3) / v_2] \quad \{v_1 = p_3 - p_2 \;\; v_2 = N - p_3\}$

$= [(71.545-33.135) / 9] / [33.135 / 20]$

$= 4.27 / 1.66 = 2.57$

Since $F^* = 2.57 > F_{0.05,9,20} = 2.39$, the null hypothesis that the response surfaces at two different level of the qualitative factor have the same shape is rejected. Since the shapes are different across levels, the test for equality of the intercept is not performed. Results of the homogeneity tests and final regression equation verify each other.

After constructing the regression equation where the qualitative factor is included as a parameter, regression analyses for two activator types and with only quantitative factors are performed separately for comparison. Two independent response surfaces are built and examined for each of the activator type.

Below regression equation (4.5) is the best model chosen for mean 7-day compressive strength when activator type is NaOH. Insignificant factors are discarded while considering adjusted multiple coefficient of determination and standard deviation estimate of the models.

$$CS7 = 15.1 - 3.41\ P + 0.928\ F + 2.64\ D + 0.985\ Fsq + 1.18\ Dsq + 0.947\ PD + 0.573\ FD \quad (4.5)$$

S = 1.12462   R-Sq = 93.6%   R-Sq(adj) = 89.9%

Durbin-Watson statistic = 2.03704

Regression results are summarized in Appendix 4.6. The regression is significant at 100% confidence level and basic regression assumptions are valid (Fig.s 4.7 and 4.8). Upper bound for Durbin-Watson statistic is 1.41 for three independent variables and 20 observations at 0.01 significance level. Since the statistic for this regression model (2.03) is greater than the upper bound value there is not sufficient evidence for residual correlation.

There is no evidence of lack of fit as it can be seen from the regression results. Table 4.7 and 4.8 summarize significance of the regression and β terms of the equation 4.5.

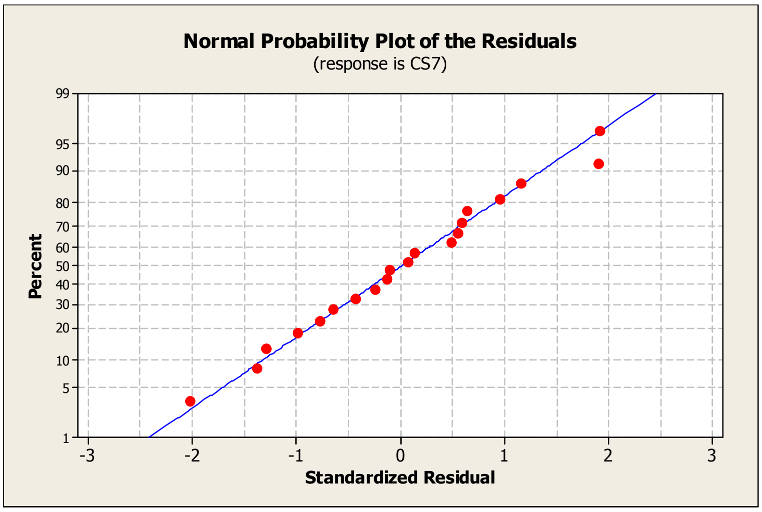

Figure 4.7 Normal probability plot of the residuals for the regression model based on the design with three quantitative variables for activator type NaOH for 7-day compressive strength

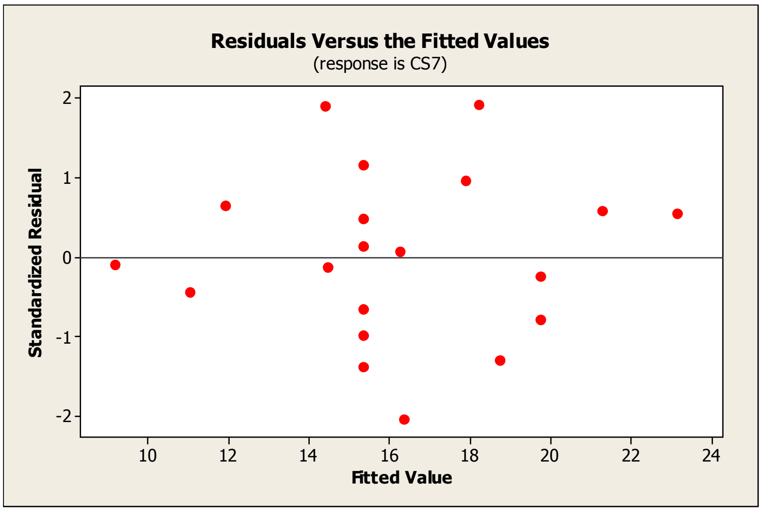

Figure 4.8 Residuals versus the fitted values plot of the regression model based on the design with three quantitative variables for activator type NaOH for 7-day compressive strength

Table 4.7 ANOVA for the significance of the regression model applied for 7-day mean compressive strength when the activator type is NaOH

Source	**DF**	**SS**	**MS**	**F**	**P**
Regression	7	223.332	31.905	25.23	0.000
Residual Error	12	15.177	1.265		
Lack of Fit	7	8.961	1.28	1.03	0.505
Pure Error	5	6.216	1.243		
Total	19	238.509			

Table 4.8 Significance of β terms of the regression model for mean 7-day compressive strength when the activator type is NaOH

Predictor	**Coef**	**SE Coef**	**T**	**P**
Constant	15.135	0.3772	40.12	0.000
P	-3.413	0.3556	-9.6	0.000
F	0.928	0.3556	2.61	0.023
D	2.639	0.3556	7.42	0.000
Fsq	0.985	0.6287	1.57	0.143
Dsq	1.18	0.6287	1.88	0.085
PD	0.9475	0.3976	2.38	0.035
FD	0.5725	0.3976	1.44	0.175

For activator Na_2SO_4, chosen best regression model is 4.6 and regression results are summarized in Appendix 4.7.

$$CS7 = 15.7 - 4.18\ P + 0.857\ F + 0.223\ D + 1.81\ Fsq + 1.65\ Dsq \qquad (4.6)$$

S = 1.45557   R-Sq = 88.6%   R-Sq(adj) = 84.5%

Durbin-Watson statistic = 2.34560

The regression is significant with a p-value of 0.000 and the total sample variation explained by this regression equation is 84.5%. The p-value for the Anderson-Darling normality test for residuals is 0.141 as noted in Fig 4.9. This value is greater than the chosen α-level of 0.10, thus the hypothesis that the data follows a normal distribution cannot be rejected. Residuals versus the fitted values plot (Fig. 4.10) does not show a specific pattern and constant variance of residuals assumption is valid. Significance of the regression and β terms are summarized in Tables 4.9 and 4.10.

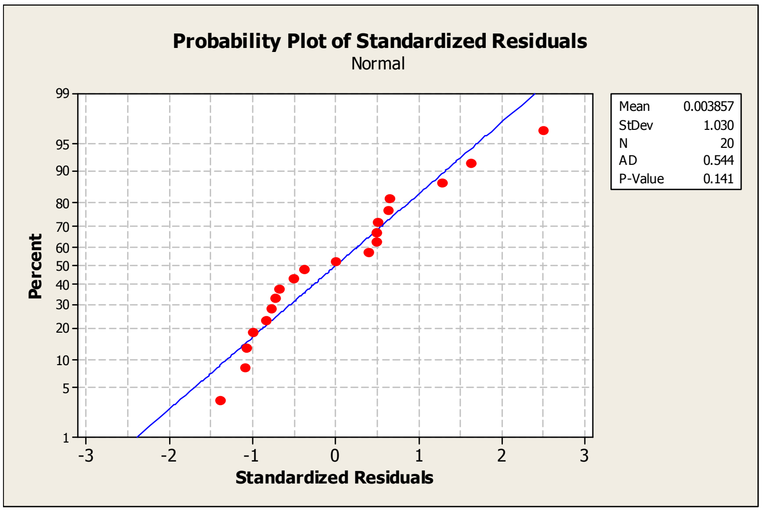

Figure 4.9 Normal probability plot of the residuals for the regression model based on the design with three quantitative variables for activator type Na_2SO_4 for 7-day compressive strength

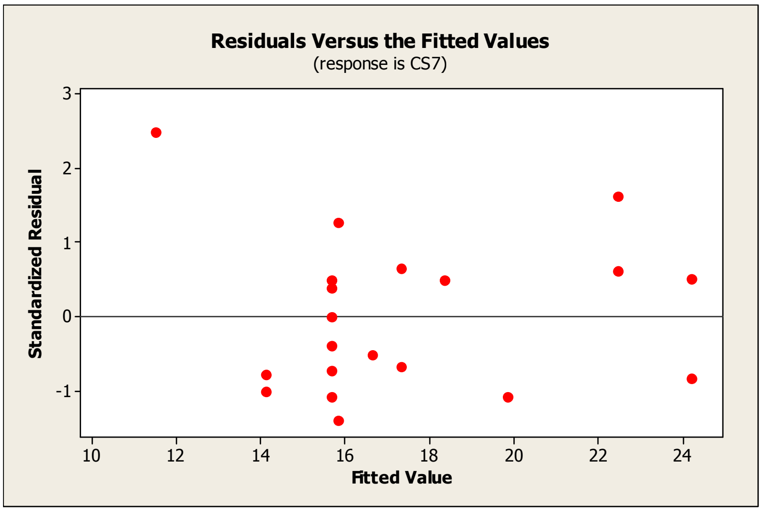

Figure 4.10 Residuals versus the fitted values plot of the regression model based on the design with three quantitative variables for activator type Na_2SO_4 for 7-day compressive strength

Table 4.9 ANOVA for the significance of the regression model applied for 7-day mean compressive strength when the activator type is NaOH

Source	DF	SS	MS	F	P
Regression	5	230.553	46.111	21.76	0.000
Residual Error	14	29.662	2.119		
Lack of Fit	9	26.187	2.91	4.19	0.065
Pure Error	5	3.475	0.695		
Total	19	260.215			

Table 4.10 Significance of β terms of the regression model for mean 7-day compressive strength when the activator type is NaOH

Predictor	Coef	SE Coef	T	P
Constant	15.6851	0.4882	32.13	0.000
P	-4.178	0.4603	-9.08	0.000
F	0.857	0.4603	1.86	0.084
D	0.223	0.4603	0.48	0.636
Fsq	1.8144	0.8137	2.23	0.043
Dsq	1.6544	0.8137	2.03	0.061

4.2. Response Surface Methodology with Economical Designs

4.2.1. Design of Experiments

As explained in section 2.2.1, economical design alternatives for response surface designs with qualitative factors are proposed in the literature. One design from Draper and John (1988) and one design from Wu and Ding (2003) with 16 runs and 4 independent variables are adopted for the data set and related regression analyses are done in the following section. The design alternative from Draper and John will be referred as DJ design and the alternative from Wu and Ding will be referred as WD design from now on. These designs are given in Appendix 4.8. Selected design from each work is the best proposed alternative among others according to alphabetical optimality criteria (A, D, G and V-optimality criteria).

4.2.2. Regression Analyses

The second-order regression equation with three quantitative and one qualitative variable has 20 β parameters to estimate so two chosen economical designs with 16 observations are not capable for fitting such an equation. At least 21 observations are required to fit such an equation. In order to decrease the number of potential predictors to a manageable number, variable screening method as stepwise regression and best subsets regression are employed. However these procedures are not recommended for final design selection since the probability of making Type I or Type II errors are extremely high (Mendenhall and Sincich, 2003). Instead they are employed for preliminary design decision. Regression equations are fit for alternative predictor sets and basic regression assumptions are checked. The best model for DJ design that achieves the highest multiple coefficient determination, minimum standard deviation estimate and significance results as follows:

$$CS7 = 16.1 - 2.80\ P + 1.22\ F + 0.972\ D + 0.351\ T - 1.76\ DT + 0.948\ PD + 0.874\ PT + 1.34\ Fsq \qquad (4.7)$$

S = 1.13455   R-Sq = 95.7%   R-Sq(adj) = 90.9%

Durbin-Watson statistic = 1.73984

Regression analysis results are given in Appendix 4.9. Lack of tit test cannot be performed since there is not enough data and pure error test cannot be done since there are no replicates. These are shortcomings of this design. On the other hand 90.9% of the sample variation in mean compressive strength can be explained by this regression, after adjusting for sample size and number of independent variables in the model. Standard deviation estimate and multiple coefficient of determination values are better with respect to equation 4.4. Durbin-Watson statistic (1.74) is higher than tabulated upper bound value of 1.66 for 4 independent variables and 16 observations and hence does not indicate autocorrelation of residuals. Normality and constant variance assumptions for residuals are satisfied (Fig.s 4.11 and 4.12). Table 4.11 and 4.12 summarize significance of the regression and individual parameters.

Table 4.11 ANOVA for the significance of the regression model applied for 7-day mean compressive strength based on DJ design

Source	DF	SS	MS	F	P
Regression	8	202.826	25.353	19.7	0.000
Residual Error	7	9.011	1.287		
Total	15	211.837			

Table 4.12 Significance of β terms of the regression model based on DJ design and applied for mean 7-day compressive strength

Predictor	Coef	SE Coef	T	P
Constant	16.1468	0.5228	30.89	0.000
P	-2.8031	0.4485	-6.25	0.000
F	1.2226	0.3588	3.41	0.011
D	0.9725	0.4485	2.17	0.067
T	0.3509	0.3637	0.96	0.367
DT	-1.757	0.4485	-3.92	0.006
PD	0.948	0.4011	2.36	0.050
PT	0.8744	0.4485	1.95	0.092
Fsq	1.3431	0.7453	1.8	0.115

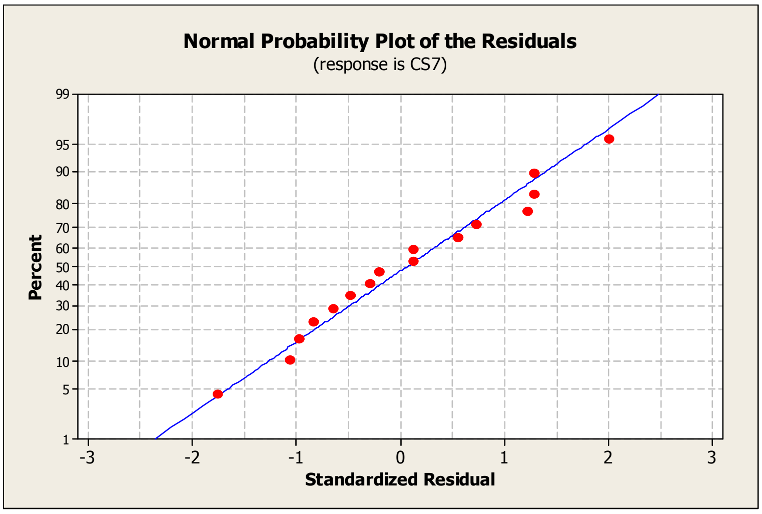

Figure 4.11 Normal probability plot of the residuals for the regression model based on DJ design and applied for mean 7-day compressive strength

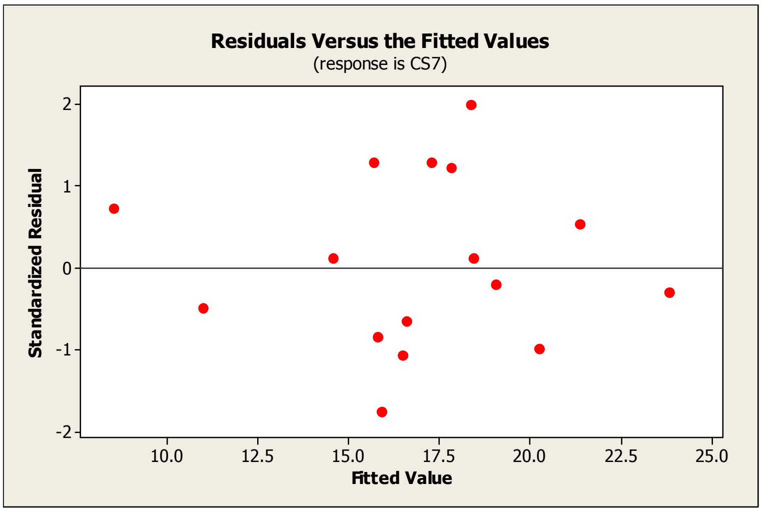

Figure 4.12 Residuals versus the fitted values plot of the regression model based on DJ design and applied for mean 7-day compressive strength

For selection of the best regression model for WD design, the same procedure followed for DJ design is used. The chosen regression model results as:

$$CS7 = 15.3 - 3.56\ P + 1.22\ F + 1.52\ D + 0.560\ T - 1.89\ DT + 1.74\ Dsq + 1.05\ FD + 1.19\ Fsq \quad (4.8)$$

S = 1.12158   R-Sq = 96.9%   R-Sq(adj) = 93.3%

Durbin-Watson statistic = 2.12921

Standard deviation estimate is slightly better than equation 4.7 and 93.3% of the sample variation is explained by this regression model. A violation for basic regression assumptions is not detected (Fig.s 4.13 and 4.14). Durbin-Watson statistic is higher than tabulated upper bound value of 1.66 for 4 independent variables and 16 observations and does not indicate dependency of residuals. ANOVA for the significance of the regression model is given in Table 4.13 and significance of the β parameters is summarized in Table 4.14.

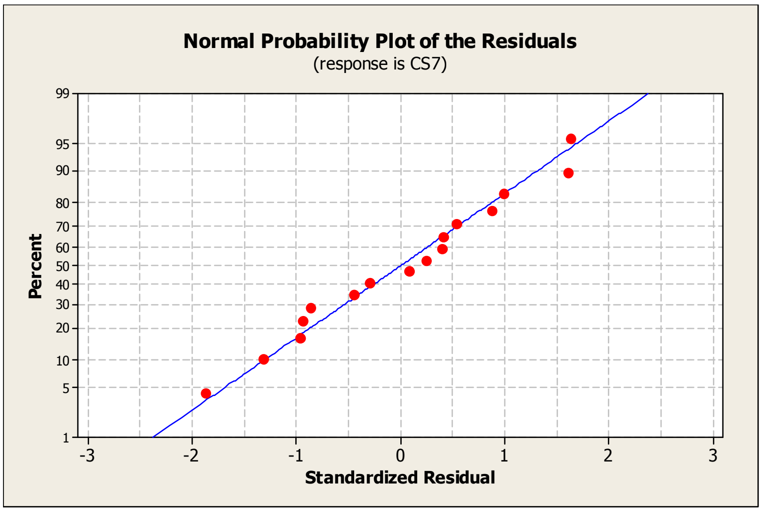

Figure 4.13 Normal probability plot of the residuals for the regression model based on WD design and applied for mean 7-day compressive strength

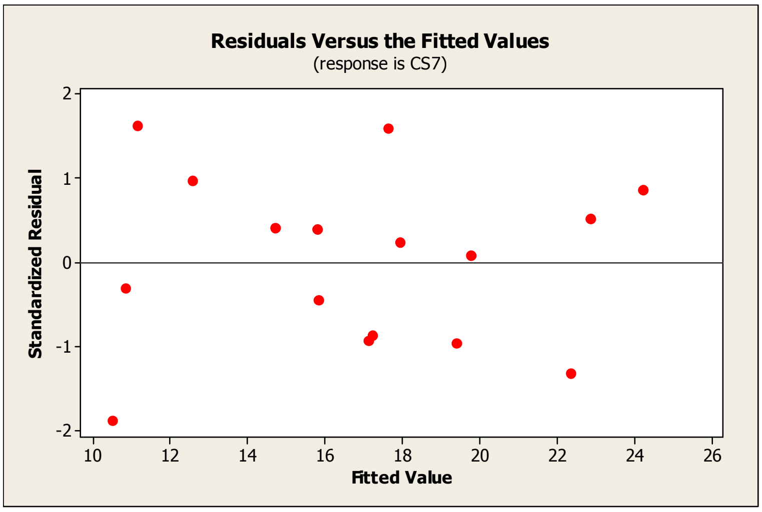

Figure 4.14 Residuals versus the fitted values plot of the regression model based on WD design and applied for mean 7-day compressive strength

Table 4.13 ANOVA for the significance of the regression model applied for 7-day mean compressive strength based on WD design

Source	DF	SS	MS	F	P
Regression	8	202.826	25.353	19.7	0.000
Residual Error	7	9.011	1.287		
Total	15	211.837			

Table 4.14 Significance of β terms of the regression model based on WD design and applied for mean 7-day compressive strength

Predictor	Coef	SE Coef	T	P
Constant	15.2764	0.5134	29.76	0.000
P	-3.5551	0.3903	-9.11	0.000
F	1.2172	0.3634	3.35	0.012
D	1.5219	0.3606	4.22	0.004
T	0.5603	0.326	1.72	0.129
DT	-1.8888	0.3955	-4.78	0.002
Dsq	1.7407	0.6639	2.62	0.034
FD	1.0535	0.4198	2.51	0.040
Fsq	1.1859	0.6964	1.7	0.132

4.3. Response Surface Optimization of Mean 7-Day Compressive Strength

Response surface optimization for the best regression models found for mean 7-day compressive strength is done by Design-Expert Optimization Module (Design-Expert, Version 7.0.0, Stat-Ease Inc.). This module searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. To use optimization, first each response should be analyzed to find an appropriate model. Optimization of one response or the simultaneous optimization of multiple responses can be performed by Design-Expert Optimization Module.

First, the desired goal for each factor and response is chosen from the menu. For compressive strength desired goal is maximization and the goal is assigned accordingly. For mean 7-day compressive strength, the limits for minimum and maximum strengths are set to 10 MPa and 30 MPa respectively. The decision is based on past experience and test results. Then maximum and minimum levels are assigned for the factors. Design-Expert Optimization Module differentiates between qualitative and quantitative factors while defining parameters, which is a great advantage for this study.

The module makes use of desirability function for optimization. Desirability is an objective function that ranges from zero outside of the limits to one at the goal. The numerical optimization finds a point that maximizes the desirability function. The value of desirability function is completely dependent on how closely the lower and upper limits are set relative to the actual optimum.

The characteristics of a goal may be altered by adjusting the weight or importance. These adjustments are especially important in simultaneous optimization of several response variables. A weight can be assigned to a goal to adjust the shape of its particular desirability function. The default value of one creates a linear function between the low value and the goal or the high value and the goal. Increased weight (up to 10) moves the result towards the goal. Reduced weight (down to 0.1) creates the opposite effect. The importance of a goal can be changed in relation to the other goals and can be assigned from 1 to 5. For several responses and factors, all goals get combined into one desirability function and this function is tried to be maximized. In Fig. 4.15, the screenshot of the assignments for mean 7-day compressive strength (when the experimental design is FCCD with 40 observations) and the desirability function graph formed by related assignments is given.

The goal seeking begins at a random starting point and proceeds up the steepest slope to a maximum. There may be two or more maximums because of curvature in the response surfaces and their combination into the desirability function. By starting from several points in the design space chances improve for finding the "best" local maximum.

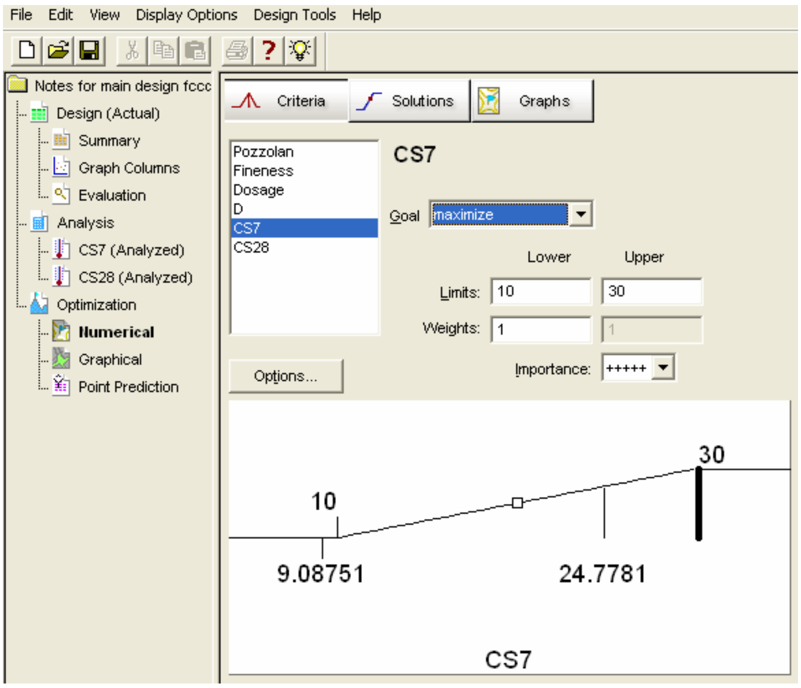

Figure 4.15 Goal and limit assignment for CS7 in Design-Expert software and desirability function for assigned case

In sections 4.1.2. and 4.2.2. best regression models for 5 different sets of observations are found. Response surface optimization for each regression model is performed and results are presented below.

FCCD for Each Level of the Qualitative Factor (40 observations)

The best regression model for the main design in the study is accepted as (Equation 4.4):

$$CS7 = 15.4 - 3.80\ P + 0.892\ F + 1.43\ D + 0.601\ T + 1.40\ Fsq + 1.42\ Dsq + 0.564\ PF + 0.662\ PD - 0.382\ PT + 0.637\ FD - 1.21\ DT \qquad (4.4)$$

Example response surface curves of 7-day mean compressive strength for equation 4.4 are given in Fig. 4.16. For each activator type, all possible subsets of 2 main factors are assigned to x-axes and y-axis indicates the response. The level of the third quantitative factor which cannot be assigned is kept constant at medium level. Fitted response surfaces verify the significant effect of activator type on the response once again.

Optimum points found by the software are presented in Table 4.15. Desirability value, 95% confidence and prediction levels for the optimum points are also indicated in the table. Table 4.16 reports the parameter levels of these optimum points. In Fig. 4.17 optimum point is also graphically shown.

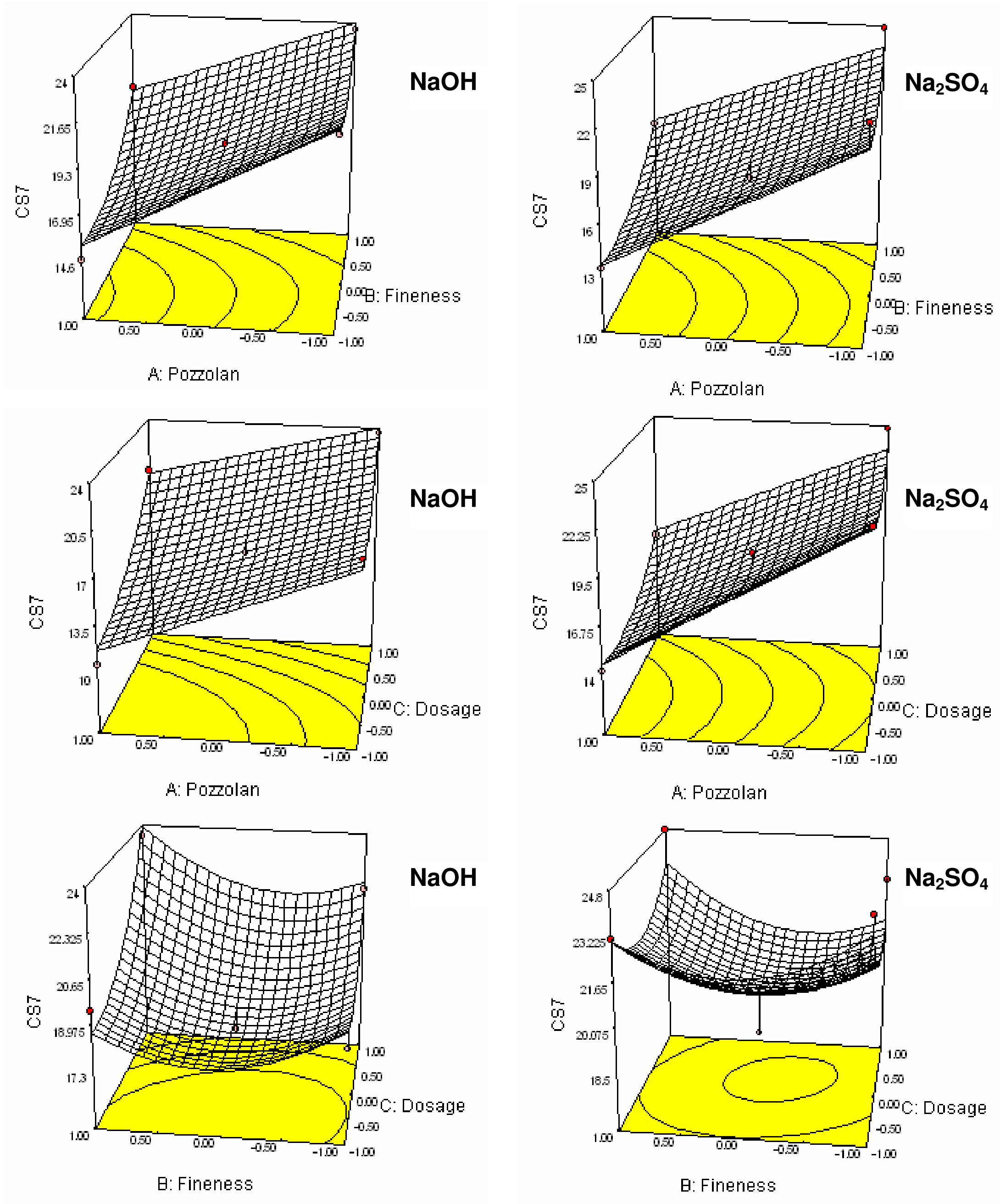

Figure 4.16 Example response surface curves of CS7 for two different types of activators (FCCD with 40 observations)

Table 4.15 Optimum CS7 responses with desirability values, 95% confidence and prediction intervals for main FCCD design for both activator types

#	Prediction (in MPa)	Desirability	95% CI	95% PI
1	23.9821	0.699	(22.23; 25.73)	(20.98; 26.98)
2	23.7533	0.688	(22.00; 25.51)	(20.75; 26.75)
3	23.7203	0.686	(22.06; 25.38)	(20.77; 26.67)
4	23.5314	0.677	(21.78; 25.28)	(20.53; 26.53)
5	23.4665	0.673	(21.88; 25.05)	(20.56; 26.37)
6	23.1352	0.657	(21.38; 24.89)	(20.14; 26.13)
7	23.0252	0.651	(21.41; 24.64)	(20.11; 25.94)
8	22.9377	0.647	(21.34; 24.53)	(20.03; 25.85)
9	22.5174	0.626	(20.92; 24.11)	(19.61; 25.43)
10	22.4047	0.620	(20.85; 23.96)	(19.52; 25.29)

Table 4.16 Parameter levels of optimum CS7 points for FCCD design at each activator type

#	P	F	D	T	CS7
1	**-1.00**	**1.00**	**1.00**	**NaOH**	**23.98**
2	**-1.00**	**-1.00**	**-1.00**	**Na_2SO_4**	**23.75**
3	-0.88	1.00	1.00	NaOH	23.72
4	**-1.00**	**1.00**	**1.00**	**Na_2SO_4**	**23.53**
5	-0.76	1.00	1.00	NaOH	23.47
6	**-1.00**	**1.00**	**-1.00**	**Na_2SO_4**	**23.14**
7	-1.00	1.00	0.82	NaOH	23.03
8	-1.00	1.00	0.78	Na_2SO_4	22.94
9	-1.00	-0.48	-1.00	Na_2SO_4	22.52
10	-1.00	1.00	-0.66	Na_2SO_4	22.40

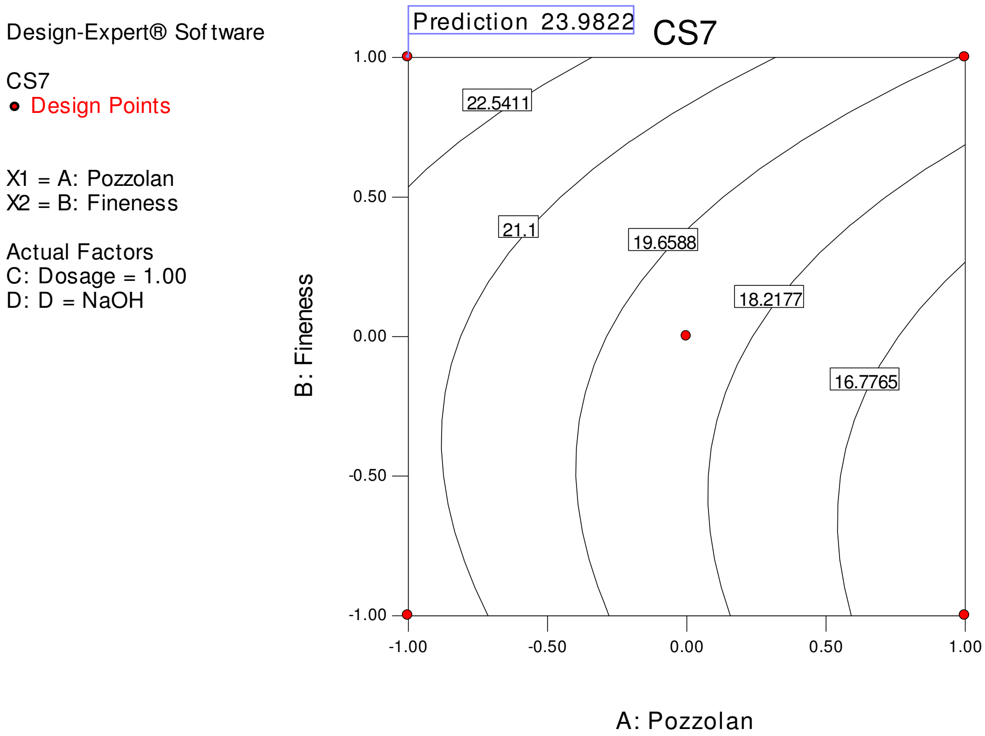

Figure 4.17 Graphical representation of optimum point for CS7 with FCCD with 40 observations

In Table 4.16, 4 optimum points are especially important and will be explained briefly:

Point #1: This point is a combination of minimum pozzolan content (35%), maximum fineness (90% passing 45 μm sieve), maximum activator dosage (1.5%) and activator type NaOH. When the response surface examples for NaOH activator (Fig. 4.16) are considered, the optimum point is expected at this point as well. The mean value for 6 experiment results performed at this point is 23.6 MPa, which is very close to predicted value of 23.98 MPa, and experiment result also falls within 95% confidence interval. Therefore, this point is very well modeled by chosen regression model. Points 3, 5 and 7 in Table 4.16 possess same sign combinations for each factor but they have slightly smaller parameter values with smaller desirability values.

