ROBUST DESIGN OF LITHIUM EXTRACTION FROM BORON CLAYS BY USING STATISTICAL DESIGN AND ANALYSIS OF EXPERIMENTS

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ABSTRACT

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In this thesis, it is aimed to design lithium extraction from boron clays using statistical design of experiments and robust design methodologies. There are several factors affecting extraction of lithium from clays. The most important of these factors have been limited to a number of six which have been gypsum to clay ratio, roasting temperature, roasting time, leaching solid to liquid ratio, leaching time and limestone to clay ratio. For every factor, three levels have been chosen and an experiment has been designed. After performing three replications for each of the experimental run, signal to noise ratio transformation, ANOVA, regression analysis and response surface methodology have been applied on the results of the experiments. Optimization and confirmation experiments have been made sequentially to find factor settings that maximize lithium extraction with minimal variation. The mean of the maximum extraction has been observed as 83.81% with a standard deviation of 4.89 and the 95% prediction interval for the mean extraction is (73.729, 94.730). This result is in agreement with the studies that have been made in

the literature. However; this study is unique in the sense that lithium is extracted from boron clays by using limestone directly from the nature, and gypsum as a waste product of boric acid production. Since these two materials add about 20% cost to the extraction process, the results of this study become important. Moreover, in this study it has been shown that statistical design of experiments help mining industry to reduce the need for standardization.

Keywords: Statistical Design of Experiments, Taguchi Method, Robust Design, Response Surface Methodology, Lithium Extraction, Boron Clays

ÖZ

BOR KİLLERİNDEN LİTYUM KAZANIMININ İSTATİSTİKSEL DENEY TASARIMI VE ANALİZİ YOLUYLA ROBUST TASARIMI

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Bu tez çalışmasında, bor killerinden lityumun kazanılmasının, istatistiksel deney tasarımı ve robust tasarım metotları uygulanarak tasarlanması amaçlanmıştır. Lityumun killerden kazanımı etkileyen çeşitli faktörler vardır. Bunlar içinde en önemlileri altı faktörde sınırlanmıştır. Bunlar jipsin kile oranı, kavurma sıcaklığı, kavurma süresi, liçin katı sıvı oranı, liç süresi, kireçtaşının kile oranıdır. Her parametre için üç seviye seçilecek şekilde, deney tasarlanmıştır. Her deney için üç tekrar yapıldıktan sonra, sinyal/gürültü oranı dönüşümü, ANOVA, regresyon analizi ve cevap yüzeyi metotları, deney sonuçları üzerinde uygulanmıştır. En yüksek lityumun çözünmesini ve en düşük sapmayı sağlayacak faktör seviyelerinin bulunması için optimizasyon ve doğrulama deneyleri bir önceki sonuçlar kullanılarak yapılmıştır. Deneyler sonucunda ortalama lityum kazanımı %83.81 olurken, standard sapma 4.89 olarak hesaplanmış, %95 tahmin aralığı ise (73.729, 94.730) olarak bulunmuştur. Elde edilen bu sonuçlar, literatürde yapılmış olan killerden lityum kazanımı çalışmaları ile uyumluluk göstermektedir. Ancak bu çalışmada killerden lityum kazanımına yeni bir bakış açısı getirilmiş ve proses esnasında kullanılan kireçtaşının doğrudan doğadan sağlanması, jips olarak ise borik asit

üretiminde açığa çıkan katı atığın kullanılması düşünülmüştür. Bu iki hammaddenin toplam proses ekonomisine yaklaşık %20'lik bir maliyet getirdiği göz önüne alındığında çok önemli olduğu düşünülmektedir. Ayrıca bu çalışmada madencilik sektöründe standardizasyona duyulan ihtiyacın istatistiksel deney tasarımının yardımıyla azaltılabileceği gösterilmiştir.

Anahtar Kelimeler: İstatistiksel Deney Tasarımı, Taguchi Metodu, Robust Tasarım, Cevap Yüzeyi Metodolojisi, Lityum Kazanımı, Bor Killeri

To Uğur and Berin Büyükburç

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CHAPTER I

INTRODUCTION

The aim of this study is to use statistical experimental design and analysis of these experiments in order to maximize the extraction of lithium from the clays of the boron fields. While achieving this aim, it is tried to make the lithium extraction robust to the variations in the process. Taguchi's L_{27} (3^{13}) orthogonal array has been chosen as the statistical experimental design. In order to analyse the robustness of the process, three replications have been performed. Signal-to-Noise (S/N) ratio, Analysis of Variance (ANOVA) and Regression Analysis (for both mean and standard deviation) and Response Surface Methodology have been used in order to maximize the mean of lithium extraction and minimize the variation.

The widest application areas of lithium and its compounds are in several industries such as glass, ceramics, lubricants, pharmaceutics, metallurgy and batteries (Fishwick, 1974). In the ceramic industry, lithium is used as an additive to frits and glazes to reduce the viscosity. In the pharmaceutics industry, it is used in the synthesis of vitamin A and in the treatment of manic-depressive disorders. As lithium has high energy density, it is a desirable electrode material in batteries. Lithium compounds like lithium carbonate (Li_2CO_3) is added to the aluminium electrolysis cells in order to increase current efficiency and thereby decreasing the power consumption (Fishwick, 1974).

It is known that lithium occurs in boron fields (Mordoğan et. al., 1995, Beşkardeş et. al., 1992 and Büyükburç et. al., 2002) all of which owned by a state-hold company, Eti Holding, Inc. Therefore, from the clays of boron minerals, lithium has been tried to be extracted and production of Li_2CO_3 has been aimed. In this study a different approach has been suggested for the extraction process design. This approach has been based on using raw materials that can be obtained from the facilities and fields of Eti Holding, Inc. Therefore, the raw material cost will be minimized so that no payment will be made for purchasing these raw materials. The studies in literature have not used or have not had any chance to use such an approach.

There are several factors affecting the Li_2CO_3 production from clays. The production steps can be simplified as pelletizing, roasting, leaching, evaporation, precipitation and filtering.

The first and main part of the process is to take lithium into the solution. The most important parameters of taking lithium into solution can be classified as; raw material to clay ratio, roasting temperature, roasting time, leaching time and leaching solid to liquid ratio. In order to perform the experiments, three levels for each factor have been determined and Taguchi's $L_{27}(3^{13})$ orthogonal array is chosen in order to estimate the main effects and some of interactions. To perform robust analysis and study the variations, three replications for each run have been obtained. S/N ratio has been estimated and analysis of variance (ANOVA) has been performed. The regression analyses for both the mean and the standard deviation have been conducted. In order to achieve the maximum solubility, response surface methodology has been used and it has been tried to find the global optimum of extraction by employing the GAMS non-linear programming and the methodology of response surfaces for 2^{nd} order surfaces, Ridge Analysis. Although after completing the designed experiments maximum extraction has been identified as 73%, applying optimization methods has increased the extraction to about 83% on the average. These methodologies have not been applied commonly in mining industry, without making any standardization to the best of our knowledge.

In Chapter II, the background on the methods used in this study has been provided. In Chapter III, problem definition and the experimental procedure have been explained. In Chapter IV, the design, analysis and conduct of experiments have been explained. In Chapter V, the optimization study has been reported. In Chapter VI, an attempt to improve the optimum points has been presented. In Chapter VII, a cost analysis for this study has been made. Finally in Chapter VIII, the results obtained from this study have been discussed and suggestions for future work have been made.

CHAPTER II

LITERATURE SURVEY

2.1. Background On Lithium Extraction

In this study, lithium has been extracted from boron fields by applying roasting and leaching processes simultaneously, and the experiments have been performed by using orthogonal arrays, and analysis of experiments (ANOVA, Regression) has been performed. On the results gained from regression, response surface and robust design methodologies have been applied.

Lithium is the third element of the periodic table coming after hydrogen and helium. It is the lightest metal and its atomic weight is 6.938. The name lithium originates from the Greek word “lithos” that means stone. The first identification of lithium was in the 19^{th} century by Johan August Arfvedson. Arfvedson had analysed the content of a mineral later called spodumene [$LiAl(Si_2O_6)$] and saw that an accounted portion of the ore was not identified (Kroschwitz, 1994). Further work resulted in extraction of a compound that had unknown chemical properties. However; it was not until 1855 that lithium was extracted as a free metal by the studies of Robert Bunsen and Augustus Matthienson. They achieved these by electrolysis of lithium chloride. In 1923, Metallgesellschaft AG in Germany did the first commercial production of lithium. The first production of lithium on an appreciable scale was during 1900’s as spodumene mineral of Etta Mine in the Black Hills of South Dakota. The large increase of lithium and its derivatives production were in the middle of 1950’s due to the thermonuclear program of Atomic Energy Commission (AEC). The program had been completed in 1960 and the lithium producers have been left with an excess capacity. However; after 1960 new application

areas of lithium were found.

The average concentration of lithium in earth's crust is about 0,006% and it is supposed that there exists 0,1 ppm lithium in seawater. The main sources of lithium are clays, minerals and brines. However; current commercial production is made from minerals and brines. The commercially important lithium minerals are spodumene, lepidolite, petalite and amblygonite (Saller and O'Driscoll, 2000). These minerals are either used directly in certain applications or they are converted in the lithium compounds such as Li_2CO_3, LiCl, LiOH. Li_2CO_3 production is made both from minerals and brines. The production is made mainly from brines as this is easier and cheaper than mineral processing.

A smectit-type clay which contained minimum lithium content of about 4500 ppm is called hectorite. This type of clay is not currently used for producing lithium but instead is used directly in different applications. Some studies were performed (Lien, 1985, May et. al., 1980 and Edlund, 1983) in order to extract lithium from these clays and then producing Li_2CO_3.

Lithium carbonate (Li_2CO_3) is the most important compound of lithium, which is a raw material for various industries as explained in Chapter 1. Li_2CO_3 is produced commercially from minerals and brines. The production route from minerals includes crushing of spodumene mineral and applying of flotation in order to produce concentrate. Then the concentrate goes through a heating process at about 1100°C and the crystal structure of spodumene is altered so it becomes more reactive to sulfuric acid. The mixture of finely ground converted spodumene and sulfuric acid is heated to 250°C and forms lithium sulphate which is a water soluble compound. After leaching with water, insoluble compounds are separated by filtration. Lithium carbonate is achieved by reacting lithium sulphate and sodium carbonate (Na_2CO_3) (Ober, 2001). As this process is energy intensive, producing lithium carbonate is expensive when compared with the production from brines and the production is shifting to that side. The production from brines mainly includes evaporation, filtration, and precipitation steps. The schematic diagram of Li_2CO_3 production from the world's largest lithium containing brine (Salar de Atacama, Chile), is shown in Figure 2.1.

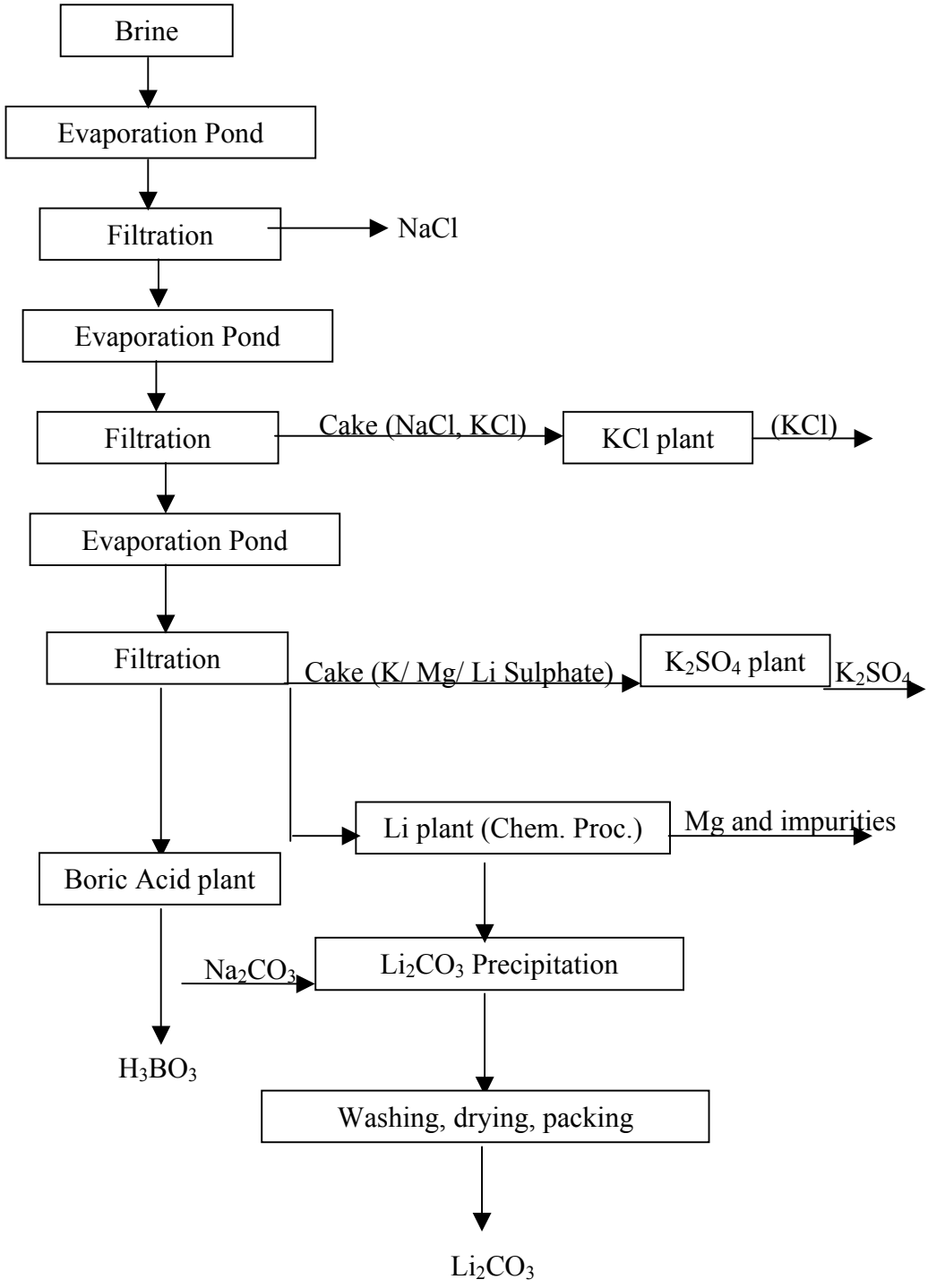


Figure 2.1. The extraction of Li_2CO_3 and other salts from brines, Salar de Atacama, Chile (Mordoğan et. al., 1995 and Coad, 1984)

Ooi et. al. (1986) have claimed that if the application of lithium in thermonuclear fusion will come to the stage, the known lithium reserves will not be enough to supply this demand, and extraction of lithium from the sea water will be needed regardless of the low concentration which is 0.17 ppm. However; before coming to the extraction from sea water, the recovery from lithium bearing clays are to be thought. By this point of view, various studies have been performed in order to extract lithium from clays. The methods to extract lithium can be classified as water disaggregation, sulfuric acid leaching, acid baking-water leaching, alkaline roast-water leach, sulfate roast-water leach, chloride roast-water leach, multiple reagent roast-water leach (May et. al., 1980), selective chlorination (Davidson, 1981) and lime-gypsum roasting-water leach (Edlund, 1983 and Lien, 1985). Among all these, lime-gypsum roasting-water leach is the most promising method. Edlund (1983) tries to optimize the lime-gypsum ratios and roasting parameters. He conducts the experiment in different atmospheres such as N_2+CO atmosphere, CO+H_2O+N_2 atmosphere. Clay:Lime:Gypsum ratio 5:3:3 is found as the optimum. The calcination time is prolonged to 4 hours and experiments are conducted for hours between 1-4. The results indicate that calcination temperature of 900°C yields the best results for batch production with a rotary furnace. According to the same study, in an electrically heated furnace the extraction yield has increased for all temperatures. Lien (1985) makes an extensive study for producing Li_2CO_3 from a montmorillonite-type clay containing %0,6 lithium. He also sets the clay:lime:gypsum ratio to 5:3:3 as optimum and conducts the experiments in the calcination temperature range of 750-1100°C for 1 hour. Lien (1985) concludes that 78-82% of lithium in the clay can be recovered. He also estimates the production cost of Li_2CO_3 and finds the cost as 1.4 fold larger than market price of Li_2CO_3. The process flow chart is given in Figure 2.2.

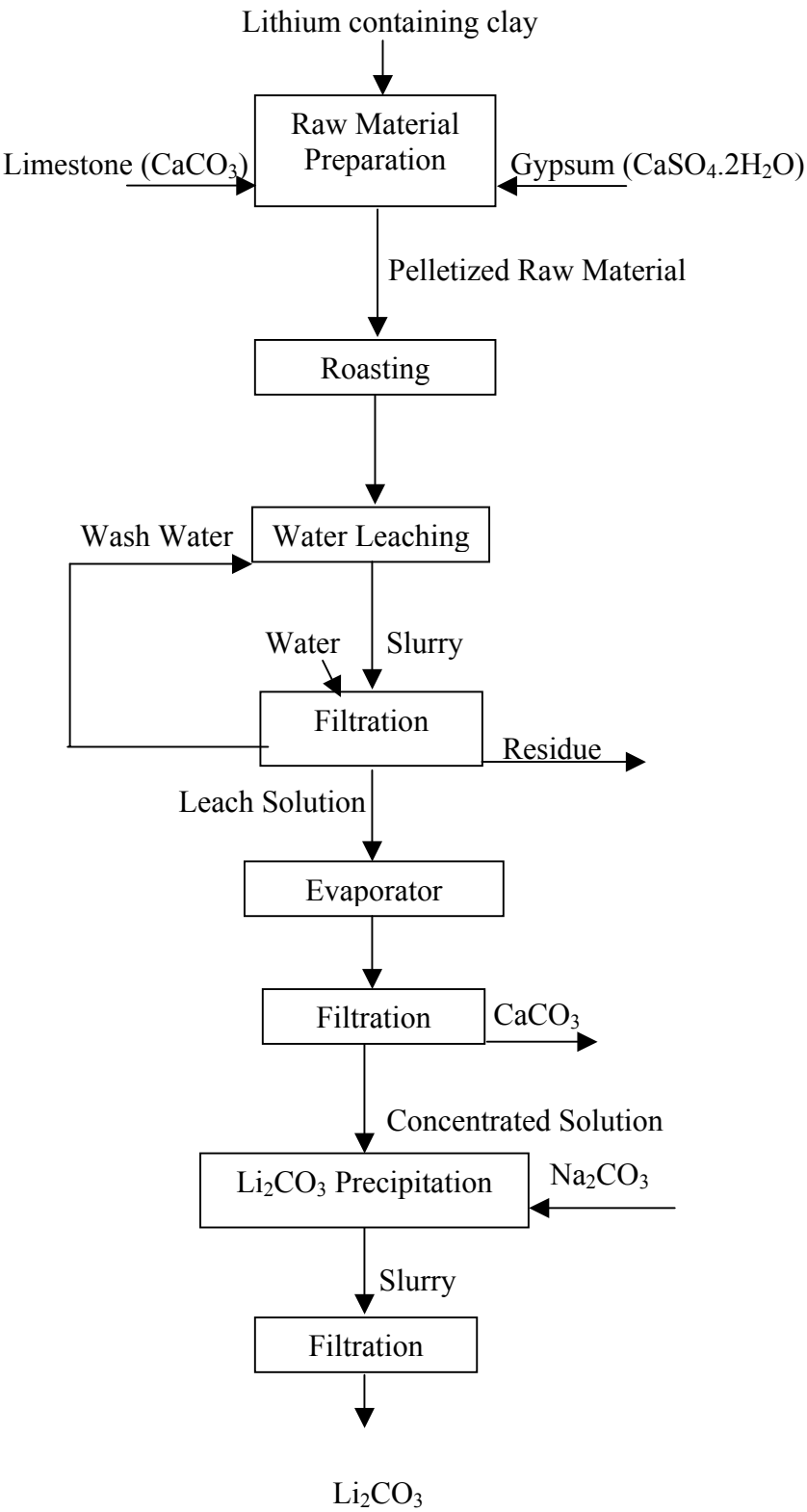


Figure 2.2. The process flowchart of Li_2CO_3 from hectorite clay (Lien, 1985)

Extraction of lithium from boron fields has been the subject of Turkish researchers (Mordoğan et.al, 1995 and Beşkardeş et.al, 1992). Mordoğan et. al. (1995) conclude that 77% of lithium from Kırka clays can be recovered by adding 16,67% gypsum to the clay but no lime. Calcination temperature and time set as 900°C and 2 hours as optimum. Leaching time and solid:liquid ratio used are 1 hour and 0.1 respectively. Beşkardeş et. al. (1992) mainly concern with the application of Bigadiç clays for industrial use and try to investigate the economy of recovering lithium. They conclude that the cost of recovering lithium is 10,95$/kg which is about 3 times the selling price of Li_2CO_3.

2.2. Background on Design and Analysis of Experiments for Optimization

In this study, natural lime-waste gypsum roasting-water leach method has been used in order to extract lithium from boron fields. The experiments have been performed by using Taguchi's L_{27} (3^{13}) orthogonal array and analysed by using robust design methodologies. S/N Ratio, ANOVA, regression and response surface are the methods that have been used to analyse the experiments and optimize the extraction of lithium.

After World War II, Japan faced the problem of reconstruction the country. The main problem was from good-quality raw material, high-quality manufacturing equipment and skilled engineers (Phadke, 1989). To meet this challenge, Genichi Taguchi was assigned and he developed the foundations of Robust Design. The Robust Design method provides a systematic and efficient approach in order to get close to the optimum by having the product functional, exhibiting high performance and robust to variations (Erdoğan, 2000).

The robust design methodology strives for:

1. Making product performance insensitive to raw material which in turn leads to independence from the grade or quality of the raw material or components in the process.

2. Making the design robust to the manufacturing variation in order to reduce labor and material cost for rework.

3. Having the design less sensitive to operating environment so that the reliability improves and operating cost decreases.

4. Using a novel development process, which will help, in using the engineering time more productively.

In order to achieve these aims, robust design simply tries to minimize the sensitivity of the process or product to the variation caused by uncontrollable factors without sacrificing the main aim, optimizing the mean (minimize, maximize or on target). The optimum settings of the controllable factors are found and set to minimize the variation. Robust Design involves eight steps which can be grouped into three categories as planning experiments, conducting them and analyzing and conforming the results (Phadke, 1989).

Planning the experiment contains;

a- Identifying of the main function

b- Identify noise factors and testing conditions for quality loss

c- Decide on the quality characteristic to observe and the objective function to be optimized

d- Identifying and levelling of the control factors

e- Choosing the most suitable experiment design and data analysis procedure

Performing the experiments contains;

f- Conducting the experiments

Analyzing and conforming the results consists of;

g- Analyzing the data and determining of optimum levels for control factors

h- Conduct the confirmation experiments and planning future actions

The Robust Design method developed by Taguchi has two major tools; signal-to-noise ratio and orthogonal arrays.

When we intentionally deal with the problem of minimizing the variation and the optimization of the response simultaneously, we can transform our data such that we can observe the variation and the mean. Taguchi recommended the transformation of the raw data to signal-to-noise ratio (S/N). S/N ratio consolidates several repetitions (at least two data points are required) into one value which reflects the amount of variation (Ross, 1988). In Robust Design, S/N ratio is used as the objective function to be maximized.