Point #2: For activator type NaOH, quadratic effect of fineness and dosage push optimum points to the minimum-maximum level combinations of these parameters as can be seen in Fig. 4.16. Especially the response curves in which these two parameters are assigned as independent variables behave differently and the effect is observed in optimum points for two activator types. For point #2, pozzolan content is again at its minimum (this is valid for all optimum points in Table 4.16). Fineness and activator dosage are also at their minimums while the activator is Na_2SO_4. Average of 6 experiments at this point is 24.39, which is a little higher than predicted value, and this value is in the confidence interval.

Point # 4: At this point pozzolan content is minimum and activator type is Na_2SO_4 again while fineness and activator dosage are at their maximums. Average of 6 replicates is 24.78 which is higher the predicted value of 23.53 but within confidence interval.

Point #6: For activator type Na_2SO_4 at minimum pozzolan content, fineness is at its maximum and activator dosage is at its minimum for this point. Average of six replicates is 23.21 which is very close to predicted value of 23.14 and it is safely covered by the confidence interval.

Among all results Point # 1 with highest predicted response, where pozzolan content is minimum, fineness and activator dosages are maximum and the activator type is NaOH, is chosen as the optimum point.

FCCD for activator type NaOH (20 observations)

Equation 4.5 below is the best regression model for the FCCD design where activator type is NaOH. In Fig. 4.18 example response curves are shown and in Tables 4.17 and 4.18 information on optimum points are summarized.

$$CS7 = 15.1 - 3.41\ P + 0.928\ F + 2.64\ D + 0.985\ Fsq + 1.18\ Dsq + 0.947\ PD + 0.573\ FD \qquad (4.5)$$

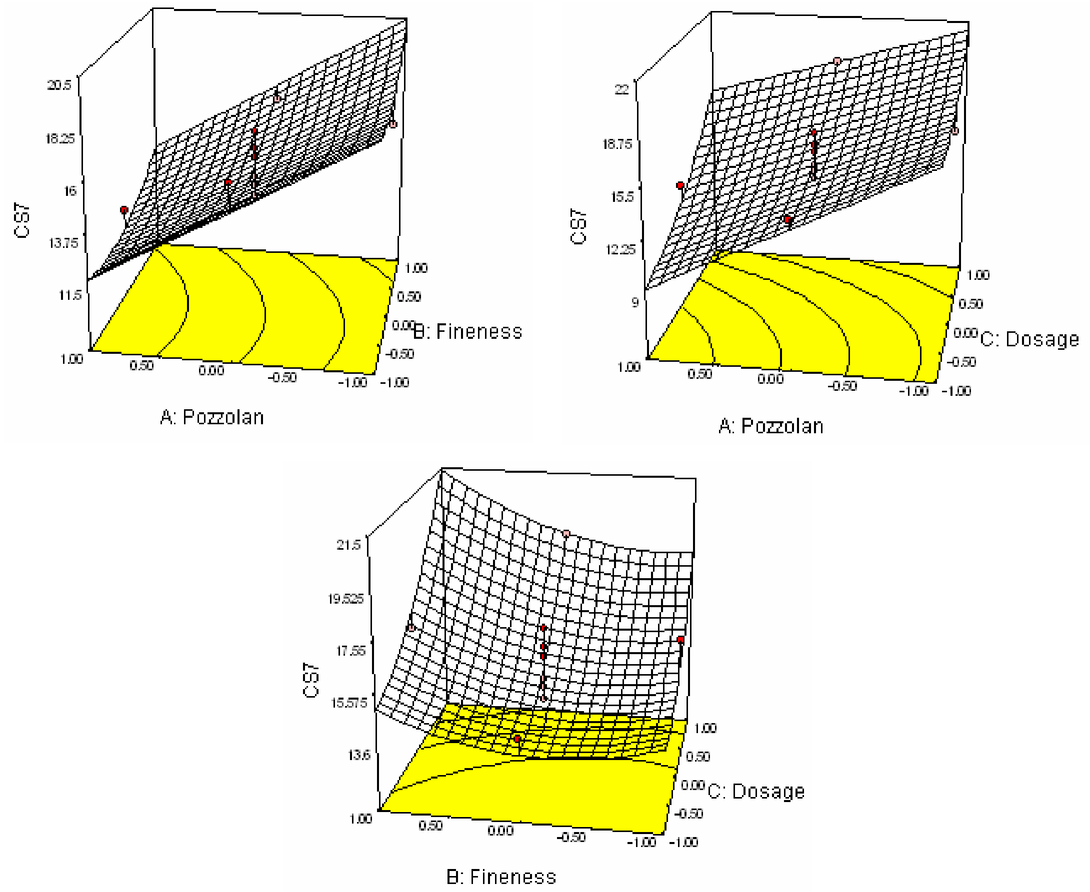

Figure 4.18 Example response surface curves of CS7 for activator type NaOH

Table 4.17 Optimum CS7 responses with desirability values, 95% confidence and prediction intervals for FCCD design for activator NaOH only

#	Prediction (in MPa)	Desirability	95% CI	95% PI
1	23.91	0.695	(21.91; 25.90)	(20.75; 27.06)
2	23.78	0.689	(21.82; 25.74)	(20.64; 26.91)
3	23.73	0.686	(21.79; 25.67)	(20.60; 26.86)
4	23.70	0.685	(21.76; 25.64)	(20.58; 26.82)
5	23.69	0.685	(21.76; 25.63)	(20.57; 26.82)
6	23.54	0.677	(21.64; 25.44)	(20.44; 26.64)
7	23.26	0.663	(21.43; 25.09)	(20.21; 26.32)
8	23.16	0.658	(21.31; 25.02)	(20.09; 26.23)
9	22.18	0.609	(20.30; 24.06)	(19.09; 25.26)
10	21.38	0.569	(19.44; 23.31)	(18.26; 24.50)

Table 4.18 Parameter levels of optimum CS7 points for FCCD design for activator NaOH only

#	P	F	D	CS7
1	-1.00	1.00	1.00	23.91
2	-0.97	1.00	0.99	23.78
3	-1.00	1.00	0.96	23.73
4	-1.00	0.94	1.00	23.70
5	-0.91	1.00	1.00	23.69
6	-0.85	1.00	1.00	23.54
7	-0.99	1.00	0.86	23.26
8	-1.00	0.77	1.00	23.16
9	-1.00	0.40	1.00	22.18
10	-1.00	-0.03	1.00	21.38

10 optimum solutions found are very similar when their signs and values are compared. Point # 1 is the chosen optimum point. This is the same point found in previous optimization with same parameter levels. Response is predicted as 23.91 and while average of 6 experiments (23.6) is included in 95% confidence interval.

FCCD for activator type Na_2SO_4 (20 observations)

When the regression is fit for FCCD when activator type is Na_2SO_4, best regression model is Equation (4.6) below. Example response curves are given in Fig. 4.19. Response surface optimization results are summarized in Tables 4.19 and 4.20.

$$CS7 = 15.7 - 4.18\ P + 0.857\ F + 0.223\ D + 1.81\ Fsq + 1.65\ Dsq \qquad (4.6)$$

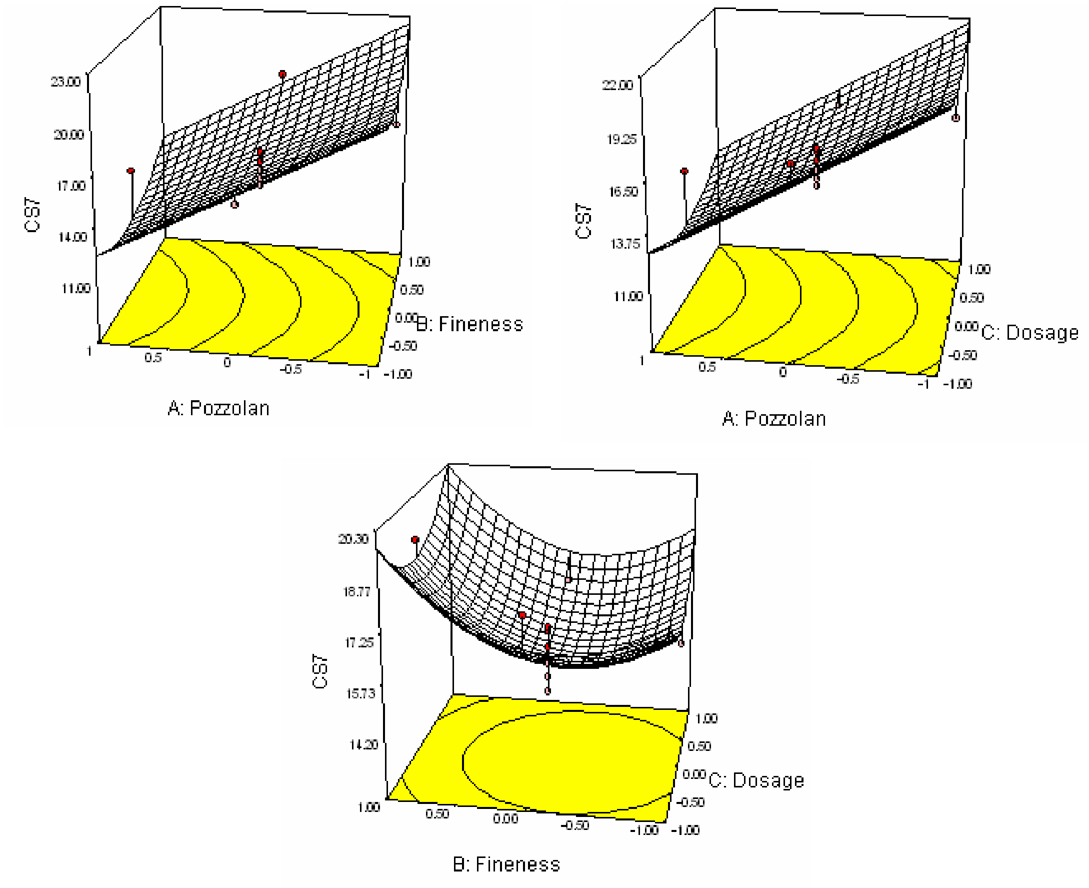

Figure 4.19 Example response surface curves of CS7 for activator type Na_2SO_4

Table 4.19 Optimum CS7 responses with desirability values, 95% confidence and prediction intervals for FCCD design for activator Na_2SO_4 only

#	Prediction (in MPa)	Desirability	95% CI	95% PI
1	24.41	0.695	(22.40; 26.41)	(20.70; 28.12)
2	24.08	0.689	(22.15; 26.01)	(20.41; 27.75)
3	24.03	0.686	(22.06; 25.99)	(20.34; 27.71)
4	23.96	0.685	(21.96; 25.97)	(20.25; 27.67)
5	23.17	0.685	(21.24; 25.09)	(19.50; 26.83)
6	23.03	0.677	(21.00; 25.06)	(19.30; 26.75)
7	22.76	0.663	(20.76; 24.75)	(19.05; 26.46)
8	22.66	0.658	(20.66; 24.66)	(18.95; 26.37)
9	22.60	0.609	(20.40; 24.79)	(18.78; 26.41)
10	22.58	0.569	(20.61; 24.55)	(18.88; 26.27)

Table 4.20 Parameter levels of optimum CS7 points for FCCD design for activator Na_2SO_4 only

#	P	F	D	CS7
1	**-1.00**	**1.00**	**1.00**	**24.41**
2	-1.00	1.00	0.90	24.08
3	-0.91	1.00	1.00	24.03
4	-1.00	1.00	-1.00	23.96
5	-1.00	1.00	-0.69	23.17
6	-1.00	1.00	0.48	23.03
7	-1.00	0.55	1.00	22.76
8	-0.99	-1.00	1.00	22.66
9	-1.00	1.00	0.14	22.60
10	-1.00	-1.00	0.97	22.58

Optimum point #1 with predicted value 24.41 has its experimental average at 24.78. Same point was predicted as 23.53 with the regression equation where activator type is a parameter so it is better modeled by this regression. However the confidence and prediction intervals of that regression are narrower.

Economical Response Surface Designs: DJ Design

Below equation (4.7) is the best regression model fit to DJ design. Response surface curves for this model can be seen in Fig. 4.20. Tables 4.21 and 4.22 outline optimal points.

$$CS7 = 16.1 - 2.80\,P + 1.22\,F + 0.972\,D + 0.351\,T - 1.76\,DT + 0.948\,PD + 0.874\,PT + 1.34\,Fsq \quad (4.7)$$

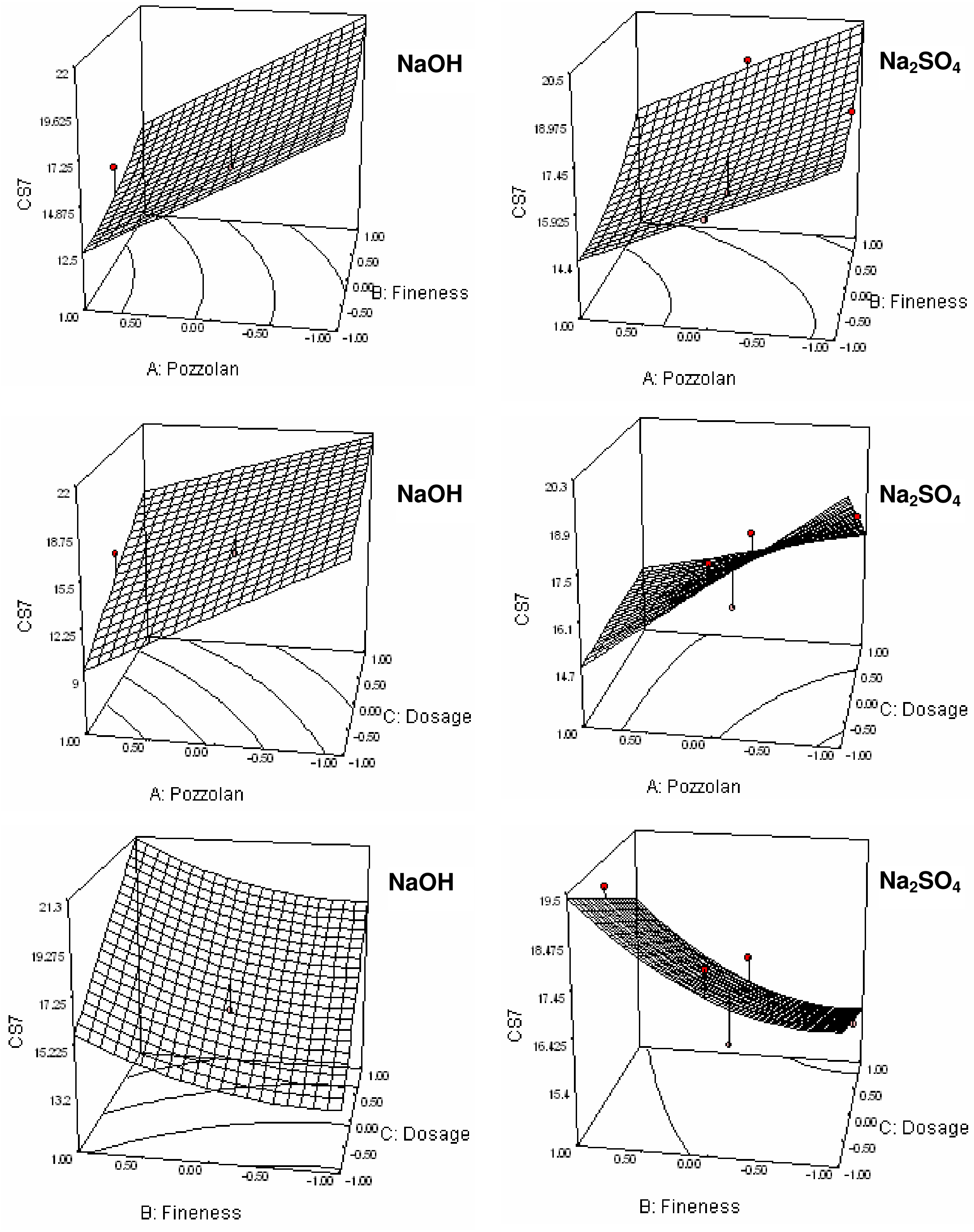

Figure 4.20 Example response surface curves of CS7 with DJ design

Table 4.21 Optimum CS7 responses with desirability values, 95% confidence and prediction intervals for DJ design

#	Prediction (in MPa)	Desirability	95% CI	95% PI
1	23.73	0.686	(21.25; 26.20)	(19.66; 27.79)
2	23.66	0.683	(21.22; 26.09)	(19.62; 27.70)
3	23.62	0.681	(21.17; 26.07)	(19.57; 27.67)
4	23.43	0.671	(21.12; 25.74)	(19.46; 27.39)
5	23.35	0.668	(21.08; 25.63)	(19.41; 27.30)
6	23.28	0.664	(20.85; 25.72)	(19.24; 27.33)
7	23.06	0.653	(20.83; 25.28)	(19.14; 26.98)
8	22.94	0.647	(20.43; 25.45)	(18.86; 27.03)
9	22.15	0.608	(17.49; 26.82)	(16.48; 27.82)
10	22.11	0.605	(20.22; 23.99)	(18.37; 25.84)

Table 4.22 Parameter levels of optimum CS7 points for DJ design

#	P	F	D	T	CS7
1	-1.00	1.00	1.00	NaOH	23.73
2	-1.00	1.00	0.96	NaOH	23.66
3	-1.00	0.96	1.00	NaOH	23.62
4	-1.00	1.00	0.83	NaOH	23.43
5	-1.00	1.00	0.79	NaOH	23.35
6	-1.00	0.82	1.00	NaOH	23.28
7	-0.74	1.00	1.00	NaOH	23.06
8	-1.00	0.67	1.00	NaOH	22.94
9	-1.00	1.00	-1.00	Na_2SO_4	22.15
10	-1.00	1.00	0.09	NaOH	22.11

As it can be seen in Table 4.22, point #1 is the optimum point with highest desirability. This is the same optimum point found for the best regression model for FCCD design with 40 observations. However example response surface curves for two designs have differences (Fig.s 4.16 and 4.19). Especially when activator type is Na_2SO_4 and one of the independent parameters is activator dosage, Fig. 4.19 show different response curves with respect to Fig.s 4.16 and 4.18. Predicted response for optimum point is 23.73, very close to experimental average 23.6.

Economical Response Surface Designs: WD Design

Response surface optimization for the best regression model below for WD design is again the point where pozzolan content is minimum, activator dosage and fineness are at their maximum levels and NaOH is the activator (Tables 4.23 and 4.24). However, the optimum point is predicted as 26.88 while the experimental average of six observations for this point is 23.6. Experimental average is not included in 95% confidence interval and it is very close to the lower limit of 95% prediction interval. In conclusion, this point is overestimated by below regression model. On the other hand, when shape of response curves is concern, response curves of WD design (Fig. 4.21) are much similar to the response curves of the main design (Fig. 4.16) with respect to the curves found by DJ design (Fig. 4.19).

$$CS7 = 15.3 - 3.56\,P + 1.22\,F + 1.52\,D + 0.560\,T - 1.89\,DT + 1.74\,Dsq + 1.05\,FD + 1.19\,Fsq \qquad (4.8)$$

Table 4.23 Optimum CS7 responses with desirability values, 95% confidence and prediction intervals for WD design

#	Prediction (in MPa)	Desirability	95% CI	95% PI
1	26.88	0.844	(24.56; 29.20)	(23.36; 30.40)
2	26.71	0.835	(24.34; 28.93)	(23.12; 30.14)
3	26.42	0.821	(24.26; 28.75)	(23.03; 29.98)
4	26.34	0.817	(24.19; 28.76)	(22.98; 29.98)
5	26.14	0.807	(24.16; 28.70)	(22.94; 29.92)
6	25.89	0.794	(24.01; 28.54)	(22.79; 29.76)
7	25.87	0.794	(23.84; 28.35)	(22.61; 29.57)
8	25.38	0.769	(23.92; 28.25)	(22.66; 29.50)
9	24.21	0.711	(23.44; 27.98)	(22.22; 29.20)
10	24.06	0.703	(23.36; 27.76)	(22.12; 29.01)

Table 4.24 Parameter levels of optimum CS7 points for WD design

#	P	F	D	T	CS7
1	-1.00	1.00	1.00	NaOH	26.88
2	-1.00	0.96	1.00	NaOH	26.71
3	-1.00	0.91	0.99	NaOH	26.42
4	-1.00	1.00	0.93	NaOH	26.34
5	-0.79	1.00	1.00	NaOH	26.14
6	-0.72	1.00	1.00	NaOH	25.89
7	-1.00	0.77	1.00	NaOH	25.87
8	-0.58	1.00	1.00	NaOH	25.38
9	-1.00	1.00	1.00	Na_2SO_4	24.21
10	-0.95	1.00	1.00	Na_2SO_4	24.06

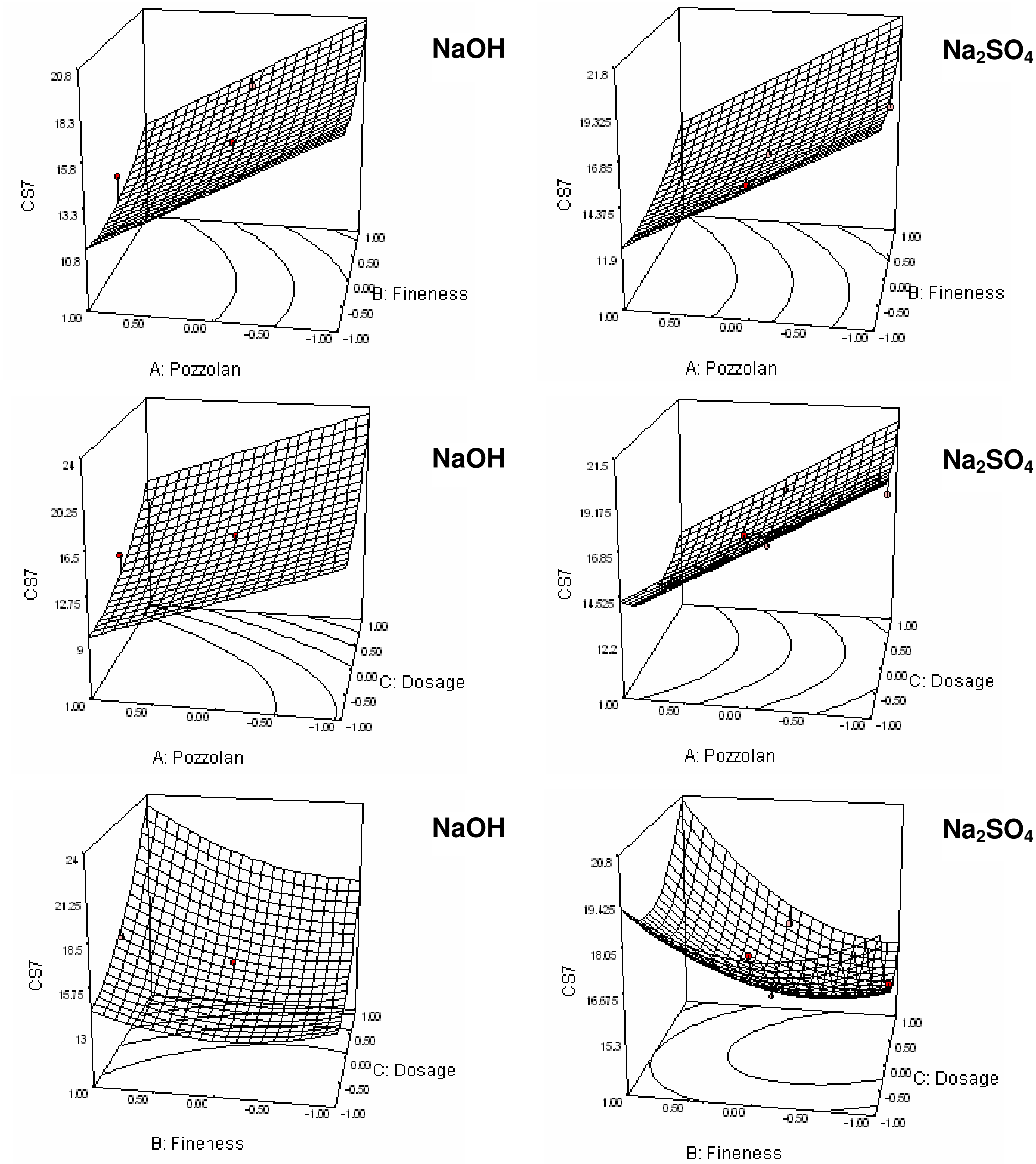

Figure 4.21 Example response surface curves of CS7 with WD design

When the total variation explained in the data and standard deviation are considered for regressions applied for 5 different response surface designs in this chapter; it can be said that they are successful and have similar performances. However for response surface optimization as the number of runs decreases confidence intervals for the mean tend to get wider. Estimated values are closer to observed values for the main FCCD design with 40 runs.

CHAPTER 5

EXPERIMENTAL DESIGN AND ANALYSIS WHEN THE RESPONSE IS 28-DAY COMPRESSIVE STRENGTH

In this chapter, response surface methodology for the second response, mean 28-day compressive strength, is performed. The same approach in chapter 4 for experimental design and regression analysis is employed. In Section 5.1, response surface methodology for mean 28-day compressive strength when face-centered central composite design (FCCD) is used for each level of the qualitative factor is explained. In section 5.2, response surface methodology for mean 28-day compressive strength with economical design alternatives proposed in the literature is given.

5.1. Response Surface Methodology when FCCD is Used for Each Level of the Qualitative Factor

5.1.1. Experimental Design

For mean 28-day compressive strength response, the same regression model in Equation 4.1 with the same independent variables is of interest. Therefore, the same design is used for experimentation and test results for 240 experiments are presented in Appendix 5.1. The parameters and levels for experimentation are repeated below for convenience:

Parameter P: Natural pozzolan replacement (% by weight)

Levels: -1: 35% 0: 45% 1: 55%

Parameter F: Amount of pozzolan passing 45 μm sieve (% by weight)

Levels: -1: 70% 0: 80% 1: 90%

Parameter D: Activator dosage (% by weight of binder)

Levels: -1: 0.5% 0: 1% 1: 1.5%

Parameter T: Activator type

Levels: -1: NaOH (sodium hydroxide)

1: Na_2SO_4 (sodium sulphate)

5.1.2. Regression Analysis

The same approach followed in Chapter 4 for regression analysis is used again in Chapter 5. As the initial step, a regression analysis for only first order main factors is employed. The regression equation is found as:

$$CS28 = 29.8 - 3.70\ P + 1.94\ F + 0.210\ D + 0.244\ T \quad (5.1)$$

S = 2.20309   R-Sq = 67.5%   R-Sq(adj) = 63.8%

Although the regression is significant with a p-value of zero (Table 5.1), it explains only 63.8% of the total variation in 28-day mean compressive strength. No violation of basic regression assumptions is detected (Fig.s 5.1 and 5.2). Table 5.2 summarizes the significance of β terms in the model. Lack of fit (Appendix 5.2) is significant and it also implies considering higher order terms in regression equation. Therefore a more adequate model with second-order terms and interactions is searched.

Table 5.1 ANOVA for the significance of the regression model applied for 28-day mean compressive strength based on face-centered central composite design with only main factors

Source	**DF**	**SS**	**MS**	**F**	**P**
Regression	4	353.099	88.275	18.190	0.000
Residual Error	35	169.876	4.854		
Lack of Fit	25	132.871	5.315	1.440	0.281
Pure Error	10	37.004	3.7		
Total	39	522.975			

Table 5.2 Significance of β terms of the regression model for 28-day mean compressive strength based on face-centered central composite design with only main factors

Predictor	**Coef**	**SE Coef**	**T**	**P**
Constant	29.8173	0.3483	85.6	0.000
P	-3.703	0.4926	-7.52	0.000
F	1.944	0.4926	3.95	0.000
D	0.2105	0.4926	0.43	0.672
T	0.2443	0.3483	0.7	0.488

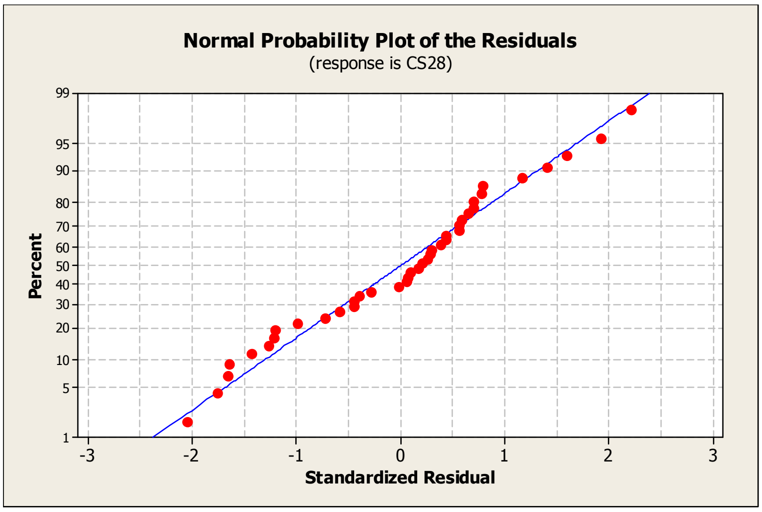

Figure 5.1 Normal probability plot of the residuals for the regression model based on face-centered central composite design and applied for CS28 with only main factors

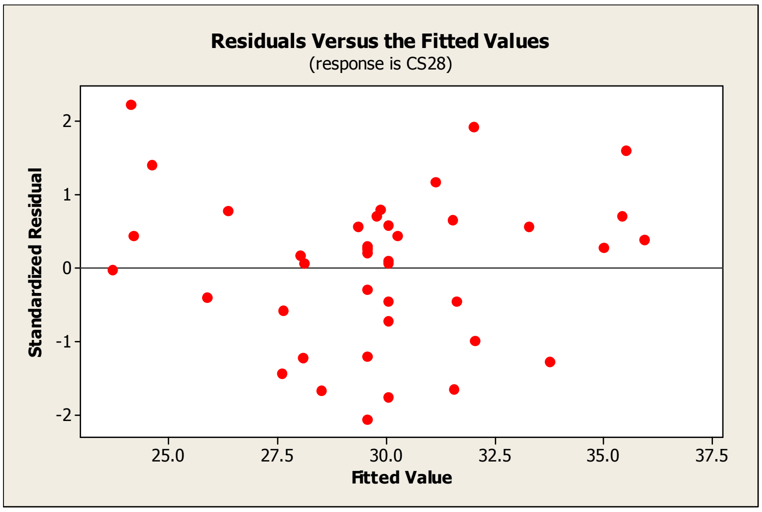

Figure 5.2 Residuals versus the fitted values plot of the regression model based on face-centered central composite design and applied for CS28 with only main factors

The regression equation when all second-order effects, two-way interaction effects for the quantitative variables and their interactions with qualitative factor are included results as equation 5.2. Regression results are in Appendix 5.3. The regression is significant at 100% confidence level (Table 5.3). No residual correlation is detected as Durbin-Watson statistic with a value of 1.80 is above the tabulated upper bound which is 1.52 with 4 independent variables and 40 observations at 0.01 significance level. Normal probability plot of residuals (Fig. 5.3) and residuals versus fitted values plot do not show any violation of basic regression assumptions. R-sq(adj) is improved with respect to previous equation but there are many insignificant β terms as it can be seen from Table 5.4. Therefore, a better regression equation with significant β terms is searched.

CS28 = 29.5 - 3.70 P + 1.94 F + 0.210 D + 0.446 T - 0.686 Psq + 0.554 Fsq
+ 0.786 Dsq - 1.61 PF + 1.05 PD + 0.116 PT + 0.064 FD + 0.133 FT
- 0.318 DT - 0.690 PsqT + 0.650 FsqT - 0.363 DsqT - 0.398 PFT
- 0.573 FDT - 0.487 PDT (5.2)

S = 2.04190 R-Sq = 84.1% R-Sq(adj) = 68.9%

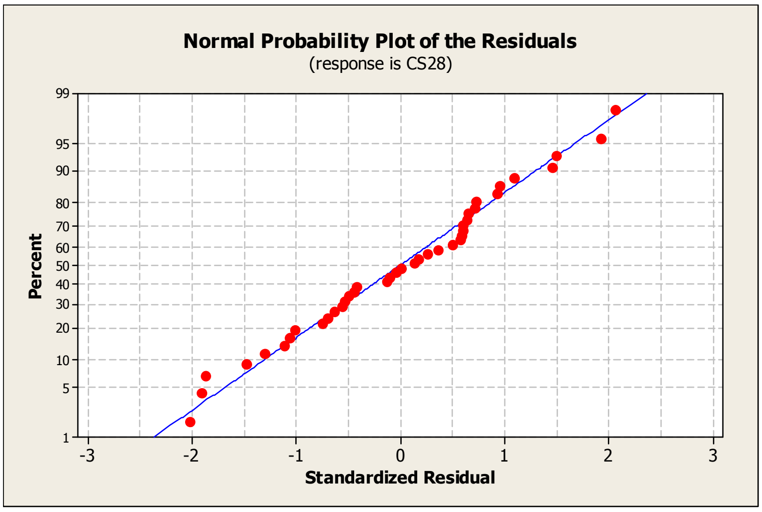

Figure 5.3 Normal probability plot of the residuals for the regression model based on face-centered central composite design and applied for CS28 involving all two-way interaction and quadratic terms

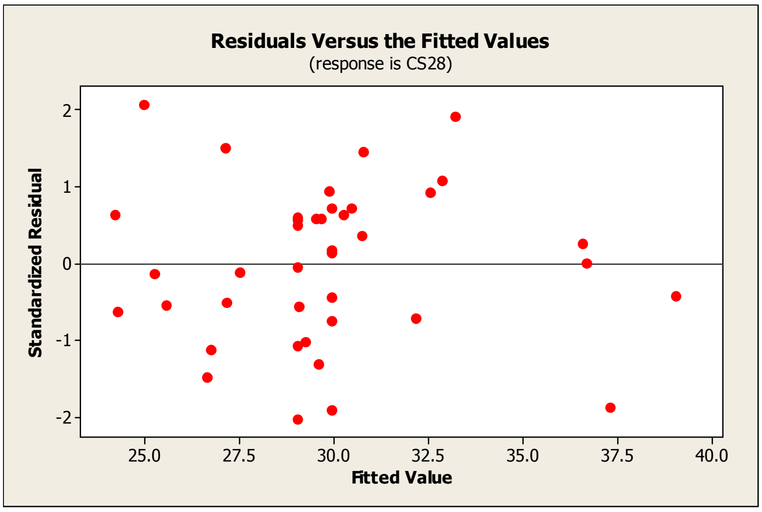

Figure 5.4 Residuals versus the fitted values plot of the regression model based on face-centered central composite design and applied for CS28 involving all two-way interaction and quadratic terms

Table 5.3 ANOVA for the significance of the regression model applied for 28-day mean compressive strength based on the face-centered central composite design involving all two-way interaction and quadratic terms

Source	**DF**	**SS**	**MS**	**F**	**P**
Regression	19	439.588	23.136	5.550	0.000
Residual Error	20	83.387	4.169		
Lack of Fit	10	46.383	4.638	1.250	0.364
Pure Error	10	37.004	3.7		
Total	39	522.975			

Table 5.4 Significance of β terms of the regression model based on face-centered central composite design and applied for mean 28-day compressive strength

Predictor	Coef	SE Coef	T	P
Constant	29.4905	0.4964	59.41	0.000
P	-3.703	0.4566	-8.11	0.000
F	1.944	0.4566	4.26	0.000
D	0.2105	0.4566	0.46	*0.650*
T	0.4462	0.4964	0.9	*0.379*
Psq	-0.6864	0.8707	-0.79	0.44
Fsq	0.5536	0.8707	0.64	*0.532*
Dsq	0.7861	0.8707	0.9	*0.377*
PF	-1.6081	0.5105	-3.15	0.005
PD	1.0481	0.5105	2.05	0.053
PT	0.116	0.4566	0.25	*0.802*
FD	0.0644	0.5105	0.13	*0.901*
FT	0.133	0.4566	0.29	*0.774*
DT	-0.3175	0.4566	-0.7	*0.495*
PsqT	-0.6905	0.8707	-0.79	*0.437*
FsqT	0.6495	0.8707	0.75	*0.464*
DsqT	-0.363	0.8707	-0.42	*0.681*
PFT	-0.3981	0.5105	-0.78	*0.445*
FDT	-0.5731	0.5105	-1.12	*0.275*
PDT	-0.4869	0.5105	-0.95	*0.352*

While searching for the best possible regression model, insignificant parameters are eliminated one by one from the regression equation, starting from the one with the highest p-value. The procedure followed in section 4.1.2. is used again in this section.

The best model satisfying basic regression assumptions results as follows:

$$CS28 = 29.8 - 3.70 P + 1.94 F - 1.61 PF \quad (5.3)$$

S = 1.91319   R-Sq = 74.8%   R-Sq(adj) = 72.7%

By equation 5.3, 73% of the total variation in mean 28-day compressive strength is explained after adjusting for sample size and number of independent variables in the model. Regression analysis is summarized in Appendix 5.4. Durbin-Watson statistic is 2.19, which is above the tabulated upper bound of 1.52 with 4 independent variables and 40 observations at 0.01 significance level; hence assumption of uncorrelated residuals is satisfied. Normal probability plot of residuals and the Anderson-Darling test result for normality supports normality assumption of residuals (Fig. 5.5). Although a slight pattern in residuals versus fitted values plot is detected, data transformations such as √y, ln(y), $\sin^{-1}\sqrt{y}$, Box-Cox (Mendenhall and Sincich, 2003) do not help in stabilizing the variance. Including other terms in the regression equation such as D and its two way interactions increase adjusted multiple coefficient of determination inconsiderably (up to 75 %, Appendix 5.5) but does not satisfy the normality assumption of residuals (Fig 5.7). In addition, the slight pattern detected in residuals versus fitted values plot of equation 5.3 is also observed in the similar plot for the regression equation in Appendix 5.5. Consequently, the regression equation 5.3 which satisfies the basic regression assumptions and explains the variation in the response as high as possible is accepted as the final equation. Significance of this regression and its β parameters are summarized in Tables 5.5 and 5.6.

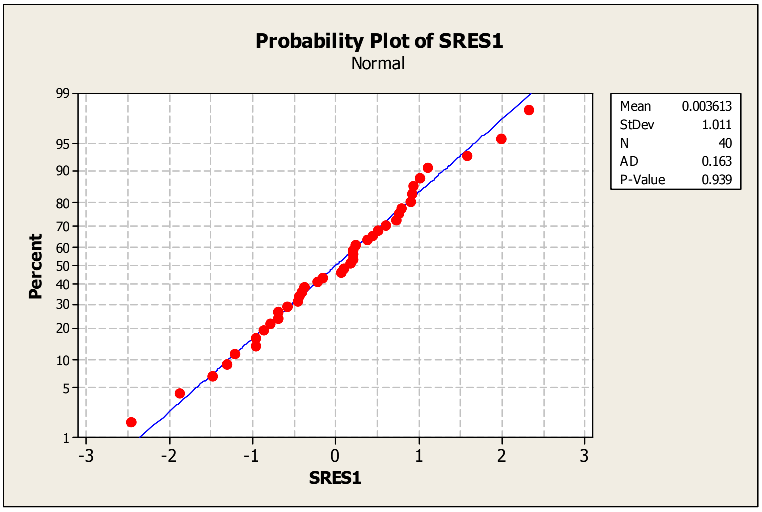

Figure 5.5 Normal probability plot of the residuals for the regression model based on face-centered central composite design and applied for mean 28-day compressive strength after elimination of insignificant terms

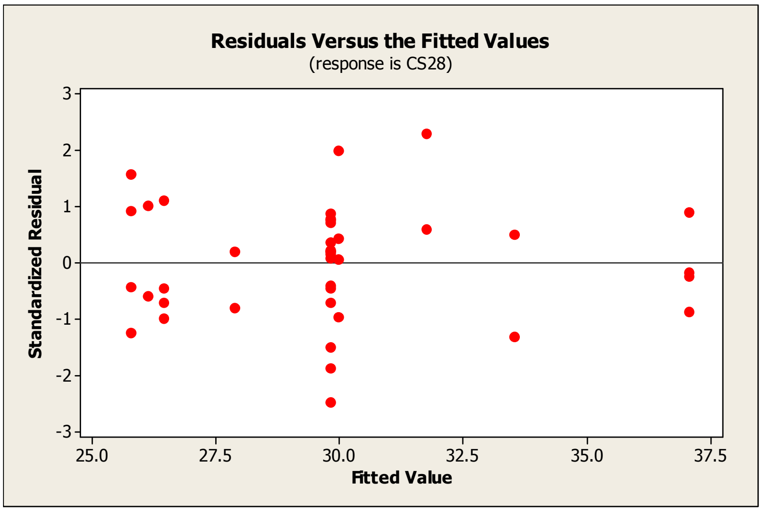

Figure 5.6 Residuals versus the fitted values plot of the regression model based on face-centered central composite design and applied for mean 28-day compressive strength after elimination of insignificant terms

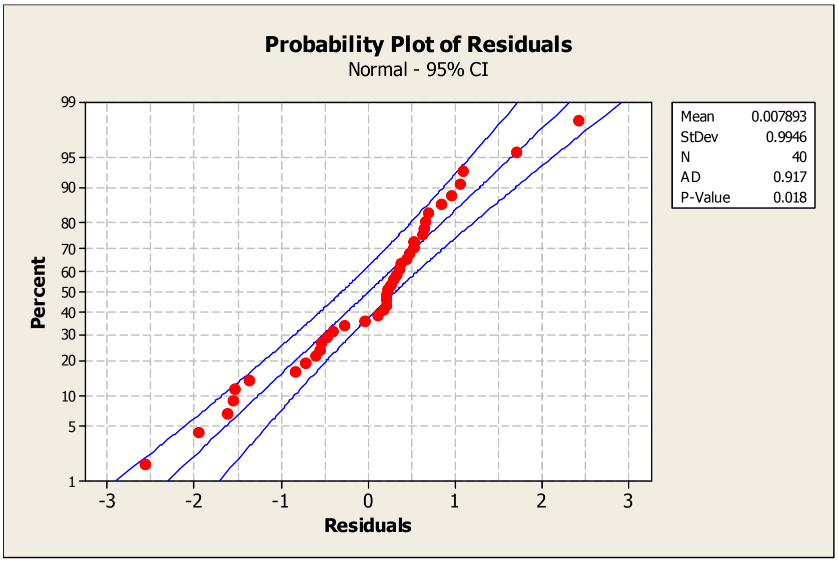

Figure 5.7 Normal probability plot of the residuals for mean 28-day compressive strength when activator dosage and its interaction with natural pozzolan replacement is included in regression parameters

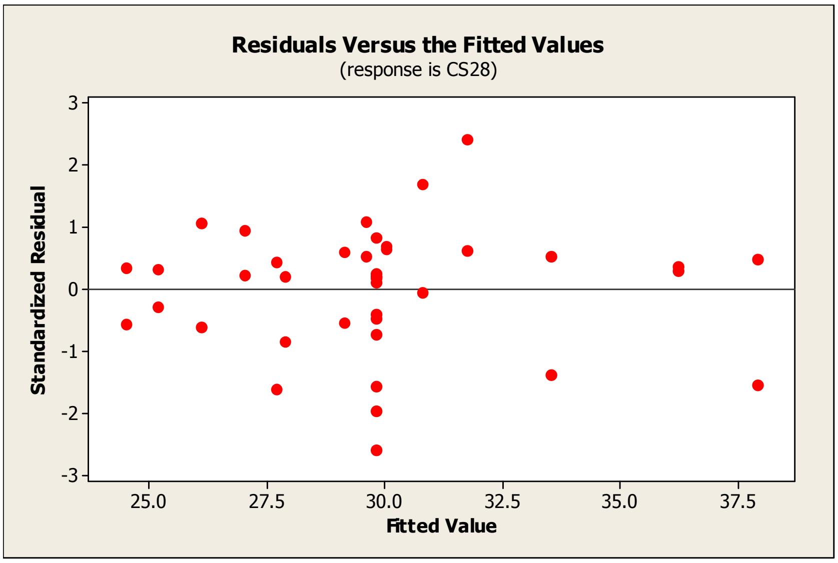

Figure 5.8 Residuals versus the fitted values plot of the regression model for mean 28-day compressive strength when activator dosage and its interaction with natural pozzolan replacement is included in regression parameters

Table 5.5 ANOVA for the significance of the regression model applied for 28-day mean compressive strength after elimination of insignificant factors

Source	DF	SS	MS	F	P
Regression	3	391.2	130.4	35.63	0.000
Residual Error	36	131.77	3.66		
Lack of Fit	5	21.47	4.29	1.21	0.329
Pure Error	31	110.3	3.56		
Total	39	522.97			

Table 5.6 Significance of β terms of the regression model applied for 28-day mean compressive strength after elimination of insignificant factors

Predictor	Coef	SE Coef	T	P
Constant	29.8173	0.3025	98.57	0.000
P	-3.703	0.4278	-8.66	0.000
F	1.944	0.4278	4.54	0.000
PF	-1.6081	0.4783	-3.36	0.002

Homogeneity of response surfaces across levels of the qualitative factor proposed by Tunalı and Batmaz (2003) performed again in this section for the mean 28-day compressive strength as response this time. Regression analyses to enable the calculation of F values for these tests are performed and given in Appendix 5.6.

Test of homogeneity of response curves:

F* = [(SSE(1) – SSE(3)) / v_1] / [SSE(3) / v_2] {$v_1 = p_3 - p_1$ $v_2 = N - p_3$}

= [(105.97-102.711) / 10] / [83.387 / 20]

= 0.3259 / 4.16935 = 0.078

Since F* = 0.078 < $F_{0.05,10,20}$ = 2.35, the hypothesis cannot be rejected at α = 0.05 level of significance. There is not sufficient evidence to reject that the second-order regression model built only with quantitative factors adequately describes the relation between mean 28-day compressive strength and these factors for each activator type. This result supports the final regression model 5.3. which does not include activator type or its interactions as significant parameters for modeling mean 28-day compressive strength.

Regression analyses for two activator types and with only quantitative factors are performed separately below. Two independent response surfaces are built and examined for each of the activator type for comparison.

Below equation is turned out to be the best regression model for mean 28-day compressive strength where activator type is NaOH (Equation 5.4).

CS28 = 29.6 - 3.82 P + 1.81 F - 1.21 PF + 1.53 PD + 0.528 D (5.4)

S = 1.87784 R-Sq = 81.1% R-Sq(adj) = 74.4%

Durbin-Watson statistic = 2.30086

The total variation explained in the sample with 20 observations is 74.4% by this regression. Basic regression assumptions hold (Fig.s 5.9 and 5.10) while the regression is significant at 100% confidence (Table 5.7). Durbin-Watson statistic (2.3, Appendix 5.7) is greater than the upper bound of 1.41 for three independent variables and 20 observations at $\alpha = 0.01$ significance level so there is not sufficient evidence to claim residual correlation. In Table 5.8 ANOVA for the significance of β parameters of this equation can be found.

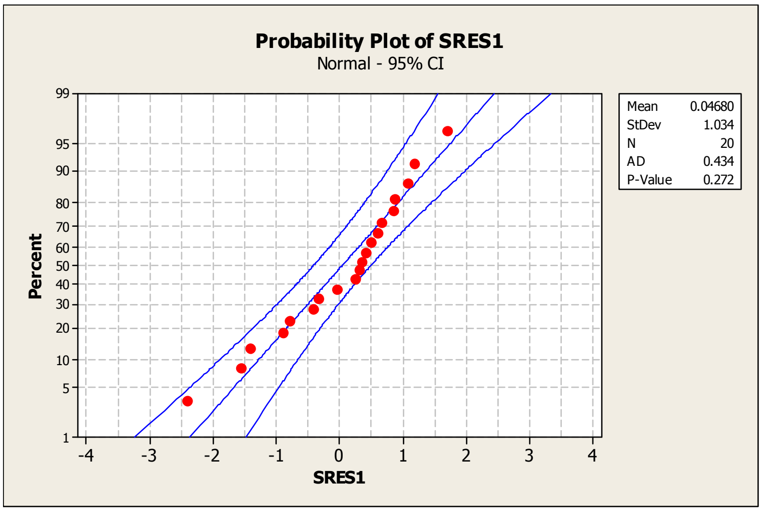

Figure 5.9 Normal probability plot of the residuals for the regression model of mean 28-day compressive strength for activator type NaOH

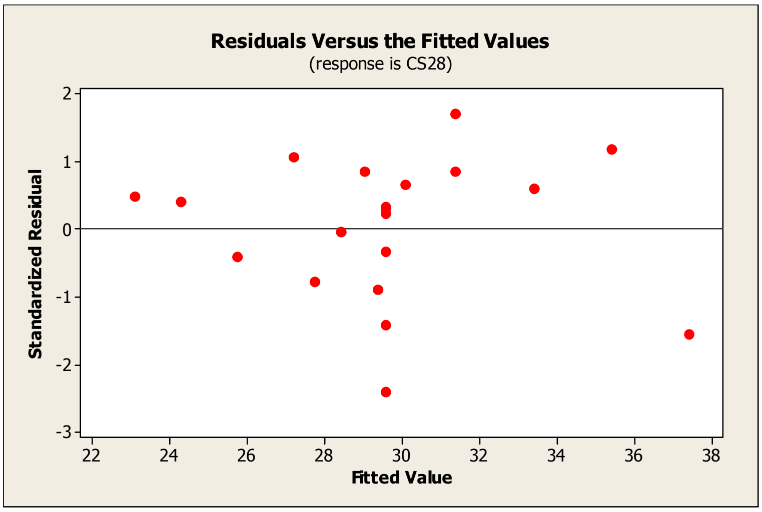

Figure 5.10 Residuals versus the fitted values plot of the regression model of mean 28-day compressive strength for activator type NaOH

Table 5.7 ANOVA for the significance of the regression model applied for 28-day mean compressive strength when the activator type is NaOH

Source	DF	SS	MS	F	P
Regression	5	211.995	42.399	12.02	0.000
Residual Error	14	49.368	3.526		
Lack of Fit	9	27.996	3.111	0.73	0.681
Pure Error	5	21.372	4.274		
Total	19	261.363			

Table 5.8 Significance of β terms of the regression model for mean 28-day compressive strength when the activator type is NaOH

Predictor	Coef	SE Coef	T	P
Constant	29.573	0.4199	70.43	0.000
P	-3.819	0.5938	-6.43	0.000
F	1.811	0.5938	3.05	0.009
PF	-1.21	0.6639	-1.82	0.090
PD	1.535	0.6639	2.31	0.037
D	0.528	0.5938	0.89	0.389

When a regression is fit for only the observations when activator type is Na_2SO_4, the best model is selected as equation (5.5). This equation can explain 73.4 % of the variation in the sample. Durbin-Watson statistic (1.56, Appendix 5.8) is greater than the upper bound of 1.41 for three independent variables and 20 observations at 0.01 significance level, therefore the assumption that residuals are not correlated holds. Residuals plots (Fig. 5.11 and 5.12) do not indicate a considerable pattern or violation of the regression assumptions so the regression analysis is also accepted to be valid. Table 5.9 and 5.10 summarize the significance of the regression and β parameters.

CS28 = 30.3 - 3.59 P + 2.08 F - 2.01 PF - 0.401 Psq (5.5)

S = 1.90467   R-Sq = 79.0%   R-Sq(adj) = 73.4%

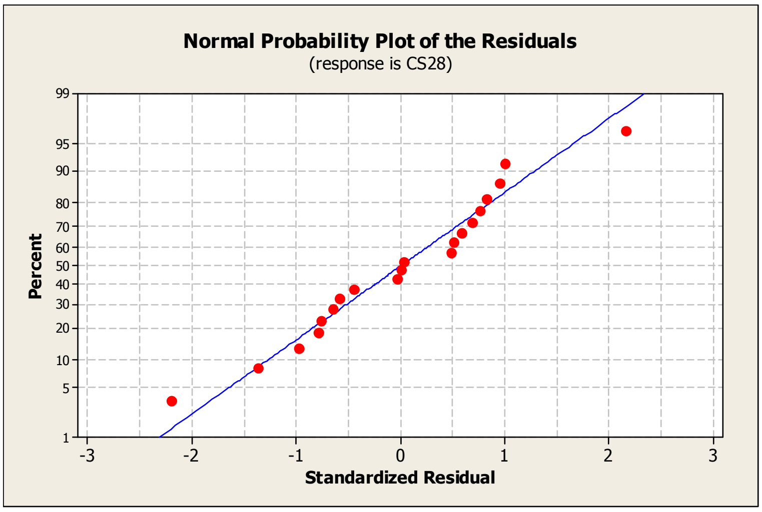

Figure 5.11 Normal probability plot of the residuals for the regression model of mean 28-day compressive strength for activator type Na_2SO_4

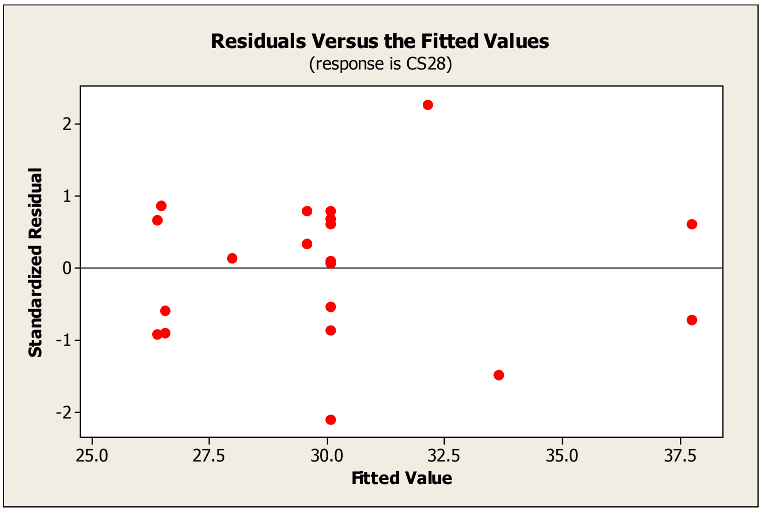

Figure 5.12 Residuals versus the fitted values plot of the regression model of mean 28-day compressive strength for activator type Na_2SO_4

Table 5.9 ANOVA for the significance of the regression model applied for 28-day mean compressive strength when the activator type is NaOH

Source	DF	SS	MS	F	P
Regression	4	204.809	51.202	14.110	0.000
Residual Error	15	54.416	3.628		
Lack of Fit	4	27.354	6.838	2.780	0.081
Pure Error	11	27.063	2.46		
Total	19	259.226			

Table 5.10 Significance of β terms of the regression model for mean 28-day compressive strength when the activator type is NaOH

Predictor	Coef	SE Coef	T	P
Constant	30.262	0.6023	50.24	0.000
P	-3.587	0.602	-5.96	0.000
F	2.077	0.602	3.45	0.004
PF	-2.0062	0.673	-2.98	0.009
Psq	-0.401	0.852	-0.47	0.645

5.2. Response Surface Methodology with Economical Designs

5.2.1. Experimental Design

Two economical design alternatives referred as DJ and WD designs used in section 4.2.1. are used here again for response mean 28-day compressive strength. Designs and corresponding test results for parameter level combinations are given in Appendix 5.9.

5.2.2. Regression Analyses

For DJ design, the best regression model among possible other alternatives is selected as follows:

$$CS28 = 30.2 - 3.19\ P + 1.94\ F - 1.21\ PF \qquad (5.6)$$

S = 2.29130   R-Sq = 70.6%   R-Sq(adj) = 63.3%

The total variation that can be explained by this regression is 63.3%. Qualitative factor activator type and quantitative factor activator dosage are not significant for this regression. Normal probability and residuals versus fitted values plots (Fig.s 5.13 and 5.14) do not indicate any violation against basic regression assumptions. Independency of residuals assumption is also valid since the statistic (1.67, Appendix 5.10) is higher than tabulated upper bound value of 1.66 for 4 independent variables and 16 observations. There is no evidence of lack of fit at 90 % confidence. ANOVA for the significance of the regression and β parameters are given in Tables 5.11 and 5.12.