A process simply consists of input, controllable and uncontrollable factors and output as shown in Figure 2.3.

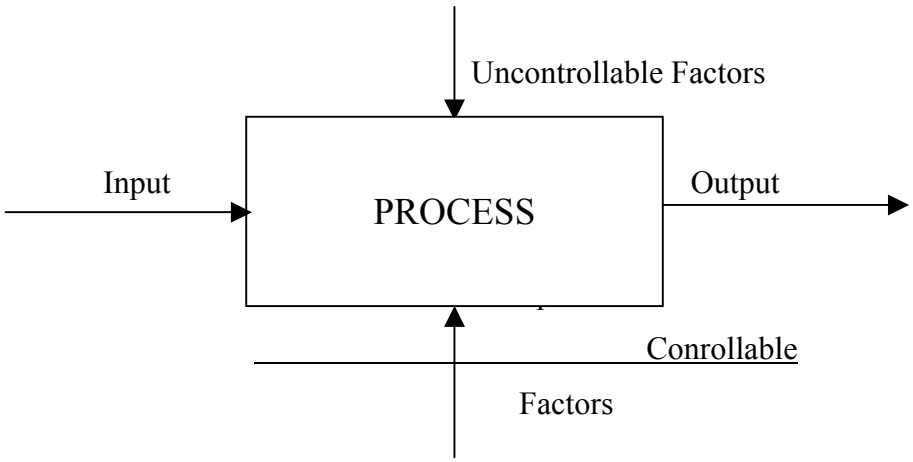


Figure 2.3. General model of a process

In S/N ratio terminology, the controllable factors for a fixed target or static problem can be considered as signal factors and these can be intentionally adjusted to accomplish a controlled change in the output of the system. Uncontrollable factors are named as noise factors and these are known to affect a system's performance. However; the settings of these factors can not be controlled or it is not feasible to control them in actual operation. Noise factors can be split into three categories as inner noise, outer noise and between-products noise. Inner noise is the internal source of variability in a product's function such as deterioration of components in response to aging. Outer noise is the one that is external sources of variability like operating environment; temperature, humidity. Between-products noise is caused by the variability in

the manufacturing procedures or equipment. Welding amperage can be an example for such a noise.

Using S/N ratio we can simply analyze the results of the experiments involving multiple runs, instead of extended and time-consuming analysis. S/N ratio lets the selection of the optimum objective with minimum variation around the target.

A classical example can be given to show the idea of S/N ratio. Let us consider a radio that the signal factor is the power of the radio signal and noise factor is interference of storm. The clearness of radio signal is the target and the storm interference is variation. The most desirable situation is strong signal and little interference whereas the least desirable situation is weak signal and strong interference. So maximizing radio signal/storm interference will be the most suited case for our problem.

There are three types of S/N ratios for static cases;

- Nominal-the-Best
- Smaller-the-Better
- Larger-the-Better

Nominal-the-Best: Nominal-the-best is the correct type when we have the following conditions;

L: Quality Loss = 0 when μ:Target=m, and σ_e:Deviation=0

To simplify, nominal-the best is a measurable characteristic with a specific user-defined target. The transformation to S/N ratio can be made by the following formula:

$$\eta = 10LOG\frac{\bar{y}^2}{s^2} \qquad [2.1]$$

where;

η = symbol for S/N; (dB)

$\bar{y} = mean = \frac{\sum_{i=1}^{n} y_i}{n}$ n= number of data points, y_i = the result of the i^{th} data

$$s = std.dev. = \sqrt{\sum_{i=1}^{n} \frac{(y_i - \bar{y})^2}{n-1}}$$

Smaller-the-Better: If we have the following criteria;

L: Quality Loss = 0 when μ=0 and σ_e:Deviation=0

then Smaller-the-Better type S/N ratio can be used. This simply corresponds to the target of achieving zero which is the smallest obtainable value, without negative values. If the system is capable of attaining both negative and positive values, then this is a case for Nominal-the-Best type.

The transformation formula for smaller-the-best type is:

$$\eta = -10LOGV_T \qquad V_T = \frac{1}{n}\sum_{i=1}^{n} y_i^2 \qquad [2.2]$$

where; n= number of replications

y_i = i^{th} value

The specific examples for smaller-the-better type problems are direct evaluation of energy, leakage of any matter (gas, solid, liquid) or pollution.

Larger-the-Better: When we have the following requirement;

L: Quality Loss = 0 when $\mu = +\infty$, and σ_e:Deviation=0

then the larger-the-better type is the most suitable one. If a system will be defined as perfect when it approaches to infinity, larger-the-better should be used. Dr.Taguchi recommends to use the inverse of the target of zero which is similar to opposite of smaller-the-better type. Therefore the transformation to the S/N ratio can be performed by the formula:

$$\eta = -10LOGV_T \qquad V_T = \frac{1}{n}\sum_{i=1}^{n} \frac{1}{y_i^2} \qquad [2.3]$$

Weld strength, profit, material strength and fuel efficiency can be the examples of larger-the-better type.

Another tool used in Robust Design methodology is orthogonal arrays. Orthogonal array is a type of statistical design of experiments and are called matrix experiments also. Ronald Fisher who introduced analysis of variance (ANOVA) was the primary founder of the statistically designed experiments. He first applied this method in agricultural studies and later statistically designed experiments have found wide applications in Medical and R&D activities. There are various kind of designs such as; one factor at a time, full factorial, fractional factorial, central composite design and orthogonal arrays. In designing, conducting and analyzing an experiment, there are major steps (Ross, 1988). These can be listed as:

1. Selection of factors and/or interactions to be evaluated
2. Selection of number of levels for the factors
3. Selection of the appropriate orthogonal arrays
4. Assignment of factors and/or interactions to columns
5. Conducting tests
6. Analyzing tests
7. Making the confirmation experiments

Orthogonal array is the foundation for designing an experiment in Taguchi methodology. Orthogonal means being balanced and not mixed. In statististical terminology, orthogonal means statistically independent. Notation of orthogonal arrays is L_a (b^c) where "L" is an symbol for orthogonal array, "a" stands for the number of experiments required for this array, "b" shows the number of test levels for each factor and "c" points out the number of factors that this array can examine. For example L_{27} (3^{13}) tells that this array requires 27 experiments, and with these, thirteen 3 level factors can be analysed.

In statistical terminology a matrix is said to be orthogonal if following two criteria occur ;

- all possible combinations of test levels occur between pairs of columns
- and each of these combinations occur an equal number of times

There are several orthogonal arrays that are used. The most widely ones are $L_4(2^3)$, $L_8(2^7)$, $L_9(3^4)$, $L_{12}(2^{11})$, $L_{16}(4^5)$, L_{18} (2^1x3^7), $L_{25}(5^6)$, $L_{27}(3^{13})$ and $L_{32}(2^{31})$. There are other orthogonal arrays that are less common such as $L_{20}(2^{19})$, $L_{98}(7^{15}x2^1)$, $L_{121}(11^{12})$, $L_{169}(13^{14})$. It is possible to create new orthogonal arrays by merging colums of the most widely used ones. Some examples for such arrays are; $L_{18}(6^1x3^6)$, $L_{27}(9^1x3^9)$, $L_{81}(9^{10})$ and $L_{128}(4^{41}x2^4)$. Ünal (2001) lists all these orthogonal arrays and in Phadke (1989), interaction tables and linear graphs of the most commonly used arrays can be found.

After performing the experiments, the analysis and model fitting of the experimental data come into nature. Model fitting is made by using regression. Regression analysis is called simple regression when the model contains only one factor. If there are more than one factor in the model, then multiple regression is performed to fit a model. When the model contains only linear terms then this model fitting is called multiple linear regression, and denoted by:

$$y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + ... + \beta_k X_k + \varepsilon \qquad [2.4]$$

When the model contains square and interaction terms then the model is called quadratic regression and the model is formulated as:

$$\eta = \beta_0 + \sum_{j=1}^{k} \beta_j x_j + \sum_{\substack{j=1 \\ \text{for } j<m}}^{k} \sum_{m=1}^{k} \beta_{jm} x_j x_m + \sum_{j=1}^{k} \beta_{jj} x_j^2 \qquad [2.5]$$

In order to find the optimum point in the model, response surface methodology can be used. An experimenter wishes to have the optimum point in his/her experimental region. An appropriate way to see whether the global optimum lies in the experimental region is to apply response surface methods. For a regression problem including only the linear terms in x_j's, it is easy for response methodology to reach to optimum by using the method called steepest ascent. This method basically tries to reach the optimum by moving b_1 units in, say X_1 direction for every b_2 units in, say X_2 direction starting at the centre

(0,0) of the experimental design if X_1 and X_2 are the only variables. Thus, the steps along the path are proportional to the regression coefficients (β_i's) (Montgomery, 1997). If second order model is necessary to explain the relationship, ridge analysis can be used.

The technique of ridge analysis was first suggested by A.E.Hoerl (1959) and later urged by R.W.Hoerl (1985). It is developed form of the steepest ascent that will apply to second-order surfaces and finds its origin in Box and Wilson (1951) (Box and Draper, 1987).

The method simply comprises the following:

Consider the 2nd order response surface in k variables $x_1, x_2,...,x_k$ that

$$\mu = b_0 + b_1x_1 + b_2x_2 + ... + b_kx_k + b_{11}x_1^2 + b_{22}x_2^2 + ... + b_{kk}x_k^2 + b_{12}x_1x_2 + b_{13}x_1x_3 + ... + b_{k-1,k}x_{k-1}x_k \quad [2.6]$$

Suppose a sphere centring at the origin [usually (0,0,...,0)] and having radius R is drawn. Then it is certain that somewhere in the sphere there will be a maximum and elsewhere a minimum. Also depending on the type of quadratic surface [2.6] values of μ which are local maxima or minima, that is maxima and minima for all nearby points on the sphere, but not absolute maxima or minima when all points of the sphere are taken into consideration (Box and Draper, 1987).

For ridge analysis, application of the method of Lagrange multipliers leads to the following equations, which must be solved for $\mathbf{x} = (x_1, x_2,\ldots,x_k)^{/}$:

$$(\mathbf{B} - \lambda\mathbf{I})\,\mathbf{x} = -1/2\,\mathbf{b} \quad [2.7]$$

$$B = \begin{bmatrix} b_{11} & 1/2b_{21} & ... & 1/2b_{1k} \\ 1/2b_{12} & b_{22} & ... & 1/2b_{2k} \\ ... & ... & ... & ... \\ 1/2b_{1k} & 1/2b_{2k} & ... & b_{kk} \end{bmatrix} \qquad \mathbf{b} = \begin{bmatrix} b_1 \\ b_2 \\ ... \\ b_k \end{bmatrix}$$

Let the eigenvalues of the matrix **B** be denoted by μ_i (i=1,...,k). Then, det (**B**-μ**I**) = **0** will provide the eigenvalues. Suppose that the largest eigenvalue for **B** is μ_L and the smallest eigenvalue is μ_s. Some assignment values to λ is given and equation [2.7] is solved and values for x_1, x_2,...,x_k are computed. Whether the assigned λ value is outside the interval [μ_s μ_L] or inside the interval gives the decision of the point, **x** = (x_1, x_2,...,x_k) as local or global maxima or minima (Box and Draper, 1987).

Contour plots and response surface graphs are two basic constitutes of response surface methodologies that help the researcher visualise the surfaces more easily. An example adapted from literature showing the response surface graphs and contour plots with the pathway that should be followed while conducting response surface methodology are given in Figures 2.4 and 2.5.

Applications of response surfaces can be read from Özler (1997), Myers (1971), Myers et. al. (1989), Lin et. al. (1995), Handle et. al. (1997) and Myers et. al. (1999). Applications of robust design can be found in Koolen (1998), Köksal et. al. (1998), Köksal (1992), Menon et. al. (2002) and Khoei et. al. (2002).

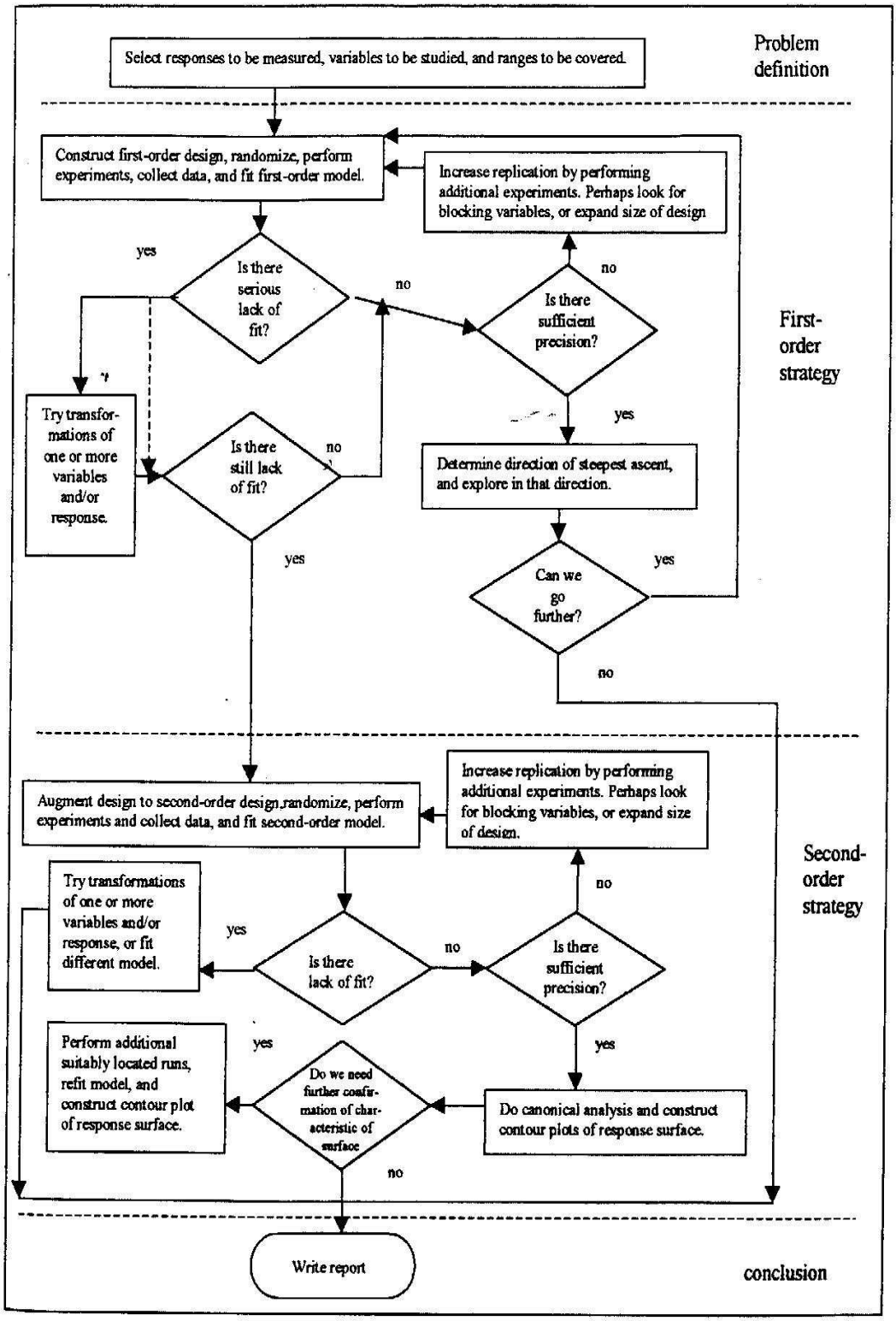


Figure 2.4. The flow diagram of Response Surface Methodology (Abacıoğlu, 1999)

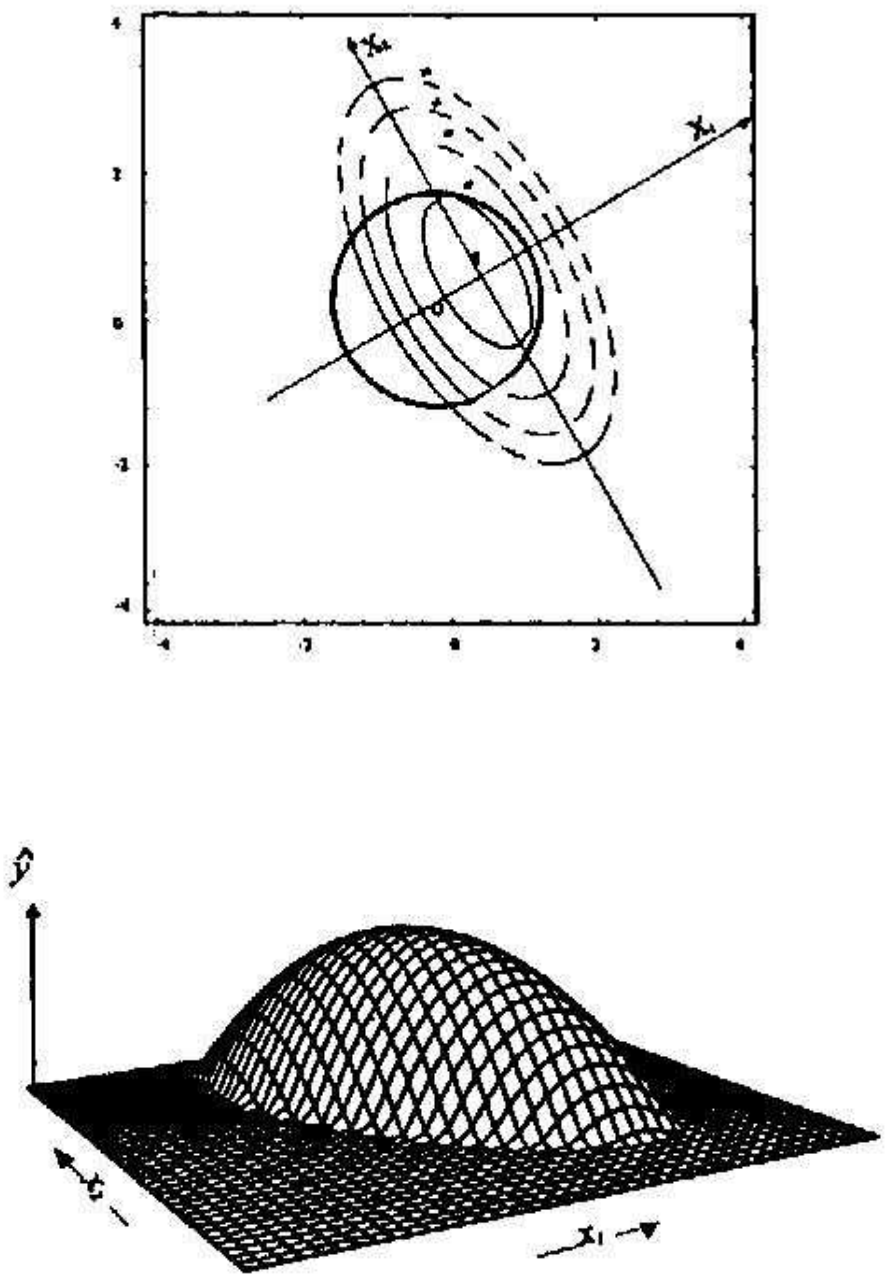


Figure 2.5. Contour plot and a response surface (George et.al, 2000).

CHAPTER III

PROBLEM DEFINITION AND EXPERIMENTAL PROCEDURE

Boron minerals in Turkey are completely owned by Eti Bor, a subsidiary of Eti Holding. Boron minerals are found in four different places in Turkey. Three different boron minerals are mined in these four locations. Colemanite ($Ca_2B_6O_{11}.5H_2O$) mineral is mined in Kestelek (Bursa), in Bigadiç (Balıkesir) and in Emet (Kütahya). Ulexite ($NaCaB_5O_9.8H_2O$) is mined in Bigadiç and Tincal ($Na_2B_4O_7.10H_2O$) is mined in Kırka (Eskişehir). After extracting the run-of-mine ore, physical (crushing, washing, sieving and so on) processes should be applied to recover the mineral. These processes are applied in order to separate the valuable part of the ore (B_2O_3) from relatively less valuable part (clay, limestone, marn, tuff) totally named as gangue minerals. These gangue minerals are stored in tailings pond as slurry or solid. Some studies have been conducted to beneficiate the clay minerals of boron fields. Some of the studies concentrate on extracting the lithium content of Bigadiç clays. Bigadiç clays contain nearly about 2500 ppm lithium (Mordoğan et. al., 1995 and Büyükburç et. al., 2002) and this can be a potential source for future use.

The extraction of lithium comprises mixing of raw materials, roasting them and leaching with water. After taking lithium in the solution, it is concentrated by evaporation and then precipitated by the addition of Na_2CO_3. Therefore we can roughly divide Li_2CO_3 production into two stages; extraction (taking into solution) and precipitation (reacting with Na_2CO_3). Extraction mostly affects the yield of the whole process as the solid part of the leaching is a residue. Extraction includes three processes; raw material preparation (crushing, grinding), roasting, leaching. During these processes, many factors cause variation that affect the extraction yield. These factors are listed in Table 3.1.

Table 3.1. Factors Affecting the Extraction of Lithium

Process	Factors Affecting Lithium Extraction
Raw Material Preparation	Mixing ratios
	The contents of the raw materials:
	a. $CaSO_4.2H_2O$ content of gypsum*
	b. $CaCO_3$ content of limestone*
	c. Lithium content of clay*
	Measurement Error
	a. Calibration of balance
Roasting	Roasting temperature
	Roasting time
	Temperature variation in the furnace
Leaching	Leaching time
	Leaching solid to liquid ratio
	Leaching temperature
	Stirring speed
	Leaching particle size
	Measurement Error
	a. Calibration of balance
	b. Accuracy of container
	c. Chemical Analyses

* The contents vary since the raw materials are from nature (limestone) or wastes (clay and gypsum).

As there is no industrial production of lithium from clays, probably some of the factors affecting the process have been neglected. Some of the factors listed above are control factors and some are noise factors. However; in order to simulate the production environment, some controllable factors not studied and certain predetermined levels are used for them. Moreover; to control some of the factors will bring additional cost to the process. This is especially valid for bringing the contents of the raw materials to minimum value (standardization). However; standardization has not been taken into consideration in this study and

contents of the raw materials have been left as a noise factor. In real production environment; as the capacities are so high, the measurements about weighting are to be based on tonnage and some variation in weighting of the solids and measuring the volume of the liquid may occur. In this study, the measurements have been made accurately so such errors in the production environment have not been simulated. Another important noise factor that can affect the yield of the extraction is, temperature variation in the furnace. In the real production environment, temperature can not be kept consistently at given levels or this is not desired, as it will increase the cost. In this study, a furnace that shows ±10°C variation has been used in order to simulate the production environment. Leaching temperature is another important factor that can affect the solubility of lithium sulphate, hence extraction. As the room temperature solubility of lithium sulphate is 40 gr/lt, it is not needed to work at high leaching temperatures. Moreover, leaching will be made at room temperature in the real production environment so this factor can be simulated, however, as solubility increases with increasing temperature, in this study it is not claimed to have robustness against leaching temperatures other than the room temperature. Stirring speed is another factor that can not be followed accurately in the production environment. Therefore, in this study stirring speed has been let to variate ±10 rotations per minute. That means the stirring speed has been left to vary between 400-420 (410±10) rpm so that noise factor can be simulated well. Leaching particle size is another factor. However; as leaching in the real production environment will be made with powder particles (particle size less than 200 μ) and as in this study the average particle size has been set around 74μ, this factor has been simulated well. In this study, pelletizing has not been made although it has been made in other studies in literature (Beşkardeş et. al. 1992, Mordoğan et. al., 1995 and Lien 1985). The results of this study do not show a considerable difference from those studies. However; if pelletizing is needed in the real production environment due to high dusting environment in roasting process, then leaching particle size should be taken into consideration. Other factors such as clay:gypsum:limestone mixing ratio, roasting temperature, roasting

time, leaching solid to liquid ratio and leaching time have been chosen as the control factors in this study. Another important noise factor is accuracy of chemical analyses. In order to overcome this factor a mass balance has been set up and if there occurs larger than 15% difference in mass balance then analyses and/or experiments have been repeated.