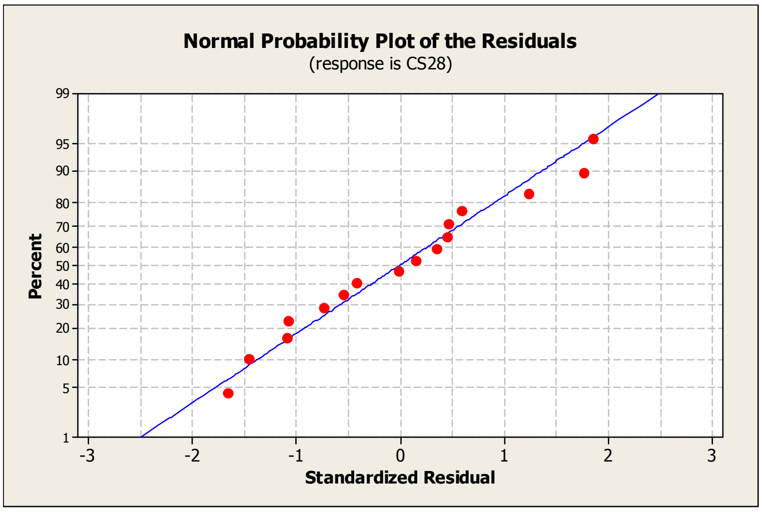

Figure 5.13 Normal probability plot of the residuals for the regression model based on DJ design and applied for mean 28-day compressive strength

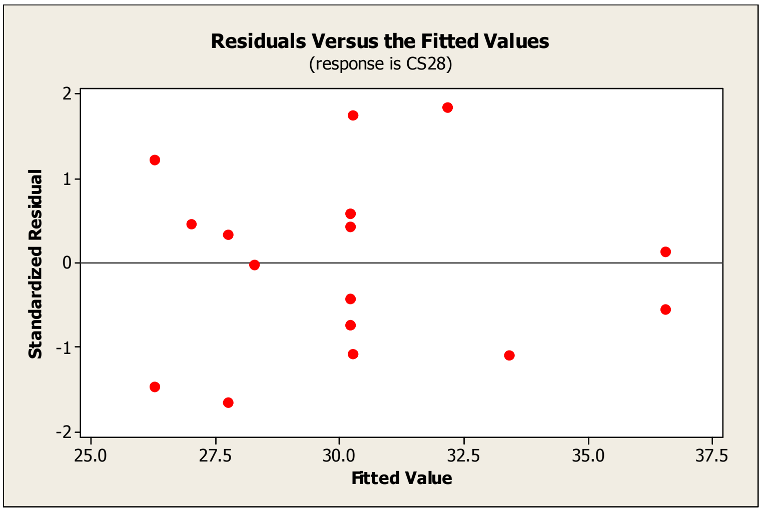

Figure 5.14 Residuals versus the fitted values plot of the regression model based on DJ design and applied for mean 28-day compressive strength

Table 5.11 ANOVA for the significance of the regression model applied for 28-day mean compressive strength based on DJ design

Source	DF	SS	MS	F	P
Regression	3	151.315	50.438	9.61	0.002
Residual Error	12	63.001	5.25		
Lack of Fit	5	24.966	4.993	0.920	0.5
Pure Error	7	38.035	5.434		
Total	15	214.316			

Table 5.12 Significance of β terms of the regression model based on DJ design and applied for mean 28-day compressive strength

Predictor	Coef	SE Coef	T	P
Constant	30.2088	0.5728	52.74	0.000
P	-3.192	0.7246	-4.41	0.001
F	1.942	0.7246	2.68	0.020
PF	-1.21	0.8101	-1.49	0.161

For WD design, below regression equation (5.7) is the most successful one when the significance of the parameters and the variation explained by the regression are considered. Equation 5.5 is significant at 100% confidence level (Table 5.13) and explains 90.7% of the variation in the sample. Activator type is not significant again in this regression equation but unlike equation 5.4 activator dosage (D) is included in the regression equation. Though activator dosage itself is not significant (Table 5.14) its two-way interaction with natural pozzolan replacement (P) is significant at 100% confidence and hence it is included in the equation. Basic regression assumptions are accepted to be valid (Fig.s 5.15 and 5.16). Durbin-Watson statistic (1.76) is higher than tabulated upper bound value of 1.66 for 4 independent variables and 16 observations and hence does not indicate autocorrelation of residuals.

$$CS28 = 29.8 - 3.89\ P + 2.03\ F - 0.007\ D - 1.44\ PF + 1.80\ PD - 1.16\ Psq + 1.32\ Fsq \qquad (5.7)$$

S = 1.25701   R-Sq = 95.0%   R-Sq(adj) = 90.7%

Durbin-Watson statistic = 1.76501

Table 5.13 ANOVA for the significance of the regression model applied for 28-day mean compressive strength based on WD design

Source	DF	SS	MS	F	P
Regression	7	241.329	34.476	21.820	0.000
Residual Error	8	12.641	1.58		
Lack of Fit	7	12.396	1.771	7.230	0.279
Pure Error	1	0.245	0.245		
Total	15	253.97			

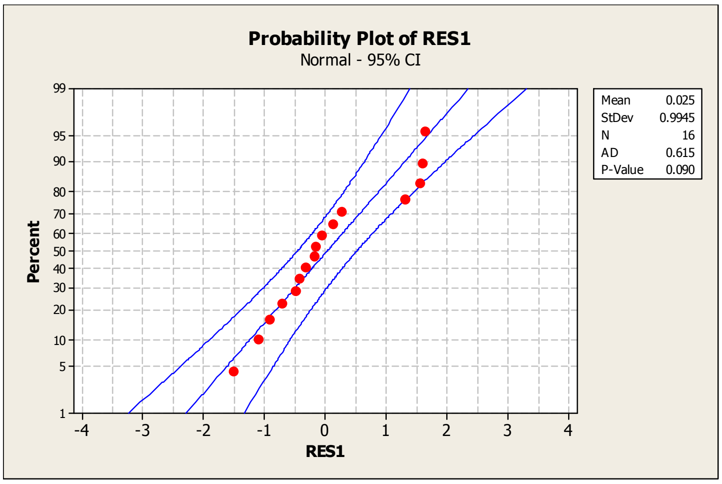

Figure 5.15 Normal probability plot of the residuals for the regression model based on WD design and applied for mean 28-day compressive strength

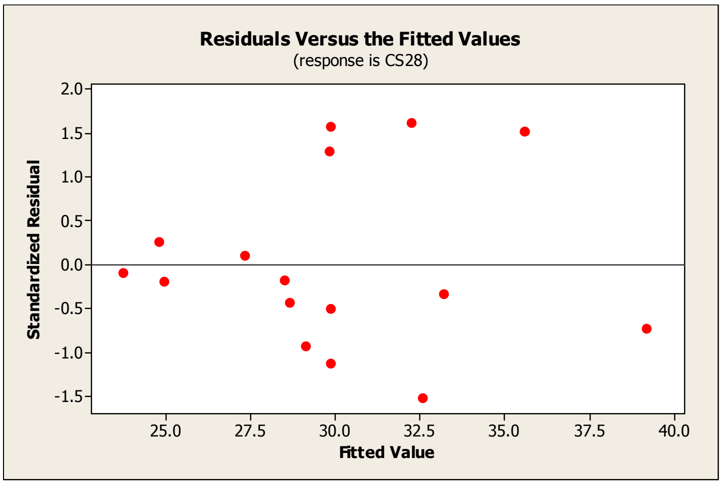

Figure 5.16 Residuals versus the fitted values plot of the regression model based on WD design and applied for mean 28-day compressive strength

Table 5.14 Significance of β terms of the regression model based on WD design and applied for mean 28-day compressive strength

Predictor	Coef	SE Coef	T	P
Constant	29.8389	0.5685	52.49	0.000
P	-3.891	0.3975	-9.79	0.000
F	2.033	0.3975	5.11	0.001
D	-0.007	0.3975	-0.02	0.986
PF	-1.4388	0.4444	-3.24	0.012
PD	1.7963	0.4444	4.04	0.004
Psq	-1.1566	0.7339	-1.58	0.154
Fsq	1.3234	0.7339	1.8	0.109

5.3. Response Surface Optimization of Mean 28-Day Compressive Strength

Response surface optimization for mean 28-day compressive strength is done by the help of Design-Expert Optimization Module as explained in section 4.3 and in the same way the optimization for mean 7-day strength optimization is done.

FCCD for Each Level of the Qualitative Factor (40 observations)

The best regression model for CS28 for the main design in the study is accepted as (Equation 5.3):

$$CS28 = 29.8 - 3.70\ P + 1.94\ F - 1.61\ PF \qquad (5.3)$$

Example response surface curves of 28-day mean compressive strength are given in Fig. 5.17. All possible subsets of 2 main quantitative factors are assigned to x-axes and y-axis indicates the response. Activator type and dosage are not included in the regression model and hence they do not have effects on the response curves and optimum result.

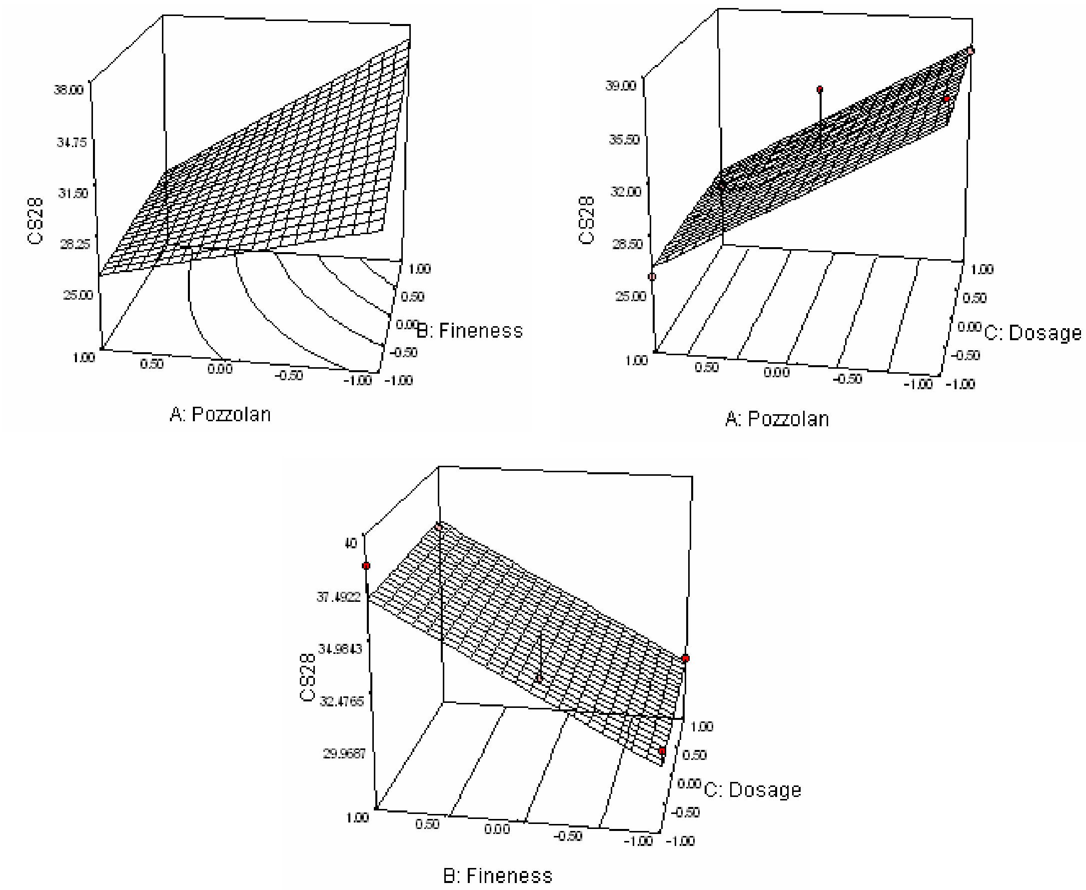

Figure 5.17 Example response surface curves of CS28 for two different types of activators (FCCD with 40 observations)

10 optimum solutions proposed by the software have the same compressive strength. Activator type and dosage values change however as previously stated these variables do not affect the value of the response.

Table 5.15 Optimum CS28 response with desirability value, 95% confidence and prediction interval for FCCD design at each activator type

#	Prediction (in MPa)	Desirability	95% CI	95% PI
1	37.07	0.628	(35.39; 38.75)	(32.84; 41.30)

Table 5.16 Parameter levels of optimum CS7 points for FCCD design at each activator type

#	P	F	D*	T*	CS28
1	-1.00	1.00	*-0.23*	*Na_2SO_4*	37.07
2	-1.00	1.00	*-0.35*	*NaOH*	37.07
3	-1.00	1.00	*0.98*	*NaOH*	37.07
4	-1.00	1.00	*0.27*	*NaOH*	37.07
5	-1.00	1.00	*-0.75*	*Na_2SO_4*	37.07
6	-1.00	1.00	*-0.49*	*NaOH*	37.07
7	-1.00	1.00	*0.14*	*NaOH*	37.07
8	-1.00	1.00	*0.45*	*NaOH*	37.07
9	-1.00	1.00	*-0.06*	*NaOH*	37.07
10	-1.00	1.00	*0.54*	*Na_2SO_4*	37.07

**Has no effect on optimization results.*

Averages of 6 replicates at 4 different activator dosage and type combinations where pozzolan content is at minimum and fineness is at maximum are 38.64, 36.68, 35.57 and 36.81. Overall average for the 24 observations is 36.92. All values are covered by the confidence interval of point #1.

FCCD for activator type NaOH (20 observations)

When the regression equation is fit for only activator type NaOH for the subset of main design with twenty observations, activator dosage is also included in the best regression model as follows:

$$CS28 = 29.6 - 3.82\ P + 1.81\ F - 1.21\ PF + 1.53\ PD + 0.528\ D \qquad (5.4)$$

Example response curves for this equation are given in Fig. 5.18 and optimization is summarized in Tables 5.17 and 5.18.

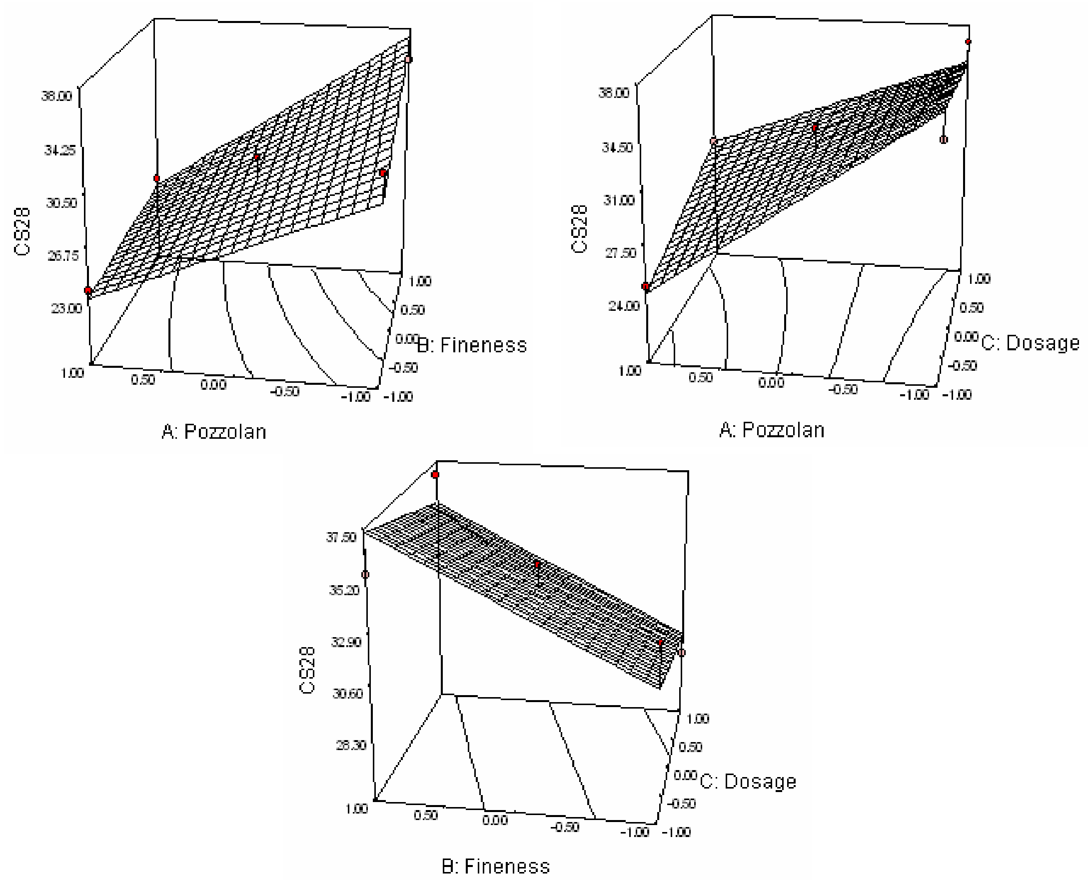

Figure 5.18 Example response surface curves of CS28for activator type NaOH

Table 5.17 Optimum CS28 response with desirability value, 95% confidence and prediction interval for FCCD design for only activator NaOH

#	Prediction (in MPa)	Desirability	95% CI	95% PI
1	37.42	0.64	(34.30; 40.54)	(32.32; 42.51)
2	37.16	0.63	(34.31; 40.00)	(32.23; 42.09)
3	36.93	0.62	(33.99; 39.87)	(31.94; 41.92)
4	36.60	0.60	(33.77; 39.44)	(31.68; 41.53)
5	36.60	0.60	(34.11; 39.09)	(31.86; 41.33)
6	35.98	0.57	(33.39; 38.58)	(31.19; 40.78)
7	35.67	0.56	(32.82; 38.51)	(30.74; 40.60)
8	35.25	0.54	(32.19; 38.31)	(30.19; 40.31)

Table 5.18 Parameter levels of optimum CS28 points for FCCD design for only activator NaOH

#	P	F	D	CS28
1	-1.00	1.00	-1.00	37.42
2	-1.00	1.00	-0.74	37.16
3	-1.00	0.84	-1.00	36.93
4	-1.00	0.73	-1.00	36.60
5	-1.00	1.00	-0.18	36.60
6	-1.00	1.00	0.43	35.98
7	-1.00	1.00	0.74	35.67
8	-1.00	0.95	1.00	35.25

Optimum point is chosen as point #1 in Table 5.18. is predicted as 37.42. The experimental average for this parameter level combination is 35.57. The point is a bit overestimated by the regression model but 35.57 is included in the confidence interval. For the 8 optimal solutions proposed, it is observed that changing activator dosage from minimum to maximum while keeping pozzolan content at its minimum and fineness at its maximum does not affect the compressive strength too much.

FCCD for activator type Na_2SO_4 (20 observations)

For the subset of observations with activator Na_2SO_4, the best regression model below does not include activator dosage as in the regression model of main design. Response surface examples are presented in Fig. 5.19 and optimal points are tabulated (Tables 5.19 and 5.20).

$$CS28 = 30.3 - 3.59\,P + 2.08\,F - 2.01\,PF - 0.401\,Psq \quad (5.5)$$

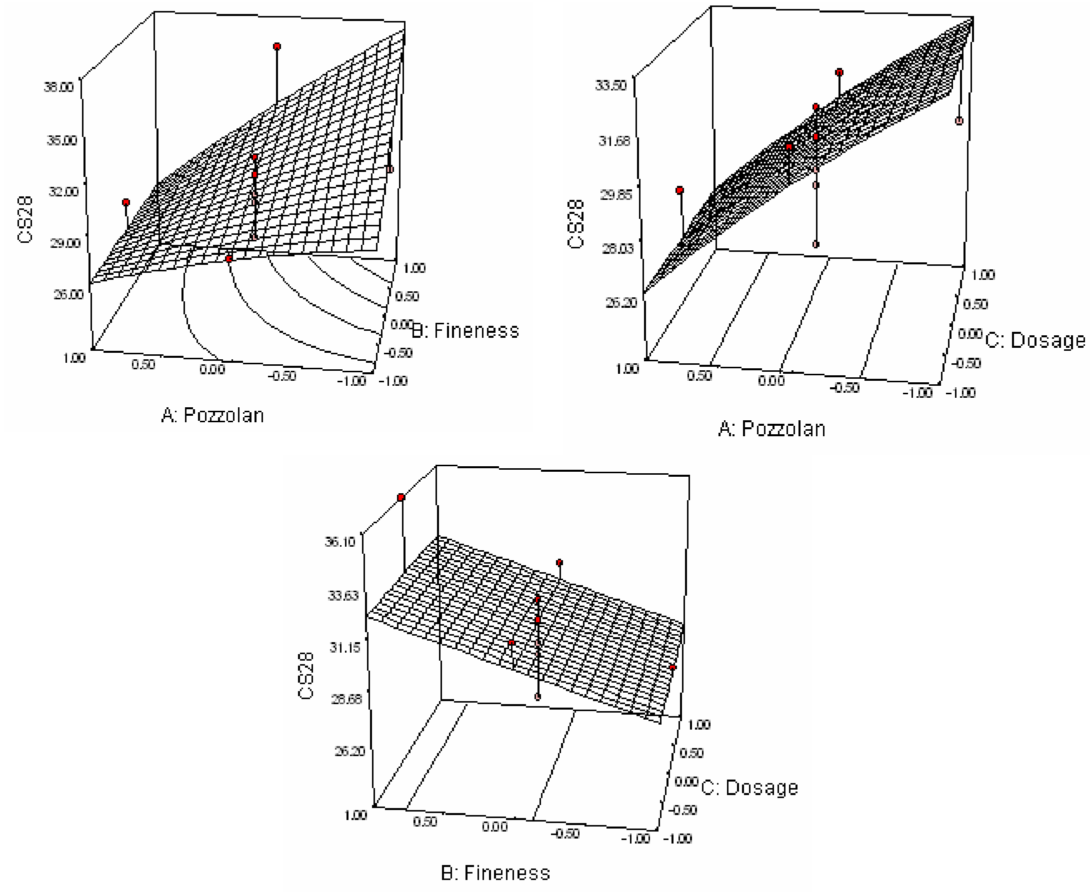

Figure 5.19 Example response surface curves of CS28for activator type Na_2SO_4

Table 5.19 Optimum CS28 response with desirability value, 95% confidence and prediction interval for FCCD design for only activator Na_2SO_4

#	Prediction (in MPa)	Desirability	95% CI	95% PI
1	37.53	0.626	(34.88; 40.18)	(32.68; 42.37)

Table 5.20 Parameter levels of optimum CS28 points for FCCD design for only activator Na_2SO_4

#	P	F	D*	CS28
1	-1.00	1.00	*-0.68*	37.53
2	-1.00	1.00	*0.07*	37.53
3	-1.00	1.00	*0.34*	37.53
4	-1.00	1.00	*0.78*	37.53
5	-1.00	1.00	*-0.81*	37.53
6	-1.00	1.00	*0.23*	37.53
7	-1.00	1.00	*-0.24*	37.53
8	-1.00	1.00	*-0.95*	37.53
9	-1.00	1.00	*-0.47*	37.53
10	-1.00	1.00	*0.60*	37.53

**Has no effect on optimization results.*

The optimality condition is again not affected by activator dosage like in the optimization result of main design and compressive strength is maximum when pozzolan content is minimum and fineness is maximum. Previously with the regression model obtained from the main design optimal result was predicted as 37.07 while prediction is 37.53 here. Optimum values are reasonably close.

Economical Response Surface Designs: DJ Design

For the first economical design alternative with qualitative variable best regression model is as follows:

$$CS28 = 30.2 - 3.19\,P + 1.94\,F - 1.21\,PF \qquad (5.6)$$

Activator dosage and type are again not significant in defining the relation between mean 28-day compressive strength and independent variables hence their level values do not affect optimality condition (Tables 5.21 and 5.22). In Fig. 5.20 example response curves can be found. Response curves are similar in shape when compared with the response surface curves of main design (Fig. 5.17).

Table 5.21 Optimum CS28 response with desirability value, 95% confidence and prediction interval for DJ design

#	Prediction (in MPa)	Desirability	95% CI	95% PI
1	36.553	0.578	(33.44; 39.66)	(30.67; 42.43)

Table 5.22 Parameter levels of optimum CS28 points for FCCD design for DJ design

#	P	F	D*	T*	CS28
1	-1.00	1.00	*-0.99*	*Na_2SO_4*	36.553
2	-1.00	1.00	*0.21*	*NaOH*	36.553
3	-1.00	1.00	*0.80*	*NaOH*	36.553
4	-1.00	1.00	*0.91*	*NaOH*	36.553
5	-1.00	1.00	*-0.40*	*NaOH*	36.553
6	-1.00	1.00	*-0.07*	*Na_2SO_4*	36.553
7	-1.00	1.00	*0.49*	*Na_2SO_4*	36.553
8	-1.00	1.00	*0.89*	*Na_2SO_4*	36.553
9	-1.00	1.00	*0.30*	*Na_2SO_4*	36.553
10	-1.00	1.00	*0.11*	*NaOH*	36.553

**Has no effect on optimization results.*

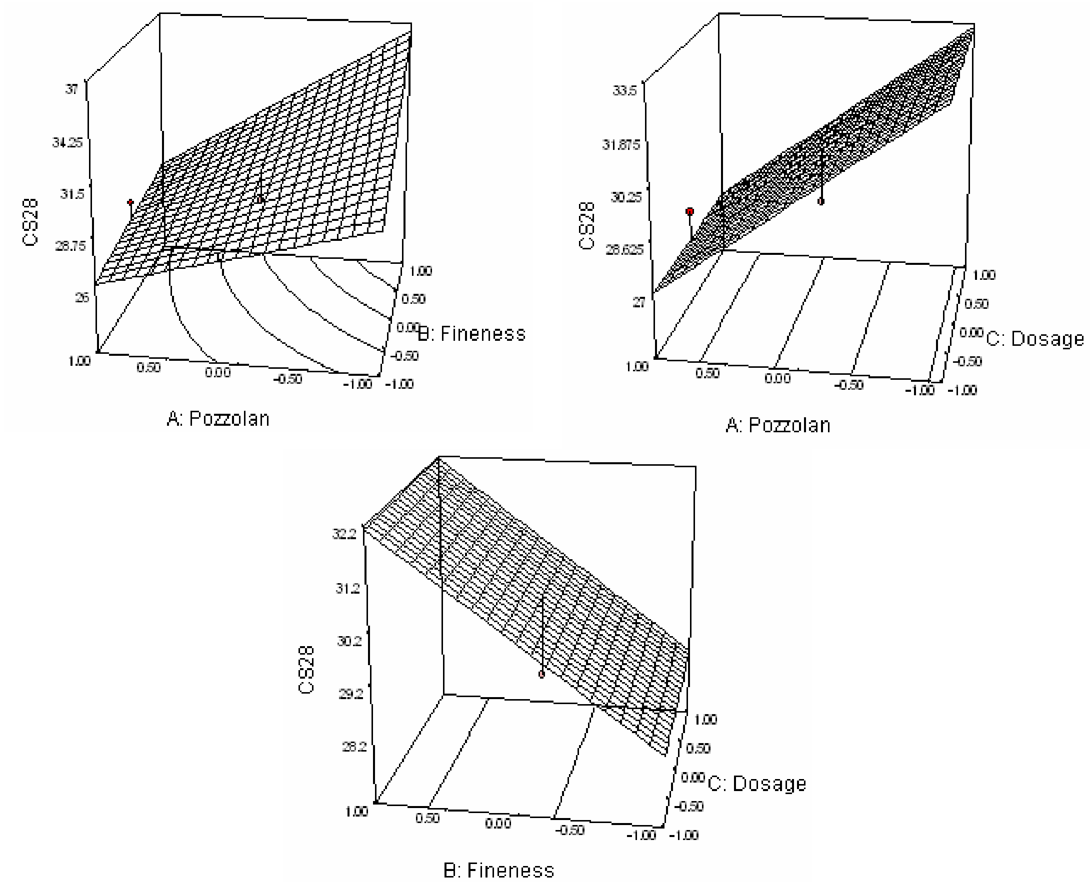

Figure 5.20 Example response surfaces of CS 28 with DJ design

Optimum 'mean 28-day compressive strength' is predicted as 36.55 by this model. Predicted value is slightly less when compared with previous predictions at the same combination of fineness and pozzolan content but closer to the experimental average of 24 observations (36.92) at the specified combination.

Economical Response Surface Designs: WD Design

Same optimality condition is found again for below regression model (5.7) for WD design (Tables 5.23 and 5.24).

$$CS28 = 29.8 - 3.89\,P + 2.03\,F - 0.007\,D - 1.44\,PF + 1.80\,PD - 1.16\,Psq + 1.32\,Fsq \quad (5.7)$$

Activator type is not significant in the regression again and hence does not affect optimality condition. The predicted response is overestimated when compared with previous results. Experimental average for same parameter level combinations is 36.92 while current prediction is 39.17. However experimental average is included in confidence and prediction intervals. Response surface examples (Fig. 5.21) have different shapes when compared with the curves of main design (5.17) due to additional parameters as activator dosage and quadratic terms of activator dosage and pozzolan content.

Table 5.23 Optimum CS28 response with desirability value, 95% confidence and prediction interval for WD design

#	Prediction (in MPa)	Desirability	95% CI	95% PI
1	39.17	0.709	(36.81; 41.53)	(35.43; 42.91)
2	39.17	0.709	(36.81; 41.53)	(35.43; 42.91)
3	38.98	0.699	(36.70; 41.26)	(35.29; 42.67)
4	38.76	0.688	(36.57; 40.96)	(35.13; 42.40)
5	38.71	0.686	(36.54; 40.89)	(35.09; 42.34)
6	38.58	0.679	(36.39; 40.77)	(34.95; 42.21)
7	38.51	0.676	(36.34; 40.69)	(34.89; 42.14)
8	38.35	0.667	(36.29; 40.41)	(34.79; 41.90)
9	38.27	0.664	(36.05; 40.50)	(34.62; 41.92)
10	38.14	0.657	(36.13; 40.15)	(34.61; 41.67)

Table 5.24 Parameter levels of optimum CS28 points for FCCD design for WD design

#	P	F	D	T*	CS28
1	-1.00	1.00	-1.00	*NaOH*	39.17
2	-1.00	1.00	-1.00	Na_2SO_4	39.17
3	-1.00	1.00	-0.89	*NaOH*	38.98
4	-1.00	1.00	-0.77	Na_2SO_4	38.76
5	-1.00	1.00	-0.75	*NaOH*	38.71
6	-0.88	1.00	-1.00	*NaOH*	38.58
7	-0.87	1.00	-1.00	Na_2SO_4	38.51
8	-1.00	1.00	-0.54	*NaOH*	38.35
9	-1.00	0.85	-1.00	Na_2SO_4	38.27
10	-1.00	1.00	-0.43	Na_2SO_4	38.14

**Has no effect on optimization results.*

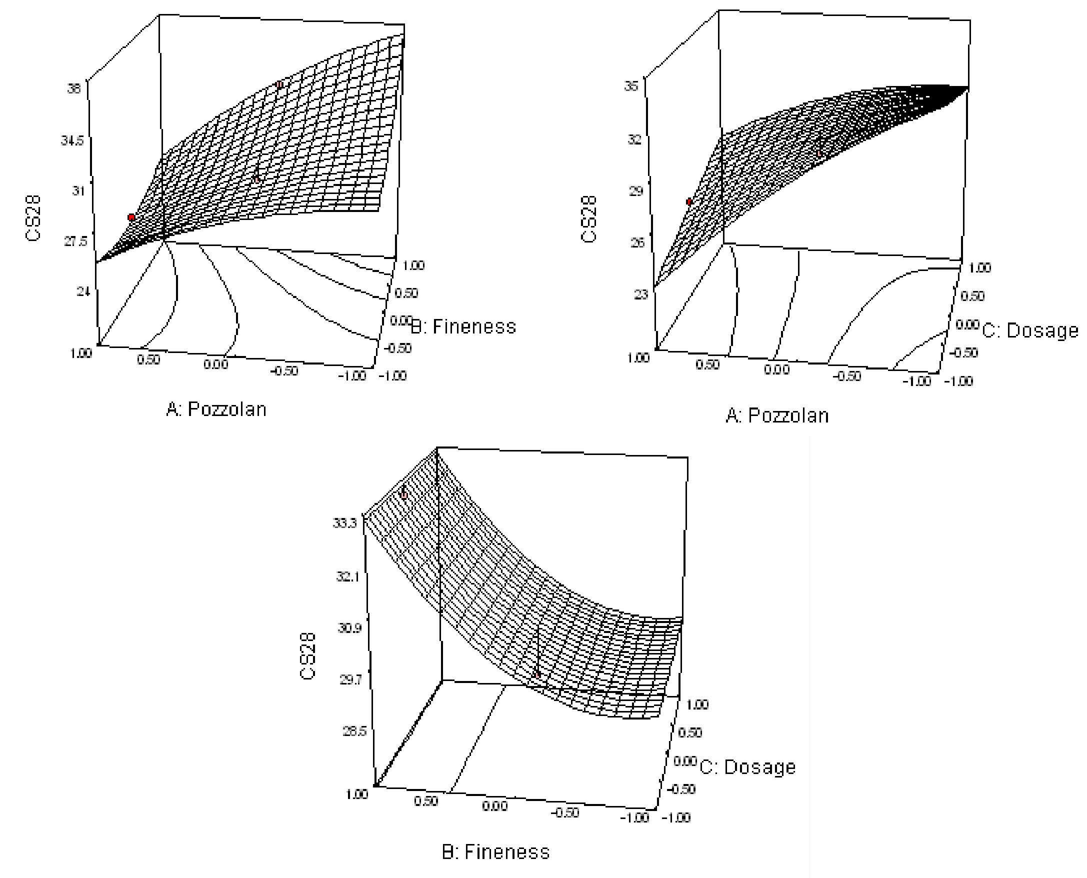

Figure 5.21 Example response surfaces of CS 28 with WD design

Regression analyses done for 28-day compressive strength for different designs result in smaller adjusted multiple coefficient of determination values when compared with 7-day compressive strength regression results. However these analyses are also successful in explaining a reasonable variation in the data of about 70 %. Economical designs are successful in explaining the variation in the data when multiple coefficient of determination values are concerned but regression analysis with the main FCCD design is superior in estimating closer values to observed values.

CHAPTER 6

SIMULTANEOUS OPTIMIZATION OF SEVERAL RESPONSE VARIABLES

Having defined and optimized two individual compressive strength responses separately in previous chapters; several responses are considered at the same time and optimal solutions satisfying all responses are presented in this chapter. In simultaneous optimization problems, it is not always possible to find global optimum solutions. In fact a basic concern in simultaneous optimization problems is to observe how responses change with respect to each other. Optimum conditions for a problem may change depending on the desired characteristics of the optimum. For example, one may not afford the optimum solution with maximum compressive strength and minimum standard deviation due to cost concerns. As long as previously defined system of parameter levels and functions are valid, parameter level selections can be based on present situation. Importance of responses may also change from time to time. Early strength may be more important than cost or vice versa for a specific case. A smaller compressive strength value with a smaller cost might be preferable due to current requirements.

Optimal solution alternatives are presented for different multiresponse systems in preceding sections. Dual response surface optimization of compressive strengths at both ages and their standard deviation estimates is also included.

6.1. Optimization of 7-Day and 28-Day Compressive Strengths

Maximization of both responses at the same time without any restrictions on independent and dependent variable space to represent basic general case is done by Design-Expert Optimization Module. The module makes use of overall composite desirability function approached which is explained in chapter 2 for optimization. A set of optimal solutions for maximization of both strength responses simultaneously when same weight and importance are assigned for both responses is tabulated in Table 6.1.

Table 6.1 Optimal solutions when both strength functions are maximized simultaneously

#	P	F	D	T	CS7	CS28	Desirability
1	-1	1	1	NaOH	23.9824	37.071	0.922
2	-1	1	1	Na_2SO_4	23.5312	37.0712	0.908
3	-1	1	0.85	NaOH	23.1731	37.0707	0.897
4	-1	1	-1	Na_2SO_4	23.1357	37.0712	0.895
5	-1	1	-0.77	Na_2SO_4	22.6129	37.0712	0.879
6	-1	1	0.73	NaOH	22.5979	37.0712	0.878
7	-1	1	-0.53	Na_2SO_4	22.2114	37.0707	0.865
8	-1	1	0.09	Na_2SO_4	21.9469	37.0711	0.857
9	-1	1	0.58	NaOH	21.9269	37.0712	0.856
10	-1	1	-0.24	NaOH	19.393	37.0603	0.767

As it will be recalled, the effect of activator type and dosage does not have statistical significant effects on compressive strength at 28 days. The optimum parameter combination (-1, 1, 1, NaOH) which is the optimum of both responses individually is the optimum solution of this analysis as well with highest desirability. The effect of activator dosage, activator type and their interactions on 7-day compressive strength is observed in suboptimal solutions presented.

6.2. Optimization of 7-Day, 28-Day Compressive Strengths and Cost Simultaneously

A simple cost analysis approach that represents the change in cost for different level combinations of parameters is applied. Costs that are constant for each experimental run such as labor cost or standard sand cost are not taken into consideration. For each run costs of cement, natural pozzolan (taking fineness into account), superplasticizer and activator are combined into a cost value. Material costs are given in Table 6.2. Energy cost for pozzolan grinding at different fineness levels is calculated by considering the time of grinding in the laboratory mill, the power of mill engine and electricity cost.

The engine of the mill consumes 1.5 kW of electricity in one hour and the cost per 1 kW consumed electricity is 1.58 TL for December, 2005. Consequently, the cost for operating the mill for 1 hour is 2.37 TL. For 10kg batches of pozzolan grinding at 70%, 80% and 90% fineness levels the mill is operated 75, 115 and 170 minutes respectively. Material costs are given in Table 6.2.

Table 6.2 Material costs

Material	Cost (TL)
Portland Cement (per ton)	105
Bulk form of volcanic tuff (per ton)	11
Superplasticizer (kg)	4.34
Energy cost for pozzolan grinding (F=70%, per 10 kg)	3
Energy cost for pozzolan grinding (F=80%, per 10 kg)	4.54
Energy cost for pozzolan grinding (F=90%, per 10 kg)	6.72
Na_2SO_4 (kg)	3
NaOH (kg)	2

Since the amount of superplasticizer used for a particular run does not depend directly on any design parameter but found by trials to satisfy flow condition; cost function cannot be written as a direct function of design parameters. First, cost for each run is calculated. The calculation is done by adding up all material costs of a run and the cost of energy spent for that particular run. Cost observations are given in Appendix 6.1. Then, regression analysis is applied to cost observations. Since only amount of superplasticizer is not a design parameter but all other parameters are direct elements of cost function; a regression with a very high adjusted multiple coefficient of determination of 99.7% is achieved. Regression analysis results for cost response are given in Appendix 6.2.

NIMBUS software is utilized for this multiresponse optimization. NIMBUS is a Nondifferentiable Interactive Multiobjective BUndle-based optimization System which has been developed at the University of Jyväskylä, Department of Mathematical Information Technology (WWW-NIMBUS, 2006). It is suitable for both differentiable and nondifferentiable multiobjective and single objective optimization problems subject to nonlinear and linear constraints with bounds for the variables. The problems to be solved are of the form

$$
\begin{array}{lll}
\textit{optimize} & \{f_1(x),......,f_k(x)\} & \\
\textit{subject to} & g_i(x) \le 0, & j = 1,\dots,m_i \\
 & g_i(x) = 0, & j = m_i,\dots,m \\
 & A_1 x \le b_1, & \\
 & A_2 x = b_{21}, & \\
\textit{and} & x^{\ell} \le x \le x^{u} &
\end{array}
$$

where k is the number of the objective functions, m is the number of the nonlinear constraints, decision vector x and its lower and upper bounds are n-dimensional vectors, b is an l-dimensional vector and A is an l X n-dimensional matrix of linear constraint coefficients. Pareto optimality is used as optimality concept.

In the NIMBUS method, the idea is that the user examines the values of the objective functions calculated at a current solution and divides the objective functions into up to five classes. The classes are functions whose values

- should be decreased,
- should be decreased down till some aspiration level,
- are satisfactory at the moment,
- are allowed to increase up till some upper bound, and
- are allowed to change freely.

A new problem is formed according to the classification and the connected information. This problem is solved alternatively by a multiobjective proximal bundle (MPB) method or genetic algorithms.

In Fig. 6.1, flowchart of the NIMBUS algorithm is provided.

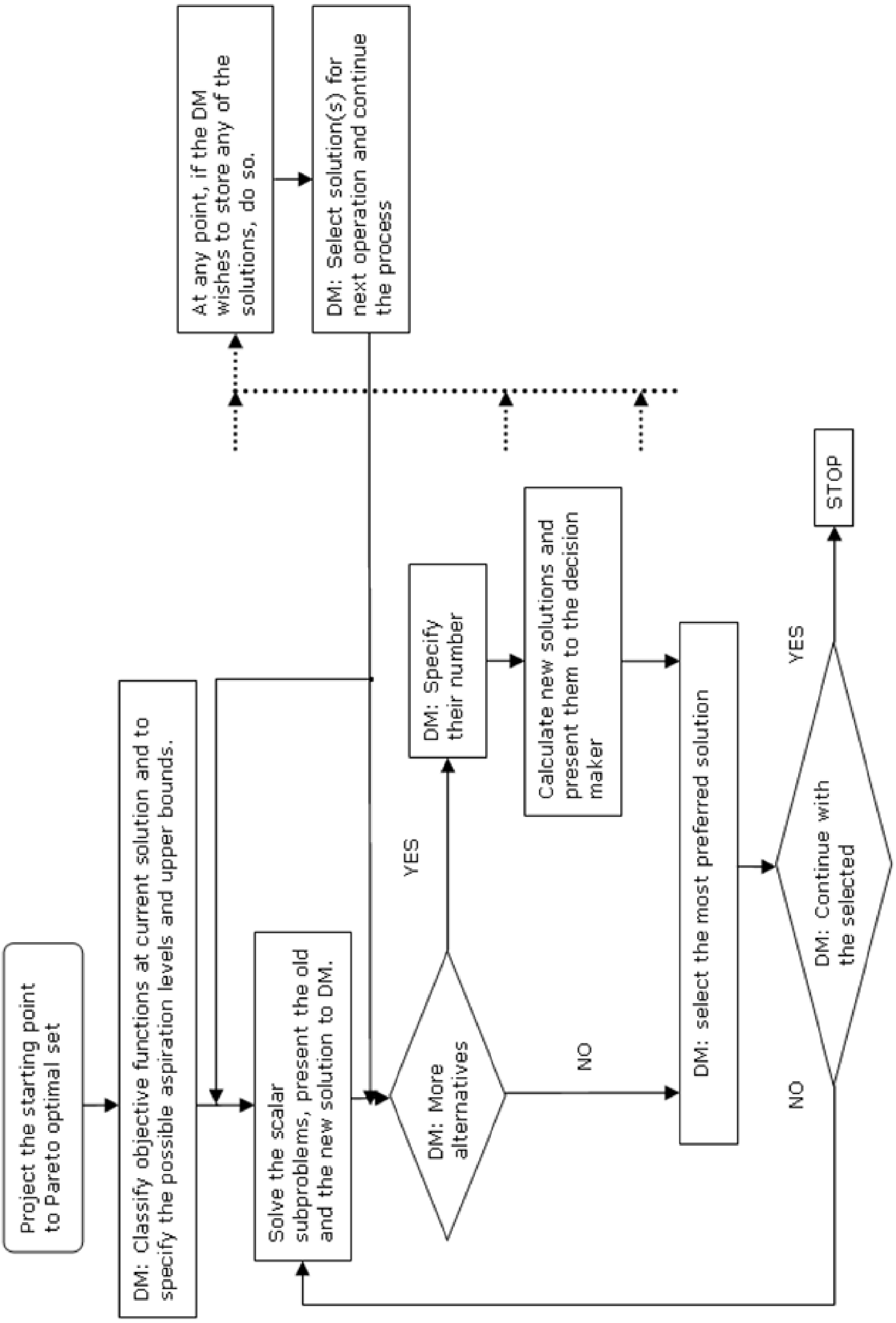

Figure 6.1 Flowchart of NIMBUS algorithm Pareto-optimal solutions for cost minimization and compressive strength maximization can be seen in Table 6.3.

Table 6.3 Pareto-optimal solutions when both strength functions are maximized and cost is minimized simultaneously

	COST (TL)	CS7 (MPa)	CS28 (MPa)	x'*
1	0.150	22.03	34.11	(-1, 0.171, -1, 1)
2	0.155	22.08	34.60	(-1, 0.310, -1, 1)
3	0.158	20.06	35.31	(-1, 0.509, -1, 0)
4	0.165	20.28	35.89	(-1, 0.672, -1, 0)
5	0.175	22.70	36.36	(-1, 0.804, -1, 1)
6	0.184	23.11	37.02	(-1, 0.990, -1, 1)
7	0.202	23.98	37.05	(-1, 1, 1, -1)

** x' represents parameter level combinations as (P,F,D,T)*

Pozzolan content is at its lower bound value for all Pareto-optimal solutions in the set. By increasing fineness, CS28 and cost increase as well however CS7 first shows a decreasing trend and then increases. Pareto-optimal solution set provides an understanding of three-response system. For the optimum point where compressive strengths are at their maximums, cost is not at its minimum and hence there is not a unique global solution. Decisions on parameter level combinations should be made considering current constraints or preferences and should be case based.

6.3. Dual Response Surface Optimization of Compressive Strength and Standard Deviation

Response surfaces for 7-day and 28-day compressive strengths are already fitted and optimized. Using 6 replicates for each run, sample standard deviations are calculated and regression equations are fit for these observations. Basic regression assumptions are satisfied and regression outputs are given in Appendix 6.3 and 6.4. Second-order regression equations are resulted as the best choice for both standard deviations. Activator type is not significant in standard deviation prediction equations. For standard deviation modeling, several data transformations are advised in statistical literature. Although residual plots of both standard deviations does not indicate a problem, data transformation as square root, log standard deviation and log variance are tried but the best result turns out to be when no transformation is applied to the data considering residual plots and adjusted multiple coefficient of determination.

Response surface plots for two fitted standard deviations possess different shapes. Fineness and activator type has no significant effect on standard deviation response for mean 7-day compressive strength where as fineness and its quadratic term are significant predictors for the standard deviation of mean 28-day compressive strength. Joint optimization for maximization of compressive strength and minimization of standard deviation is performed by NIMBUS algorithm. However, adjusted multiple coefficient of determination for both standard deviations are low. Although the regressions are statistically significant estimated functions are not very successful in explaining the total variation in the data.

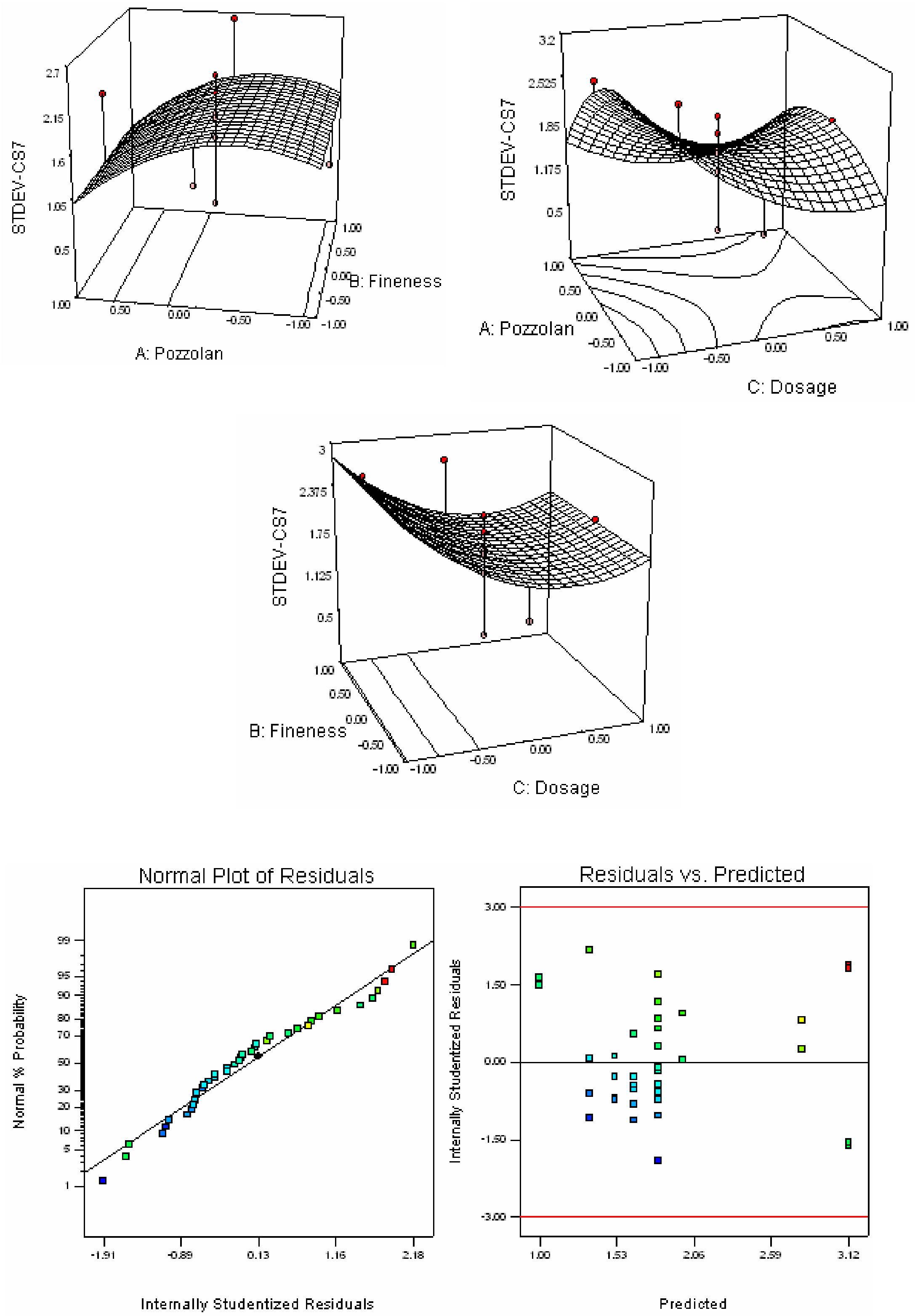

Figure 6.2 Response surface examples for two dimensional parameter planes and residual plots when the response is standard deviation of CS7

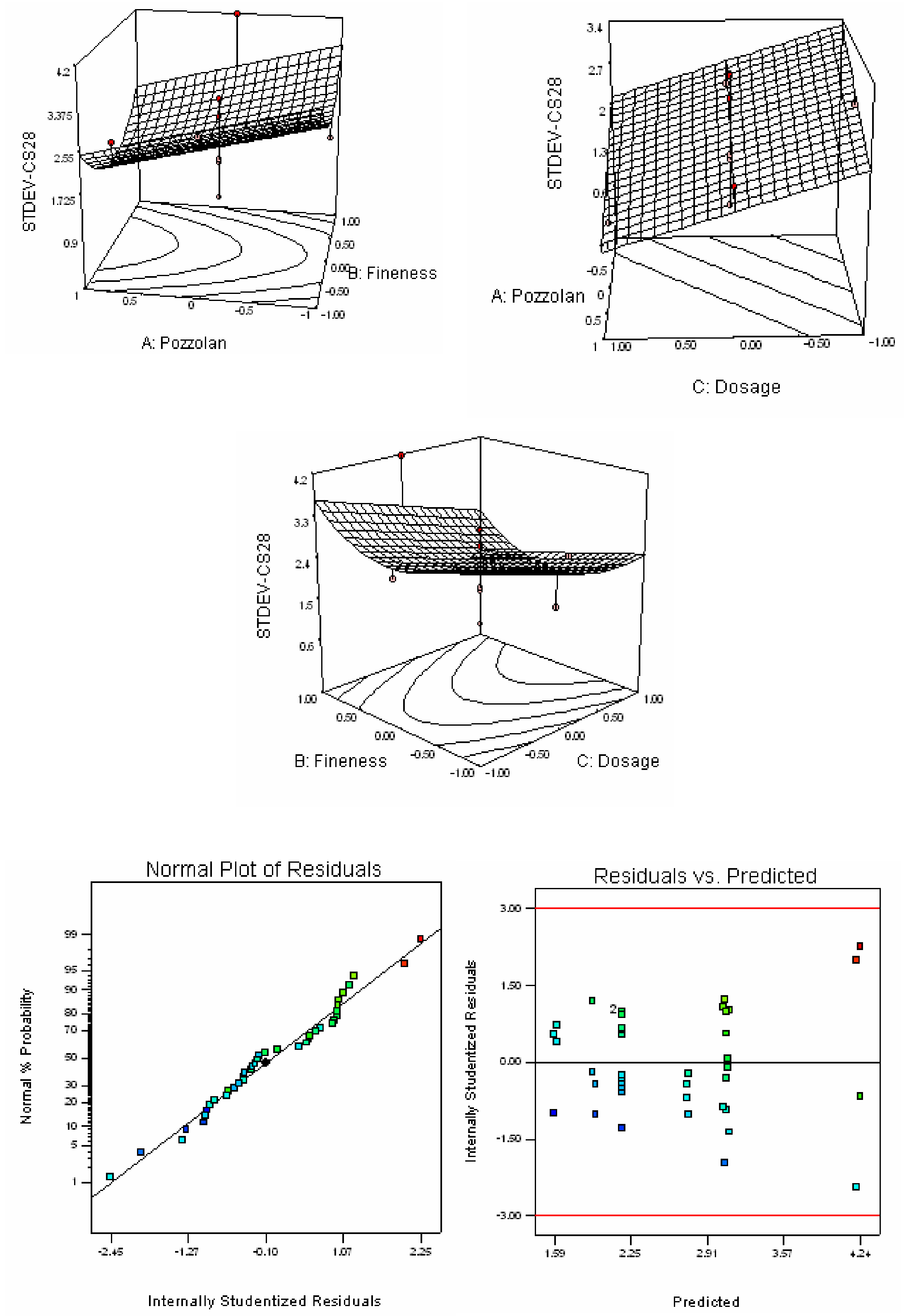

Figure 6.3 Response surface examples for two dimensional parameter planes and residual plots when the response is standard deviation of CS28

In Tables 6.4 and 6.5, pareto-optimal solution sets for dual response surface optimization are indicated. As strength increases standard deviation also increases so the decision maker should choose among alternatives with tolerable standard deviation.

Table 6.4 Pareto-optimal solutions for dual response surface optimization for CS7

#	CS7	STDEV	x'
1	14.594	1.003	(1, 1, -0.056, 1)
2	15.861	1.105	(1, 1, 0.364, -1)
3	16.712	1.200	(1, 1, 0.527, -1)
4	22.892	1.314	(-1, 1, 0.765, 1)
5	23.146	1.318	(-1, 1, 0.840, -1)
6	23.588	1.330	(-1, 1, 0.926, -1)
7	23.757	1.336	(-1, 1, 0.958, -1)
8	23.864	1.341	(-1, 1, 0.978, -1)
9	23.980	1.346	(-1, 1, 1, -1)

Table 6.5 Pareto-optimal solutions for dual response surface optimization for CS28

#	CS 28	STDEV	X'
1	26.102	1.020	(1, 0.007, 1)
2	27.507	1.229	(0.639, 0.081, 1)
3	29.168	1.471	(0.227, 0.132, 1)
4	31.093	1.746	(-0.232, 0.187, 1)
5	33.286	2.053	(-0.735, 0.244, 1)
6	34.904	2.288	(-1, 0.395, 1)
7	35.517	2.437	(-1, 0.568, 1)
8	35.673	2.483	(-1, 0.612, 1)
9	36.379	2.738	(-1, 0.811, 1)
10	37.050	3.047	(-1, 1, 1, -1)

6.4. Optimization of Strength to Cost Ratio

In concrete industry, strength to cost ratio is an important parameter. Achieving a high strength to cost ratio, in another saying spending minimum per cost of attained strength, is desirable. To present a basic application for such optimization strength to cost ratios for 7-day and 28-day are calculated and regressions are fit (named as Ratio 7 and Ratio 28) to the data as it can be seen in Appendix 6.5 and 6.6. Initially quadratic models are fit to untransformed data and lack of fit test result is significant. A Box-Cox transformation applied to both data sets at both ages solves lack of fit problem and significant models with high multiple coefficient of determination values are obtained (94% and 93% respectively).

Optimization of strength to cost ratios by Design-Expert Optimization Module resulted as in Tables 6.6 and 6.7. For both responses the point where pozzolan content, fineness and activator dosage are at their lower bound values and when activator type is Na_2SO_4 is found as the optimum point.

Table 6.6 Optimal solutions when strength to cost ratio is maximized at 7 days

#	Pozzolan	Fineness	Dosage	Type	$(\text{Ratio 7})^{0.15}$	Desirability
1	-1	-1	-1	Na_2SO_4	2.2078	0.9616
2	-1	-0.89	-1	Na_2SO_4	2.1966	0.9370
3	-1	-1	-0.82	Na_2SO_4	2.1946	0.9328
4	-1	-1	-0.71	Na_2SO_4	2.1870	0.9162
5	-1	-1	-0.54	Na_2SO_4	2.1761	0.8924
6	-1	-1	-0.3	Na_2SO_4	2.1627	0.8632
7	-1	-1	-1	NaOH	2.1531	0.8424
8	-1	-1	-0.08	Na_2SO_4	2.1517	0.8393
9	-1	-1	1	NaOH	2.1434	0.8213
10	-1	-1	-0.68	NaOH	2.1430	0.8205

Table 6.7 Optimal solutions when strength to cost ratio is maximized at 28 days

#	Pozzolan	Fineness	Dosage	Type*	$(\text{Ratio } 28)^{0.29}$	Desirability
1	-1	-1	-1	Na_2SO_4	5.0434	0.9073
2	-1	-1	-1	NaOH	5.0434	0.9073
3	-1	-0.89	-1	Na_2SO_4	5.0282	0.8967
4	-1	-0.86	-1	NaOH	5.0229	0.8930
5	-0.89	-1	-1	NaOH	5.0103	0.8842
6	-1	-1	-0.75	NaOH	5.0096	0.8838
7	-1	-0.98	-0.7	Na_2SO_4	5.0004	0.8774
8	-1	-0.69	-1	Na_2SO_4	4.9991	0.8764
9	-1	-1	-0.51	Na_2SO_4	4.9781	0.8618
10	-1	-1	0.1	Na_2SO_4	4.8953	0.8041

CHAPTER 7

CONCLUSIONS

Response surface methodology is applied in this study to optimize parameters of chemically activated mortars containing high volumes of pozzolan to obtain maximum 7-day and 28-day compressive strengths. A face-centered central composite design is chosen as the main design of this study since one of the research interests is to statistically identify potential relations of two-way interactions and quadratic terms of process parameters with compressive strength. Special focus is on early strength improvement by chemical activation because addition of natural pozzolan delays strength development. Despite this drawback, the use of natural pozzolans in cement and concrete systems leads to better durability, low permeability and high ultimate strength. What is more, pozzolan usage is an environment friendly approach that can reduce the CO_2 emission produced by the cement industry. Therefore, efforts to accelerate widespread usage of pozzolan as a Portland cement replacement are necessary for sustainable development of concrete industry.

Four process parameters as amount of natural pozzolan replacement, pozzolan fineness, activator dosage and type are included in this research. Activator type is a qualitative variable and presence of a qualitative variable in response surface methodology necessitates special attention in experimental design and analysis. Regression equations for both responses are fit considering 5 different experimental designs. These regression equations, their adjusted multiple coefficient determination (R^2_{adj}) values and standard deviation of the error estimates are tabulated in Tables 7.1 and 7.2.

Table 7.1 Comparison of regression equation parameters when the response is 7-day compressive strength

Equation	R^2_{adj}	S	N	Coef.	P	F	D	T	Psq	Fsq	Dsq	PF	PD	FD	PT	FT	DT
4.4 **Main FCCD** 40 runs	89.3%	1.18	40	15.4	-3.8	0.892	1.43	0.601		1.40	1.42	0.565	0.662	0.637	-0.38		-1.21
4.5 **FCCD for only NaOH** 20 runs	89.9%	1.12	20	15.1	-3.41	0.928	2.64	*		0.985	1.18		0.947	0.573	*	*	*
4.6 **FCCD for only Na_2SO_4** 20 runs	84.5%	1.46	20	15.7	-4.18	0.857	0.223	*		1.81	1.65				*	*	*
4.7 **DJ design** 16 runs	90.9%	1.13	16	16.1	-2.80	1.22	0.972	0.351		1.34			0.948		0.874		-1.76
4.8 **WD design** 16 runs	93.3%	1.12	16	15.3	-3.56	1.22	1.52	0.56		1.19	1.74			1.05			-1.89

Table 7.2 Comparison of regression equation parameters when the response is 28-day compressive strength

Equation	R^2_{adj}	S	N	Coef.	P	F	D	T	Psq	Fsq	Dsq	PF	PD	FD	PT	FT	DT
5.3 **Main FCCD** 40 runs	72.7%	1.91	40	29.8	-3.70	1.94						-1.61					
5.4 **FCCD for only NaOH** 20 runs	74.4%	1.88	20	29.6	-3.82	1.81		*			0.528	-1.21	1.53		*	*	*
5.5 **FCCD for only Na_2SO_4** 20 runs	73.4%	1.90	20	30.3	-3.59	2.08		*	-0.40			-2.01			*	*	*
5.6 **DJ design** 16 runs	63.3%	2.29	16	30.2	-3.19	1.94						-1.21					
5.7 **WD design** 16 runs	90.7%	1.26	16	29.8	-3.89	2.03	-0.007		-1.16	1.32		-1.44	1.8				

Different regression equations fit for 5 different designs are all successful in statistically explaining the variance in the data with high R^2_{adj} values. 2nd and 3rd experimental designs are half parts of the main design repeated for two qualitative levels. Separate analysis for these designs are done to see the difference in their regression equations and to evaluate the case when the qualitative factor is not defined as a system parameter. Obviously activator type cannot appear in the regression equation for these designs. For 7-day compressive strength response surfaces for different qualitative levels are different. Estimate of standard deviation (S) for all regression equations is approximately the same. The highest standard deviation estimate is for the case when FCCD is analyzed for only Na_2SO_4 activator. The R^2_{adj} value for this regression is also smaller when compared with others. Overall, significant regression equations for 7-day compressive strength are found. Main effects, quadratic effects and two-way interaction effects of variables appeared in regression equations.

For 28-day compressive strength, regression analyses are carried out with the same approach. Activator type was not significant at any of the regression equations. Response surfaces formed by only quantitative factors are statistically sufficient in explaining the relationship between the response and parameter for both levels of the qualitative factor. Activator dosage appeared only when FCCD is analyzed for Na_2SO_4 activator alone, with 20 runs. R^2_{adj} values are smaller for 28-day compressive strength equations. Pozzolan content and fineness together with their interaction effects explain about 70 % of the variation in data at average. The maximum R^2_{adj} value is achieved for the same case again, when regression analysis is separately done on the data activated by Na_2SO_4.

In regression analysis mean values for each run are modeled instead of single observations for this study. Compressive strength measurements of single mortar cubes show high standard deviations. Even when they are obtained from the same mixture and kept under the same conditions single observations may have large deviations from the mean; this is the nature of compressive strength measurements data. From construction materials point of view, the value of the average compressive strength measurements of replications is important. When regression analyses are applied for single observations and for both 7-day and 28-day compressive strengths with the parameters of best regression equations of main design; multiple coefficient of determination decreases and standard deviation increases significantly for both responses (Appendix 7.1). For 7-day compressive strength multiple coefficient of determination decreases from 89.3% to 71.3% while standard deviation increases from 1.18 to 2.16 MPa when the regression is applied to single observations. Since the method of least squares is applied in regression, the same regression equations are obtained with the same parameters when the mean or single observations are modeled. For 28-day compressive strength multiple coefficient of determination decreases to 48.5% from 72.7 % and standard deviation increases to 3.2 from 1.91 MPa. So, when regression is applied to single observations the same regression equations are obtained but with poorer standard deviation values and the total variation explained by the regression equation decreases considerably. The mean compressive strength value of replications is valuable and used in practice therefore it is used in regression analyses.

After fitting regression equations for both responses and different designs response surface optimization for each regression equation is done. Results are tabulated in Table 7.3.