3.1 RAW MATERIAL PREPARATION

Three raw materials are used in extracting lithium. First one is the clay from boron fields and the others are gypsum and limestone. The studies about extracting lithium from clays present that the process is cost-sensitive. (Beşkardeş, 1992 and Lien, 1985). In order to decrease the cost, the reagents (gypsum and limestone) are not purchased from chemical suppliers or from mining companies. Instead the materials that belong the Eti Holding are tried. Instead of purchasing gypsum from outside markets, solid waste of boric acid production plant is used. Chemical analyses of this waste show that it can be a candidate to be used instead of gypsum. Also in Bigadiç mine, there is a place rich in limestone content. Therefore the limestone used in the experiments are from Bigadiç fields which belong to Eti Holding. Also the chemical analyses of this pit show a great hope to substitute limestone. The chemical analyses of the samples are given in Table 3.2.

Table 3.2. The chemical analyses of raw materials

Sample	**CaO (%)**	**CO_2 (%)**	**SO_4 (%)**	**Li (ppm)**	**SiO_2 (%)**
Limestone	49,74	38,37	0,26	64	7,91
Gypsum	27,89	0,64	50,26	98	5,84
Clay	10,03	4,55	0,21	2150	39,01

As these materials are natural, the chemical analyses show variability.

All the materials are crushed under a size of 1,3 cm. In order to have an efficient roasting, these materials should be mixed vigorously. For achieving appropriate mixing, it is thought to grind them together. The studies on that subject add pelletizing of the ground materials. This is done in order to minimize the weight loss, hence lithium loss during roasting. In this study, pelletizing is

not included. The pictures of raw materials and the grinding machine are given in Figure 3.1.

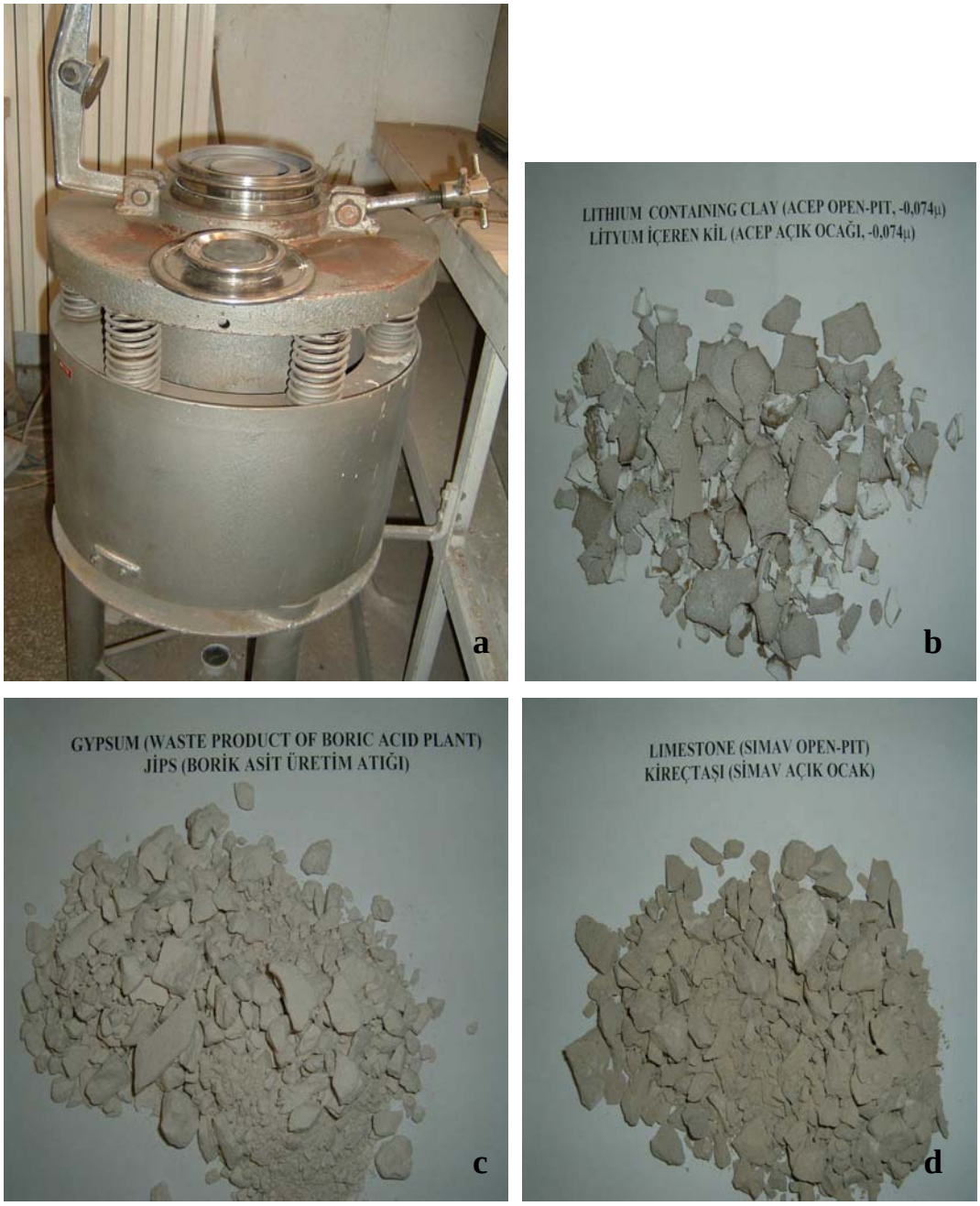


Figure 3.1. Pictures of raw materials and grinding machine a-) grinding machine b-) Lithium containing clay, c-) waste of boric acid plant, gypsum, d-) limestone

3.2 ROASTING

The identification of the lithium phase is almost difficult in the clay since lithium content is in ppm. Therefore it is assumed that lithium is with silicate minerals with the formula $Li_2Si_2O_5$. In order to make an efficient leach, this

lithium phase must be converted to a water soluble phase such as Li_2SO_4 (water solubility is about 40 gr/lt). This can be achieved by roasting at high temperatures (higher than 800°C). During roasting the following reactions occur.

$$CaSO_4.2H_2O + SiO_2 \Rightarrow CaSiO_3 + SO_2 + ½\ O_2 + 2H_2O \quad (1)$$

$$Li_2Si_2O_5 + SO_2 + ½\ O_2 \Rightarrow Li_2SO_4 + 2SiO_2 \quad (2)$$

An important point to consider here is that the 2nd reaction is reversible. Free SiO_2 tends to react with Li_2SO_4 and results in lithium silicate mineral. Hence in order to prevent the back reaction, $CaCO_3$ is added. This material does not stop the back reaction but limits it. CaO reacts with SiO_2 to form $CaSiO_3$. CO_2 is lost to furnace atmosphere. An electric driven muffle furnace that can reach to the temperatures of 1200°C is used. The required temperature can be adjusted. However; the heating and cooling time can not be seen on the furnace. Roasting experiments are performed in a mullite crucible that can resist high temperatures. The picture of the furnace and the roasted material in the crucible are given in Figure 3.2.

Figure 3.2. The muffle furnace and roasts in the crucible

3.3 LEACHING

After calcining, the roasts are weighted, the weight loss is recorded. Lithium analysis is applied to a portion of the roast and the other portion is leached with water. Distilled water is used during the experiments, as other solvents such as sulfuric acid and hydrochloric acid are expensive. Also they are such powerful solvents that they extract some undesired materials as well like iron (Fe), magnesium (Mg) and aluminium (Al). The reactor used for leaching has a volume of 1liter and is connected to a cryostat that sets the temperature to the desired point. However; during the experiments room temperature is used. This is due to high solubility of Li_2SO_4 in water (about 40 gr/lt at 20°C). Moreover, it is tried not to include any more energy consuming items in the process by leaching at high temperatures. The reactor also has 6 necks to dip in thermometers, pH meters and rods to take liquid samples. A mixer is dipped from the middle neck of the reactor to make a homogeneous mixing.

When the literature is examined it is seen that mixing speed does not have an important affect on the leaching performance (Mordoğan et. al., 1995). Preliminary experiments are performed in order to see if it is important for Bigadiç clays. As a result, it is concluded that it does not have a considerable effect on leaching. Therefore mixing speed is set to 400 rpm based on preliminary experiments. The leaching experiments are performed with different time and solid to liquid ratio. At the end of the leaching the slurry are filtered. By this, solution is separated from the slurry. Filtration is performed by using the thinnest filter paper. Lithium analysis is applied to the solution and the solid part (which is a residue) is dried and analysed for lithium content. The final point is the calculation of the lithium extraction from the clay. Lithium analyses have been made using AAS (Atomic Absorption Spectrophotometer) which has lithium detection limit of 0.02 ppm.

The picture of the reactor can be seen in Figure 3.3.

Figure 3.3 The picture of reactor and cryostat

Figure 3.4 shows the process flow chart of this study.

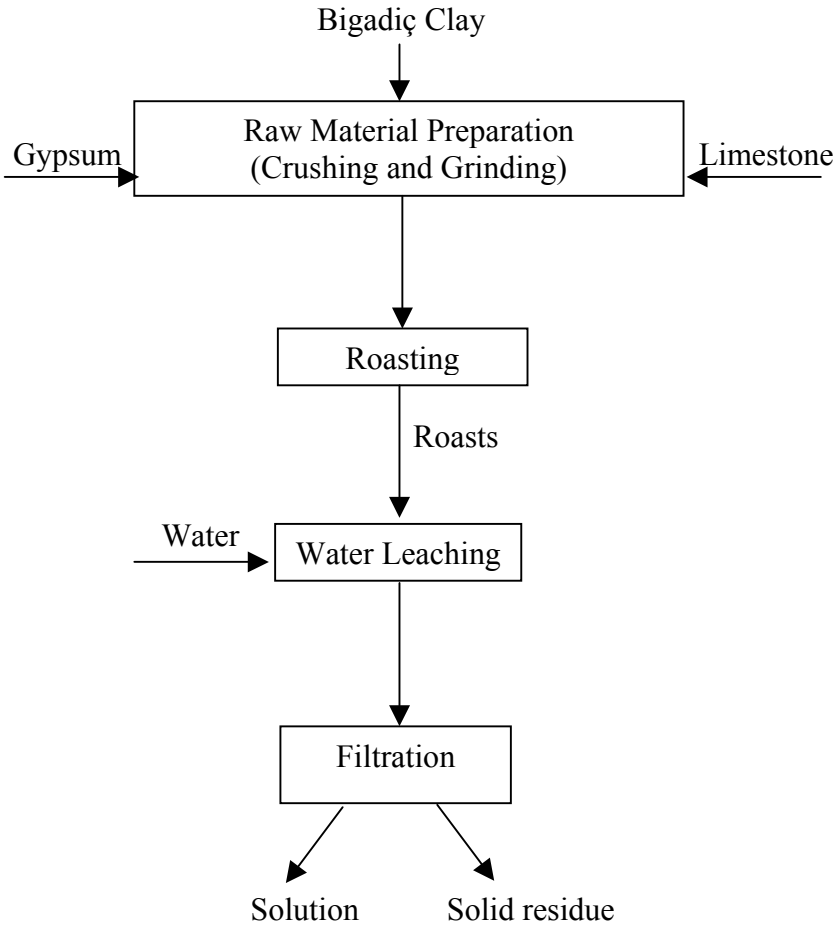


Figure 3.4. The process flow chart used in this study.

CHAPTER IV

DESIGN, CONDUCT AND ANALYSIS OF THE EXPERIMENTS

4.1. Design and Conduct of the Experiments

4.1.1 Deciding on the Levels of Control Factors:

Extraction of lithium from boron clays mainly comprises 3 steps; raw material preparation, roasting and leaching.

In the raw material preparation step, the most important parameter is the addition ratio of gypsum and limestone to the clay. The studies that have been done, have showed that clay:gypsum:limestone optimum mixing ratio is about 5:3:3 (Mordoğan et. al, 1994) or 5:2:2 (Lien, 1985). So in this study 5:3:3 ratio is treated as the center in choosing the levels of gypsum and limestone. In fact, if we increase the content of gypsum and limestone, it will not bring an additional raw material cost (as raw materials used are wastes) to the process if transportation cost is ignored. However; due to the back reaction characteristic of roasting and equilibrium concentration of leaching processes, the additional amount of gypsum and limestone should be closely examined.

Roasting is the most important process as the conversion of lithium silicate minerals to lithium sulphate takes place in this process. As the reaction of conversion is reversible, the time and temperature of roasting need close attention. The addition of limestone ($CaCO_3$) is for limiting the back reaction. $CaCO_3$ decomposes to CaO and CO_2 at about temperatures higher than 800°C and the decomposed product CaO reacts with free SiO_2, and hence preventing the back reaction. The studies for setting the optimum roasting temperature result in different temperatures, from 850°C to 1000°C due to the different

characteristics of the processes and the used clays (Mordoğan et. al, 1994 and Lien, 1985). As the optimum roasting time strictly depends on the roasting temperature, its levels are based on the roasting temperature. Higher temperatures and prolonged time of roasting result in a decrease of extraction percentage. As a result, the roasting temperature levels are set at 850°C, 950°C and 1050°C, and levels of the time are chosen as 30, 60 and 120 minutes.

As the prolonged time and higher temperatures decrease the lithium content, it is believed that there occurs an interaction between time and temperature in that period. So in choosing the appropriate orthogonal array, this interaction is taken into account.

There are several important factors for leaching. These are leaching temperature, mixing speed, leaching particle size, leaching time and leaching solid:liquid ratio. The reasons of ignoring temperature and stirring speed are explained in Chapter III. It is aimed not to make any regulation on the particle size of the leach feed. There has been made no operation on particle size and it has been used as it has left roasting, however, if there occurs strong agglomeration, the roasts have been ground. In the choice of leaching time and solid to liquid ratio, two important parameters are considered: The leaching equilibrium of the reaction, and the contamination of the solution with impurities such as Fe, Al and Mg. After examining the studies, leaching time of one hour with a solid to liquid ratio of about 0.1-0.4 is chosen as the most appropriate (Mordoğan et. al, 1994 and Lien, 1985). So in choosing the levels of leaching, these parameters are taken into consideration. The chosen levels of the factors are shown Table 4.1.

Table 4.1. The levels of the factors

Factors	*Level 1*	*Level 2*	*Level 3*
A. Gypsum/Clay Ratio*	1.5/5	3/5	4.5/5
B. Roasting Temperature (°C)	850	950	1050
C. Roasting Time (min)	60**	30	120
D. Leach Solid to Liquid Ratio	0.1	0.2	0.4
E. Leach Time (min)	30	60	120
F. Limestone/Clay Ratio*	1.5/5	3/5	4.5/5

* Gypsum and Limestone will also point the same factor (gypsum/clay ratio and limestone/clay ratio, respectively) hereafter.
** At first 90 minutes was thought to be appropriate for the 2nd level. However; after some experiences, it is believed that 30 minutes is better.

4.1.2. Designing the Experimental Layout

For this experiment an orthogonal array is decided to be used for its various advantages (Phadke, 1989). In order to decide which orthogonal array is the most suitable one, we determined the degrees of freedom needed to estimate all of the main effects and important interaction effects.

Factors	df
Gypsum	2
Roasting Temp.	2
Roasting Time	2
Leach S:L Ratio	2
Leach Time	2
Limestone	2
Overall Mean	1
TOTAL	13

Also it is important to estimate the interaction between roasting time and roasting temperature. Therefore additional 4 degrees of freedom should be reserved for estimation of this interaction. So we need at least 17 experiments. It is clear that we need to have an orthogonal array with at least 3 levels, 8 columns (6 for the main effects and 2 for the interaction) and 17 rows (run).

When the orthogonal arrays available in the literature are examined, it is observed that L_{27} (3^{13}) is the most suitable one. If this array is used there are left four more columns for estimating any other interaction, and one level for estimating the error. Therefore, as roasting temperature seems to be the most important factor, the gypsum and roasting temperature interaction, and leaching solid to liquid ratio and roasting temperature interaction can be estimated as well.

As a result, the factors are assigned to the columns of the orthogonal array as shown in Table 4.2.

Table 4.2. The assignment of factors to the columns of L_{27} (3^{13}) array

Factors	*Column numbers*	*df*
Gypsum Ratio	1	2
Roasting Temperature	2	2
Roasting Time	5	2
Leaching S:L Ratio	6	2
Leaching Time	7	2
Limestone Ratio	10	2
Gypsum x Roasting Temperature	3,4	4
Roasting Temperature x Roasting Time	8,11	4
Roasting Temperature x Leach Solid to Liquid Ratio	9,12	4
Error	13	2
Overall Mean		1
TOTAL		27

The $L_{27}(3^{13})$ O.A. and its interaction tables are given in Appendix 4A.1 and 4A.2. The factors are assigned to columns according to interaction table of $L_{27}(3^{13})$.

The experiments are repeated three times in order to effectively calculate the noise factors such as the variation of the contents of the raw materials, temperature variation in the furnace and leaching temperature.

While performing the experiments, the samples for roasting are placed in the furnace when the temperature reaches the desired value and then are taken out as soon as the roasting time is completed. Two samples, which have the same roasting time and temperature, are roasted together. The results of the experiments are given in Table 4.3.

After the experiments are conducted; average, standard deviation and signal-to-noise ratio of the results belonging to each run (experimental setting) are computed.

After estimating the average and standard deviation, Signal-to-Noise ratio is calculated by using the Larger-the-Better criteria. The formula for this criterion is:

$$\eta = -10LOGV_T \qquad V_T = \frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2} \qquad [4.1]$$

For the 1st experiment, the computation is given as follows:

Results are: 13.76, 24.18 and 26.00

$$V_T = \frac{1}{3}\left(\frac{1}{13.76^2} + \frac{1}{24.18^2} + \frac{1}{26.00^2}\right) \quad \Rightarrow \quad V_T = 0.0028237$$

η = -10LOG(0.0028237) $\Rightarrow$ η = 25.49175

The complete results of average, standard deviation and S/N ratio are given in Table 4.4.

4.2. Analysis of the Results

4.2.1. ANOVA

ANOVA of the S/N ratio values is performed by using the statistical package program MINITAB. The ANOVA table obtained is given in Table 4.5.

Table 4.3. The Results of The Experiments

Run	A	B	C	D	E	F	EXTRACTION RESULTS (%)		
	Gypsum/Clay	Ro. Te.,°C	Ro. Ti., min	Leach S/L	Le. Ti., min	Limestone/Clay	1	2	3
1	1.5/5	850	60	0.1	30	1.5/5	13.76	24.18	26.00
2	1.5/5	850	30	0.2	60	3/5	5.22	6.51	6.14
3	1.5/5	850	120	0.4	120	4.5/5	8.11	11.03	7.21
4	1.5/5	950	60	0.1	30	3/5	27.66	30.44	30.74
5	1.5/5	950	30	0.2	60	4.5/5	17.65	7.81	8.85
6	1.5/5	950	120	0.4	120	1.5/5	70.35	73.42	65.80
7	1.5/5	1050	60	0.1	30	4.5/5	11.97	6.29	8.72
8	1.5/5	1050	30	0.2	60	1.5/5	44.26	43.69	25.89
9	1.5/5	1050	120	0.4	120	3/5	36.13	50.68	25.73
10	3/5	850	60	0.2	120	4.5/5	8.15	6.56	4.90
11	3/5	850	30	0.4	30	1.5/5	6.93	4.34	4.65
12	3/5	850	120	0.1	60	4.5/5	27.65	6.71	10.99
13	3/5	950	60	0.2	120	1.5/5	55.70	64.63	55.86
14	3/5	950	30	0.4	30	3/5	39.52	18.27	13.42
15	3/5	950	120	0.1	60	4.5/5	22.95	23.36	19.19
16	3/5	1050	60	0.2	120	3/5	52.83	65.64	44.61
17	3/5	1050	30	0.4	30	4.5/5	10.55	28.40	28.65
18	3/5	1050	120	0.1	60	1.5/5	18.70	25.80	24.25
19	4.5/5	850	60	0.4	60	3/5	10.86	4.37	7.18
20	4.5/5	850	30	0.1	120	4.5/5	3.00	2.79	3.10
21	4.5/5	850	120	0.2	30	1.5/5	30.17	28.20	23.78
22	4.5/5	950	60	0.4	60	4.5/5	28.93	27.30	26.16
23	4.5/5	950	30	0.1	120	1.5/5	30.93	30.64	30.53
24	4.5/5	950	120	0.2	30	3/5	64.69	65.81	52.74
25	4.5/5	1050	60	0.4	60	1.5/5	11.45	14.06	15.52
26	4.5/5	1050	30	0.1	120	3/5	42.53	49.82	45.24
27	4.5/5	1050	120	0.2	30	4.5/5	46.80	65.75	54.91

Table 4.4. The Average, Standard Deviation and S/N Ratio of Experiments

Run	A	B	C	D	E	F			
	Gypsum/Clay	Ro.Te.,°C	Ro.Ti., min	Leach S/L	Le.Ti. ,min	Limestone/Clay	AVER.	STD.DEV.	S/N RATIO
1	1.5/5	850	60	0.1	30	1.5/5	21.313	6.6044	25.49180
2	1.5/5	850	30	0.2	60	3/5	5.957	0.6643	15.38497
3	1.5/5	850	120	0.4	120	4.5/5	8.783	1.9970	18.47098
4	1.5/5	950	60	0.1	30	3/5	29.613	1.6983	29.39990
5	1.5/5	950	30	0.2	60	4.5/5	11.437	5.4060	19.66948
6	1.5/5	950	120	0.4	120	1.5/5	69.857	3.8339	36.85758
7	1.5/5	1050	60	0.1	30	4.5/5	8.993	2.8498	18.20008
8	1.5/5	1050	30	0.2	60	1.5/5	37.947	10.4453	30.74645
9	1.5/5	1050	120	0.4	120	3/5	37.513	12.5324	30.51278
10	3/5	850	60	0.2	120	4.5/5	6.537	1.6251	15.74346
11	3/5	850	30	0.4	30	1.5/5	5.307	1.4144	13.97356
12	3/5	850	120	0.1	60	4.5/5	15.117	11.0631	19.74724
13	3/5	950	60	0.2	120	1.5/5	58.730	5.1102	35.31552
14	3/5	950	30	0.4	30	3/5	23.737	13.8822	25.13866
15	3/5	950	120	0.1	60	4.5/5	21.833	2.2984	26.67787
16	3/5	1050	60	0.2	120	3/5	54.360	10.5982	34.38546
17	3/5	1050	30	0.4	30	4.5/5	22.533	10.3786	24.18595
18	3/5	1050	120	0.1	60	1.5/5	22.917	3.7331	26.94470
19	4.5/5	850	60	0.4	60	3/5	7.470	3.2547	15.72724
20	4.5/5	850	30	0.1	120	4.5/5	2.963	0.1582	9.41022
21	4.5/5	850	120	0.2	30	1.5/5	27.383	3.2723	28.61751
22	4.5/5	950	60	0.4	60	4.5/5	27.463	1.3922	28.75297
23	4.5/5	950	30	0.1	120	1.5/5	30.700	0.2066	29.74238
24	4.5/5	950	120	0.2	30	3/5	61.080	7.2443	35.58371
25	4.5/5	1050	60	0.4	60	1.5/5	13.677	2.0619	22.50835
26	4.5/5	1050	30	0.1	120	3/5	45.863	3.6848	33.17449
27	4.5/5	1050	120	0.2	30	4.5/5	55.820	9.5077	34.68712

Table 4.5. ANOVA of S/N Ratio Values

Source	df	Sum of Squares	Mean Square	F	P
Gypsum	2	16.56	8.28	0.40	0.716
Roasting Temp.	2	728.96	364.48	17.44	0.054
Roasting Time	2	179.77	89.88	4.30	0.189
Leach S/L Ratio	2	79.48	39.74	1.90	0.345
Leaching Time	2	85.93	42.97	2.06	0.327
Limestone	2	183.50	91.75	4.39	0.186
Gypsum x Ro. Te.	4	32.64	8.16	0.39	0.808
Ro. Te. x Ro. Time	4	118.68	29.67	1.42	0.453
Ro. Te. x Leach S/L	4	56.47	14.12	0.68	0.670
Error	2	41.81	20.90		
TOTAL	26	1523.81			

The results show that the interaction factors do not have any significant effect on the leaching of lithium. Also the interaction graphs prove this corollary. The interaction graphs are given in Figures 4.1, 4.2 and 4.3 for Gypsum x Roasting Temperature, Roasting Temperature x Roasting Time and Roasting Temperature x Leach S/L Ratio, respectively.