Table 7.3 Optimum parameter level combinations for compressive strengths

Response	**# of Runs**	**Equation**	**Best levels**				**Estimated response (MPa)**	**95% CI**
			P	**F**	**D**	**T**		
CS7	40	4.4	-1.00	1.00	1.00	NaOH	23.98	(22.23; 25.73)
	20	4.5	-1.00	1.00	1.00	*	23.91	(21.91; 25.90)
	20	4.6	-1.00	1.00	1.00	*	24.41	(22.40; 26.41)
	16	4.7	-1.00	1.00	1.00	NaOH	23.73	(21.25; 26.20)
	16	4.8	-1.00	1.00	1.00	NaOH	26.88	(24.56; 29.20)
CS28	40	5.5	-1.00	1.00	*-0.23*	*Na_2SO_4*	37.07	(35.39; 38.75)
	20	5.6	-1.00	1.00	-1.00	*	37.42	(34.30; 40.54)
	20	5.7	-1.00	1.00	*-0.68*	*	37.53	(34.88; 40.18)
	16	5.8	-1.00	1.00	*-0.99*	*Na_2SO_4*	36.55	(33.44; 39.66)
	16	5.9	-1.00	1.00	-1.00	*NaOH*	39.17	(36.81; 41.53)

** pre-determine, either NaOH or Na_2SO_4, does not affect optimization*
(level values in italic: parameter does not appear in regression equation)

For strength maximization, minimum pozzolan content (35%) and maximum fineness (90%) are reported as optimum parameter levels for both responses and for all designs. Activator dosage at its upper bound (1.5%) is the optimum level for 7-day compressive strength. For 28-day compressive strength however, activator dosage is at its minimum for strength maximization for two equations that the dosage is a significant parameter. NaOH is the optimal chemical activator for 7-day compressive strength whereas activator type does not affect optimality in 28-day compressive strength. For optimal parameter levels of CS7, the experimental average is 23.6 MPa. The first 4 regression equations predict close values to this average however the 5^{th} (WD design) regression overestimates the compressive strength. The experimental average is even not in its confidence level. The experimental compressive strength average of 24 cubes in the study is 36.92. While the main design and DJ design estimates close values to this average; regression by WD design overestimates the strength again and the experimental average is hardly in the confidence interval. As the number of runs in the design decreases, confidence intervals tend to get wider. Confidence intervals as narrow as possible are favorable. This is another drawback of economical response surface designs. If we compare the two economical designs, DJ design is much more successful in explaining the variation and estimating reasonable values. Since optimal points are at the borders of the design, moving in these directions for the parameters and experimenting more may be a future research.

The economical designs seemed reasonably successful for explaining the variation in the data with defined process parameters. However, important problems from response design perspective are present. Due to lack of repetitions on the same run, lack of fit test cannot be performed. Design matrix evaluation for response surface quadratic model of both economical designs and the main FCCD design are presented in Appendix 7.2-7.4. For three designs, no aliases are found for quadratic model. Main FCCD design utilized in the study is quite successful with good lack of fit detectability, Ideal VIF values of 1 for all main terms and two way interactions and very high power values. On comparison with the same criteria, DJ design is superior to WD design (which is consistent with regression results) but poor when compared with main design. VIF values are enormously high indicating high correlation among factors. Two designs do not have degrees of freedom for pure error and hence lack of fit test cannot be performed. Power values for DJ design is less than half when compared with the main design and for WD design they are even worse. Finally standard errors of design plots are drawn for three designs and compared (Fig.s 7.1-3). The goal for these plots is contour plots as circles in circles where standard error of two designs are equal for two points that are at the same distance from the center and this is called rotatability. The worst case is WD design again. Although main design is not rotatable, it is nearly rotatable and acceptable according to this criterion. In conclusion, response surface methodology applications with only economical designs might be risky so matrix designs should be evaluated carefully and bigger data sets, like the main design of this study, better be preferred when affordable.

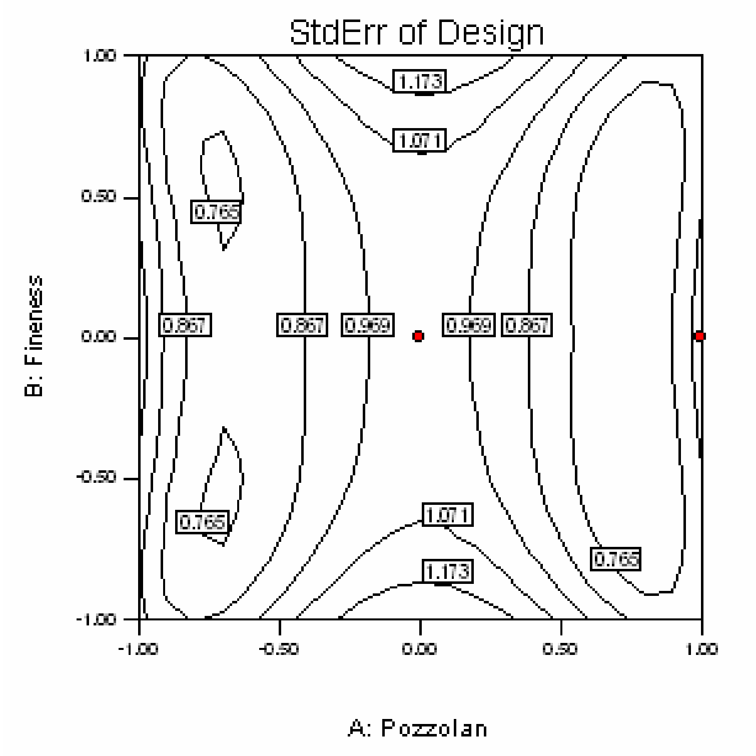

Figure 7.1 Standard error of design plot for DJ design (quadratic model)

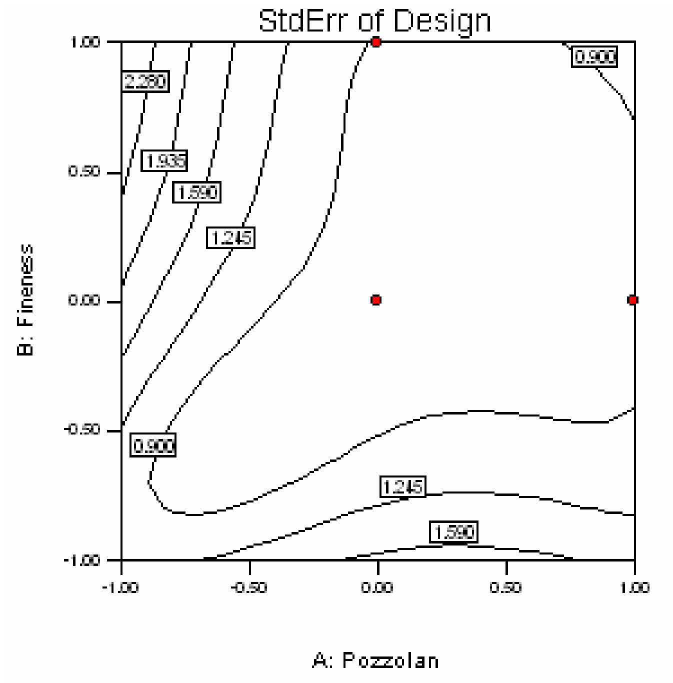

Figure 7.2 Standard error of design plot for WD design (quadratic model)

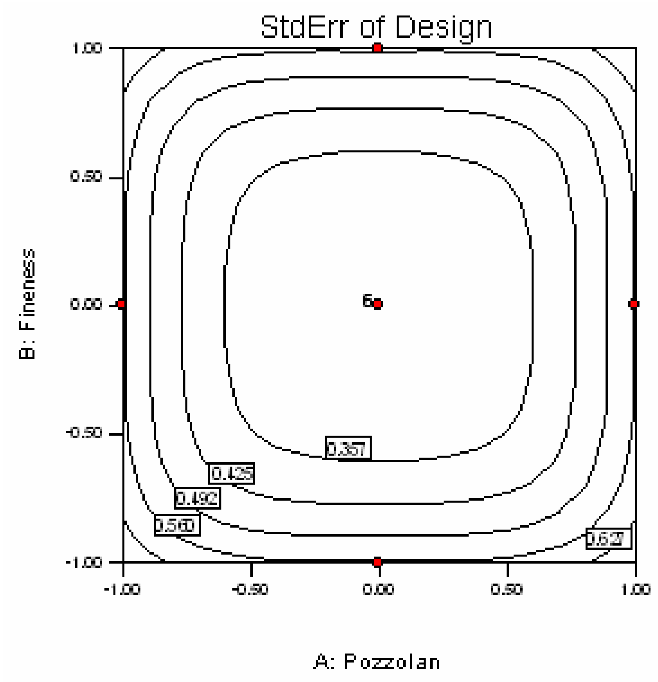

Figure 7.3 Standard error of design plot for main FCCD design with 40 runs (quadratic model)

After maximizing strength responses individually simultaneous optimization for several responses is applied. In RSM problems there are usually other responses to consider while optimizing one. Therefore, exploration of respective behavior of several responses is enlightening on such systems. Optimal settings for maximization of both compressive strengths were the same and as a result of optimization of both, the same level combination where minimum pozzolan content (35%), maximum fineness (90%) maximum activator dosage (1.5%) and NaOH as chemical activator is the optimal setting once again. When cost is introduced to this system as a third response, it is seen that there is a trade off between cost and 28-day compressive strength for all Pareto-optimal solutions. Both increase in the same direction so a compromise is necessary. Activator dosage is set to its minimum for 9 of the Pareto optimal solutions. CS7 first decreases, then increase by increasing fineness. Optimal settings when several criteria are considered are shaped according to own judgment but multiresponse analysis definitely provide an understanding of the system.

Dual response surface optimization is applied for both compressive strength responses. As strength increases standard deviation also increases so again a point of compromise should be the optimal setting based on decision maker's preference.

Optimal settings for maximization of "strength to cost" ratio is different from the optimal settings for previous compressive strength maximization cases. Pozzolan content is reported as minimum (35%) again but activator dosage (0.5%) and fineness (1.5%) are at their lower bounds unlike previous cases. On the contrary to previous choice, Na_2SO_4 is proposed as the optimal activator for this case.

Results of simultaneous optimization studies underlined the fact that systems' optimal parameter levels for different responses vary and in addition optimal settings of a system for a particular response may also vary when considered with any other response on the system.

Although best chosen regression models are statistically adequate in general, for standard deviation estimates only, significant models but with low multiple coefficient of determination values are found. A parameter optimization study with other parameters that are considered as potential parameters for standard deviation estimate may be a further study.

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Appendix 4.1 Face-centered central composite design repeated for each level of the qualitative factor and its results for 7-day compressive strength

Exp. run order	Std. order	Parameters				RESULTS						
		P	F	D	T	Run-1	Run-2	Run-3	Run-4	Run-5	Run-6	μ (MPa)
4	1	-1	-1	-1	-1	16,08	18,04	20,01	20,79	20,79	16,48	18,70
2	2	1	-1	-1	-1	9,02	9,81	7,06	9,41	9,02	10,20	9,09
31	3	-1	1	-1	-1	23,93	23,93	16,08	16,08	14,91	22,36	19,55
30	4	1	1	-1	-1	10,98	12,55	10,59	10,20	10,20	9,41	10,66
32	5	-1	-1	1	-1	22,75	21,57	20,79	23,93	20,01	21,57	21,77
33	6	1	-1	1	-1	14,91	16,08	16,08	12,94	14,51	13,34	14,64
3	7	-1	1	1	-1	24,32	24,71	23,54	23,93	21,97	23,14	23,60
40	8	1	1	1	-1	18,44	20,01	19,22	19,61	20,40	21,18	19,81
15	9	-1	0	0	-1	17,26	16,87	15,69	17,26	19,22	17,65	17,33
22	10	1	0	0	-1	9,02	13,34	12,94	12,16	13,73	14,51	12,62
29	11	0	-1	0	-1	16,08	18,04	18,04	14,91	15,30	16,48	16,48
23	12	0	1	0	-1	17,26	19,22	16,48	15,30	18,04	11,77	16,34
35	13	0	0	-1	-1	16,87	17,65	15,30	14,12	12,16	9,81	14,32
36	14	0	0	1	-1	20,79	16,87	20,40	16,48	20,79	18,04	18,89
10	15	0	0	0	-1	14,91	16,48	17,26	14,91	16,87	12,55	15,49
5	16	0	0	0	-1	18,44	14,91	14,51	16,48	15,69	15,30	15,89
28	17	0	0	0	-1	16,87	17,65	12,55	14,51	12,16	13,73	14,58
34	18	0	0	0	-1	13,73	13,73	13,73	14,51	14,91	14,51	14,19
9	19	0	0	0	-1	16,48	17,26	18,44	16,08	18,04	13,73	16,67
19	20	0	0	0	-1	11,38	12,55	13,34	17,26	14,51	13,34	13,73
11	21	-1	-1	-1	1	30,99	25,11	25,50	18,04	22,36	24,32	24,39
37	22	1	-1	-1	1	13,73	13,34	14,12	9,81	13,73	12,94	12,94
1	23	-1	1	-1	1	21,97	20,01	23,93	26,28	24,32	22,75	23,21
39	24	1	1	-1	1	16,08	15,69	13,34	13,73	13,34	12,94	14,19
27	25	-1	-1	1	1	22,36	22,75	23,14	24,32	23,54	23,14	23,21
12	26	1	-1	1	1	13,73	11,77	14,91	11,38	14,12	13,34	13,21
21	27	-1	1	1	1	21,18	21,97	25,11	27,85	25,50	27,07	24,78
7	28	1	1	1	1	19,22	14,12	18,04	17,26	19,22	16,08	17,33
16	29	-1	0	0	1	18,44	19,61	15,69	18,44	19,61	19,22	18,50
25	30	1	0	0	1	16,87	12,94	12,94	16,08	12,55	16,48	14,64
26	31	0	-1	0	1	18,83	12,94	18,04	15,69	17,26	13,73	16,08
17	32	0	1	0	1	18,44	17,65	18,83	18,44	22,36	17,65	18,89
38	33	0	0	-1	1	22,36	18,44	21,18	16,87	16,48	13,34	18,11
8	34	0	0	1	1	19,61	15,69	16,08	18,04	17,65	12,16	16,54
13	35	0	0	0	1	13,73	16,08	12,16	14,91	14,91	13,73	14,25
24	36	0	0	0	1	18,04	15,30	16,08	14,91	17,65	15,30	16,21
14	37	0	0	0	1	13,34	10,59	17,26	18,83	16,48	14,51	15,17
6	38	0	0	0	1	17,26	14,91	12,94	15,30	15,30	12,55	14,71
18	39	0	0	0	1	14,12	16,87	16,08	14,91	15,30	16,87	15,69
20	40	0	0	0	1	18,83	15,30	16,87	16,87	15,69	14,51	16,34

Appendix 4.2 The regression analysis for 7-day compressive strength that includes only main factor terms

```
The regression equation is
CS7 = 16.8 - 3.80 P + 0.892 F + 1.43 D + 0.601 T

Predictor     Coef  SE Coef      T      P  VIF
Constant   16.8184   0.3313  50.76  0.000
P          -3.7952   0.4686  -8.10  0.000  1.0
F           0.8924   0.4686   1.90  0.065  1.0
D           1.4318   0.4686   3.06  0.004  1.0
T           0.6015   0.3313   1.82  0.078  1.0

S = 2.09556   R-Sq = 70.0%   R-Sq(adj) = 66.6%

PRESS = 211.375   R-Sq(pred) = 58.81%

Analysis of Variance

Source          DF       SS      MS      F      P
Regression       4  359.465  89.866  20.46  0.000
Residual Error  35  153.698   4.391
  Lack of Fit   25  143.986   5.759   5.93  0.003
  Pure Error    10    9.712   0.971
Total           39  513.163


 28 rows with no replicates


Source  DF   Seq SS
P        1  288.067
F        1   15.928
D        1   40.999
T        1   14.471

Unusual Observations

Obs      P     CS7     Fit  SE Fit  Residual  St Resid
  1  -1.00  24.386  18.891   0.937     5.495     2.93R
 40   1.00  19.809  14.746   0.937     5.063     2.70R

R denotes an observation with a large standardized residual.


Durbin-Watson statistic = 1.24653


Lack of fit test
Possible curvature in variable P  (P-Value = 0.022 )


Possible curvature in variable F  (P-Value = 0.007 )


Possible curvature in variable D  (P-Value = 0.006 )

Possible lack of fit at outer X-values (P-Value = 0.020)
Overall lack of fit test is significant at P = 0.006
```

Appendix 4.3 Regression analysis based on face-centered central composite design and applied for CS7 involving all two-way interaction and quadratic terms

```
The regression equation is
CS7 = 15.4 - 3.80 P + 0.892 F + 1.43 D + 0.215 T + 0.162 Psq + 1.34 Fsq
      + 1.36 Dsq + 0.564 PF + 0.662 PD - 0.382 PT + 0.637 FD - 0.036 FT
       - 1.21 DT + 0.492 PsqT + 0.230 FsqT + 0.051 DsqT + 0.057 PFT
       + 0.065 FDT - 0.286 PDT
```

Predictor	Coef	SE Coef	T	P	VIF
Constant	15.3905	0.3129	49.19	0.000	
P	-3.7952	0.2878	-13.19	0.000	1.0
F	0.8924	0.2878	3.10	0.006	1.0
D	1.4318	0.2878	4.97	0.000	1.0
T	0.2151	0.3129	0.69	0.500	2.4
Psq	0.1620	0.5488	0.30	0.771	1.8
Fsq	1.3388	0.5488	2.44	0.024	1.8
Dsq	1.3551	0.5488	2.47	0.023	1.8
PF	0.5639	0.3218	1.75	0.095	1.0
PD	0.6619	0.3218	2.06	0.053	1.0
PT	-0.3825	0.2878	-1.33	0.199	1.0
FD	0.6374	0.3218	1.98	0.062	1.0
FT	-0.0360	0.2878	-0.12	0.902	1.0
DT	-1.2095	0.2878	-4.20	0.000	1.0
PsqT	0.4918	0.5488	0.90	0.381	3.6
FsqT	0.2303	0.5488	0.42	0.679	3.6
DsqT	0.0505	0.5488	0.09	0.928	3.6
PFT	0.0572	0.3218	0.18	0.861	1.0
FDT	0.0654	0.3218	0.20	0.841	1.0
PDT	-0.2860	0.3218	-0.89	0.385	1.0

S = 1.28716   R-Sq = 93.5%   R-Sq(adj) = 87.4%

PRESS = 203.932   R-Sq(pred) = 60.26%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	19	480.028	25.265	15.25	0.000
Residual Error	20	33.135	1.657		
Lack of Fit	10	23.423	2.342	2.41	0.091
Pure Error	10	9.712	0.971		
Total	39	513.163			

28 rows with no replicates

Source	DF	Seq SS
P	1	288.067
F	1	15.928
D	1	40.999
T	1	14.471
Psq	1	31.623
Fsq	1	21.831
Dsq	1	10.100
PF	1	5.087
PD	1	7.011
PT	1	2.926
FD	1	6.501
FT	1	0.026
DT	1	29.257
PsqT	1	4.360
FsqT	1	0.398
DsqT	1	0.014
PFT	1	0.052
FDT	1	0.068
PDT	1	1.309

Unusual Observations

Obs	P	CS7	Fit	SE Fit	Residual	St Resid
11	-1.00	18.502	20.437	0.902	-1.935	-2.11R
29	1.00	14.645	12.082	0.902	2.563	2.79R

R denotes an observation with a large standardized residual.

Durbin-Watson statistic = 1.82212

* ERROR * Not enough data for lack of fit test

Appendix 4.4 Regression analysis for the model applied for 7-day mean compressive strength based on the face-centered central composite design after elimination of insignificant terms

```
The regression equation is
CS7 = 15.4 - 3.80 P + 0.892 F + 1.43 D + 0.601 T + 1.40 Fsq + 1.42 Dsq
      + 0.564 PF + 0.662 PD - 0.382 PT + 0.637 FD - 1.21 DT


Predictor     Coef  SE Coef       T      P  VIF
Constant   15.4107   0.2817   54.70  0.000
P          -3.7952   0.2656  -14.29  0.000  1.0
F           0.8924   0.2656    3.36  0.002  1.0
D           1.4318   0.2656    5.39  0.000  1.0
T           0.6015   0.1878    3.20  0.003  1.0
Fsq         1.3995   0.4695    2.98  0.006  1.6
Dsq         1.4158   0.4695    3.02  0.005  1.6
PF          0.5639   0.2970    1.90  0.068  1.0
PD          0.6619   0.2970    2.23  0.034  1.0
PT         -0.3825   0.2656   -1.44  0.161  1.0
FD          0.6374   0.2970    2.15  0.041  1.0
DT         -1.2095   0.2656   -4.55  0.000  1.0


S = 1.18784   R-Sq = 92.3%   R-Sq(adj) = 89.3%

PRESS = 81.9124   R-Sq(pred) = 84.04%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression      11  473.656  43.060  30.52  0.000
Residual Error  28   39.507   1.411
  Lack of Fit   18   29.795   1.655   1.70  0.196
  Pure Error    10    9.712   0.971
Total           39  513.163


 28 rows with no replicates


Source  DF   Seq SS
P        1  288.067
F        1   15.928
D        1   40.999
T        1   14.471
Fsq      1   50.580
Dsq      1   12.829
PF       1    5.087
PD       1    7.011
PT       1    2.926
FD       1    6.501
DT       1   29.257


Durbin-Watson statistic = 1.67856

No evidence of lack of fit (P >= 0.1).
```

Appendix 4.5 Regression analyses in order to check the significance of the interaction between levels of the qualitative factor and quantitative factors proposed by Batmaz and Tunali (2003) for mean 7-day compressive strength

Regression Analysis: CS7 versus P, F, D, Psq, Fsq, Dsq, PF, PD, FD *(to calculate SSE1)*

```
The regression equation is
CS7 = 15.4 - 3.80 P + 0.892 F + 1.43 D + 0.162 Psq + 1.34 Fsq + 1.36 Dsq
      + 0.564 PF + 0.662 PD + 0.637 FD


Predictor      Coef  SE Coef       T      P  VIF
Constant    15.3905   0.4116   37.39  0.000
P           -3.7952   0.3786  -10.02  0.000  1.0
F            0.8924   0.3786    2.36  0.025  1.0
D            1.4318   0.3786    3.78  0.001  1.0
Psq          0.1620   0.7220    0.22  0.824  1.8
Fsq          1.3388   0.7220    1.85  0.074  1.8
Dsq          1.3551   0.7220    1.88  0.070  1.8
PF           0.5639   0.4233    1.33  0.193  1.0
PD           0.6619   0.4233    1.56  0.128  1.0
FD           0.6374   0.4233    1.51  0.143  1.0


S = 1.69328   R-Sq = 83.2%   R-Sq(adj) = 78.2%

PRESS = 190.360   R-Sq(pred) = 62.90%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression       9  427.147  47.461  16.55  0.000
Residual Error  30   86.016   2.867
  Lack of Fit    5   17.596   3.519   1.29  0.301
  Pure Error    25   68.421   2.737
Total           39  513.163


Source  DF   Seq SS
P        1  288.067
F        1   15.928
D        1   40.999
Psq      1   31.623
Fsq      1   21.831
Dsq      1   10.100
PF       1    5.087
PD       1    7.011
FD       1    6.501

Unusual Observations

Obs      P     CS7     Fit  SE Fit  Residual  St Resid
  1  -1.00  24.386  21.581   1.066     2.805     2.13R
  3  -1.00  18.698  21.581   1.066    -2.883    -2.19R

R denotes an observation with a large standardized residual.
```

```
Durbin-Watson statistic = 1.95328

Possible lack of fit at outer X-values (P-Value = 0.086)
Overall lack of fit test is significant at P = 0.086
```

Regression Analysis: CS7 versus P, F, D, Psq, Fsq, Dsq, PF, PD, FD, T *(to calculate SSE2)*

```
The regression equation is
CS7 = 15.4 - 3.80 P + 0.892 F + 1.43 D + 0.162 Psq + 1.34 Fsq + 1.36 Dsq
      + 0.564 PF + 0.662 PD + 0.637 FD + 0.601 T


Predictor     Coef  SE Coef       T      P  VIF
Constant   15.3905   0.3818   40.31  0.000
P          -3.7952   0.3512  -10.81  0.000  1.0
F           0.8924   0.3512    2.54  0.017  1.0
D           1.4318   0.3512    4.08  0.000  1.0
Psq         0.1620   0.6697    0.24  0.811  1.8
Fsq         1.3388   0.6697    2.00  0.055  1.8
Dsq         1.3551   0.6697    2.02  0.052  1.8
PF          0.5639   0.3927    1.44  0.162  1.0
PD          0.6619   0.3927    1.69  0.103  1.0
FD          0.6374   0.3927    1.62  0.115  1.0
T           0.6015   0.2483    2.42  0.022  1.0


S = 1.57070   R-Sq = 86.1%   R-Sq(adj) = 81.3%

PRESS = 162.985   R-Sq(pred) = 68.24%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression      10  441.618  44.162  17.90  0.000
Residual Error  29   71.545   2.467
  Lack of Fit   19   61.833   3.254   3.35  0.027
  Pure Error    10    9.712   0.971
Total           39  513.163


 28 rows with no replicates


Source  DF   Seq SS
P        1  288.067
F        1   15.928
D        1   40.999
Psq      1   31.623
Fsq      1   21.831
Dsq      1   10.100
PF       1    5.087
PD       1    7.011
FD       1    6.501
T        1   14.471


Durbin-Watson statistic = 1.80577

Possible lack of fit at outer X-values (P-Value = 0.029)
Overall lack of fit test is significant at P = 0.029
```

Regression Analysis: CS7 versus P, F, D, Psq, Fsq, Dsq, PF, PD, FD, T, PT, FT, DT, PFT, PDT, FDT, PsqT, FsqT, DsqT
(to calculate SSE3)

```
The regression equation is
CS7 = 15.4 - 3.80 P + 0.892 F + 1.43 D + 0.162 Psq + 1.34 Fsq + 1.36 Dsq
      + 0.564 PF + 0.662 PD + 0.637 FD + 0.215 T - 0.382 PT - 0.036 FT
      - 1.21 DT + 0.057 PFT - 0.286 PDT + 0.065 FDT + 0.492 PsqT
      + 0.230 FsqT + 0.051 DsqT
```

Predictor	Coef	SE Coef	T	P	VIF
Constant	15.3905	0.3129	49.19	0.000	
P	-3.7952	0.2878	-13.19	0.000	1.0
F	0.8924	0.2878	3.10	0.006	1.0
D	1.4318	0.2878	4.97	0.000	1.0
Psq	0.1620	0.5488	0.30	0.771	1.8
Fsq	1.3388	0.5488	2.44	0.024	1.8
Dsq	1.3551	0.5488	2.47	0.023	1.8
PF	0.5639	0.3218	1.75	0.095	1.0
PD	0.6619	0.3218	2.06	0.053	1.0
FD	0.6374	0.3218	1.98	0.062	1.0
T	0.2151	0.3129	0.69	0.500	2.4
PT	-0.3825	0.2878	-1.33	0.199	1.0
FT	-0.0360	0.2878	-0.12	0.902	1.0
DT	-1.2095	0.2878	-4.20	0.000	1.0
PFT	0.0572	0.3218	0.18	0.861	1.0
PDT	-0.2860	0.3218	-0.89	0.385	1.0
FDT	0.0654	0.3218	0.20	0.841	1.0
PsqT	0.4918	0.5488	0.90	0.381	3.6
FsqT	0.2303	0.5488	0.42	0.679	3.6
DsqT	0.0505	0.5488	0.09	0.928	3.6

S = 1.28716   R-Sq = 93.5%   R-Sq(adj) = 87.4%

PRESS = 203.932   R-Sq(pred) = 60.26%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	19	480.028	25.265	15.25	0.000
Residual Error	20	***33.135***	1.657		
Lack of Fit	10	23.423	2.342	2.41	0.091
Pure Error	10	9.712	0.971		
Total	39	513.163			

28 rows with no replicates

Source	DF	Seq SS
P	1	288.067
F	1	15.928
D	1	40.999
Psq	1	31.623
Fsq	1	21.831
Dsq	1	10.100
PF	1	5.087
PD	1	7.011
FD	1	6.501
T	1	14.471
PT	1	2.926
FT	1	0.026
DT	1	29.257
PFT	1	0.052
PDT	1	1.309
FDT	1	0.068
PsqT	1	4.360
FsqT	1	0.398
DsqT	1	0.014

Unusual Observations

Obs	P	CS7	Fit	SE Fit	Residual	St Resid
11	-1.00	18.502	20.437	0.902	-1.935	-2.11R
29	1.00	14.645	12.082	0.902	2.563	2.79R

R denotes an observation with a large standardized residual.

Durbin-Watson statistic = 1.82212

* ERROR * Not enough data for lack of fit test

Appendix 4.6 Regression analysis for mean 7-day compressive strength when activator type is NaOH (with basic FCCD design with 20 observations)

```
The regression equation is
CS7 = 15.1 - 3.41 P + 0.928 F + 2.64 D + 0.985 Fsq + 1.18 Dsq + 0.947 PD
      + 0.573 FD


Predictor     Coef  SE Coef      T      P  VIF
Constant   15.1350   0.3772  40.12  0.000
P          -3.4130   0.3556  -9.60  0.000  1.0
F           0.9280   0.3556   2.61  0.023  1.0
D           2.6390   0.3556   7.42  0.000  1.0
Fsq         0.9850   0.6287   1.57  0.143  1.6
Dsq         1.1800   0.6287   1.88  0.085  1.6
PD          0.9475   0.3976   2.38  0.035  1.0
FD          0.5725   0.3976   1.44  0.175  1.0


S = 1.12462   R-Sq = 93.6%   R-Sq(adj) = 89.9%

PRESS = 54.5894   R-Sq(pred) = 77.11%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression       7  223.332  31.905  25.23  0.000
Residual Error  12   15.177   1.265
  Lack of Fit    7    8.961   1.280   1.03  0.505
  Pure Error     5    6.216   1.243
Total           19  238.509


 14 rows with no replicates


Source  DF   Seq SS
P        1  116.486
F        1    8.612
D        1   69.643
Fsq      1   14.331
Dsq      1    4.456
PD       1    7.182
FD       1    2.622


Unusual Observations

Obs     P     CS7     Fit  SE Fit  Residual  St Resid
  5  1.00  14.640  15.973   0.915    -1.333     -2.04R

R denotes an observation with a large standardized residual.


Durbin-Watson statistic = 2.03704

No evidence of lack of fit (P >= 0.1).
```

Appendix 4.7 Regression analysis for mean 7-day compressive strength when activator type Na_2SO_4 (with basic FCCD design with 20 observations)

```
The regression equation is
CS7 = 15.7 - 4.18 P + 0.857 F + 0.223 D + 1.81 Fsq + 1.65 Dsq


Predictor     Coef  SE Coef      T      P  VIF
Constant   15.6851   0.4882  32.13  0.000
P          -4.1780   0.4603  -9.08  0.000  1.0
F           0.8570   0.4603   1.86  0.084  1.0
D           0.2230   0.4603   0.48  0.636  1.0
Fsq         1.8144   0.8137   2.23  0.043  1.6
Dsq         1.6544   0.8137   2.03  0.061  1.6


S = 1.45557   R-Sq = 88.6%   R-Sq(adj) = 84.5%

PRESS = 64.1475   R-Sq(pred) = 75.35%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression       5  230.553  46.111  21.76  0.000
Residual Error  14   29.662   2.119
  Lack of Fit    9   26.187   2.910   4.19  0.065
  Pure Error     5    3.475   0.695
Total           19  260.215


 14 rows with no replicates


Source  DF   Seq SS
P        1  174.557
F        1    7.344
D        1    0.497
Fsq      1   39.396
Dsq      1    8.758


Durbin-Watson statistic = 2.34560

No evidence of lack of fit (P >= 0.1).
```

Appendix 4.8 Economic design alternatives for mean 7-day compressive strength

Main FCCD (40 0bservations)

Condition number:	5.5
D-optimality (determinant of XTX):	1.47640E+17
A-optimality (trace of inv(XTX)):	1.11705
G-optimality (avg leverage/max leverage):	0.612326
V-optimality (average leverage):	0.35
Maximum leverage:	0.571591

WD (16 observations)

Condition number:	68.0873
D-optimality (determinant of XTX):	1.24613E+10
A-optimality (trace of inv(XTX)):	8.36393
G-optimality (avg leverage/max leverage):	0.875
V-optimality (average leverage):	0.875
Maximum leverage:	1

DJ (16 observations)

Condition number:	8.81560
D-optimality (determinant of XTX):	3.99432E+11
A-optimality (trace of inv(XTX)):	3.22110
G-optimality (avg leverage/max leverage):	0.894231
V-optimality (average leverage):	0.875
Maximum leverage:	0.978495

WD Design					DJ Design				
Parameters				μ (MPa)	Parameters				μ (MPa)
P	F	D	T		P	F	D	T	
-1	1	-1	1	23.21	-1	0	0	1	18.50
-1	1	1	1	24.78	-1	1	-1	-1	19.55
1	-1	1	1	13.21	-1	1	1	-1	23.60
1	1	1	-1	19.81	0	1	0	1	18.89
-1	-1	-1	-1	18.70	0	0	-1	1	18.11
1	-1	-1	-1	9.09	-1	-1	-1	-1	18.70
-1	-1	1	-1	21.77	-1	-1	1	-1	21.77
1	1	-1	-1	10.66	0	0	0	-1	15.09
0	0	0	1	15.40	0	0	0	1	15.40
0	0	0	-1	15.09	1	1	-1	-1	10.66
1	0	0	-1	12.62	1	1	1	-1	19.81
-1	0	0	1	18.50	0	0	1	1	16.54
0	1	0	-1	16.34	0	-1	0	1	16.08
0	-1	0	1	16.08	1	-1	-1	-1	9.09
0	0	1	1	16.54	1	-1	1	-1	14.64
0	0	-1	1	18.11	1	0	0	1	14.64

Appendix 4.9 Regression analysis for mean 7-day compressive strength with DJ design

```
The regression equation is
CS7 = 16.1 - 2.80 P + 1.22 F + 0.972 D + 0.351 T - 1.76 DT + 0.948 PD
+ 0.874 PT + 1.34 Fsq


Predictor     Coef  SE Coef      T      P  VIF
Constant   16.1468   0.5228  30.89  0.000
P          -2.8031   0.4485  -6.25  0.000  1.6
F           1.2226   0.3588   3.41  0.011  1.0
D           0.9725   0.4485   2.17  0.067  1.6
T           0.3509   0.3637   0.96  0.367  1.6
DT         -1.7570   0.4485  -3.92  0.006  1.6
PD          0.9480   0.4011   2.36  0.050  1.0
PT          0.8744   0.4485   1.95  0.092  1.6
Fsq         1.3431   0.7453   1.80  0.115  1.6


S = 1.13455   R-Sq = 95.7%   R-Sq(adj) = 90.9%

PRESS = 51.4452   R-Sq(pred) = 75.71%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression       8  202.826  25.353  19.70  0.000
Residual Error   7    9.011   1.287
Total           15  211.837


No replicates.
Cannot do pure error test.


Source  DF   Seq SS
P        1  110.738
F        1   14.947
D        1   41.075
T        1    0.046
DT       1   19.758
PD       1    7.189
PT       1    4.893
Fsq      1    4.180


Durbin-Watson statistic = 1.73984

* ERROR * Not enough data for lack of fit test
```

Appendix 4.10 Regression analysis for mean 7-day compressive strength with WD design

```
The regression equation is
CS7 = 15.3 - 3.56 P + 1.22 F + 1.52 D + 0.560 T - 1.89 DT + 1.74 Dsq
+ 1.05 FD + 1.19 Fsq


Predictor     Coef  SE Coef      T      P  VIF
Constant   15.2764   0.5134  29.76  0.000
P          -3.5551   0.3903  -9.11  0.000  1.2
F           1.2172   0.3634   3.35  0.012  1.0
D           1.5219   0.3606   4.22  0.004  1.0
T           0.5603   0.3260   1.72  0.129  1.4
DT         -1.8888   0.3955  -4.78  0.002  1.2
Dsq         1.7407   0.6639   2.62  0.034  1.3
FD          1.0535   0.4198   2.51  0.040  1.1
Fsq         1.1859   0.6964   1.70  0.132  1.4


S = 1.12158   R-Sq = 96.9%   R-Sq(adj) = 93.3%

PRESS = 53.4695   R-Sq(pred) = 80.89%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression       8  271.049  33.881  26.93  0.000
Residual Error   7    8.806   1.258
Total           15  279.854


No replicates.
Cannot do pure error test.


Source  DF   Seq SS
P        1  172.806
F        1   25.440
D        1   26.700
T        1    0.246
DT       1   16.882
Dsq      1   18.322
FD       1    7.004
Fsq      1    3.648


Durbin-Watson statistic = 2.12921

* ERROR * Not enough data for lack of fit test
```

Appendix 5.1 Face-centered central composite design repeated for each level of the qualitative factor and its results for 28-day compressive strength

Exp. run order	Std. order	Parameters				RESULTS						
		P	F	D	T	Run-1	Run-2	Run-3	Run-4	Run-5	Run-6	μ (MPa)
4	1	-1	-1	-1	-1	29,03	34,91	28,64	34,52	37,27	36,09	33,41
2	2	1	-1	-1	-1	24,71	22,75	23,14	27,07	21,57	22,75	23,67
31	3	-1	1	-1	-1	29,03	41,97	42,36	37,66	32,17	30,20	35,57
30	4	1	1	-1	-1	21,97	25,89	27,46	25,89	25,50	21,97	24,78
32	5	-1	-1	1	-1	26,67	24,32	32,17	27,46	30,60	28,64	28,31
33	6	1	-1	1	-1	29,42	28,24	30,20	27,07	29,81	26,28	28,50
3	7	-1	1	1	-1	36,48	38,44	29,42	40,40	36,48	39,62	36,81
40	8	1	1	1	-1	28,64	27,46	25,50	28,64	29,42	30,60	28,37
15	9	-1	0	0	-1	33,73	32,95	37,27	33,73	32,17	36,87	34,45
22	10	1	0	0	-1	23,93	22,75	24,32	23,54	27,46	28,24	25,04
29	11	0	-1	0	-1	27,07	29,81	29,42	25,50	25,50	21,18	26,41
23	12	0	1	0	-1	33,73	32,17	34,52	33,73	31,38	31,77	32,88
35	13	0	0	-1	-1	32,56	30,60	27,46	32,17	29,81	30,60	30,53
36	14	0	0	1	-1	30,60	33,34	32,56	31,38	27,46	32,17	31,25
10	15	0	0	0	-1	28,64	25,11	25,89	19,61	24,71	27,07	25,17
5	16	0	0	0	-1	27,85	33,34	29,81	28,64	30,20	30,20	30,01
28	17	0	0	0	-1	28,24	31,38	27,46	30,60	32,56	30,60	30,14
34	18	0	0	0	-1	25,50	29,42	26,67	25,11	27,07	28,24	27,00
9	19	0	0	0	-1	33,34	32,56	29,03	31,77	28,24	26,28	30,20
19	20	0	0	0	-1	31,38	30,60	23,93	31,77	29,42	26,67	28,96
11	21	-1	-1	-1	1	36,48	21,18	29,03	38,44	29,42	29,81	30,73
37	22	1	-1	-1	1	25,69	30,99	27,85	23,54	22,36	20,01	25,07
1	23	-1	1	-1	1	40,80	36,09	38,44	40,40	40,01	36,09	38,64
39	24	1	1	-1	1	30,60	21,57	28,64	25,11	27,46	20,79	25,69
27	25	-1	-1	1	1	29,42	29,81	23,93	32,95	34,13	30,20	30,07
12	26	1	-1	1	1	27,07	27,07	27,07	27,46	29,42	26,28	27,39
21	27	-1	1	1	1	39,62	36,09	36,48	34,13	39,23	34,52	36,68
7	28	1	1	1	1	22,36	26,67	24,71	29,81	21,97	25,89	25,24
16	29	-1	0	0	1	28,24	34,52	32,17	31,38	31,77	28,64	31,12
25	30	1	0	0	1	29,81	27,85	24,32	28,64	27,85	29,42	27,98
26	31	0	-1	0	1	31,77	23,93	31,38	27,07	26,67	28,64	28,24
17	32	0	1	0	1	38,44	34,52	28,64	36,48	37,27	40,80	36,02
38	33	0	0	-1	1	34,13	30,60	33,73	28,64	33,34	28,64	31,51
8	34	0	0	1	1	31,38	31,38	30,20	31,38	32,17	30,60	31,19
13	35	0	0	0	1	34,91	30,20	33,73	27,07	32,95	29,03	31,32
24	36	0	0	0	1	31,77	29,42	30,20	30,20	29,03	30,60	30,20
14	37	0	0	0	1	30,60	26,67	28,24	24,32	29,81	31,38	28,50
6	38	0	0	0	1	25,89	29,03	29,03	26,28	26,67	20,79	26,28
18	39	0	0	0	1	30,99	30,20	30,60	27,07	30,60	32,17	30,27
20	40	0	0	0	1	28,64	29,03	31,77	29,03	26,28	29,81	29,09

Appendix 5.2 The regression analysis for 28-day compressive strength that includes only main factor terms

```
The regression equation is
CS28 = 29.8 - 3.70 P + 1.94 F + 0.210 D + 0.244 T


Predictor     Coef  SE Coef      T      P  VIF
Constant   29.8173   0.3483  85.60  0.000
P          -3.7030   0.4926  -7.52  0.000  1.0
F           1.9440   0.4926   3.95  0.000  1.0
D           0.2105   0.4926   0.43  0.672  1.0
T           0.2443   0.3483   0.70  0.488  1.0


S = 2.20309   R-Sq = 67.5%   R-Sq(adj) = 63.8%

PRESS = 231.694   R-Sq(pred) = 55.70%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression       4  353.099  88.275  18.19  0.000
Residual Error  35  169.876   4.854
  Lack of Fit   25  132.871   5.315   1.44  0.281
  Pure Error    10   37.004   3.700
Total           39  522.975


 28 rows with no replicates


Source  DF   Seq SS
P        1  274.244
F        1   75.583
D        1    0.886
T        1    2.386


Unusual Observations

Obs     P    CS28     Fit  SE Fit  Residual  St Resid
 10  1.00  28.500  24.137   0.985     4.363     2.21R
 21  0.00  25.170  29.573   0.493    -4.403    -2.05R

R denotes an observation with a large standardized residual.


Durbin-Watson statistic = 1.85702


Lack of fit test
Possible interaction in variable P (P-Value = 0.070)

Overall lack of fit test is significant at P = 0.070
```

Appendix 5.3 Regression analysis based on face-centered central composite design and applied for CS28 involving all two-way interactions and quadratic terms

Regression Analysis: CS28 versus P, F, ...

The regression equation is

```
CS28 = 29.5 - 3.70 P + 1.94 F + 0.210 D + 0.446 T - 0.686 Psq + 0.554
Fsq
       + 0.786 Dsq - 1.61 PF + 1.05 PD + 0.116 PT + 0.064 FD + 0.133 FT
       - 0.318 DT - 0.690 PsqT + 0.650 FsqT - 0.363 DsqT - 0.398 PFT
       - 0.573 FDT - 0.487 PDT
```

Predictor	Coef	SE Coef	T	P	VIF
Constant	29.4905	0.4964	59.41	0.000	
P	-3.7030	0.4566	-8.11	0.000	1.0
F	1.9440	0.4566	4.26	0.000	1.0
D	0.2105	0.4566	0.46	0.650	1.0
T	0.4462	0.4964	0.90	0.379	2.4
Psq	-0.6864	0.8707	-0.79	0.440	1.8
Fsq	0.5536	0.8707	0.64	0.532	1.8
Dsq	0.7861	0.8707	0.90	0.377	1.8
PF	-1.6081	0.5105	-3.15	0.005	1.0
PD	1.0481	0.5105	2.05	0.053	1.0
PT	0.1160	0.4566	0.25	0.802	1.0
FD	0.0644	0.5105	0.13	0.901	1.0
FT	0.1330	0.4566	0.29	0.774	1.0
DT	-0.3175	0.4566	-0.70	0.495	1.0
PsqT	-0.6905	0.8707	-0.79	0.437	3.6
FsqT	0.6495	0.8707	0.75	0.464	3.6
DsqT	-0.3630	0.8707	-0.42	0.681	3.6
PFT	-0.3981	0.5105	-0.78	0.445	1.0
FDT	-0.5731	0.5105	-1.12	0.275	1.0
PDT	-0.4869	0.5105	-0.95	0.352	1.0

S = 2.04190   R-Sq = 84.1%   R-Sq(adj) = 68.9%

PRESS = 475.818   R-Sq(pred) = 9.02%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	19	439.588	23.136	5.55	0.000
Residual Error	20	83.387	4.169		
Lack of Fit	10	46.383	4.638	1.25	0.364
Pure Error	10	37.004	3.700		
Total	39	522.975			

28 rows with no replicates

Source	DF	Seq SS
P	1	274.244
F	1	75.583
D	1	0.886
T	1	2.386
Psq	1	0.138
Fsq	1	4.607
Dsq	1	3.399
PF	1	41.377
PD	1	17.577
PT	1	0.269
FD	1	0.066
FT	1	0.354
DT	1	2.016
PsqT	1	2.688
FsqT	1	1.687
DsqT	1	0.725
PFT	1	2.536
FDT	1	5.256
PDT	1	3.793

Unusual Observations

Obs	P	CS28	Fit	SE Fit	Residual	St Resid
21	0.00	25.170	29.044	0.702	-3.874	-2.02R
29	1.00	27.980	24.973	1.431	3.007	2.06R

R denotes an observation with a large standardized residual.

Durbin-Watson statistic = 1.80818

* ERROR * Not enough data for lack of fit test

Appendix 5.4 Regression analysis for the model applied for 28-day mean compressive strength based on the face-centered central composite design after elimination of insignificant terms

```
The regression equation is
CS28 = 29.8 - 3.70 P + 1.94 F - 1.61 PF


Predictor      Coef  SE Coef      T      P  VIF
Constant    29.8173   0.3025  98.57  0.000
P           -3.7030   0.4278  -8.66  0.000  1.0
F            1.9440   0.4278   4.54  0.000  1.0
PF          -1.6081   0.4783  -3.36  0.002  1.0


S = 1.91319   R-Sq = 74.8%   R-Sq(adj) = 72.7%

PRESS = 162.638   R-Sq(pred) = 68.90%


Analysis of Variance

 Source          DF      SS      MS      F      P
Regression        3  391.20  130.40  35.63  0.000
Residual Error   36  131.77    3.66
  Lack of Fit     5   21.47    4.29   1.21  0.329
  Pure Error     31  110.30    3.56
Total            39  522.97


Source  DF  Seq SS
P        1  274.24
F        1   75.58
PF       1   41.38


Unusual Observations

Obs     P    CS28     Fit  SE Fit  Residual  St Resid
 21  0.00  25.170  29.817   0.303    -4.647     -2.46R
 35  0.00  36.020  31.761   0.524     4.259      2.31R

R denotes an observation with a large standardized residual.


Durbin-Watson statistic = 2.19336

No evidence of lack of fit (P >= 0.1).
```

Appendix 5.5 Regression analysis for mean 28-day compressive strength when activator dosage and its interaction with natural pozzolan content is included in regression parameters

Regression Analysis: CS28 versus P, F, D, PF, PD

```
The regression equation is
CS28 = 29.8 - 3.70 P + 1.94 F + 0.210 D - 1.61 PF + 1.05 PD


Predictor      Coef  SE Coef       T      P  VIF
Constant    29.8173   0.2886  103.30  0.000
P           -3.7030   0.4082   -9.07  0.000  1.0
F            1.9440   0.4082    4.76  0.000  1.0
D            0.2105   0.4082    0.52  0.609  1.0
PF          -1.6081   0.4564   -3.52  0.001  1.0
PD           1.0481   0.4564    2.30  0.028  1.0


S = 1.82554   R-Sq = 78.3%   R-Sq(adj) = 75.1%

PRESS = 148.735   R-Sq(pred) = 71.56%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression       5  409.667  81.933  24.59  0.000
Residual Error  34  113.308   3.333
  Lack of Fit    9   41.125   4.569   1.58  0.175
  Pure Error    25   72.182   2.887
Total           39  522.975


Source  DF   Seq SS
P        1  274.244
F        1   75.583
D        1    0.886
PF       1   41.377
PD       1   17.577


Unusual Observations

Obs     P    CS28     Fit  SE Fit  Residual  St Resid
 21  0.00  25.170  29.817   0.289    -4.647     -2.58R
 35  0.00  36.020  31.761   0.500     4.259      2.43R

R denotes an observation with a large standardized residual.


Durbin-Watson statistic = 1.91513

No evidence of lack of fit (P >= 0.1).
```

Appendix 5.6 Regression analyses in order to check the significance of the interaction between levels of the qualitative factor and quantitative factors proposed by Batmaz and Tunali (2003) for mean 28-day compressive strength

Regression Analysis: CS28 versus P, F, D, Psq, Fsq, Dsq, PF, PD, FD *(to calculate SSE1)*

```
The regression equation is
CS28 = 29.5 - 3.70 P + 1.94 F + 0.210 D - 0.686 Psq + 0.554 Fsq + 0.786
Dsq
       - 1.61 PF + 1.05 PD + 0.064 FD

Predictor     Coef  SE Coef      T      P  VIF
Constant   29.4905   0.4550  64.82  0.000
P          -3.7030   0.4185  -8.85  0.000  1.0
F           1.9440   0.4185   4.64  0.000  1.0
D           0.2105   0.4185   0.50  0.619  1.0
Psq        -0.6864   0.7981  -0.86  0.397  1.8
Fsq         0.5536   0.7981   0.69  0.493  1.8
Dsq         0.7861   0.7981   0.99  0.332  1.8
PF         -1.6081   0.4679  -3.44  0.002  1.0
PD          1.0481   0.4679   2.24  0.033  1.0
FD          0.0644   0.4679   0.14  0.891  1.0

S = 1.87170   R-Sq = 79.9%   R-Sq(adj) = 73.9%
PRESS = 183.405   R-Sq(pred) = 64.93%

Analysis of Variance

Source          DF       SS      MS      F      P
Regression       9  417.878  46.431  13.25  0.000
Residual Error  30  105.097   3.503
  Lack of Fit    5   32.915   6.583   2.28  0.077
  Pure Error    25   72.182   2.887
Total           39  522.975

Source  DF   Seq SS
P        1  274.244
F        1   75.583
D        1    0.886
Psq      1    0.138
Fsq      1    4.607
Dsq      1    3.399
PF       1   41.377
PD       1   17.577
FD       1    0.066

Unusual Observations

Obs     P    CS28     Fit  SE Fit  Residual  St Resid
 21  0.00  25.170  29.491   0.455    -4.321    -2.38R
 35  0.00  36.020  31.988   0.927     4.032     2.48R
R denotes an observation with a large standardized residual.

Durbin-Watson statistic = 1.98380

No evidence of lack of fit (P >= 0.1).
```

Regression Analysis: CS28 versus P, F, D, Psq, Fsq, Dsq, PF, PD, FD, T *(to calculate SSE2)*

The regression equation is
CS28 = 29.5 - 3.70 P + 1.94 F + 0.210 D - 0.686 Psq + 0.554 Fsq + 0.786 Dsq
- 1.61 PF + 1.05 PD + 0.064 FD + 0.244 T

Predictor	Coef	SE Coef	T	P	VIF
Constant	29.4905	0.4575	64.46	0.000	
P	-3.7030	0.4208	-8.80	0.000	1.0
F	1.9440	0.4208	4.62	0.000	1.0
D	0.2105	0.4208	0.50	0.621	1.0
Psq	-0.6864	0.8025	-0.86	0.399	1.8
Fsq	0.5536	0.8025	0.69	0.496	1.8
Dsq	0.7861	0.8025	0.98	0.335	1.8
PF	-1.6081	0.4705	-3.42	0.002	1.0
PD	1.0481	0.4705	2.23	0.034	1.0
FD	0.0644	0.4705	0.14	0.892	1.0
T	0.2443	0.2976	0.82	0.418	1.0

S = 1.88196   R-Sq = 80.4%   R-Sq(adj) = 73.6%
PRESS = 194.247   R-Sq(pred) = 62.86%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	10	420.264	42.026	11.87	0.000
Residual Error	29	***102.711***	3.542		
Lack of Fit	19	65.707	3.458	0.93	0.571
Pure Error	10	37.004	3.700		
Total	39	522.975			

28 rows with no replicates

Source	DF	Seq SS
P	1	274.244
F	1	75.583
D	1	0.886
Psq	1	0.138
Fsq	1	4.607
Dsq	1	3.399
PF	1	41.377
PD	1	17.577
FD	1	0.066
T	1	2.386

Unusual Observations

Obs	P	CS28	Fit	SE Fit	Residual	St Resid
21	0.00	25.170	29.246	0.546	-4.076	-2.26R
35	0.00	36.020	32.232	0.979	3.788	2.36R
38	1.00	25.240	28.344	1.222	-3.104	-2.17R

R denotes an observation with a large standardized residual.

Durbin-Watson statistic = 1.90645

No evidence of lack of fit (P >= 0.1).

Regression Analysis: CS28 versus P, F, D, Psq, Fsq, Dsq, PF, PD, FD, T, PT, FT, DT, PFT, PDT, FDT, PsqT, FsqT, DsqT
(to calculate SSE3)

```
The regression equation is
CS28 = 29.5 - 3.70 P + 1.94 F + 0.210 D + 0.446 T - 0.686 Psq + 0.554
Fsq
       + 0.786 Dsq - 1.61 PF + 1.05 PD + 0.116 PT + 0.064 FD + 0.133 FT
       - 0.318 DT - 0.690 PsqT + 0.650 FsqT - 0.363 DsqT - 0.398 PFT
       - 0.573 FDT - 0.487 PDT
```

Predictor	Coef	SE Coef	T	P	VIF
Constant	29.4905	0.4964	59.41	0.000	
P	-3.7030	0.4566	-8.11	0.000	1.0
F	1.9440	0.4566	4.26	0.000	1.0
D	0.2105	0.4566	0.46	0.650	1.0
T	0.4462	0.4964	0.90	0.379	2.4
Psq	-0.6864	0.8707	-0.79	0.440	1.8
Fsq	0.5536	0.8707	0.64	0.532	1.8
Dsq	0.7861	0.8707	0.90	0.377	1.8
PF	-1.6081	0.5105	-3.15	0.005	1.0
PD	1.0481	0.5105	2.05	0.053	1.0
PT	0.1160	0.4566	0.25	0.802	1.0
FD	0.0644	0.5105	0.13	0.901	1.0
FT	0.1330	0.4566	0.29	0.774	1.0
DT	-0.3175	0.4566	-0.70	0.495	1.0
PsqT	-0.6905	0.8707	-0.79	0.437	3.6
FsqT	0.6495	0.8707	0.75	0.464	3.6
DsqT	-0.3630	0.8707	-0.42	0.681	3.6
PFT	-0.3981	0.5105	-0.78	0.445	1.0
FDT	-0.5731	0.5105	-1.12	0.275	1.0
PDT	-0.4869	0.5105	-0.95	0.352	1.0

S = 2.04190   R-Sq = 84.1%   R-Sq(adj) = 68.9%

PRESS = 475.818   R-Sq(pred) = 9.02%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	19	439.588	23.136	5.55	0.000
Residual Error	20	***83.387***	4.169		
Lack of Fit	10	46.383	4.638	1.25	0.364
Pure Error	10	37.004	3.700		
Total	39	522.975			

28 rows with no replicates

Source	DF	Seq SS
P	1	274.244
F	1	75.583
D	1	0.886
T	1	2.386
Psq	1	0.138
Fsq	1	4.607
Dsq	1	3.399
PF	1	41.377
PD	1	17.577
PT	1	0.269
FD	1	0.066
FT	1	0.354
DT	1	2.016
PsqT	1	2.688
FsqT	1	1.687
DsqT	1	0.725
PFT	1	2.536
FDT	1	5.256
PDT	1	3.793

Unusual Observations

Obs	P	CS28	Fit	SE Fit	Residual	St Resid
21	0.00	25.170	29.044	0.702	-3.874	-2.02R
29	1.00	27.980	24.973	1.431	3.007	2.06R

R denotes an observation with a large standardized residual.

Durbin-Watson statistic = 1.80818

* ERROR * Not enough data for lack of fit test

Appendix 5.7 Regression analysis for activator type NaOH

Regression Analysis: CS28 versus P, F, PF, PD, D

The regression equation is
CS28 = 29.6 - 3.82 P + 1.81 F - 1.21 PF + 1.53 PD + 0.528 D

Predictor	Coef	SE Coef	T	P	VIF
Constant	29.5730	0.4199	70.43	0.000	
P	-3.8190	0.5938	-6.43	0.000	1.0
F	1.8110	0.5938	3.05	0.009	1.0
PF	-1.2100	0.6639	-1.82	0.090	1.0
PD	1.5350	0.6639	2.31	0.037	1.0
D	0.5280	0.5938	0.89	0.389	1.0

S = 1.87784   R-Sq = 81.1%   R-Sq(adj) = 74.4%

PRESS = 123.368   R-Sq(pred) = 52.80%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	5	211.995	42.399	12.02	0.000
Residual Error	14	49.368	3.526		
Lack of Fit	9	27.996	3.111	0.73	0.681
Pure Error	5	21.372	4.274		
Total	19	261.363			

14 rows with no replicates

Source	DF	Seq SS
P	1	145.848
F	1	32.797
PF	1	11.713
PD	1	18.850
D	1	2.788

Durbin-Watson statistic = 2.30086

No evidence of lack of fit (P >= 0.1).

Appendix 5.8 Regression analysis for activator type Na_2SO_4

The regression equation is
CS28 = 30.3 - 3.59 P + 2.08 F - 2.01 PF - 0.401 Psq

Predictor	Coef	SE Coef	T	P	VIF
Constant	30.2620	0.6023	50.24	0.000	
P	-3.5870	0.6023	-5.96	0.000	1.0
F	2.0770	0.6023	3.45	0.004	1.0
PF	-2.0062	0.6734	-2.98	0.009	1.0
Psq	-0.4010	0.8518	-0.47	0.645	1.0

S = 1.90467   R-Sq = 79.0%   R-Sq(adj) = 73.4%

PRESS = 89.8529   R-Sq(pred) = 65.34%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	4	204.809	51.202	14.11	0.000
Residual Error	15	54.416	3.628		
Lack of Fit	4	27.354	6.838	2.78	0.081
Pure Error	11	27.063	2.460		
Total	19	259.226			

4 rows with no replicates

Source	DF	Seq SS
P	1	128.666
F	1	43.139
PF	1	32.200
Psq	1	0.804

Obs	P	CS28	Fit	SE Fit	Residual	St Resid
1	-1.00	30.730	29.365	1.242	1.365	0.95
2	-1.00	30.070	29.365	1.242	0.705	0.49
3	0.00	28.240	28.185	0.852	0.055	0.03
4	1.00	25.070	26.203	1.242	-1.133	-0.78
5	1.00	27.390	26.203	1.242	1.187	0.82
6	-1.00	31.120	33.448	0.852	-2.328	-1.37
7	0.00	31.510	30.262	0.602	1.248	0.69
8	0.00	31.320	30.262	0.602	1.058	0.59
9	0.00	30.200	30.262	0.602	-0.062	-0.03
10	0.00	28.500	30.262	0.602	-1.762	-0.98
11	0.00	26.280	30.262	0.602	-3.982	-2.20R
12	0.00	30.270	30.262	0.602	0.008	0.00
13	0.00	29.090	30.262	0.602	-1.172	-0.65
14	0.00	31.190	30.262	0.602	0.928	0.51
15	1.00	27.980	26.274	0.852	1.706	1.00
16	-1.00	38.640	37.531	1.242	1.109	0.77
17	-1.00	36.680	37.531	1.242	-0.851	-0.59
18	0.00	36.020	32.339	0.852	3.681	2.16R
19	1.00	25.690	26.345	1.242	-0.655	-0.45
20	1.00	25.240	26.345	1.242	-1.105	-0.76

R denotes an observation with a large standardized residual.

Durbin-Watson statistic = 1.98417

No evidence of lack of fit (P >= 0.1).

Appendix 5.9 Economic design alternatives for mean 28-day compressive strength

Main FCCD (40 0bservations)

```
Condition number:                                    5.5
D-optimality (determinant of XTX):          1.47640E+17
A-optimality (trace of inv(XTX)):               1.11705
G-optimality (avg leverage/max leverage):      0.612326
V-optimality (average leverage):                   0.35
Maximum leverage:                              0.571591
```

WD (16 observations)

```
Condition number:                               68.0873
D-optimality (determinant of XTX):          1.24613E+10
A-optimality (trace of inv(XTX)):               8.36393
G-optimality (avg leverage/max leverage):         0.875
V-optimality (average leverage):                  0.875
Maximum leverage:                                     1
```

DJ (16 observations)

```
Condition number:                               8.81560
D-optimality (determinant of XTX):          3.99432E+11
A-optimality (trace of inv(XTX)):               3.22110
G-optimality (avg leverage/max leverage):      0.894231
V-optimality (average leverage):                  0.875
Maximum leverage:                              0.978495
```

WD Design					DJ Design				
Parameters				μ (MPa)	Parameters				μ (MPa)
P	F	D	T		P	F	D	T	
-1	1	-1	1	38.64	-1	0	0	1	31.12
-1	1	1	1	36.68	-1	1	-1	-1	35.57
1	-1	1	1	27.39	-1	1	1	-1	36.81
1	1	1	-1	28.37	0	1	0	1	36.02
-1	-1	-1	-1	33.41	0	0	-1	1	31.51
1	-1	-1	-1	23.67	-1	-1	-1	-1	33.41
-1	-1	1	-1	28.31	-1	-1	1	-1	28.31
1	1	-1	-1	24.78	0	0	0	-1	28.58
0	0	0	1	29.28	0	0	0	1	29.28
0	0	0	-1	28.58	1	1	-1	-1	24.78
1	0	0	-1	25.04	1	1	1	-1	28.37
-1	0	0	1	31.12	0	0	1	1	31.19
0	1	0	-1	32.88	0	-1	0	1	28.24
0	-1	0	1	28.24	1	-1	-1	-1	23.67
0	0	1	1	31.19	1	-1	1	-1	28.50
0	0	-1	1	31.51	1	0	0	1	27.98

Appendix 5.10 Regression analysis for DJ design

The regression equation is
CS28 = 30.2 - 3.19 P + 1.94 F - 1.21 PF

Predictor	Coef	SE Coef	T	P	VIF
Constant	30.2088	0.5728	52.74	0.000	
P	-3.1920	0.7246	-4.41	0.001	1.0
F	1.9420	0.7246	2.68	0.020	1.0
PF	-1.2100	0.8101	-1.49	0.161	1.0

S = 2.29130   R-Sq = 70.6%   R-Sq(adj) = 63.3%

PRESS = 132.341   R-Sq(pred) = 38.25%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	3	151.315	50.438	9.61	0.002
Residual Error	12	63.001	5.250		
Lack of Fit	5	24.966	4.993	0.92	0.520
Pure Error	7	38.035	5.434		
Total	15	214.316			

4 rows with no replicates

Source	DF	Seq SS
P	1	101.889
F	1	37.714
PF	1	11.713

Durbin-Watson statistic = 1.67027

No evidence of lack of fit (P >= 0.1).