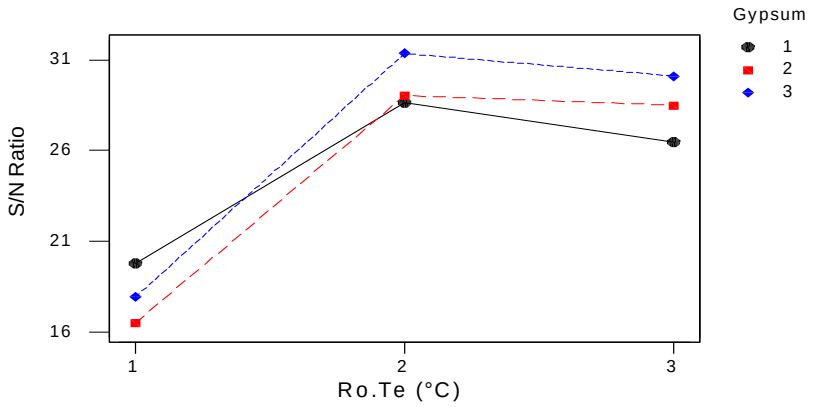


Figure 4.1. The interaction plot for Roasting Temperature x Gypsum

The plot in Figure 4.1 implies not a strong interaction, however, we can conclude a slight interaction between roasting temperatures of 850°C and 950°C and gypsum ratios of 1.5 and 4.5.

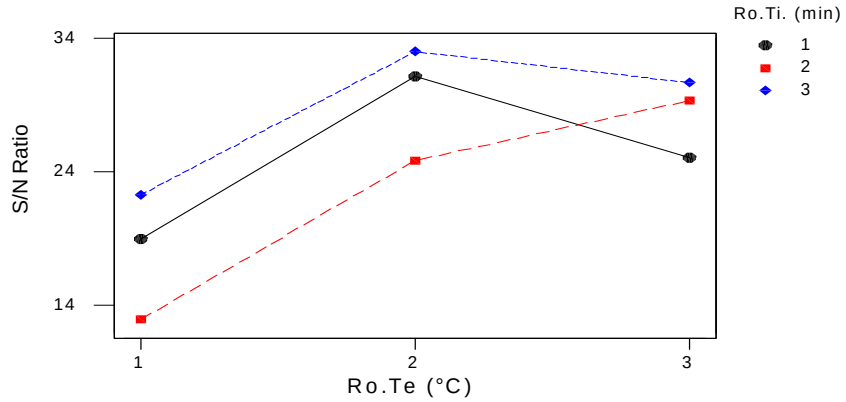


Figure 4.2. The interaction plot for Roasting Temperature x Roasting Time

As it is seen from the plot, there is no interaction between 850-950°C of roasting temperatures. However; we can conclude that an interaction may exist for roasting temperatures more than 950°C and roasting time between 30-60 minutes.

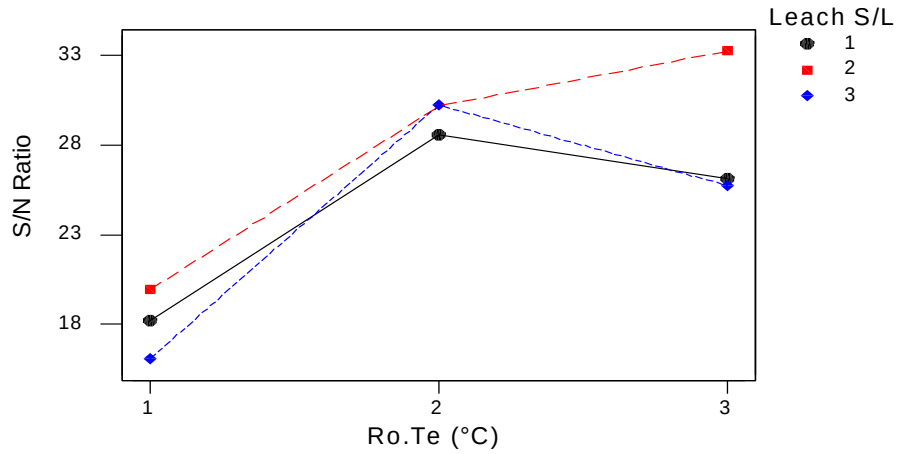


Figure 4.3. The interaction plot for Roasting Temperature x Leach S/L Ratio

The interaction plot in Figure 4.3 indicates a possibility of a strong interaction for the leaching solid-liquid ratios of between 0.1 and 0.4.

As ANOVA shows that the interaction terms are not significant within the experimental region, a new ANOVA is performed by pooling the interaction terms to error. New results are given in Table 4.6.

Table 4.6 ANOVA of S/N Ratio without interaction terms

Source	df	Sum of Squares	Mean Square	F	P
Gypsum	2	16.56	8.28	0.46	0.638
Roasting Temperature	2	728.96	364.48	20.44	0.000
Roasting Time	2	179.77	89.88	5.04	0.022
Leach S/L Ratio	2	79.48	39.74	2.23	0.144
Leaching Time	2	85.93	42.97	2.41	0.126
Limestone	2	183.50	91.75	5.15	0.021
Error	14	249.60	17.83		
TOTAL	26	1523.81			

When ANOVA of main factors are examined, it is observed that, gypsum has a very high p-value that it is not a significant factor. Therefore, it is thought to perform ANOVA without Gypsum. The results are given in Table 4.7.

Table 4.7. ANOVA of S/N Ratio without interaction terms and Gypsum

Source	df	Sum of Squares	Mean Square	F	P
Roasting Temperature	2	728.96	364.48	21.91	0.000
Roasting Time	2	179.77	89.88	5.40	0.016
Leach S/L Ratio	2	79.48	39.74	2.39	0.124
Leaching Time	2	85.93	42.97	2.58	0.107
Limestone	2	183.50	91.75	5.52	0.015
Error	16	266.16	16.64		
TOTAL	26	1523.81			

These results show that at the significance level of α=0.15, Roasting Temperature, Roasting Time, Leach S/L Ratio, Leaching Time and Limestone are significant.

The residual plots of the model are given in Figure 4.4 and 4.5.

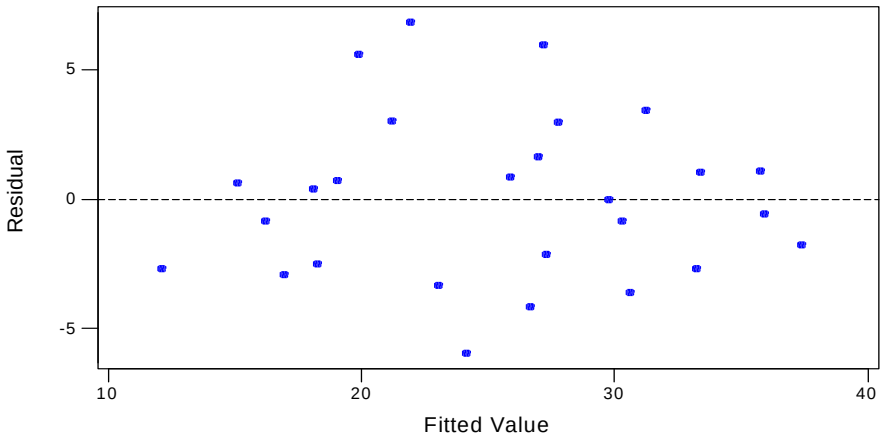


Figure 4.4. The residuals versus fitted values of the model found by ANOVA for S/N ratio.

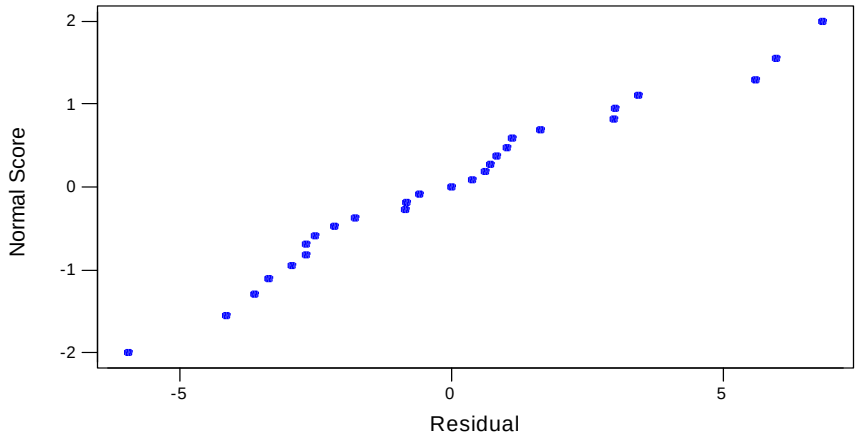


Figure 4.5. Normal probability plot for the model found by ANOVA for S/N Ratio

Both figures show no abnormality for validation of the assumptions of errors.

The main effects plot is plotted. By using the main effects plot and level averages, the optimum point that increases S/N ratio is found.

Table 4.8. Level averages of the factors

Gypsum			Ro.Te. °C		
1.5	*3*	*4.5*	*850*	*950*	*1050*
24.9705	24.6792	26.2471	18.0630	29.6820	28.3717
Ro.Ti. min			Leach S/L		
30	*60*	*120*	*0.1*	*0.2*	*0.4*
22.3807	25.0583	28.6777	24.3099	27.7926	24.0142
Lea.Ti. min			Limestone		
30	*60*	*120*	*1.5*	*3*	*4.5*
26.1420	22.9066	27.0681	27.7998	26.5616	21.7553

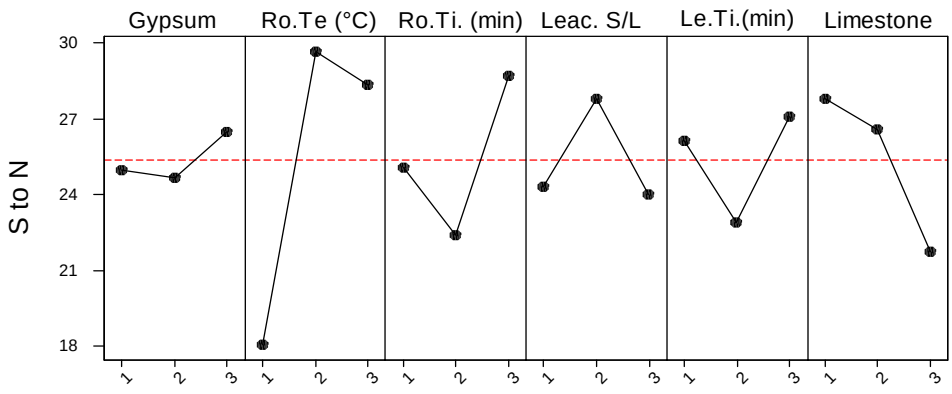


Figure 4.6. Main Effects Plots of Signal-to-Noise Ratio

As it is seen from Figure 4.6, the optimum points are 2nd level for Roasting Temperature, 3rd level for Roasting Time, 2nd level for Leach S/L Ratio, 3rd level for Leach Time and 1st level for Limestone.

That is, if we assign letters to factors like; A for Gypsum, B for Roasting Temperature, C for Roasting Time, D for Leach S/L Ratio, E for Leach Time and F for Limestone, the notation of optimum points are;

$A_3B_2C_3D_2E_3F_1$

Although gypsum has not been found significant, it has to be used in the experiment. Hence the level that seems to yield the highest extraction has been used for gypsum. We need to predict the results of the extraction percent and estimate the 95% confidence interval for this fit value. The superscripts imply the average effect of the factors.

$$E(\eta) = \overline{T} + (\overline{B}_2 - \overline{T}) + (\overline{C}_3 - \overline{T}) + (\overline{D}_2 - \overline{T}) + (\overline{E}_3 - \overline{T}) + (\overline{F}_1 - \overline{T}) \quad [4.2]$$

$$E(\eta) = 25.37 + (29.68 - 25.37) + (28.68 - 25.37) + (27.79 - 25.37) + (27.07 - 25.37) + (27.80 - 25.37)$$

$$E(\eta) = 25.37 + 4.31 + 3.31 + 2.42 + 1.70 + 2.43$$

$$E(\eta) = 39.54$$

The confidence interval for signal to noise ratio should be calculated before conducting the experiment.

$$C.I. = \sqrt{F_{\alpha,1,n_e} V_e (\frac{1}{N_{EFF}} + \frac{1}{r})} \qquad [4.3]$$

where;

$F_{\alpha,1,n_e}$ = Tabulated F-value for 1-α (α=0.95) confidence level with 1 and degrees of freedom of error

V_e = Pooled error variance

N_{EFF}= Effective sample size = $\frac{\text{Total degrees of freedom}}{\text{Degrees of freedom used in calculating S/N}}$

r= sample size for the confirmation experiment,

$F_{0.05,1,16}$ = 4.49

V_e = 16.64

N_{EFF} = 26 / 11 = 2.364

r = 1, as only one S/N ratio will be estimated from the experiments

$$C.I. = \sqrt{4.49 * 16.64 (\frac{1}{2.364} + 1)} = 10.31$$

Therefore the value for S/N ratio of the confirmation experiment is expected to be between;

$$\eta = \left\{ 29.23 \, , \, 49.85 \right\}$$

with 95% confidence

In order to have an idea about the mean extraction at the optimal levels we can predict a value for the mean. In order to predict the mean more accurately, ANOVA has been performed on the individual results rather than the average of the replications. ANOVA table of the model for the mean can be seen in Table 4.9.

Table 4.9. ANOVA table for the mean

Source	df	Sum of Squares	Mean Square	F	P
Gypsum	2	376.8	188.4	3.37	0.041
Roasting Temperature	2	10590	5295	94.71	0.000
Roasting Time	2	3127.7	1563.9	27.97	0.000
Leach S/L Ratio	2	2807.2	1403.6	25.11	0.000
Leaching Time	2	3883.3	1941.7	34.73	0.000
Limestone	2	3097.8	1548.9	27.70	0.000
Ro. Te. x Ro. Ti.	4	2198.7	549.7	9.83	0.000
Ro. Te. x Leach S/L	4	2254.2	563.5	10.08	0.000
Error	60	3354.5	55.9		
TOTAL	80	31690.2			

In order to estimate the effects of factors the experiments have been treated individually. The residual plots for the mean model can be seen in Appendix 4A.3. The best level for roasting temperature conflicts with the best level of interaction between roasting temperature and leach solid to liquid ratio. The level averages for the mean and the comparison of the best levels can be found in Appendix 4A.4. Since we are aiming to maximize the mean extraction with minimal variation, the choice of best levels has been based on the S/N analysis. This is the combination $A_3B_2C_3D_2E_3F_1$. The predicted value for the mean has been found as 73.13 for this combination.

To predict the standard deviation at the optimal levels of the factors, the following formula of S/N can be used.

$$\eta = -10LOG(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}) \cong -10LOG\left[\frac{1}{\bar{y}^2}(1+3\frac{s^2}{\bar{y}^2})\right] \qquad [4.4]$$

From Equation [4.4], s can be estimated by putting 39.54 and 73.13 for η and $\overline{y}$ respectively. However; solving for s will yield a negative value for s^2. This might be due to the cumulative effect of prediction errors of both S/N Ratio and the mean. Hence we have decided to model the standard deviation and make a prediction directly from this model. ANOVA table of the model for standard deviation can be seen in Table 4.10.

Table 4.10. ANOVA table for the standard deviation

Source	df	Sum of Squares	Mean Square	F	P
Gypsum	2	47.787	23.893	9.51	0.014
Roasting Temperature	2	74.433	37.217	14.81	0.005
Roasting Time	2	22.926	11.463	4.56	0.062
Leach S/L Ratio	2	30.213	15.107	6.01	0.037
Leaching Time	2	20.973	10.486	4.17	0.073
Limestone	2	60.124	30.062	11.96	0.008
Ro. Te. x Ro. Ti.	4	53.451	13.363	5.32	0.036
Ro. Te. x Leach S/L	4	118.978	29.744	11.84	0.005
Error	6	15.079	2.513		
TOTAL	26	443.963			

The residual plots for the standard deviation model can be seen in Appendix 4A.5. The best levels considering both the mean and the standard deviation had been found based on S/N analysis as $A_3B_2C_3D_2E_3F_1$. The predicted value for standard deviation at these levels has been found as 2.514, and the computation of this value with the level averages can be found in Appendix 4A.6.

These fitted values of S/N, mean and standard deviation seem to be worth to try.

The confirmation experiment has been performed twice. The results of the confirmation experiment yield the values of 56.87% and 67.79% with a standard deviation of 5.46. S/N ratio for these experiments has been found as 35.794, which is in the prediction interval. This leads to a conclusion that the "optimum" settings found by using the Taguchi method are confirmed.

In the following sections, we try to find even better settings for the design parameters by utilizing regression and response surface methodologies.

4.2. Regression Analysis

4.2.1 Modelling the Mean Response

In order to model the mean response, MINITAB package program is used. ANOVA has shown us that only linear terms will not be enough to explain the extraction of lithium from clays. However; it is worth to try regression analysis with only linear terms.

$\mu = - 87.0 + 1.52*A + 0.110*B + 0.166* C - 2.8*D + 0.103*E - 4.50*F$ [4.5]

Table 4.11. ANOVA for Regression Analysis for the mean including only main factors

Source	dF	Sum of Squares	Mean Squares	F	p
Regression	6	4555.3	759.2	2.89	0.034
Residual Error	20	5249.3	262.5		
TOTAL	26	9804.6			

$R^2 = 46.5\%$ $R^2_{(adj)} = 30.4\%$ $S = 16.20$

Durbin Watson = 2.44

The residual versus fitted values plot shows a violation (Figure 4.7) of constant variance assumption of residuals, and also R^2(adj) value is so low that the model will not be adequate enough to explain the mean extraction of lithium from boron clays. Besides these, Durbin-Watson statistic is so high. In Figure 8, normal probability plot of residuals can be seen. Table 4.12 shows the significance of β terms of the general linear model. This Table indicates that roasting temperature, roasting time and limestone are significant at the p (0.15) level of significance.

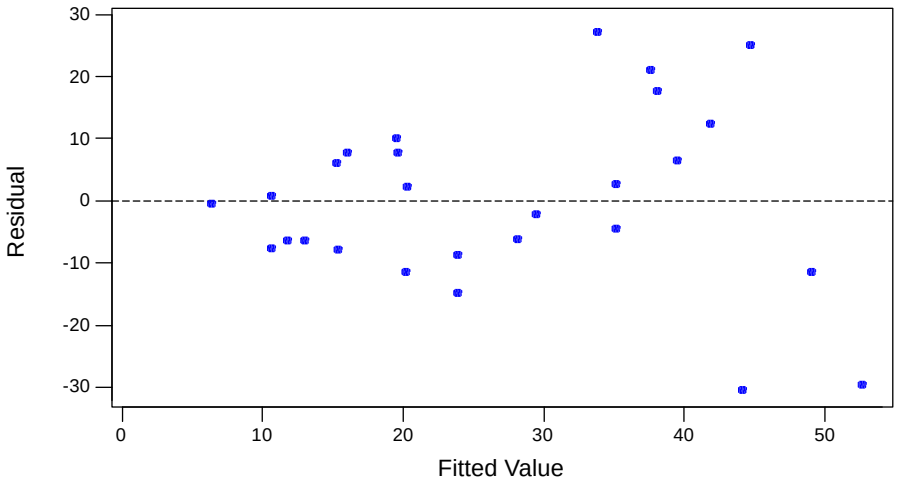


Figure 4.7. Residual versus fitted values of the residuals of general linear model [4.5] with only main factors.

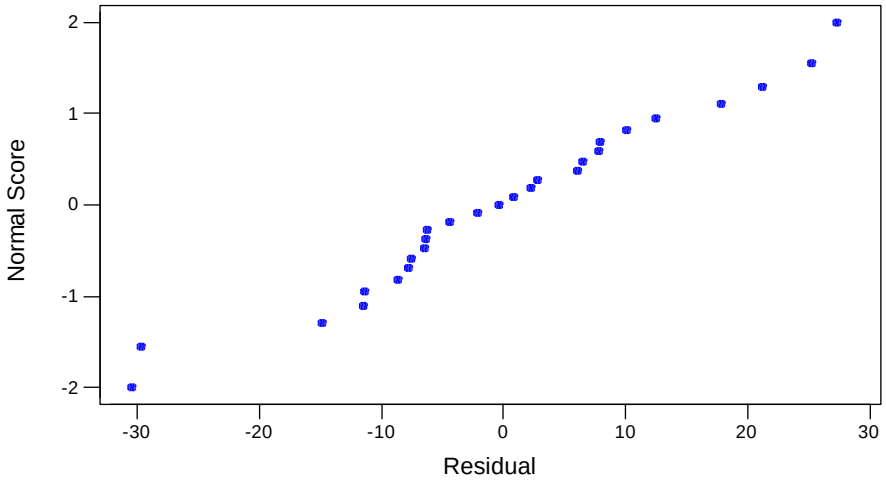


Figure 4.8. Normal probability plot of the residuals of general linear model [4.5] with only main factors.

Table 4.12. Significance of β terms of the General Linear Model [4.5]

Predictor	Coefficient	Standard Error	T	p
Constant	-86.95	39.30	-2.21	0.039
Gyspsum	1.519	2.546	0.60	0.557
Roasting Temp.	0.11044	0.03819	2.89	0.009
Roasting Time	0.16603	0.08333	1.99	0.060
Leach S:L Ratio	-2.76	25	-0.11	0.913
Leach Time	0.10307	0.08333	1.24	0.230
Limestone	-4.499	2.546	-1.77	0.092

The sequential sum of squares of the main factors are given in Appendix 4A.7.

Under these circumstances, it is decided to perform a new regression model by employing interaction and square terms.

We have 26 degrees of freedom to introduce to the new model. Main factors and square factors use 12 degrees of freedom. In order to estimate all two-way interaction terms, 15 degrees of freedom are needed. However; there are only 14 degrees of freedom to use so an interaction could not be estimated. This interaction is chosen as the one between Leach Time and Limestone.

MINITAB package program is used in order to model the quadratic regression with two-way interactions. However; while performing regression analysis, MINITAB has found some correlation between some interaction and quadratic factors. These are automatically disregarded from the regression analysis. The interaction factors that are correlated with other variables are A*E, C*E and D*E. The square factors that are correlated are C^2, D^2 and E^2.

The regression model and the ANOVA of the regression obtained can be seen in Equation [4.6].

$$\mu = -1332 + 17.2*A + 2.89*B - 0.105*C - 98.5*D + 0.631*E - 50.18*F + 0.019*AB + 0.195*AC - 1.49*AD + 5.20*AF - 0.001*BC - 0.14*BD - 0.0006*BE + 0.055*BF + 3.75*CD - 0.013*CF - 2.97*DF - 9.80*A^2 - 0.0015*B^2 - 3.49*F^2 \quad [4.6]$$

Table 4.13. ANOVA for Regression Analysis for the mean including main, interaction and square factors

Source	dF	Sum of Squares	Mean Squares	F	p
Regression	20	9736.54	486.83	42.94	0.000
Residual Error	6	68.02	11.34		
TOTAL	26	9804.56			

$R^2 = 99.3\ \%$ $R^2_{(adj)} = 97.0$ $S = 3.367$

Durbin Watson = 1.96

This model is much more adequate for explaining the mean extraction of lithium from boron clays. R^2 and $R^2_{(adj)}$ values are adequately high. Standard deviation of the error is much smaller than the regression model including only main factors. Also Durbin-Watson statistic shows no correlation of errors. The residuals versus fitted values and normal probability plots are shown in Figures 4.9 and 4.10, respectively.

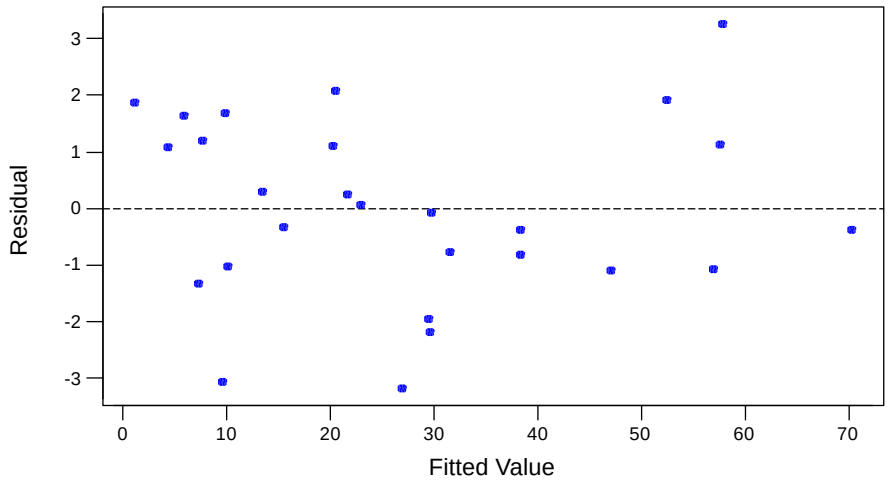


Figure 4.9. Residual vs fitted values of the residuals of quadratic model [4.6] with interaction factors.

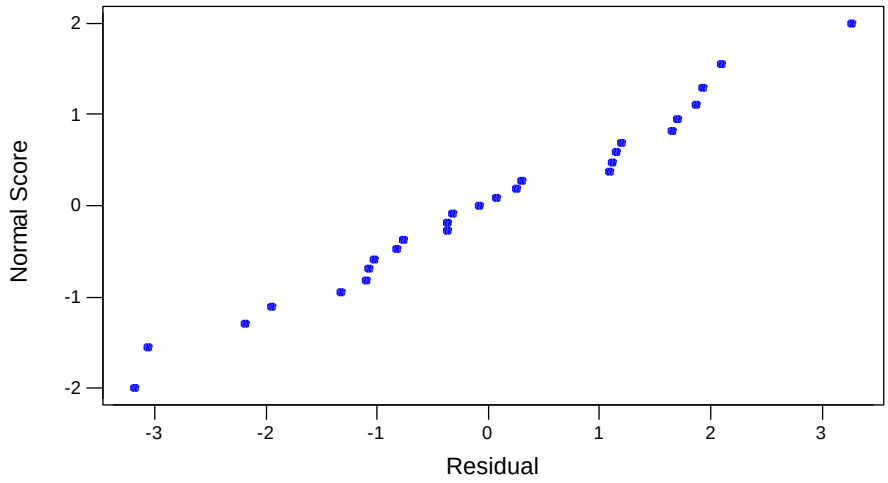


Figure 4.10. Normal probability plot of the residuals of quadratic model [4.6] with interaction factors.

Residuals versus fitted values and normal probability plot indicate that errors have normal distribution with constant variance. With these and Durbin Watson test, it is inferred that the assumptions about errors for a adequate model is achieved. In that point, it is necessary to make a β significance test.

Table 4.14. Significance of β terms of quadratic model [4.6]

Predictor	Coefficient	Standard Error	T	p
Constant	-1332.1	129.5	-10.29	0.000
A	17.17	17.08	1.01	0.354
B	2.8857	0.2644	10.91	0.000
C	-0.1051	0.3143	-0.33	0.749
D	-98.52	95.90	-1.03	0.344
E	0.6312	0.4228	1.49	0.186
F	-50.18	10.84	-4.63	0.004
A*B	0.018944	0.007003	2.71	0.035
A*C	0.19532	0.02154	9.07	0.000
A*D	-1.491	6.461	-0.23	0.825
A*F	5.2019	0.4669	11.14	0.000
B*C	-0.0012118	0.0002335	-5.19	0.002
B*D	-0.14162	0.06711	-2.11	0.079
B*E	-0.0006306	0.0003968	-1.59	0.163
B*F	0.05452	0.01212	4.50	0.004
C*D	3.7501	0.8618	4.35	0.005
C*F	-0.01341	0.01557	-0.86	0.422
D*F	-2.967	4.474	-0.66	0.532
A^2	-9.804	2.563	-3.82	0.009
B^2	-0.0014914	0.0001375	-10.85	0.000
F^2	-3.4884	0.8082	-4.32	0.005

The sequential sum of squares of the model are given in Appendix 4A.8.

When the p-values of factors are examined, it is seen that some of the factors have significantly high values, which can lead the model deviate from being adequate. Therefore, it is thought to improve the p-values of the model by disregarding the ones that have a high p-value. This must be accomplished without sacrificing normality, constant variance and error correlation properties of the previous model.

The model improvement starts with disregarding the factor having the highest p-value. After disregarding a factor, all assumptions of the model are checked and looked for the best model.

Eventually, the model with valid normality, constant variance and no error correlation assumption, and large R^2 and $R^2_{(adj)}$ values is the model that do not have the interaction factor, A*D. The model and ANOVA are given below. The main factors have been left in the model without considering their p-value.

$$\mu = -1332 + 18.2*A + 2.89*B - 0.121*C - 108*D + 0.629*E - 50.2*F + 0.0189*AB + 0.195*AC + 5.20*AF - 0.00121*BC - 0.142*BD - 0.000631*BE + 0.0545*BF + 3.82*CD - 0.0134*CF - 2.97*DF - 10.0*A^2 - 0.00149*B^2 - 3.49*F^2 \quad [4.7]$$

Table 4.15. ANOVA for the improved quadratic regression model [4.7]

Source	dF	Sum of Squares	Mean Squares	F	p
Regression	19	9735.94	512.42	52.27	0.000
Residual Error	7	68.62	9.80		
TOTAL	26	9804.56			

R^2=99.3% $R^2_{(adj)}$= 97.4% S=3.131

Durbin Watson=1.99

This model is better than the previous one for both $R^2_{(adj)}$ value, S value and Durbin Watson statistic. The residual plots of the improved quadratic model can be seen in Figures 4.11 and 4.12.

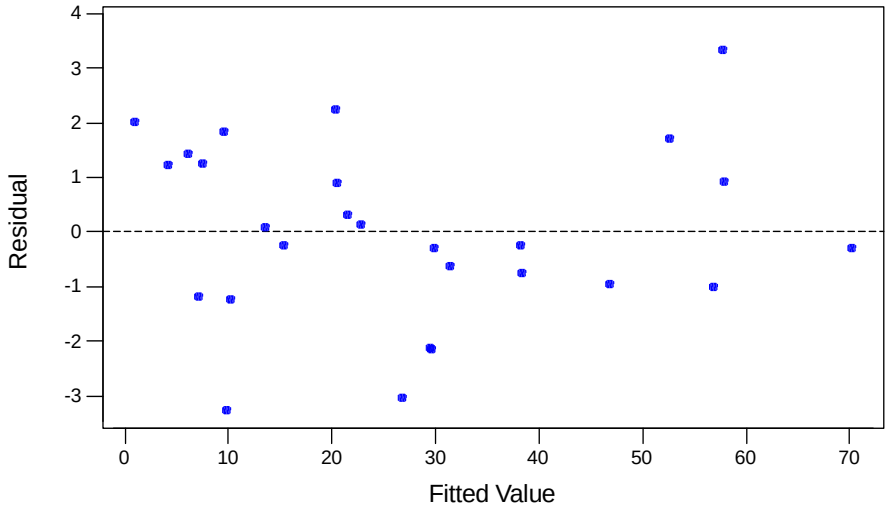


Figure 4.11. Residual vs fitted values of the residuals of improved quadratic model [4.7].

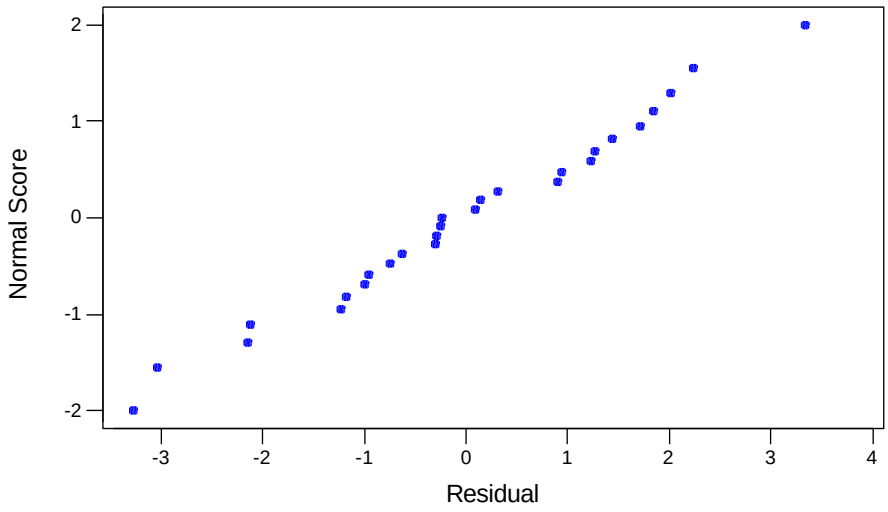


Figure 4.12. Normal probability plot of the residuals of improved quadratic model [4.7].

The normal probability plot and residual versus fitted values plot of the residuals do not show any deviation from the residual assumptions. When we investigate the β significance value of the factors, there are still some interaction factors having high p-values such as the interactions between Roasting Temperature and Leaching Time, Roasting Time and Limestone Ratio, Leaching S/L Ratio and Limestone Ratio. The β significance table and the sequential sum of squares of the model are given in Table 4.16 and Appendix 4A.9.

Table 4.16. Significance of β terms of the improved quadratic model [4.7]

Predictor	Coefficient	Standard Error	T	p
Constant	-1331.6	120.4	-11.06	0.000
A	18.19	15.34	1.19	0.354
B	2.8857	0.2459	11.73	0.000
C	-0.1209	0.2853	-0.42	0.749
D	-108.21	80.18	-1.35	0.344
E	0.6288	0.3930	1.60	0.186
F	-50.18	10.08	-4.98	0.004
A*B	0.018944	0.006512	2.91	0.035
A*C	0.19532	0.02003	9.75	0.000
A*F	5.2019	0.4341	11.98	0.000
B*C	-0.0012118	0.0002172	-5.58	0.002
B*D	-0.14162	0.06241	-2.27	0.079
B*E	-0.0006306	0.0003690	-1.71	0.163
B*F	0.05452	0.01127	4.84	0.004
C*D	3.8247	0.7430	5.15	0.005
C*F	-0.01341	0.01448	-0.93	0.422
D*F	-2.967	4.160	-0.71	0.532
A^2	-10.02	2.220	-4.51	0.009
B^2	-0.0014914	0.0001278	-11.67	0.000
F^2	-3.4884	0.7515	-4.64	0.005

Then it is tried to drop these factors from the model and achieve all interaction and square factors with p-value less than 10%. However; when we have this model, we have seen that Durbin Watson statistic falls to 1.38 and this is an evidence of a positive correlation between the residuals. Also R^2 and S value of this model is slightly worse.

In appendix 4A.10, the quadratic regression model with no p-value greater than 10% can be found.

As a result, it is decided to keep the improved quadratic model [4.7] as the most adequate one for the problem of extraction of lithium from boron clays.

4.2.2 Modelling the Standard Deviation

As we have made 3 repetitions for every run, we can make an analysis of standard deviation of the extraction values by regression. The standard deviation of the experimental results can be seen in Table 4.4. As the model for the mean shows that linear regression is not enough to explain the mean extraction of lithium, it is decided to perform modelling of the standard deviation by using quadratic and interaction factors. However; for illustrative purposes, the model that include only the main factors is tried and as expected very low values of R^2 and $R^2_{(adj)}$ is obtained (26.7% and 4.7%, respectively). The quadratic model and the ANOVA of the regression can be seen in equation [4.8] and Table 4.17.

$$s = 45 + 13.6*A - 0.122*B + 0.074*C - 102*D - 0.030*E + 1.8*F - 0.00751*AB + 0.0264*AC - 7.24*AD + 0.624*AF - 0.000232*BC + 0.116*BD + 0.000009*BE + 0.0029*BF + 0.14*CD + 0.0137*CF + 4.05*DF - 1.48*A^2 + 0.000076*B^2 - 1.39*F^2 \quad [4.8]$$

Table 4.17. ANOVA for quadratic regression analysis of the standard deviation

Source	dF	Sum of Squares	Mean Squares	F	p
Regression	20	350.10	17.51	1.12	0.482
Residual Error	6	93.86	15.64		
TOTAL	26	443.96			

R^2 = 78.9% $R^2_{(adj)}$ = 8.4% S = 3.955

Durbin Watson: 2.64

There is a big difference between R^2 and $R^2_{(adj)}$ value. This means that there are some unnecessary terms in the model. However; although there are unnecessary terms, the model only explains 78.9% of the standard deviation values. Also Durbin Watson test statistic is not acceptable. The residuals versus fitted values and normal probability plots are given in Figures 4.13 and 4.14, respectively.

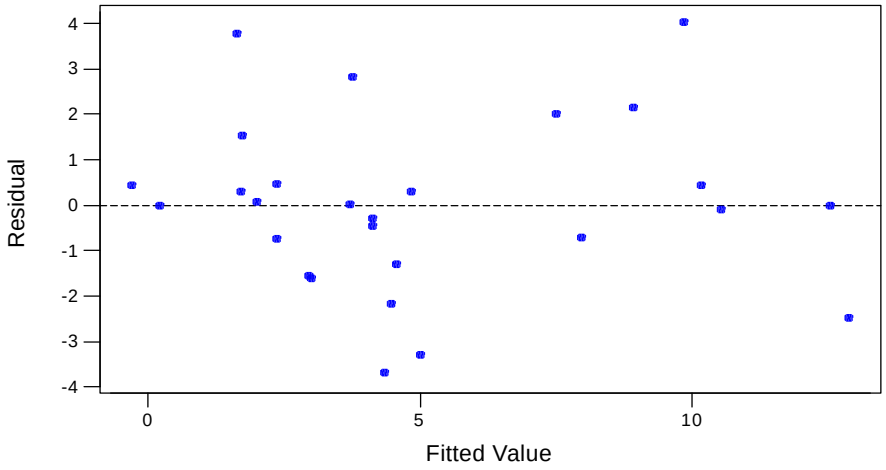


Figure 4.13. Residuals versus fitted values plot of the quadratic regression model [4.8] for the standard deviation

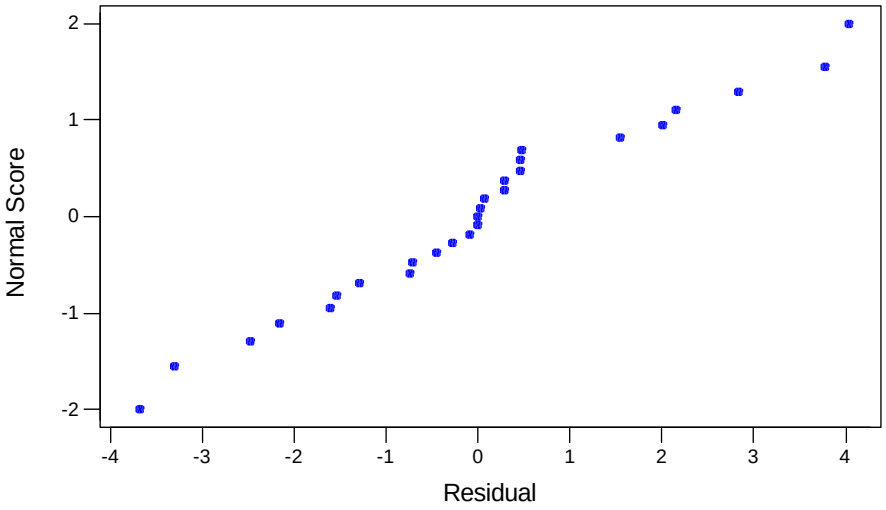


Figure 4.14. Normal probability plot of the quadratic regression model [4.8] for the standard deviation

Although the residuals versus fitted values and normal probability plots of the residuals do not show significant violation of constant variance and normal distribution assumptions, the β significance test of the factors show that none of the factors are significant at 10% confidence interval. The table of β significance test is given in Table 4.18.

Table 4.18. Significance of β terms of quadratic model [4.8]

Predictor	Coefficient	Standard Error	T	p
Constant	45.1	152.1	0.30	0.777
A	13.56	20.07	0.68	0.524
B	-0.1224	0.3106	-0.39	0.707
C	0.0744	0.3692	0.20	0.847
D	-102.0	112.7	-0.91	0.400
E	-0.0302	0.4966	-0.06	0.953
F	1.79	12.73	0.14	0.893
A*B	-0.007507	0.008226	-0.91	0.397
A*C	0.02637	0.02530	1.04	0.337
A*D	-7.244	7.589	-0.95	0.377
A*F	0.6242	0.5484	1.14	0.298
B*C	-0.0002319	0.0002743	-0.85	0.430
B*D	0.11557	0.07883	1.47	0.193
B*E	0.0000093	0.0004661	0.02	0.985
B*F	0.00292	0.1424	0.20	0.844
C*D	0.141	1.012	0.14	0.893
C*F	0.01369	0.01829	0.75	0.482
D*F	4.052	5.256	0.77	0.470
A^2	-1.480	3.011	-0.49	0.641
B^2	0.0000761	0.0001615	0.47	0.654
F^2	-1.3938	0.9494	-1.47	0.192

As it is seen from Table 4.18, none of the factors is significant at 10% significance level. Some trials are performed in order to have the factors having p-value less than 10%. However; the largest $R^2_{(adj)}$ value is obtained as 50.6 which is still low and Durbin Watson statistic for this model is 2.70 indicating a negative correlation of errors. The best achieved regression model can be seen in the Appendix 4A.11.

It is inferred that it is not possible to model the standard deviation without any transformation. It is decided to transform all standard deviation data by using $logs^2$ transformation. The $logs^2$ values are given in Appendix 4A.12.

The model and ANOVA of the regression analysis of the transformed standard deviation values can be seen in Equation [4.9] and Table 4.19.

$$\begin{aligned}\text{Log } s^2 = {} & 9.1 + 1.81*A - 0.0249*B + 0.0583*C - 8.2*D - 0.058*E + 0.17*F \\ & -0.00003*AB + 0.00824*AC + 0.35*AD + 0.145*AF - 0\ .000099*BC \\ & + 0.0026*BD + 0.000054*BE + 0.00051*BF + 0.087*CD \\ & - 0.00035*CF + 0.33*DF - 0.499*A^2 + 0.000016*B^2 - 0.185*F^2 \quad [4.9]\end{aligned}$$

Table 4.19. ANOVA for quadratic regression analysis for modelling log s^2

Source	dF	Sum of Squares	Mean Squares	F	p
Regression	20	21.0721	1.0536	1.28	0.408
Residual Error	6	5.9576	0.8263		
TOTAL	26	26.0297			

$R^2 = 81.0\%$ $R^2_{(adj)} = 17.5\%$ $S = 0.9090$
Durbin Watson= 2.12

The quadratic regression model for log s^2 seems better than that of s, however, still $R^2_{(adj)}$ value is so low that this model is not enough to explain the standard deviation of extraction of lithium from boron clays. Durbin Watson statistic measure is close to 2. Hence it can be concluded that there occurs no correlation between the residuals of quadratic regression model for log s^2. The residual versus fitted values and normal probability plots are given in Figures 4.15 and 4.16.