Appendix 5.11 Regression analysis for WD design

The regression equation is
CS28 = 29.8 - 3.89 P + 2.03 F - 0.007 D - 1.44 PF + 1.80 PD - 1.16 Psq + 1.32 Fsq

Predictor	Coef	SE Coef	T	P	VIF
Constant	29.8389	0.5685	52.49	0.000	
P	-3.8910	0.3975	-9.79	0.000	1.0
F	2.0330	0.3975	5.11	0.001	1.0
D	-0.0070	0.3975	-0.02	0.986	1.0
PF	-1.4388	0.4444	-3.24	0.012	1.0
PD	1.7963	0.4444	4.04	0.004	1.0
Psq	-1.1566	0.7339	-1.58	0.154	1.3
Fsq	1.3234	0.7339	1.80	0.109	1.3

S = 1.25701   R-Sq = 95.0%   R-Sq(adj) = 90.7%

PRESS = 48.6838   R-Sq(pred) = 80.83%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	7	241.329	34.476	21.82	0.000
Residual Error	8	12.641	1.580		
Lack of Fit	7	12.396	1.771	7.23	0.279
Pure Error	1	0.245	0.245		
Total	15	253.970			

14 rows with no replicates

Source	DF	Seq SS
P	1	151.399
F	1	41.331
D	1	0.000
PF	1	16.560
PD	1	25.812
Psq	1	1.089
Fsq	1	5.137

Durbin-Watson statistic = 1.76501

Appendix 6.1. Observations of standard deviation estimates of 7-day and 28-day compressive strengths (MPa) and cost values (TL)

Std #	Run #	P	F	D	T	Stdev7	Stdev28	COST
1	4	-1.00	-1.00	-1.00	-1	2.12935	3.6749	0.11525
2	2	1.00	-1.00	-1.00	-1	1.0932	1.94821	0.13802
3	31	-1.00	1.00	-1.00	-1	4.2857	5.91095	0.18035
4	30	1.00	1.00	-1.00	-1	1.06467	2.27942	0.24032
5	32	-1.00	-1.00	1.00	-1	1.39792	2.81139	0.14044
6	33	1.00	-1.00	1.00	-1	1.32831	1.58209	0.16647
7	3	-1.00	1.00	1.00	-1	0.974105	3.95716	0.20554
8	40	1.00	1.00	1.00	-1	0.952811	1.74841	0.26877
9	15	-1.00	0.00	0.00	-1	1.14812	2.1112	0.14286
10	22	1.00	0.00	0.00	-1	1.92836	2.25226	0.18884
11	29	0.00	-1.00	0.00	-1	1.33601	3.16417	0.13150
12	23	0.00	1.00	0.00	-1	2.60987	1.27512	0.21564
13	35	0.00	0.00	-1.00	-1	2.95374	1.83011	0.15912
14	36	0.00	0.00	1.00	-1	2.00657	2.08554	0.18192
15	10	0.00	0.00	0.00	-1	1.74988	3.07289	0.16737
16	5	0.00	0.00	0.00	-1	1.41976	1.88533	0.16737
17	28	0.00	0.00	0.00	-1	2.25226	1.92836	0.16737
18	34	0.00	0.00	0.00	-1	0.521384	1.6347	0.16737
19	9	0.00	0.00	0.00	-1	1.6963	2.77374	0.16737
20	19	0.00	0.00	0.00	-1	2.0155	3.07289	0.16737
21	11	-1.00	-1.00	-1.00	1	4.23514	6.15078	0.11775
22	37	1.00	-1.00	-1.00	1	1.58856	3.9625	0.14399
23	1	-1.00	1.00	-1.00	1	2.15449	2.13055	0.18285
24	39	1.00	1.00	-1.00	1	1.34557	3.92854	0.24846
25	27	-1.00	-1.00	1.00	1	0.675639	3.54923	0.13601
26	12	1.00	-1.00	1.00	1	1.37386	1.06467	0.16203
27	21	-1.00	1.00	1.00	1	2.68829	2.31071	0.19959
28	7	1.00	1.00	1.00	1	1.97566	2.92144	0.26693
29	16	-1.00	0.00	0.00	1	1.47644	2.34923	0.15003
30	25	1.00	0.00	0.00	1	2.02565	1.96394	0.19523
31	26	0.00	-1.00	0.00	1	2.3796	2.99769	0.13989
32	17	0.00	1.00	0.00	1	1.76156	4.1766	0.22407
33	38	0.00	0.00	-1.00	1	3.30452	2.55023	0.16487
34	8	0.00	0.00	1.00	1	2.57126	0.690655	0.18456
35	13	0.00	0.00	0.00	1	1.35128	3.03257	0.17411
36	24	0.00	0.00	0.00	1	1.32831	0.960851	0.17411
37	14	0.00	0.00	0.00	1	2.97364	2.65662	0.17411
38	6	0.00	0.00	0.00	1	1.7322	3.01815	0.17411
39	18	0.00	0.00	0.00	1	1.1095	1.70835	0.17411
40	20	0.00	0.00	0.00	1	1.52261	1.77895	0.17411

Appendix 6.2. Regression output for cost function from Design-Expert software

Response 1 COST

ANOVA for Response Surface Reduced Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.051	8	6.35E-03	1344.78	< 0.0001	significant
A-Pozzolan	*0.01*	*1*	*0.01*	*2130.27*	*< 0.0001*	
B-Fineness	*0.035*	*1*	*0.035*	*7496.64*	*< 0.0001*	
C-Dosage	*2.45E-03*	*1*	*2.45E-03*	*518.7*	*< 0.0001*	
D-Type	*1.67E-04*	*1*	*1.67E-04*	*35.31*	*< 0.0001*	
AB	*1.50E-03*	*1*	*1.50E-03*	*318.56*	*< 0.0001*	
CD	*7.56E-05*	*1*	*7.56E-05*	*16.02*	*0.0004*	
B2	*4.54E-04*	*1*	*4.54E-04*	*96.19*	*< 0.0001*	
C2	*6.81E-05*	*1*	*6.81E-05*	*14.43*	*0.0006*	
Residual	1.46E-04	31	4.72E-06			
Lack of Fit	*1.46E-04*	*21*	*6.97E-06*			
Pure Error	*0*	*10*	*0*			
Cor Total	0.051	39				

The Model F-value of 1344.78 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.
Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, C, D, AB, CD, B2, C2 are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy),
model reduction may improve your model.

Std. Dev.	2.17E-03	R-Squared	0.9971
Mean	0.18	Adj R-Squared	0.9964
C.V. %	1.23	Pred R-Squared	0.9945
PRESS	2.82E-04	Adeq Precision	150.58

The "Pred R-Squared" of 0.9945 is in reasonable agreement with the "Adj R-Squared" of 0.9964.
"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 150.580 indicates an adequate signal. This model can be used to navigate the design space.

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	0.17	1	5.15E-04	0.17	0.17	
A-Pozzolan	0.022	1	4.86E-04	0.021	0.023	1
B-Fineness	0.042	1	4.86E-04	0.041	0.043	1
C-Dosage	0.011	1	4.86E-04	0.01	0.012	1
D-Type	2.04E-03	1	3.44E-04	1.34E-03	2.74E-03	1
AB	9.69E-03	1	5.43E-04	8.59E-03	0.011	1
CD	-1.94E-03	1	4.86E-04	-2.94E-03	-9.54E-04	1
B2	8.42E-03	1	8.59E-04	6.67E-03	0.01	1.56
C2	3.26E-03	1	8.59E-04	1.51E-03	5.01E-03	1.56

Final Equation in Terms of Coded Factors:

COST	=
0.17	
0.022	* A
0.042	* B
0.011	* C
2.04E-03	* D
9.69E-03	* A * B
-1.94E-03	* C * D
8.42E-03	* B2
3.26E-03	* C2

Final Equation in Terms of Actual Factors:

Type	NaOH
COST	=
0.16812	
0.02242	* Pozzolan
0.042058	* Fineness
0.013007	* Dosage
9.69E-03	* Pozzolan * Fineness
8.42E-03	* Fineness2
3.26E-03	* Dosage2

Type	Na2SO4
COST	=
0.1722	
0.02242	* Pozzolan
0.042058	* Fineness
9.12E-03	* Dosage
9.69E-03	* Pozzolan * Fineness
8.42E-03	* Fineness2
3.26E-03	* Dosage2

Appendix 6.3. Regression output for standard deviation of CS7 from Design-Expert software

Response 1 STDEV-CS7

ANOVA for Response Surface Reduced Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	11.42913	5	2.285827	4.6967	0.0023	significant
A-Pozzolan	2.105047	1	2.105047	4.325252	0.0452	
C-Dosage	3.370616	1	3.370616	6.925622	0.0127	
AC	3.617009	1	3.617009	7.431888	0.0101	
A^2	1.506694	1	1.506694	3.095813	0.0875	
C^2	2.146861	1	2.146861	4.411168	0.0432	
Residual	16.54739	34	0.486688			
Lack of Fit	12.46461	24	0.519359	1.272071	0.3581	not significant
Pure Error	4.08278	10	0.408278			
Cor Total	27.97652	39				

The Model F-value of 4.70 implies the model is significant. There is only a 0.23% chance that a "Model F-Value" this large could occur due to noise.

The "Lack of Fit F-value" of 1.27 implies the Lack of Fit is not significant relative to the pure error. There is a 35.81% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	0.69763	R-Squared	0.408526
Mean	1.86094	Adj R-Squared	0.321544
C.V. %	37.48806	Pred R-Squared	0.142562
PRESS	23.98813	Adeq Precision	7.824155

The "Pred R-Squared" of 0.1426 is in reasonable agreement with the "Adj R-Squared" of 0.3215.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 7.824 indicates an adequate signal. This model can be used to navigate the design space.

Factor	**Coefficient Estimate**	**df**	**Standard Error**	**95% CI Low**	**95% CI High**	**VIF**
Intercept	1.813952	1	0.165458	1.477702	2.150202	
A-Pozzolan	-0.32443	1	0.155995	-0.64145	-0.00741	1
C-Dosage	-0.41053	1	0.155995	-0.72754	-0.09351	1
AC	0.475461	1	0.174408	0.121022	0.8299	1
A^2	-0.4852	1	0.275763	-1.04562	0.075215	1.5625
C^2	0.579178	1	0.275763	0.018761	1.139595	1.5625

Final Equation in Terms of Coded Factors:

STDEV-CS7=	
1.813952	
-0.32443	* A
-0.41053	* C
0.475461	* A * C
-0.4852	* A^2
0.579178	* C^2

Final Equation in Terms of Actual Factors:

STDEV-CS7=	
1.813952	
-0.32443	* Pozzolan
-0.41053	* Dosage
0.475461	* Pozzolan * Dosage
-0.4852	* Pozzolan^2
0.579178	* Dosage^2

Appendix 6.4 Regression output for standard deviation of CS28 from Design-Expert software

ANOVA for Response Surface Reduced Quadratic Model
Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	21.44354	4	5.360885	5.925107	0.0009	significant
A-Pozzolan	6.389731	1	6.389731	7.062237	0.0118	
B-Fineness	0.003558	1	0.003558	0.003932	0.9504	
C-Dosage	6.780193	1	6.780193	7.493794	0.0097	
B^2	8.270057	1	8.270057	9.140464	0.0047	
Residual	31.6671	35	0.904774			
Lack of Fit	26.02381	25	1.040953	1.844585	0.1564	not significant
Pure Error	5.643288	10	0.564329			
Cor Total	53.11064	39				

The Model F-value of 5.93 implies the model is significant. There is only
a 0.09% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, C, B ++2+- are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy),
model reduction may improve your model.

The "Lack of Fit F-value" of 1.84 implies the Lack of Fit is not significant relative to the pure
error. There is a 15.64% chance that a "Lack of Fit F-value" this large could occur due
to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	0.951196	R-Squared	0.403752
Mean	2.622527	Adj R-Squared	0.33561
C.V. %	36.27021	Pred R-Squared	0.165484
PRESS	44.32169	Adeq Precision	7.887209

The "Pred R-Squared" of 0.1655 is in reasonable agreement with the "Adj R-Squared" of 0.3356.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your
ratio of 7.887 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	2.167828	1	0.212694	1.736036	2.59962	
A-	-0.56523	1	0.212694	-0.99702	-0.13344	1

Pozzolan						
B-Fineness	-0.01334	1	0.212694	-0.44513	0.418455	1
C-Dosage	-0.58225	1	0.212694	-1.01404	-0.15045	1
B^2	0.909399	1	0.300795	0.298753	1.520044	1

Final Equation in Terms of Coded Factors:

STDEV-CS28=
2.167828
-0.56523 * A
-0.01334 * B
-0.58225 * C
0.909399 * B^2

Final Equation in Terms of Actual Factors:

STDEV-CS28=
2.167828
-0.56523 * Pozzolan
-0.01334 * Fineness
-0.58225 * Dosage
0.909399 * Fineness^2

Appendix 6.5 Regression output for strength to cost ratio at 7 days

Use your mouse to right click on individual cells for definitions.

Response	2	Ratio 7				
Transform:	Power	Lambda:	0.15	Constant:	0	

ANOVA for Response Surface Reduced Quadratic Model

Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	0.299012	9	0.033224	63.5373	< 0.0001	significant
A-Pozzolan	0.213492	1	0.213492	408.285	< 0.0001	
B-Fineness	0.057662	1	0.057662	110.2737	< 0.0001	
C-Dosage	0.001042	1	0.001042	1.992447	0.1684	
D-Type	0.002377	1	0.002377	4.546576	0.0413	
AC	0.005538	1	0.005538	10.59077	0.0028	
BC	0.002753	1	0.002753	5.264072	0.0289	
CD	0.007731	1	0.007731	14.78573	0.0006	
B^2	0.001772	1	0.001772	3.388324	0.0756	
C^2	0.001597	1	0.001597	3.05391	0.0908	
Residual	0.015687	30	0.000523			
Lack of Fit	0.012045	20	0.000602	1.653904	0.2081	not significant
Pure Error	0.003642	10	0.000364			
Cor Total	0.314699	39				

The Model F-value of 63.54 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, D, AC, BC, CD are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Lack of Fit F-value" of 1.65 implies the Lack of Fit is not significant relative to the pure error. There is a 20.81% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	0.022867	R-Squared	0.950153
Mean	1.982738	Adj R-Squared	0.935198
C.V. %	1.153304	Pred R-Squared	0.906489
PRESS	0.029428	Adeq Precision	37.80189

The "Pred R-Squared" of 0.9065 is in reasonable agreement with the "Adj R-Squared" of 0.9352.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 37.802 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	1.966521	1	0.005423	1.955445	1.977597	
A-Pozzolan	-0.10332	1	0.005113	-0.11376	-0.09288	1
B-Fineness	-0.05369	1	0.005113	-0.06414	-0.04325	1
C-Dosage	0.007218	1	0.005113	-0.00323	0.01766	1
D-Type	0.007709	1	0.003616	0.000325	0.015093	1
AC	0.018604	1	0.005717	0.006929	0.030279	1
BC	0.013116	1	0.005717	0.001441	0.024791	1
CD	-0.01966	1	0.005113	-0.0301	-0.00922	1
B^2	0.016638	1	0.009039	-0.00182	0.035098	1.5625
C^2	0.015796	1	0.009039	-0.00266	0.034256	1.5625

Final Equation in Terms of Coded Factors:

(Ratio 7)^0.15	=
1.966521	
-0.10332	* A
-0.05369	* B
0.007218	* C
0.007709	* D
0.018604	* A * C
0.013116	* B * C
-0.01966	* C * D
0.016638	* B^2
0.015796	* C^2

Appendix 6.6 Regression output for strength to cost ratio at 28 days

Response		3	Ratio 28				
Transform:	Power		Lambda:	0.29	Constant:	0	

ANOVA for Response Surface Reduced 2FI Model
Analysis of variance table [Partial sum of squares - Type III]

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	3.180808	5	0.636162	101.0892	< 0.0001	significant
A-Pozzolan	1.942042	1	1.942042	308.5998	< 0.0001	
B-Fineness	0.973213	1	0.973213	154.6483	< 0.0001	
C-Dosage	0.11046	1	0.11046	17.55265	0.0002	
AB	0.097939	1	0.097939	15.56297	0.0004	
AC	0.057154	1	0.057154	9.082084	0.0049	
Residual	0.213965	34	0.006293			
Lack of Fit	0.13791	24	0.005746	0.755541	0.7262	not significant
Pure Error	0.076055	10	0.007605			
Cor Total	3.394773	39				

The Model F-value of 101.09 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, B, C, AB, AC are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

The "Lack of Fit F-value" of 0.76 implies the Lack of Fit is not significant relative to the pure error. There is a 72.62% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good -- we want the model to fit.

Std. Dev.	0.079329	R-Squared	0.936972
Mean	4.45538	Adj R-Squared	0.927704
C.V. %	1.780519	Pred R-Squared	0.913225
PRESS	0.294583	Adeq Precision	39.48194

The "Pred R-Squared" of 0.9132 is in reasonable agreement with the "Adj R-Squared" of 0.9277.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 39.482 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	4.45538	1	0.012543	4.429889	4.48087	
A-Pozzolan	-0.31161	1	0.017738	-0.34766	-0.27556	1
B-Fineness	-0.22059	1	0.017738	-0.25664	-0.18454	1
C-Dosage	-0.07432	1	0.017738	-0.11037	-0.03827	1

AB	-0.07824	1	0.019832	-0.11854	-0.03793	1
AC	0.059767	1	0.019832	0.019463	0.100071	1

Final Equation in Terms of Coded Factors:

(Ratio 28)^0.29	=
4.45538	
-0.31161	* A
-0.22059	* B
-0.07432	* C
-0.07824	* A * B
0.059767	* A * C

Final Equation in Terms of Actual Factors:

(Ratio 28)^0.29	=
4.45538	
-0.31161	* Pozzolan
-0.22059	* Fineness
-0.07432	* Dosage
-0.07824	* Pozzolan * Fineness
0.059767	* Pozzolan * Dosage

Appendix 7.1 Regression analyses for both responses when the regression is applied to single observations instead of mean values of replications

Regression Analysis: CS7 versus P; F; D; T; Fsq; Dsq; PF; PD; PT; FD; DT

```
The regression equation is
CS7 = 15,4 - 3,80 P + 0,893 F + 1,43 D + 0,602 T + 1,40 Fsq + 1,42 Dsq
      + 0,563 PF + 0,662 PD - 0,382 PT + 0,638 FD - 1,21 DT


Predictor      Coef  SE Coef       T      P  VIF
Constant    15,4110   0,2097   73,48  0,000
P           -3,7956   0,1977  -19,20  0,000  1,0
F            0,8926   0,1977    4,51  0,000  1,0
D            1,4316   0,1977    7,24  0,000  1,0
T            0,6015   0,1398    4,30  0,000  1,0
Fsq          1,3992   0,3495    4,00  0,000  1,6
Dsq          1,4159   0,3495    4,05  0,000  1,6
PF           0,5634   0,2211    2,55  0,011  1,0
PD           0,6622   0,2211    3,00  0,003  1,0
PT          -0,3824   0,1977   -1,93  0,054  1,0
FD           0,6376   0,2211    2,88  0,004  1,0
DT          -1,2098   0,1977   -6,12  0,000  1,0


S = 2,16594   R-Sq = 72,7%   R-Sq(adj) = 71,3%

PRESS = 1190,96   R-Sq(pred) = 69,56%


Analysis of Variance

Source           DF       SS      MS      F      P
Regression       11  2842,32  258,39  55,08  0,000
Residual Error  228  1069,62    4,69
  Lack of Fit    18   178,83    9,94   2,34  0,002
  Pure Error    210   890,78    4,24
Total           239  3911,93


Source  DF   Seq SS
P        1  1728,77
F        1    95,60
D        1   245,93
T        1    86,84
Fsq      1   303,41
Dsq      1    76,98
PF       1    30,48
PD       1    42,10
PT       1    17,55
FD       1    39,03
DT       1   175,62


Unusual Observations

Obs      P     CS7     Fit  SE Fit  Residual  St Resid
  1  -1,00  30,990  23,754   0,637     7,236     3,50R
  4  -1,00  18,040  23,754   0,637    -5,714    -2,76R
```

63	-1,00	15,690	20,191	0,376	-4,501	-2,11R
73	0,00	22,360	17,207	0,464	5,153	2,44R
98	0,00	10,590	16,013	0,252	-5,423	-2,52R
162	0,00	12,160	17,650	0,464	-5,490	-2,59R
169	1,00	16,870	11,835	0,376	5,035	2,36R
174	1,00	16,480	11,835	0,376	4,645	2,18R
190	-1,00	27,850	23,532	0,637	4,318	2,09R
193	-1,00	23,930	18,750	0,637	5,180	2,50R
194	-1,00	23,930	18,750	0,637	5,180	2,50R
216	0,00	11,770	17,101	0,419	-5,331	-2,51R

R denotes an observation with a large standardized residual.

Durbin-Watson statistic = 1,69377

Lack of fit test
Possible interaction in variable P (P-Value = 0,011)

Possible interaction in variable D (P-Value = 0,008)

Possible interaction in variable Fsq (P-Value = 0,056)

Possible interaction in variable Dsq (P-Value = 0,007)

Overall lack of fit test is significant at P = 0,007

Regression Analysis: CS28 versus P; F; PF

The regression equation is
CS28 = 29,8 - 3,70 P + 1,94 F - 1,61 PF

Predictor	Coef	SE Coef	T	P	VIF
Constant	29,8178	0,2072	143,91	0,000	
P	-3,7018	0,2930	-12,63	0,000	1,0
F	1,9435	0,2930	6,63	0,000	1,0
PF	-1,6074	0,3276	-4,91	0,000	1,0

S = 3,20994   R-Sq = 49,1%   R-Sq(adj) = 48,5%

PRESS = 2528,94   R-Sq(pred) = 47,06%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	3	2345,73	781,91	75,89	0,000
Residual Error	236	2431,68	10,30		
Lack of Fit	5	129,03	25,81	2,59	0,027
Pure Error	231	2302,64	9,97		
Total	239	4777,41			

Source	DF	Seq SS
P	1	1644,43
F	1	453,26
PF	1	248,04

Unusual Observations

Obs	P	CS28	Fit	SE Fit	Residual	St Resid
1	-1,00	36,480	29,969	0,567	6,511	2,06R
2	-1,00	21,180	29,969	0,567	-8,789	-2,78R
4	-1,00	38,440	29,969	0,567	8,471	2,68R
17	-1,00	37,270	29,969	0,567	7,301	2,31R
36	0,00	21,180	27,874	0,359	-6,694	-2,10R
108	0,00	20,790	29,818	0,207	-9,028	-2,82R
124	0,00	19,610	29,818	0,207	-10,208	-3,19R
193	-1,00	29,030	37,071	0,567	-8,041	-2,54R
198	-1,00	30,200	37,071	0,567	-6,871	-2,17R
201	-1,00	29,420	37,071	0,567	-7,651	-2,42R
205	0,00	38,440	31,761	0,359	6,679	2,09R
210	0,00	40,800	31,761	0,359	9,039	2,83R

R denotes an observation with a large standardized residual.

Durbin-Watson statistic = 1,70858

Possible lack of fit at outer X-values (P-Value = 0,024)
Overall lack of fit test is significant at P = 0,024

Appendix 7.2 Design matrix evaluation for response surface quadratic model (Main FCCD design with 40 runs)

4 Factors: A, B, C, D

Design Matrix Evaluation for Response Surface Quadratic Model

No aliases found for Quadratic Model

Aliases are calculated based on your response selection,
taking into account missing datapoints, if necessary.
Watch for aliases among terms you need to estimate.

Degrees of Freedom for Evaluation

Model	13
Residuals	26
Lack 0f Fit	16
Pure Error	10
Corr Total	39

A recommendation is a minimum of 3 lack of fit df and 4 df for pure error.
This ensures a valid lack of fit test.
Fewer df will lead to a test that may not detect lack of fit.

Term	StdErr**	VIF	Ri-Squared	Power at 5 % alpha level for effect of 0.5 Std. Dev.	1 Std. Dev.	2 Std. Dev.
A	0.22	1	0	19.0 %	57.7 %	99.0 %
B	0.22	1	0	19.0 %	57.7 %	99.0 %
C	0.22	1	0	19.0 %	57.7 %	99.0 %
D	0.16	1	0	33.1 %	86.1 %	99.9 %
AB	0.25	1	0	16.1 %	48.6 %	97.1 %
AC	0.25	1	0	16.1 %	48.6 %	97.1 %
AD	0.22	1	0	19.0 %	57.7 %	99.0 %
BC	0.25	1	0	16.1 %	48.6 %	97.1 %
BD	0.22	1	0	19.0 %	57.7 %	99.0 %
CD	0.22	1	0	19.0 %	57.7 %	99.0 %
A^2	0.43	1.818182	0.45	20.4 %	61.7 %	99.5 %
B^2	0.43	1.818182	0.45	20.4 %	61.7 %	99.5 %
C^2	0.43	1.818182	0.45	20.4 %	61.7 %	99.5 %

**Basis Std. Dev. = 1.0

For Categorical Terms, The minimum Power for each group of terms is reported.
Standard errors should be similar within type of coefficient. Smaller is better.
Ideal VIF is 1.0. VIF's above 10 are cause for alarm,
indicating coefficients are poorly estimated due to multicollinearity.
Ideal Ri-squared is 0.0. High Ri-squared means terms are correlated with each other,
possibly leading to poor models.
Power should be approximately 80% for the effect you want to detect.
Be sure to set the Model (on previous screen) to be an estimate of the terms you expect to be significant.

Appendix 7.3 Design matrix evaluation for response surface quadratic model (DJ design wit 16 runs)

4 Factors: A, B, C, D

Design Matrix Evaluation for Response Surface Quadratic Model

No aliases found for Quadratic Model

Aliases are calculated based on your response selection,
taking into account missing datapoints, if necessary.
Watch for aliases among terms you need to estimate.

Degrees of Freedom for Evaluation

Model	13
Residuals	2
Lack 0f Fit	2
Pure Error	0
Corr Total	15

A recommendation is a minimum of 3 lack of fit df and 4 df for pure error.
This ensures a valid lack of fit test.
Fewer df will lead to a test that may not detect lack of fit.

				Power at 5 % alpha level for effect of		
Term	StdErr**	VIF	Ri-Squared	0.5 Std. Dev.	1 Std. Dev.	2 Std. Dev.
A	0.979796	9.6	0.895833	7.7 %	15.5 %	40.6 %
B	0.395285	1.5625	0.36	7.9 %	15.9 %	41.7 %
C	0.395285	1.5625	0.36	7.9 %	15.9 %	41.7 %
D	0.583095	5.1	0.803922	6.7 %	11.8 %	29.4 %
AB	0.353553	1	0	7.3 %	13.8 %	35.7 %
AC	0.353553	1	0	7.3 %	13.8 %	35.7 %
AD	1.05	10.74938	0.906971	5.3 %	6.0 %	9.1 %
BC	0.353553	1	0	7.3 %	13.8 %	35.7 %
BD	0.395285	1.5625	0.36	6.8 %	12.1 %	30.5 %
CD	0.395285	1.5625	0.36	6.8 %	12.1 %	30.5 %
A^2	1.386542	7.209375	0.861292	5.6 %	7.4 %	14.2 %
B^2	0.707107	1.875	0.466667	7.3 %	13.8 %	35.7 %
C^2	0.707107	1.875	0.466667	7.3 %	13.8 %	35.7 %

**Basis Std. Dev. = 1.0

For Categorical Terms, The minimum Power for each group of terms is reported.
Standard errors should be similar within type of coefficient. Smaller is better.
Ideal VIF is 1.0. VIF's above 10 are cause for alarm,
indicating coefficients are poorly estimated due to multicollinearity.
Ideal Ri-squared is 0.0. High Ri-squared means terms are correlated with each other,
possibly leading to poor models.
Power should be approximately 80% for the effect you want to detect.
Be sure to set the Model (on previous screen) to be an estimate of the terms you expect to be significant.

Appendix 7.4 Design matrix evaluation for response surface quadratic model (WD design wit 16 runs)

4 Factors: A, B, C, D

Design Matrix Evaluation for Response Surface Quadratic Model

No aliases found for Quadratic Model

Aliases are calculated based on your response selection,
taking into account missing datapoints, if necessary.
Watch for aliases among terms you need to estimate.

Degrees of Freedom for Evaluation

Model	13
Residuals	2
Lack 0f Fit	2
Pure Error	0
Corr Total	15

A recommendation is a minimum of 3 lack of fit df and 4 df for pure error.
This ensures a valid lack of fit test.
Fewer df will lead to a test that may not detect lack of fit.

				Power at 5 % alpha level for effect of		
Term	StdErr**	VIF	Ri-Squared	0.5 Std. Dev.	1 Std. Dev.	2 Std. Dev.
A	0.90	8.12	0.88	6.1 %	9.4 %	21.3 %
B	0.68	4.61	0.78	6.1 %	9.4 %	21.5 %
C	0.41	1.71	0.41	7.3 %	14.0 %	36.1 %
D	0.60	5.85	0.83	6.8 %	12.2 %	30.6 %
AB	0.72	4.16	0.76	5.6 %	7.2 %	13.5 %
AC	0.53	2.26	0.56	6.0 %	9.0 %	20.1 %
AD	0.94	7.97	0.87	5.3 %	6.3 %	10.1 %
BC	0.53	2.26	0.56	6.0 %	9.0 %	20.1 %
BD	1.00	10.02	0.90	5.3 %	6.1 %	9.5 %
CD	0.43	1.79	0.44	6.6 %	11.1 %	27.1 %
A^2	1.05	4.13	0.76	6.0 %	9.1 %	20.4 %
B^2	0.93	3.22	0.69	6.3 %	10.2 %	24.3 %
C^2	1.06	4.23	0.76	6.0 %	9.0 %	20.1 %

**Basis Std. Dev. = 1.0

For Categorical Terms, The minimum Power for each group of terms is reported.
Standard errors should be similar within type of coefficient. Smaller is better.
Ideal VIF is 1.0. VIF's above 10 are cause for alarm,
indicating coefficients are poorly estimated due to multicollinearity.
Ideal Ri-squared is 0.0. High Ri-squared means terms are correlated with each other,
possibly leading to poor models.
Power should be approximately 80% for the effect you want to detect.
Be sure to set the Model (on previous screen) to be an estimate of the terms you expect to be significant.