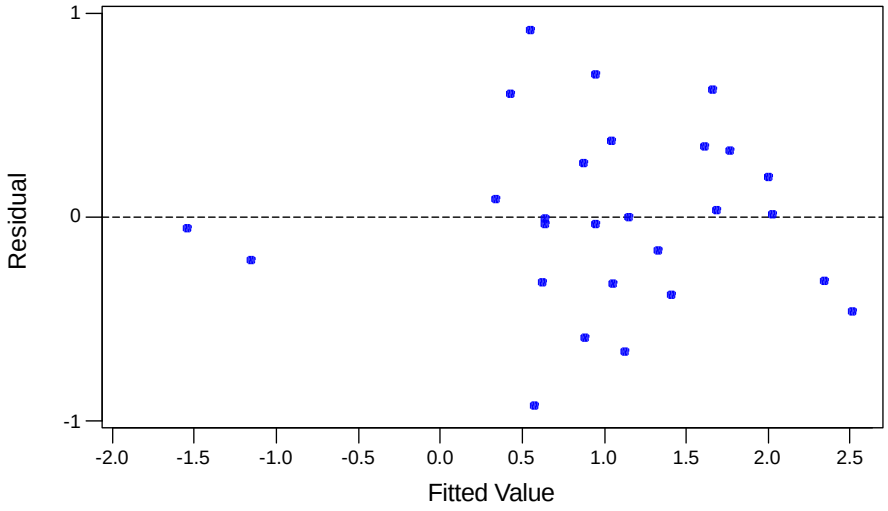


Figure 4.15. Residuals versus fitted values plot of the quadratic regression model [4.9] for log s^2

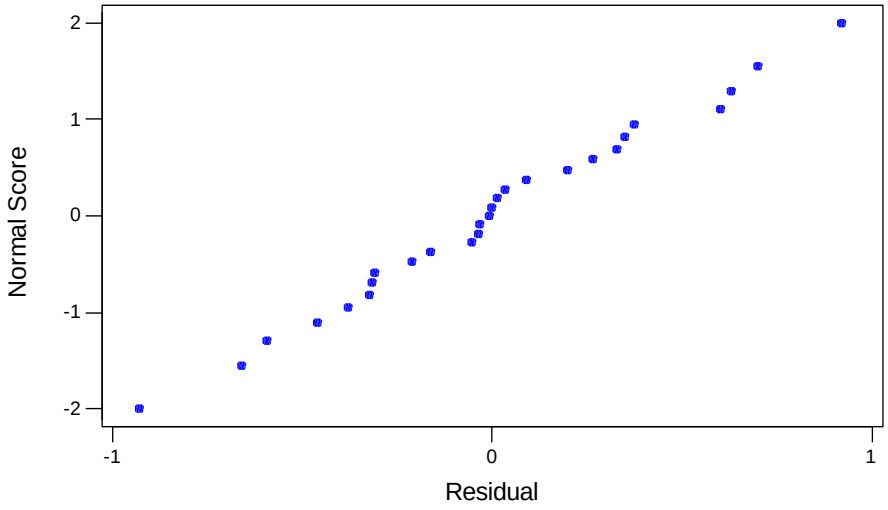


Figure 4.16. Normal probability plot of the quadratic regression model [4.9] for log s^2

Although it is seen no problem in the plot of normal probability of residuals, residuals versus fitted values do not indicate constant variance. Moreover, β significance test of the parameters indicate that some improvements are needed to be made in order to have the model more explanatory. Table 4.20 shows the β significance of the factors and sequential sum of squares can be seen in Appendix 4A.13.

Table 4.20. Significance of β terms of quadratic model [4.9] for log s^2

Predictor	Coefficient	Standard Error	T	p
Constant	9.10	34.96	0.26	0.803
A	1.815	4.611	0.39	0.708
B	-0.02486	0.07139	-0.35	0.740
C	0.05833	0.08486	0.69	0.518
D	-8.19	25.89	-0.32	0.762
E	-0.0577	0.1141	-0.51	0.631
F	0.167	2.925	0.06	0.956
A*B	-0.000025	0.001891	-0.01	0.990
A*C	0.008236	0.005814	1.42	0.206
A*D	0.348	1.744	0.20	0.848
A*F	0.1453	0.1260	1.15	0.293
B*C	-0.00009883	0.00006305	-1.57	0.168
B*D	0.00260	0.01812	0.14	0.891
B*E	0.0000543	0.0001071	0.51	0.630
B*F	0.000507	0.003273	0.15	0.882
C*D	0.0873	0.2327	0.38	0.720
C*F	-0.000353	0.004203	-0.08	0.936
D*F	0.325	1.208	0.27	0.797
A^2	-0.4990	0.6921	-0.72	0.498
B^2	0.00001626	0.00003711	0.44	0.677
F^2	-0.1847	0.2182	-0.85	0.430

As it is seen from the table of β significance, none of the factor has a p-value less than 10%. This result together with the low value of $R^2_{(adj)}$ strongly suggest that some terms in the quadratic regression model are unnecessary. Therefore, some trials are performed to increase $R^2_{(adj)}$ and to decrease the remaining factors significance level. For this purpose, factors are removed from the model starting from the factor that has the largest p-value. After several trials of getting an adequate model, the best model having the largest $R^2_{(adj)}$ value with no factors having a p-value larger than 10% is obtained as in Equation [4.10]. ANOVA of this model is given in Table 4.21.

$$\text{Log } s^2 = -4.00 + 0.0905*C + 0.00632*AC + 0.670*AD + 0.158*AF - 0.000106*BC + 0.00117*BF - 0.212*A^2 + 0.000005*B^2 - 0.271*F^2 \quad [4.10]$$

Table 4.21. ANOVA for improvedquadratic regression analysis for log s^2

Source	dF	Sum of Squares	Mean Squares	F	p
Regression	9	20.2778	2.2531	6.66	0.000
Residual Error	17	5.7519	0.3383		
TOTAL	26	26.0297			

R^2 = 77.9% $R^2_{(adj)}$ = 66.2% S = 0.5817
Durbin Watson= 2.43

There are significant improvements in the model in $R^2_{(adj)}$ value and S value. However; Durbin Watson statistics measure gets worse than the previous one. It is now important for checking the normal probability and residual versus fitted values plot. Figures 4.17 and 4.18 show the residual plots and Table 4.22 shows β significance test. In Appendix 4A.14, the sequential sum of squares can be found.

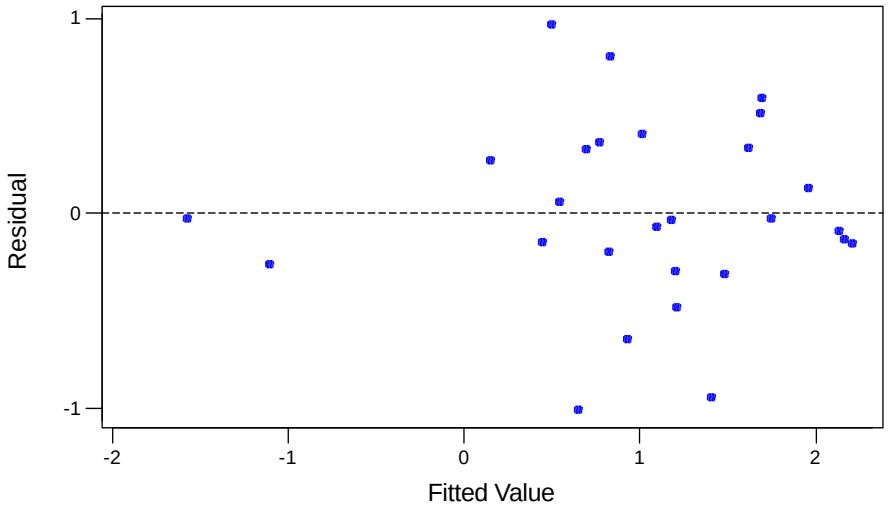


Figure 4.17. Residuals versus fitted values plot of the improved quadratic regression model [4.10] for log s^2

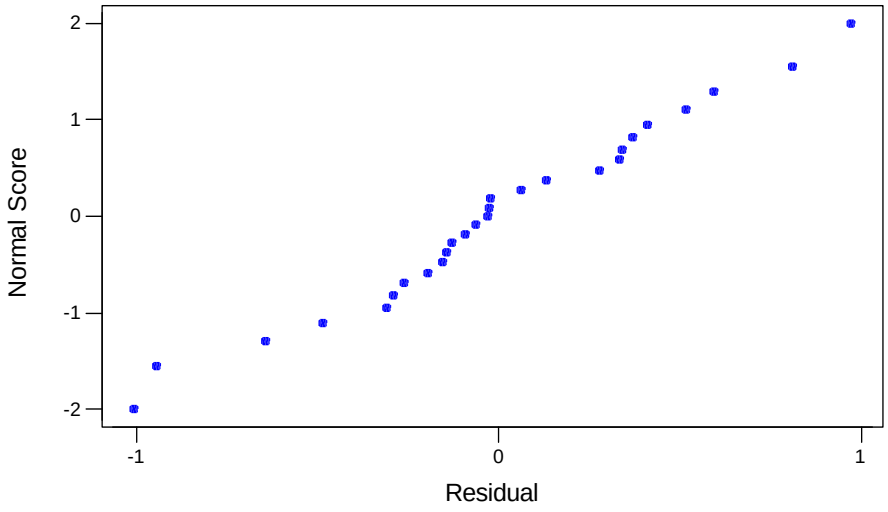


Figure 4.18. Normal probability plot of the improved quadratic regression model [4.10] for log s^2

Table 4.22. Significance of β terms of improved quadratic model [4.10] of log s^2

Predictor	Coefficient	Standard Error	T	p
Constant	-4.005	1.499	-2.67	0.016
C	0.09051	0.03739	2.42	0.027
A*C	0.006320	0.002397	2.64	0.017
A*D	0.67	0.2775	2.41	0.027
A*F	0.15803	0.07296	2.17	0.045
B*C	-0.00010596	0.00003840	-2.76	0.013
B*F	0.0011689	0.0006075	1.92	0.071
A^2	-0.21231	0.04785	-4.44	0.000
B^2	0.00000468	0.00000191	2.45	0.025
F^2	-0.27210	0.09254	-2.93	0.009

As it is seen from Table 4.22, all the factors in the improved quadratic regression model are important with at least p significance level, but unfortunately Durbin Watson test statistic for this model indicates a negative correlation between the errors. Tabulated values of Durbin-Watson (Mendenhall et. al, 1996, p.825-826) indicate that negative correlation is possibly significant in this case. Moreover, the randomness in the residuals versus fitted values graph is not achieved yet, therefore it is worth to try some higher order terms such as A^3, B^3, C^3, D^3, E^3, F^3.

When the cubic terms are added to the improved quadratic model, there is no significant improvement in the model. In contrast, $R^2_{(adj)}$ is decreased to 52.2% while R^2 value is increased to 79.8. This wide gap between R^2 and $R^2_{(adj)}$ is an indication of unnecessary terms in the model. The residual versus fitted values plot still needs improvement and Durbin Watson statistic decreases only little to 2.37 which is still an evidence for negative correlation. So some corrections are tried to be made on the model in order to decrease the gap between R^2 and $R^2_{(adj)}$ and decreasing the Durbin-Watson statistics. Also it is aimed to improve the residuals versus fitted plot. The best model that is

achieved can be seen in Equation [4.11] and Table 4.23 shows the results of ANOVA.

$$\text{Log } s^2 = -2.58 + 0.0592*C + 0.00858*AC - 0.000081*BC + 0.000873*BF - 0.0273*A^3 + 0.0000000015*B^3 + 10.6*D^3 - 0.0298*F^3 \quad [4.11]$$

Table 4.23. ANOVA for cubic regression analysis for log s^2

Source	dF	Sum of Squares	Mean Squares	F	p
Regression	8	19.1354	2.3919	6.24	0.001
Residual Error	18	6.8943	0.3830		
TOTAL	26	26.0297			

$R^2 = 73.5\%$ $R^2_{(adj)} = 61.7\%$ $S = 0.6189$

Durbin Watson = 2.09

Although this model has a larger S value, smaller $R^2_{(adj)}$ value and smaller R^2 value than the previous one, the Durbin Watson test statistic decreases to a level that we can assume there is no correlation between the residuals. The residuals versus fitted values and normal probability plot seem to be acceptable for all practical purposes. These plots can be seen in Figures 4.19 and 4.20, respectively.

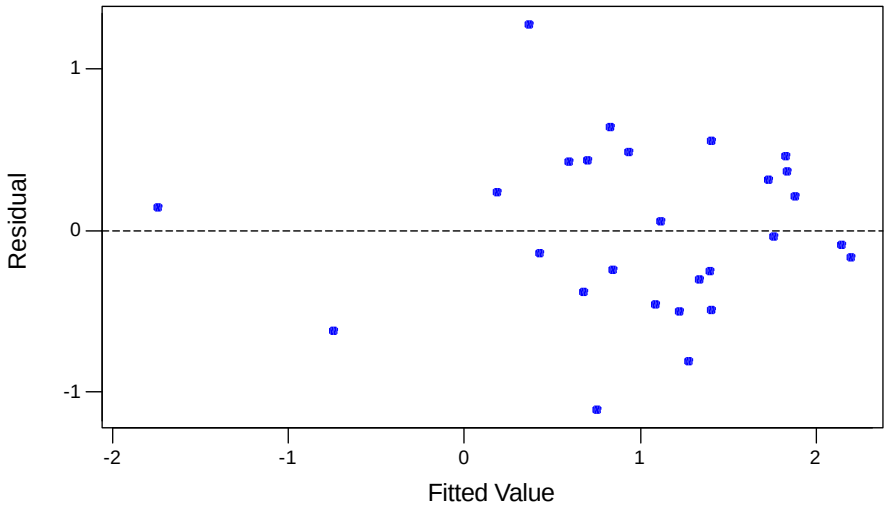


Figure 4.19. Residuals versus fitted values plot of the cubic regression model [4.11] for log s^2

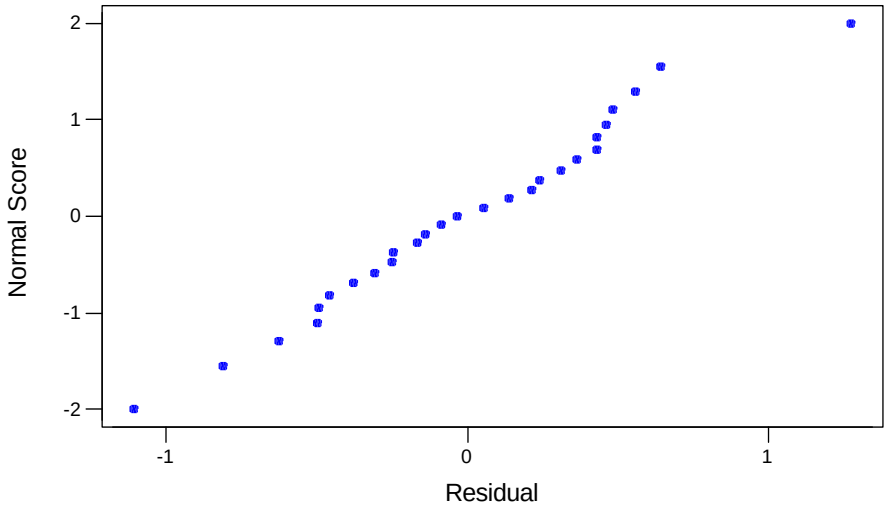


Figure 4.20. Normal probability plot of cubic model [4.11] for log s^2

The β significance test of the factors and the sequential sum of squares can be seen in Table 4.24 and Appendix 4A.15, respectively.

Table 4.24. Significance of β terms of cubic regression model for log s^2

Predictor	Coefficient	Standard Error	T	p
Constant	-2.579	1.094	-2.36	0.030
C	0.05921	0.3772	1.57	0.134
A*C	0.008584	0.002529	3.39	0.003
B*C	-0.00008092	0.0003786	2.31	0.033
B*F	0.000873	0.00003874	-2.09	0.051
A^3	-0.02728	0.0065	-4.20	0.001
B^3	0.0000000015	0.00000000	2.46	0.024
D^3	10.609	4.543	2.34	0.031
F^3	-0.02979	0.01192	-2.50	0.022

When Table 4.24 is examined, it is seen that roasting time has a p-value larger than 10%. However; removing roasting time from the model makes it worse in the manner that $R^2_{(adj)}$ has been decreased to 58.8% and Durbin Watson statistic has been increased to 2.55 indicating a negative correlation of residuals.

Eventually, standard deviation of extraction of lithium from boron clays can be modelled, however, this model is not so adequate to explain the standard deviation of the extraction results of lithium from boron clays. The best model fitted is given in Equation [4.11].

CHAPTER V

OPTIMIZATION

In Chapter 4, functional relationships between the performance measures; mean and standard deviation, and control the factors (Gypsum, Roasting Temperature, Roasting Time, Leaching S/L Ratio, Leaching Time, and Limestone) have been modelled.

In this chapter, optimal factor levels are found by solving a non-linear programming problem. The problem can simply be stated as follows;

$$\underset{A,B,C,D,E,F}{\text{Maximize}}\ \mu$$

subject to

$$\log s^2 \leq d$$

Here, d is some limit that we can accept for log s^2 value. Recall that in this study we would like to achieve maximum mean lithium extraction with as small variation as possible in the repeat extraction levels at the same factor settings. As far as the range of factor levels is concerned, we try both within and beyond the experimental region.

For solving this problem, some optimization algorithms have been used. These are MINITAB Response Optimizer, GAMS Non-Linear Programming and Ridge Analysis.

In using MINITAB optimization, the optimum point differs based on the starting point that is defined to program. Therefore, one optimum point is found based on the program's default starting point, and 9 more optimum points are found by specifying a different starting point each time. Same procedure has been applied for GAMS Non-Linear Programming. However; only one optimum is proposed by Ridge Analysis.

Furthermore, an optimum point is obtained by GAMS Non-linear programming for the surface outside the experimental region.

5.1 Minitab Response Optimizer

MINITAB Response Optimizer requires a minimum and a target value for maximization problems. Therefore it is decided to define a minimum value of 70 and a target value of 82. These values are chosen because 70 is the largest average extraction that is reached by the designed experiments and 82 is the largest extraction of lithium from clays due to economic considerations in the literature. Minimization of log s^2 could not be computed by MINITAB as it could not solve the problem of cubic models. MINITAB response optimizer provides %95 prediction interval for both the mean and the standard deviation at the optimum. The optimal factor settings that have been found from the model [4.7] have been put to the model [4.11] and fitted value and 95% prediction interval has been found for log s^2

As the response surface algorithm in MINITAB stops whenever it faces a point at which the first derivative is zero and as there are a lot of such points in the response surface area of lithium extraction, the points which are near 70 in the prediction interval has been treated as local (or global) optimum. In Table 5.1, the values can be seen. The starting points and the optimum points found by MINITAB can be seen in Appendix 5A.1.

Table 5.1. The prediction intervals for mean and standard deviation computed by MINITAB Response Optimizer

Optimum Points	Mean	Log s^2	s	% 95 Pred. Int. for Mean	% 95 Pred. Int. for log s^2
1	61.439	1.142	3.724	(50.237, 72.641)	(-0.309, 2.592)
2	99.977	2.481	17.398	(71.812, 128.141)	(0.982, 3.980)
3	22.956	-1.069	0.292	(11.191, 34.722)	(-2.593, 0.454)
4	61.867	1.000	3.163	(47.254, 79.479)	(-0.537, 2.537)
5	56.206	1.475	5.464	(43.762, 68.650)	(-0.092, 2.859)
6	66.075	1.893	8.841	(51.932, 80.218)	(0.460, 3.327)
7	83.032	1.930	9.226	(68.024, 98.040)	(0.283, 3.577)
8	71.928	1.217	4.060	(60.136, 83.720)	(-0.180, 2.614)
9	85.779	1.850	8.414	(63.591, 107.967)	(0.263, 3.436)
10	31.390	0.033	1.038	(20.325, 42.455)	(-1.384, 1.451)

As it is seen from Table 5.1, the prediction intervals for log s^2 are very wide. This is due to the fact that it can not be modelled adequately. From these ten optimum points, three points are chosen and experiments are conducted. These points are the optimum points of 1, 4 and 7. Points 3, 5, 10 have not been tested as they have yielded low values for the mean. Points 6 and 8 have not been tested as they have relatively high variances and high roasting temperatures that in turn will affect the economy of the process. Instead, point 1 (which has a high roasting temperature) has been tested. Points 9 and 7 have similar measures for the mean and the standard deviation, however, point 7 has a narrower prediction interval for the mean. Point 2 has a relatively high prediction for the standard deviation and also the mean estimated seems to be too high to obtain so it has not been tested. Point 4 has been chosen to try as it has relatively high mean value with low standard deviation. In order to estimate standard deviation, two repetitions have been applied for each experiment.

Optimum No:1

For this experiment; gypsum ratio, roasting temperature, roasting time, leach solid/liquid ratio, leaching time and limestone ratio are 1.5, 987°C, 30 min., 0.1, 120 min. and 1.5, respectively. The results of the experiments are 61,39% and 63.32%. Both of the results are in the prediction interval for the mean.

Standard deviation (log s^2) of these experiments is 0.540, which is still in prediction interval for standard deviation (log s^2).

Hence we can easily conclude that this point has been modelled well by the regression model for the mean and log s^2. However; we have had larger extraction values for lithium which was on the average 69.857 for the experiment number 6 in the orthogonal array design. It is certain that we could not have an improvement by conducting the experiments of this point.

Optimum No:4

For this experiment; gypsum ratio, roasting temperature, roasting time, leach solid/liquid ratio, leaching time and limestone ratio are 1.5, 878°C, 120 min., 0.36, 120 min. and 1.5, respectively. The results of the experiments are 43,13% and 43,08%. These points are just outside the lower limit of prediction interval for mean.

Standard deviation (log s^2) of these two experiments is –2.912 which is outside the lower limit of prediction interval for log s^2.

Therefore, it can be concluded that this point has not been modelled well by the regression model formulated for the mean and log s^2. Moreover, we have not seen any improvement of maximization of extraction of lithium from clays.

Optimum No:7

For this experiment; gypsum ratio, roasting temperature, roasting time, leach solid/liquid ratio, leaching time and limestone ratio are 4.5, 850°C, 120 min., 0.4, 120 min. and 1.5, respectively. The results of the experiments are 15,76% and 29,63%. These points are very far from the lower limit of prediction interval for mean.

Standard deviation (log s^2) of these two experiments is 1.983 which is in the prediction interval for standard deviation (log s^2).

So, this point can be modelled well by the regression for log s^2, however, it has modelled very badly by the regression for the mean. Moreover, there has been no improvement for the extraction maximization of lithium from boron clays.

5.2 GAMS Non-Linear Programming:

In Minitab package program, it is not possible to find the optimum point for the models having cubic terms. Therefore log s^2 could not have been considered by MINITAB Response Optimizer and optimum values and prediction intervals have not been found. In order to overcome this drawback, GAMS non-linear programming has been applied. Again 10 optimum points have been found by GAMS. Nine of these points have been found by defining a starting point and one without defining any starting point.

In the GAMS program, the model for mean is tried to be maximized. It is asked to the program that the mean be smaller than 100 and the regression model for log s^2 be smaller than 1. The non-linear program is given below:

Maximize

$$Z=-1331.6+18.19*A+2.8857*B-0.1209*C-108.21*D+0.6288*E-50.18*F+0.018944*A*B+0.19532*A*C+5.2019*A*F-0.0012118*B*C-0.14162*B*D-0.0006306*B*E+0.05452*B*F+3.8247*C*D-0.01341*C*F - 2.967*D*F - 10.02*A*A-0.0014914*B*B - 3.4884*F*F$$

Subject to

$$-2.579+0.05921*C+0.008584*A*C - 0.00008092*B*C + 0.000873*B*F-0.02728*A*A*A+0.0000000015*B*B*B+10.609*D*D*D-0.02979*F*F*F \leq 1$$

$$-1331.6+18.19*A+2.8857*B-0.1209*C-108.21*D + 0.6288*E - 50.18*F+0.018944*A*B+0.19532*A*C+5.2019*A*F-0.0012118*B*C-0.14162*B*D-0.0006306*B*E+0.05452*B*F+3.8247*C*D-0.01341*C*F-2.967*D*F-10.02*A*A-0.0014914*B*B- 3.4884*F*F \leq 100$$

$$1.5 \leq A \leq 4.5$$

$$850 \leq B \leq 1050$$

$$30 \leq C \leq 120$$

$$0.1 \leq D \leq 0.4$$

$$30 \leq E \leq 120$$

$$1.5 \leq F \leq 4.5$$

The code for solving this non-linear optimization problem by GAMS Non-Linear programming package can be seen in Appendix 5A.2. Also in Appendix 5A.3 the starting points defined to the GAMS program and optimum points found by the program can be seen. GAMS is using the Abadie-Carpentier method while optimizing non-linear problems.

As the coefficient for cubic term of roasting temperature (B^3) is very low (8 zeros after decimal) and as MINITAB has not given the values beyond 8 digits after decimal, a coefficient has been assigned for this parameter. Th coefficient of B^3 has been assigned as 0.0000000015. However; due to that

assignment, the values of log s^2 differ for GAMS and MINITAB program. So, fitted value and prediction interval of log s^2 values for GAMS output is found by MINITAB.

The fitted values of extraction of optimum points found by GAMS and fitted values of log s^2 and prediction intervals for both mean and log s^2 found by MINITAB for these two performance measures can be seen in Table 5.2.

Table 5.2. Mean values computed from GAMS and standard deviation with prediction intervals for both mean and log s^2 computed by MINITAB Response Optimizer

Optimum Points	Mean	Log s^2	s	% 95 Pred. Int. for Mean	% 95 Pred. Int. for log s^2
1	74.692	1.492	5.572	(62.449, 86.935)	(0.820, 2.902)
2	74.692	1.492	5.572	(62.449, 86.935)	(0.820, 2.902)
3	74.692	1.492	5.572	(62.449, 86.935)	(0.820, 2.902)
4	74.919	1.732	7.345	(51.122, 98.715)	(0.299, 3.164)
5	99.967	2.026	10.304	(84.455, 115.480)	(0.473, 3.579)
6	74.919	1.732	7.345	(51.122, 98.715)	(0.299, 3.164)
7	74.692	1.492	5.572	(62.449, 86.935)	(0.820, 2.902)
8	27.627	1.025	3.255	(17.073, 38.181)	(-0.498, 2.549)
9	74.692	1.492	5.572	(62.449, 86.935)	(0.820, 2.902)
10	99.969	2.373	15.364	(83.675, 116.263)	(0.890, 3.846)

As it is obvious from Table 5.2, five points (1, 2, 3, 7, 9) of the ten optimum points yield the same result. This point has been found by GAMS also without defining any starting point. Although, the fitted value for mean seems low, prediction intervals (compared with those of other points) for the mean and the standard deviation make it a valuable alternative to try. Point 4 and 6 have not been tested as they have yielded almost the same mean value with these five points. Point 8 has predicted a significantly low value for mean. Points 5 and 10 have predicted high mean values. However; they have both high roasting temperature and time and wide prediction intervals for the mean and standard

deviation. Therefore they have not been tried. So, the point where gypsum, roasting temperature, roasting time, leach S/L ratio, leaching time and limestone take the values of 2.787, 989, 30, 0.1, 120 and 2.512, respectively has been tried.

The results of the experiments yield the extraction values of %55.06 and %50.00. These results are both less than the lower limit of the prediction interval for the mean. The log s^2 for these results is 1.107 which is inside the prediction intervals for standard deviation.

So, this point has been modelled well with the regression for standard deviation (but standard deviation has a wide gap) and could not have been modelled by the regression model for the mean. It should have been said that GAMS Non-linear programming could not predict the fitted values well for the mean values. Moreover, it has been seen that modelling of standard deviation with log s^2 do not yield satisfactory results for GAMS. Apart from the misfit problem, there has been no any improvement achieved for extraction of lithium from boron clays.

5.3 Ridge Analysis

Ridge Analysis is the technique of steepest ascent applied to second order surfaces.

It is worth to apply this technique to the regression model for the mean, however, it is not possible to apply it to the model of log s^2 as this model is a third-order model. The idea of the model has been explained in Chapter II. Therefore, the technique tries to solve the following equation;

$(\mathbf{B}- \lambda\mathbf{I})\mathbf{x} = -1/2\ \mathbf{b}$

In our model,

B=

	A	B	C	D	E	F
A	-10.02	0.0095	0.098	0	0	2.6
B	0.0095	-0.0015	-0.0006	-0.071	-0.00032	0.027
C	0.098	-0.0006	0	1.912	0	-0.0067
D	-0.75	-0.071	1.912	0	0	-1.484
E	0	-0.00032	0	0	0	0
F	2.6	0.027	-0.0067	-1.484	0	-3.49

$$\mathbf{b}=\begin{bmatrix}18.19\\2.886\\-0.1209\\-108.21\\0.6288\\-50.18\end{bmatrix}$$

I is the identity matrix,

λ is an arbitrary value and the eigenvalues of B is denoted by δ.

The detailed formulation of the problem is given in the Appendix 5A.4.

The eigenvalues, δ , of the matrix B is found using MATLAB.

The eigenvalues are; -10.9511, -3.4231, -1.2753, -0.013, 0.0001, 2.1392.

So a GAMS program for solving the formulation of Ridge Analysis, which comprises 6 equations, 2 inequalities and 7 unknowns, is proposed and the code is given in Appendix 5A.5. The equations are;

$$(-10.02-\lambda)*A+0.0095*B+0.098*C+2.6*F= -9.095 \quad [5.1]$$

$$0.0095*A-(0.0015+\lambda)*B-0.0006*C-0.071*D-0.00032*E+0.027*F=-1.443 \quad [5.2]$$

$$0.098*A-0.0006*B-\lambda*C+1.912*D-0.0067*F=0.06045 \quad [5.3]$$

$$-0.071*B+1.912*C-\lambda*D-1.484*F=54.105 \quad [5.4]$$

$$-0.00032*B-\lambda*E=-0.3144 \quad [5.5]$$

$$2.6*A+0.027*B-0.0067*C-1.484*D-(3.49+\lambda)*F=25.09 \quad [5.6]$$

$$\lambda \leq 2.1392 \quad [5.7]$$

$$\lambda \geq -10.9511 \quad [5.8]$$

This is the program for finding the value of λ inside the region of eigenvalues of matrix B. The solution of the program yields the values of 3.16, 983, 67, 0.187, 46, 2.6 and 0 for A, B, C, D, E, F and λ, respectively. According to ridge analysis technique this point is a local optimum.

The formulation for finding the value of λ (so that location of the global optimum) outside the region of eigenvalues of matrix B yield an infeasible solution. That means ridge analysis could not propose a global optimum for this model. The model and solution can be seen in Appendix 5A.6.

MINITAB has been used for finding the mean and standard deviation of local optimum value proposed by Ridge Analysis. The fitted values and prediction intervals for both performance measures are estimated by using MINITAB. The fitted value for mean is 59.90 and prediction interval is (45.895, 73.898). The fitted value for standard deviation (log s^2) is 1.587 and the prediction interval is (0.216, 2.958). Although the prediction interval for standard deviation is wide, prediction interval for mean makes this point a candidate to be tried.

Therefore two experiments have been performed and the results are; 77.49% and 72,91%. The standard deviation (log s^2) for these results is 1.021. One of the results is just inside the prediction interval and the other is just outside the prediction interval. Also, standard deviation is inside the prediction interval. It can be concluded that the regression model fitted for mean and standard deviation can predict the results of the Ridge Analysis well.

Apart from the adequacy of the regression model for this point, what is more important is, an improvement in extraction of lithium has been achieved. 77.49% is the best result that has ever been obtained.

5.4 Optimization Outside the Response Surface

By changing the limits of the factors that have been introduced to the GAMS non-linear program, it is possible to find out optimum points outside the experimental region. Again the same algorithm of MINITAB Response Optimizer and GAMS non-linear programming have been applied to outside the experimental region. 10 optimum points have been computed by GAMS. As we have been dealing with outside region, by nature the model could not be used to predict the results of the experiment. However; it is decided to use GAMS and

the predicted results are found as 100 for the mean and less than 1.4 for log s^2 that makes s being less than 5. While choosing the experiments to conduct, another important criterion that has been considered is the economy of the process. For example; roasting temperatures and leaching time have been chosen as low as possible. 10 optimum points that have been computed by GAMS outside the experimental region can be seen in Table 5.3.

Table 5.3. The optimum points found by GAMS outside the experimental region

Opt. No	A	B	C	D	E	F	s	Mean
1	2.159	852	145	0.341	240	0.764	1.464	100
2	2.068	810	127	0.500	42	0.500	3.548	100
3	2.734	906	108	0.500	38	0.910	3.158	100
4	2.943	851	111	0.500	44	0.843	4.592	100
5	5.000	930	127	0.500	70	0.910	2.150	100
6	2.488	821	119	0.500	42	0.500	3.981	100
7	4.622	900	166	0.329	70	0.537	2.934	100
8	1.498	825	139	0.442	240	1.496	2.523	100
9	2.643	921	105	0.500	50	1.064	3.162	100
10	1.921	944	111	0.500	240	1.709	3.162	100

When we consider the economy of the process, the 2nd and 6th optimum points seem to be the most economical processes as the roasting temperature is low; as in the vicinity of 800°C, and leaching time is also low; just about 45 minutes. Therefore, 6th experiment has been conducted twice. However; the results have been surprisingly low; 24.48% and 29.79%. As such a low values are obtained for extraction of lithium from clays at very low temperatures, it has been thought to make one more experiment with higher roasting temperatures. From Table 5.3, the most suitable and relatively economic one is the 3rd optimum point. Hence this point has been conducted twice.

The results have not been as low as those of the 6th point but they have been far from being an global optimum for the extraction of lithium from boron clays. The results have been 61.61% and 53.63%. These situations can be observed for outside the experimental region, since the response surface may change their shapes at another region.

CHAPTER VI

AN ATTEMPT TO IMPROVE THE OPTIMUM POINT

6.1. An Improved Experimental Design and Analysis

In Chapter 5, we have tried to model the mean and standard deviation of extraction of lithium from boron clays. We have benefited from the response surface modelling for achieving extraction as high as possible. However; except for Ridge Analysis, no improvement can be made. Ridge Analysis has yielded the results of 77.49% and 72.91%, which 77.49% is the highest value ever obtained. However; the roasting temperature has been so high (around 980°C) that extraction will not be economical. It is aimed in this chapter to get an optimum with less cost.

Therefore, it has been thought to add the information obtained from the optimum points tried to our response surfaces so that a new model can be set up. Following this, a total of 6 points tried before have been appended to the experimental layout (three of these have been found using MINITAB, and the rest from ANOVA, GAMS Non-linear programming and Ridge Analysis). Furthermore, one more point had been tried out of curiosity after investigating the literature and experiencing the results of the experiments, the chemical mechanism of roasting temperature and solubility equilibrium of leaching. At this point, gypsum, roasting temperature, roasting time, leach S/L ratio, leach time and limestone take the values of 1.5, 918°C, 120 min., 0.17, 120 min. and 1.5 respectively. Although the fitted value (22.58%) and the prediction interval (-2.30, 47.47) of the regression model for the mean does not show good results, this point had been tried. The results of the experiment have been 73.76% and 70.46%, which are higher values than many obtained so far except Ridge Analysis results. Therefore, this point has been added to the response surface modelling, as well. The seven points that have been treated as a part of the

experimental design and added to the model can be seen in Table 6.1.

Table 6.1 The points that have been added to the model

No	Found from	A	B	C	D	E	F
1	GAMS	2.772	984	30	0.1	120	2.458
2	Ridge Analy.	3.178	986	67	0.187	33	2.6
3	MINITAB	4.5	850	120	0.4	120	1.5
4	MINITAB	1.5	987	30	0.1	120	1.5
5	MINITAB	1.5	878	120	0.36	120	1.5
6	ANOVA	4.5	950	120	0.2	120	1.5
7	Experience	1.5	918	120	0.17	120	1.5

These points have been appended in the experimental design. The model for the mean extraction has been found after several attempts in order to satisfy the assumptions for residuals. The best model that has been formulated with the ANOVA table can be seen in Equation [6.1] and in Table 6.2. The starting model can be seen in Appendix 6A.1.

$$\mu = 769 + 78.2*A - 1.85*B - 1.38*C + 343*D - 9.46*E + 266*F + 0.0181*AB - 0.254*AC + 93.2*AD + 5.12*AF - 0.00115*BC - 0.135*BD + 0.00819*BE - 0.297*BF + 9.09*CD + 0.0116*CE - 0.0124*CF - 4.09*DE - 0.584*EF - 17.4*A^2 + 0.00114*B^2 + + 0.00614*C^2 - 1864*D^2 + 0.0162*E^2 + 8.23*F^2 \quad [6.1]$$

Table 6.2 ANOVA for Regression Analysis for model comprising optimum points

Source	dF	Sum of Squares	Mean Squares	F	p
Regression	25	16252.85	650.11	68.46	0.000
Residual Error	8	75.97	9.50		
TOTAL	33	16328.83			

$R^2 = 99.5\%$ $R^2_{(adj)} = 98.1\%$ $S = 3.082$

Durbin-Watson statistic = 1.96

The model has expectedly high value of $R^2_{(adj)}$, and the Durbin-Watson statistic shows no correlation between the residuals. p-value of the model is so low that it can be concluded that this model is significant. The residuals versus fitted values plot and the normal probability plot can be seen Figures 6.1 and 6.2, respectively.

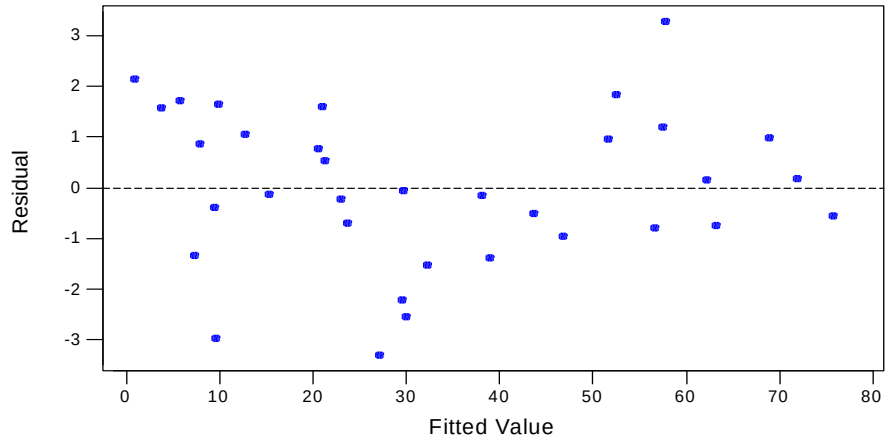


Figure 6.1. The residuals versus fitted values plot for the regression model [6.1] including optimum points.

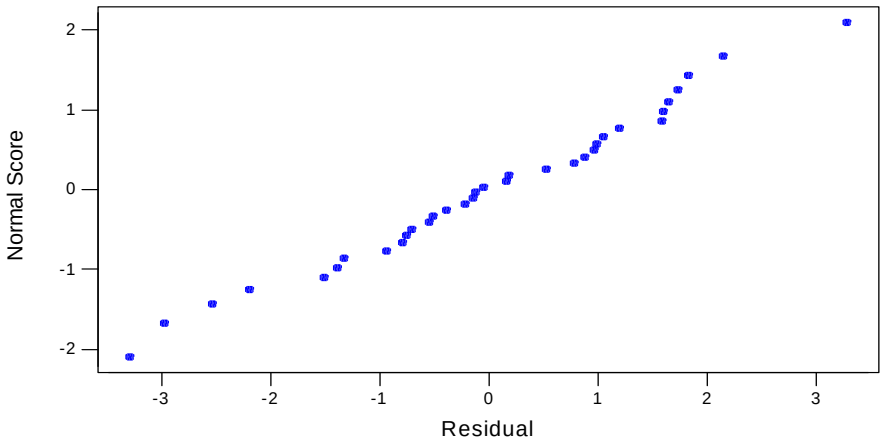


Figure 6.2. The normal probability plot of residuals for the regression model [6.1] including optimum points.

Both plots show no violation of the assumptions made for residuals. Residual versus fitted values plot shows that the variance of the residuals is constant. Normal probability plot resembles a straight line leading in a conclusion for normal distribution of residuals.

The β significance table of the parameters can be seen in Table 6.3.

Table 6.3. Significance of β terms of the model [6.1] including optimum points

Predictor	Coefficient	Standard Error	T	p
Constant	768.8	332.8	2.31	0.050
A	78.16	13.52	5.78	0.000
B	-1.8507	0.7148	-2.59	0.032
C	-1.3787	0.4912	-2.81	0.023
D	342.71	72.37	4.74	0.001
E	-9.458	1.507	-6.28	0.000
F	266.01	42.32	6.29	0.000
A*B	0.018113	0.006303	2.87	0.021
A*C	-0.25436	0.05986	-4.25	0.003
A*D	93.18	20.50	4.55	0.002
A*F	5.1191	0.4145	12.35	0.000
B*C	-0.0011513	0.0002031	-5.67	0.000
B*D	-0.13523	0.06076	-2.23	0.057
B*E	0.008193	0.001166	7.03	0.000
B*F	-0.29740	0.04633	-6.42	0.000
C*D	9.0914	0.8654	10.51	0.000
C*E	0.011571	0.001322	8.75	0.000
C*F	-0.01238	0.01421	-0.87	0.409
D*E	-4.0865	0.7233	-5.65	0.000
E*F	-0.58447	0.08325	-7.02	0.000
A^2	-17.383	2.087	-8.33	0.000
B^2	0.0011381	0.0003914	2.91	0.020
C^2	0.006138	0.003136	1.96	0.086
D^2	-1863.7	225.5	-8.27	0.000
E^2	0.016426	0.002986	5.44	0.001
F^2	8.235	1.666	4.94	0.001

The β significance table has implied that every term has a p-value of at most 10% except roasting time and limestone interaction factor. However; excluding this term from the model makes it worse in the manner that Durbin-Watson statistic shows a positive correlation. The model with no factor having p-value higher than 10% and the sum of squares of the best model can be seen in Appendix 6A.2 and 6A.3. Therefore this model is thought to be the best regression model that comprises optimum points for mean.

At this point, it will be beneficial to look for log s^2 model. The formulation and the ANOVA of the log s^2 model can be seen below.

$$\begin{aligned}\text{Log } s^2 = {} & 386 - 2.40*A - 0.979*B + 0.441*C + 309*D - 1.48*E + 63.8*F \\ & -0.0762*AC + 28.9*AD + 0.240*AE \ -0.000081*BC + 0.00180*BE \\ & -0.0697*BF + 3.12*CD - 0.00450*CE - 3.66*DE - 0.117*EF \\ & - 4.17*A^2 + 0.000546*B^2 - 536*D^2 + 0.00134*E^2 + 2.16*F^2 \end{aligned} \quad [6.2]$$

Table 6.4. ANOVA for Regression Analysis for model of log s^2 comprising optimum points

Source	dF	Sum of Squares	Mean Squares	F	p
Regression	21	36.8068	1.7527	3.26	0.019
Residual Error	12	6.4433	0.5369		
TOTAL	33	43.2501			

$R^2 = 85.1\%$ $R^2_{(adj)} = 59.0\%$ $S = 0.7328$

Durbin-Watson statistic = 2.07

The Durbin-Watson statistic of the model shows no correlation between the residuals. R^2 value is 85.1% and $R^2_{(adj)}$ value is 59% which is low value. Moreover, the gap between the values of R^2 and $R^2_{(adj)}$ is wide. This means that we have some unnecessary terms in our model. However; trying to decrease the number of factors in the model do not improve the adequacy of the model so that this model has been chosen as the best model for log s^2 with the optimum points included. The residuals versus fitted values and normal probability plot have implied that the assumptions made about the residuals are satisfied. The plots

and the β significance test of the factors can be seen in the following pages.

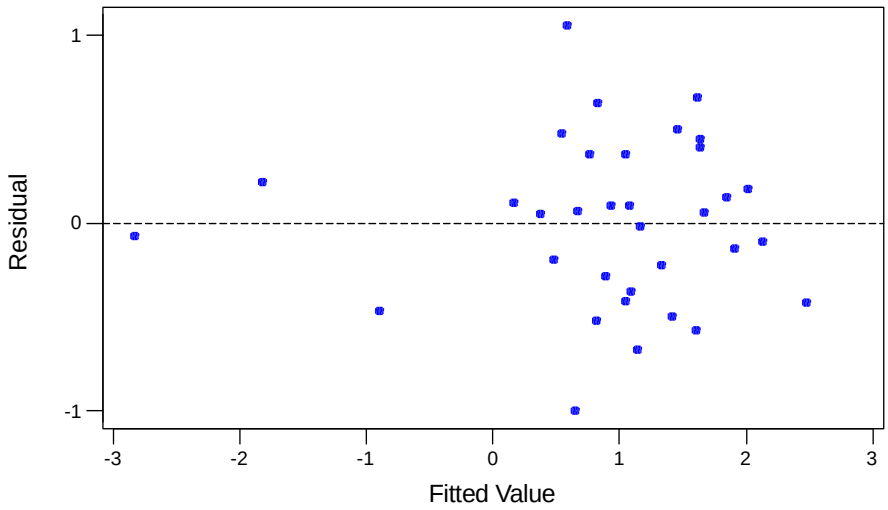


Figure 6.3. The residual versus fitted values plot for the regression model of log s^2 [6.2] including optimum points

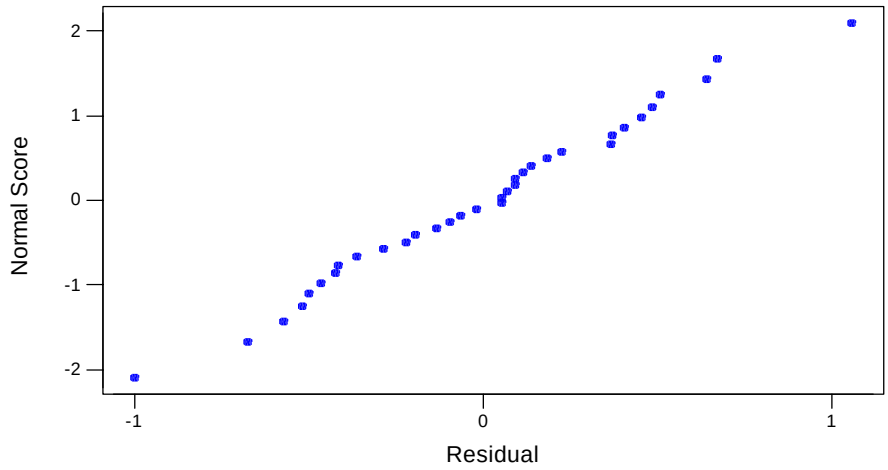


Figure 6.4. The normal probability plot of residuals for the regression model of log s^2 [6.2] including optimum points

Table 6.5. Significance of β terms of the regression model [6.2] including optimum points for log s^2

Predictor	Coefficient	Standard Error	T	p
Constant	386.3	100.0	3.86	0.002
A	-2.397	2.581	-0.93	0.371
B	-0.9791	0.2496	-3.92	0.002
C	0.4412	0.1380	3.20	0.008
D	308.64	86.16	3.58	0.004
E	-1.4801	0.3342	-4.43	0.001
F	63.80	15.63	4.08	0.002
A*C	-0.07619	0.2346	-3.25	0.007
A*D	28.917	7.496	3.86	0.002
A*E	0.23968	0.06506	3.68	0.003
B*C	-0.00008124	0.00004605	-1.76	0.103
B*E	0.0018038	0.0004253	4.24	0.001
B*F	-0.06965	0.01727	-4.03	0.002
C*D	3.1239	0.8306	3.76	0.003
C*E	-0.004496	0.001396	-3.22	0.007
D*E	-3.6604	0.9857	-3.71	0.003
E*F	-0.11725	0.03032	-3.87	0.002
A^2	-4.168	1.043	-4.00	0.002
B^2	0.0005459	0.0001381	3.95	0.002
D^2	-536.4	144.3	-3.72	0.003
E^2	0.0013444	0.0003905	3.44	0.005
F^2	2.1556	0.5963	3.61	0.004

Modelling of log s^2 with optimum points included could not have been modelled adequately. However; this model is simpler than the previous one.

MINITAB Response Optimizer is used to obtain new optimal points. and see if both models could predict the results of the experiment. Fortunately, as log s^2 have been modelled with addition of quadratic terms, it is now possible to make a dual approach to the optimization using MINITAB. In other words, In MINITAB Response Optimizer we can define limits for both the mean and log s^2 and require an optimum point that will maximize extraction with minimum variation. Therefore, for mean a minimum value of 70 and a target value of 100 whereas for log s^2, a maximum value of 1.6 (s will be 6.31 then) and a target value of 1 (s will be 3.162 then) have been defined as limits for MINITAB Response Optimizer. Same algorithm with the one that has been applied in the previous chapters has been applied. The Optimizer has found 10 points. The starting and optimum points can be seen in Appendix 6A.4 and the mean and the log s^2 values with the prediction interval for both measures can be seen in Table 6.6.

Table 6.6. The prediction intervals for the mean and the standard deviation computed by MINITAB Response Optimizer that use models [6.1] and [6.2]

Optimum Points	Mean	Log s^2	s	% 95 Pred. Int. for Mean	% 95 Pred. Int. for log s^2
1	71.930	0.669	2.160	(61.908, 81.953)	(-1.572, 2.910)
2	80.423	1.640	6.607	(69.620, 91.226)	(-0.703, 3.982)
3	74.437	0.999	3.159	(64.067, 84.807)	(-1.234, 3.233)
4	84.229	5.427	517.01	(73.729, 94.730)	(1.510, 9.343)
5	63.522	2.059	10.703	(53.701, 73.343)	(-0.561, 4.678)
6	94.599	6.367	1525.81	(82.016, 107.182)	(2.209, 10.526)
7	123.874	-10.646	$4.8x10^{-6}$	(75.216, 172.532)	(-23.273, 1.982)
8	95.439	1.387	4.937	(80.563, 110.314)	(-1.393, 4.167)
9	125.099	15.432	$5.2x10^{7}$	(99.660, 150.538)	(7.622, 23.201)
10	86.509	0.892	2.793	(75.316, 97.702)	(-1.557, 3.341)

From Table 6.6, it can be seen that standard deviation has a wide gap for most of the points. The smallest standard deviation are obtained at points 1 and 10 which we have already tested (point 10 is approximately the same as the point found by Ridge Analysis and point 1 has earlier been found by intuition). Log s^2 for points 10 and 1 are 1.021 and 0.736, respectively. They are both in the prediction interval for log s^2. However; recall that the mean extraction results obtained from these two experiments have not been satisfactorily and economically high (highest value for point 10 is 77.49%, and for point 1 is 73.76%). Hence, it is decided to look for a point to get higher mean extraction values more economically at the expense of standard deviation. Undesirability of low roasting temperatures has eliminated points 3, 8, 9, 2 and 6. Point 7 has been found without defining any starting point and it is shown here for illustrative purposes. Also experiences about the extraction mechanism has shown that roasting temperatures about 850°C result in low yields. Hence we are left with only two alternatives; points 4 and 5. Although point 5 has a narrower prediction interval for log s^2, point 4 has predicted mean extraction values much higher with a narrower prediction interval. Therefore it is decided to conduct experiments for point 4. Gypsum, roasting temperatures, roasting time, leach solid to liquid ratio, leaching time and limestone take the values of 1.5, 915, 120, 0.26, 120 and 1.5, respectively.

At first, two experiments have been conducted for this point and the results have been: 74.87 and 83.01%. The standard deviation of these two experiments is 5.756 (log s^2 is 1.520) which is an acceptable value. More importantly both of the results have been between the prediction interval limits for the mean. Also 83.01% is the largest extraction value of lithium from boron clays obtained experimentally. Hence we have conducted 4 more repetitions at this point to assure the persistence of these results and the results are; 83.84%, 85.54%, 86.39% and 89.22%. All of them are in the prediction interval (73.729, 94.730) for the mean and they are the highest that have been achieved so far. The mean of all these six experiments is 83.81% and the standard deviation is

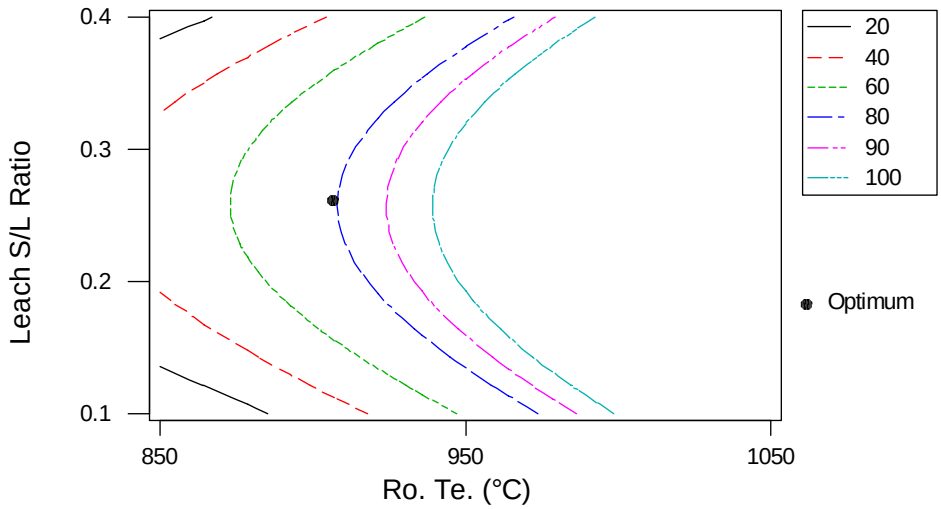
4.888. (log s^2 is 1.378) which is still an acceptable value although it is outside the prediction interval (1.510, 9.343) for log s^2 .From these 6 experiments, the lowest 3 mean values (74.87%, 83.01%, 83.84%) and the highest 3 mean values (85.54%, 86.39%, 89.22%) have been grouped with each other and Signal-to-Noise ratios have been calculated. For the lower group, S/N ratio is 38.097 and for the higher group, 38.794. They are much better than the ANOVA results. As a result, it can be concluded that the model for the means including the optimum points has successfully found the optimum (or a highly desirable point) and can predict the results well. The model is adequate at that point.

Gaining knowledge from these experiments and examining the literature has led us to think of an experiment at increased time of roasting and leaching and beyond the experimental region. For this purpose, point 7 of Table 6.1 has been used. Only roasting leaching time has been altered. Firstly the experiments have been performed at 120 minutes of roasting time and 180 minutes of leaching time. The results that have been obtained were 82,89% and 82.22%, (log s^2 is –0.649) which are not significantly different from the optimum point, that have been found from model including the optimum points.

Furthermore as a last experiment, increasing of roasting and leaching time by 60 minutes have been thought. The results of the experiment show values of 86.70% and 93.53% (log s^2 is 1.368). These results have been the highest of all experiments that have been conducted and log s^2 is an acceptable value. However; as the roasting and leaching time prolonged by a significant value, the comparison of economic value of these results and the optimum point, found by the model including the local optima, should be considered.

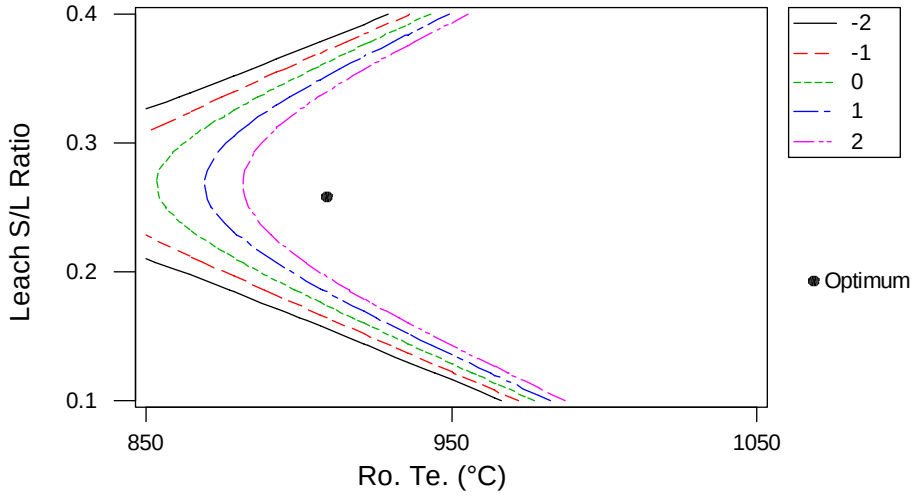
As a result, this study can claim that in the experimental region at least 74.87% and at most 89.22% (both are in the prediction interval) mean extraction has been achieved with an acceptable standard deviation. The points that would yield this result with an economical process should be 1.5, 915°C, 120, 0.26, 120 and 1.5 for gypsum, roasting temperature, roasting time, leach solid to liquid ratio, leaching time and limestone, respectively. Higher extraction values can be achieved but increasing roasting and leaching time will affect the economy of the process significantly.

For illustrative purposes, contour plots of roasting temperature versus leaching solid to liquid ratio drawn for both the mean and log s^2 can be seen from Figures 6.5 and 6.6.



Hold values: Gypsum: 1.5, Ro.Ti.: 120.0, Leach Ti.: 120.0, Limestone: 1.5

Figure 6.5. Contour plot of roasting temperature versus leaching solid to liquid ratio for mean



Hold values: Gypsum: 1.5, Ro.Ti: 120, Leach Ti.: 120, Limestone: 1.5

Figure 6.6. Contour plot of roasting temperature versus leaching solid to liquid ratio for log s^2

6.2. Comparison of Results to Relevant Literature Work

There are some studies that have tried to extract lithium from clays. These studies have been pointed out in Chapter II. From these, the most important and the relevant ones are Mordoğan et. al. (1995), Beşkardeş et. al. (1992) and Lien (1985). Mordoğan et. al. (1995) and Beşkardeş et. al (1992) have studied the boron clays whereas Lien (1985) has studied montmorillonite type clay which does not contain boron. The optimum points that have been found by these studies and the economic analysis of them can be seen in Table 6.7. Crocker et. al. (1988) is a modification of the study of Lien (1985) in order to decrease the cost of the process by decreasing the raw materials.

Table 6.7. Comparison of Results to Other Studies

	This Study	*Mordoğan 1995*	*Beşkardeş 1992*	*Crocker 1988*
Field	Bigadiç	Kırka	Bigadiç	Nevada
Lithium Content (ppm)	2000	2800	2007	6000
Optimum Points				
Clay	5	5	5	5
Gypsum	1.5	0.834	1.5	2
Roasting Temp. (°C)	915	900	850	900
Roasting Time (min.)	120	120	120	120
Leaching S/L Ratio	0.26	0.1	0.5	0.665
Leaching Time (min.)	120	60	----	5
Limestone	1.5	0	1.5	2
Performance Measures				
Average Extraction (%)	83.81	77.00	72.78	84.00
Cost ($/kg Li_2CO_3)	6.91	----	10.65	4.45
Standard Deviation	4.89	----	----	----

As it is seen from Table 6.7, the optimum point found in this study is somewhat

similar to those of the other studies, although in this study natural and waste raw materials are used, which reduces cost and saves the environment.

The extraction values achieved in this study are the highest for boron clays and nearly the same with those of Crocker et. al. (1988). Mordoğan et. al. (1995) have studied Kırka clays which has a different composition than Bigadiç clays so they do not need to use limestone. The main difference of this study from other studies is high leaching time, however, it is seen from Figure 4.6 that 30 minutes of leaching time can be enough for high extraction. A confirmation experiment has been done for decreasing leaching time (other points remaining the same) and has resulted in about 80% extraction. Further experiments are still being conducted. Another important factor is leaching solid to liquid ratio which is high for this study compared to Beşkardeş et. al. (1992) and Crocker et. al. (1988). This factor is important in the sense that high liquid amount needs more water to evaporate and this in turn increases the cost significantly. Experiments are still being conducted in order to increase the solid to liquid ratio. The author's opinion is that there will not be high differences in the extraction values for that factor.

The cost of producing lithium carbonate from clays is lowest for Crocker et. al's (1988) study but this is mainly due to the higher lithium content of the clay used in that study. The detailed cost analysis made for this study by a similar approach with Crocker et. al (1988) is given in Chapter VII.

Only this study has focused on variation of the extraction results. This performance measure has not been considered in the other studies. An acceptable standard deviation (4.89) has been achieved in this study.

CHAPTER VII

ECONOMIC IMPACT AND ANALYSIS OF THE STUDY

This study aims to design the extraction process so that high extraction results are achieved without costly control on noise factors. Here, major savings come from the use of limestone directly from the nature and gypsum as a waste product of boric acid production. In traditional practice, to achieve high lithium extraction results reagent grade raw materials are used which add further cost to process. Hence, we have made a cost analysis in order to see overall savings resulted from this study. In this analysis we have used the study of Crocker et. al. (1988) for comparison. The results of the annual operating cost analysis are summarized in Table 7.1.

It has been intended to develop a rough cost estimate assuming the worst case and the cost analysis is done based on processing 1000 tons/day. According to Crocker et. al. (1988) clay:gypsum:limestone ratio is 5:2:2, however we have found the optimum ratio as 5:1.5:5:1.5. Therefore, in Crocker et. al. (1988) about 1900 tons/day of raw materials can be processed, while we can process about 1600 tons/day of raw materials. Furthermore, some cost figures such as those for depreciation, taxes, insurance, balls, chemicals, and process water for our case have been found simply by adjusting the corresponding Crocker et. al. (1988) figures by the capacity (i.e. by multiplying them by 1600/1900). Evaporation and leaching costs have been taken as the same.

Table 7.1. Comparison of operating cost of the proposed lithium extraction process to that of Crocker et. al. (1988)

	Crocker et. al. (1988), $		**This study, $**	
	Annual	*kg Li_2CO_3*	*Annual*	*kg Li_2CO_3*
Lithium content (ppm)	6000		2000	
I. Direct Costs				
A. Raw Materials				
Clay	0	0.000	0	0.000
Limestone	3.395.700	0.437	0	0.000
Gypsum	3.326.400	0.428	1.414.000	0.514
Soda Ash	2.313.000	0.297	936.000	0.342
Balls	122.300	0.015	103.000	0.037
Chemicals	3.600	0.002	3.000	0.001
Total	9.161.000	1.179	2.456.000	0.894
B. Utilities				
Electric Power	1.190.600	0.152	1.920.000	0.698
Process Water	63.000	0.009	53.000	0.019
Fuel	8.240.100	1.057	6.294.000	2.289
Total	9.493.700	1.218	8.267.000	3.006
C. Direct Labor				
Labor	1.437.100	0.186	189.000	0.069
Supervision	215.600	0.029	28.000	0.010
Total	1.652.700	0.215	217.000	0.079
D. Maintenance				
Labor	1.437.100	0.218	224.000	0.081
Supervision	340.000	0.045	45.000	0.016
Materials	1.700.100	0.218	1.432.000	0.521
Total	3.740.100	0.471	1.701.000	0.619
E. Payroll Overhead	1.292.400	0.166	170.000	0.062
F. Operating Supplies	748.000	0.098	340.000	0.124
TOTAL DIRECT COST	**26.087.900**	**3.347**	**13.151.000**	**4.782**
II. Indirect Costs	2.157.100	0.278	767.000	0.279
III. Fixed Costs				
Taxes	811.400	0.105	684.000	0.249
Insurance	811.400	0.105	684.000	0.249
Depreciation, 20 yr	4.755.500	0.612	4.005.000	1.456
TOTAL PRODUCTION COST	**34.623.300**	**4.45**	**19.291.000**	**7.014**
Annual Production (ton)	***7785***		***2750***	
Waste Reducing Gain	-----	-----	-1.200.000	-0.436
TOTAL PRODUCTION COST	**34.623.300**	**4.45**	**18.091.000**	**6.578**

In Crocker et. al. (1988), unit cost of electricity is taken as 0.047 $/kW.h, however, for Turkey unit cost of electricity is assumed as 0.09 $/kW.h. Crocker et. al. (1988) have used heavy oil for fuel (0.85 $/gal and 1 gallon gives 153.000 Btu of heat) and we have used natural gas as the fuel (0.02 $/1000 kcal). Labor cost is 11.75 $/hr in Crocker et. al. (1988) and we have taken the labor cost as 13.500 $/annual per person on the average.

Some cost figures seem to be higher with respect to unit cost of Li_2CO_3. This is due to the fact that in our study annual production of Li_2CO_3 is about three times less than Crocker et. al. (1988) study as the lithium content of Bigadiç clays is much lower (2000 ppm) than that of Crocker et. Al. (1988) study (6000 ppm).

Although it is intended to develop an estimate for the worst case, evaporation cost (that will be added to fuel part) has been taken as the same as that of Crocker et. al (1988) study, although we have higher water amount to evaporate, hence higher cost.

Some cost figures such as those for gypsum and waste reducing gain can not be displayed here as they are confidential for Eti Holding. Waste reducing gain has been estimated assuming that the leaching residue will find an application area. This point is discussed in detail later both in this section and in Chapter 8.

The operating cost of Li_2CO_3 from boron clays that contain 2000 ppm lithium has been estimated as 6.578 $/kg whereas, the same figure for Crocker et. al. (1988) study is 4.45 $/kg. On the other hand, if the study done by Crocker et. al (1988) had lithium content of 2000 ppm in their clays, then the operating cost would roughly be around 13.35$/kg. In this study, the ratio of raw materials to clay has been decreased and also the raw materials that will not bring any additional cost to Eti Holding, Inc have been used. This has brought about 50% savings in the operating cost. However; when we consider the import price of Li_2CO_3 in Turkey in year 2002 (3.98$/kg) this process is not be preferable as of the current time. If the selling price of Li_2CO_3 in the world market is about 3.5$/kg, then, in order for this process to be preferable Bigadiç clays should contain around 3500 ppm lithium, or Li_2CO_3 selling price should increase to

about 6 $/kg.

Another important point to consider is the application of the residue of the leaching process. This residue is a waste in this study, however, by changing the amounts of raw materials (hence probably decreasing extraction yield) this residue can be used in other industries. This adjustment will bring additional cost reduction to process. An economic off-set should be made with the possible usage of the residue and extraction percentage. Moreover, possible application of the leaching residue will result in a significant benefit to society such as decreasing further the solid wastes to environment. In case that this residue is not used, about 30% waste reduction can been achieved at the optimal settings.

While making the cost analysis, natural gas has been used as the fuel source and it is seen that it has added about 35% cost to the process. Decreasing the cost of fuel as well as the cost of electricity (about 10% cost to the process) will bring significant cost improvements. Also pelletizing has been added in the cost analysis. However; a pilot scale study should be conducted to decide whether pelletizing is necessary or not.

The price of Li_2CO_3 has increased about 5-10% in year 2001 and it is predicted that the price will increase in the following years. So the price trend of Li_2CO_3 should be followed to determine when the proposed extraction process need to be put in action.

In addition to all these, the amount and grade of lithium reserves of boron clays (especially Bigadiç clays) should be determined and if a field containing about 3000 ppm lithium is found, it should be stored in a separate place. An estimation of process cost in that case might indicate that extracting lithium locally using the proposed approach is more economical than importing it.

CHAPTER VIII

CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

In mining industry, it has not been straightforward to make a standardization as the industry strongly depends on natural factors. In this study, a methodology has been demonstrated for achieving the desired result (lithium extraction) independent of the grade of the raw materials that has been input. All the raw materials have been chosen as they are solid wastes from production facilities or gangue minerals. In other words, the need for standardization is sought to be reduced. This study specifically has been concentrated on the extraction of lithium from boron clays by using a solid waste of boric acid production, gypsum and a calcium carbonate rich field in boron mines that could not been utilized, otherwise.

In this study, evaluation of optimum extraction of lithium from boron clays has been examined. The procedure has been based on two main performance measures; mean of extraction and the standard deviation of the extraction values. Statistical experimental design principles more specifically orthogonal arrays have been used in such a study for the first time to the best of our knowledge.

The objective of robust extraction of lithium is to find optimal settings of parameters which produce the maximum extraction with minimum variation around this maximum.

In this study, guidelines for the conduct of experiments have been developed and data collection and transformation methods have been presented.

Data analysis has been performed for modelling both the mean and the standard deviation. A methodology called S/N transformation comprising both of these performance measures has been utilized.

While seeking to reach the optimum settings of parameters, 4 different optimization algorithms have been used. These are ANOVA, Regression modelling, Non-linear programming, and response surface methods applied to second-order surfaces, Ridge Analysis. A widely used method of robust design, ANOVA, has been performed by making Signal-to-Noise ratio transformation of data. The results obtained from ANOVA do not yield satisfactory extraction values. The reason for this lack of achieving may be two fold; ANOVA has taken only the linear terms into consideration, and we are confined to only the experimental levels of the factors for the optimum.

Modelling through regression has been separated into two parts. The mean and the standard deviation has been modelled. MINITAB 13.3 package program has been used for modelling. Mean has been modelled with high values of adjusted multiple coefficient of determination $R^2_{(adj)}$. Also the assumptions about the residuals for mean has been met satisfactorily. No correlation has been observed for errors. Prediction intervals for mean mostly have been narrow enough. The standard deviation could not be modelled as adequately as the mean. Although residuals confirm all assumptions and no correlations have been observed between them, there has been a wide gap between multiple coefficient of determination (R^2) and adjusted multiple coefficient of determination ($R^2_{(adj)}$). Prediction intervals for the standard deviation have been too wide. The confirmation experiments for regression modelling have shown variability among different points for both the mean and the standard deviation. However; an improvement from the experimental results obtained could not be achieved by the tested optimal points. For this case, a further modelling have been tried and this modelling is based on the addition of optimal points to the first model. This model has shown an adequate fit to the mean whereas standard deviation still could not be modelled as adequately as the mean. There are several reasons for this lack of fit. One and the most important reason is that the raw materials used for this study have been chosen from nature as they are and have not been processed for standardization before beginning of the tests.

Especially, limestone $CaCO_3$ content has shown a significant variability. The model that has treated the optimal points as a part of experimental design has concluded in an extraction of lithium that has been the highest of all tests. Also the standard deviation at these optimal settings is found experimentally to be acceptable although it could not be predicted by the model of the standard deviation.

Another optimization tool that has been tried in this study is Non-linear programming. Dual responses have been tried to be solved for this purpose; maximization of the mean of extraction of lithium and minimization of the standard deviation around the mean. Non-linear programming has been made by using GAMS software. The results obtained from this study has yielded sub-optimal points which have not shown a significant improvement of the experimentally obtained results. Also by incorporating the non-linear optimization technique, some points outside the experimental region that can lead to the desired results have been found. While computing these points, economic considerations have been considered and the points that might bring cost reduction have been tried. However; satisfactory extraction values could not be achieved, either.

The last optimization algorithm that has been used in this study is the method that has been applied to second-order surfaces of response surface methodology, Ridge Analysis. This method has comprised some matrix algebra and MATLAB package program has been used for solving the equations. Ridge Analysis have predicted the results of the experiment for both performance measures satisfactorily. Moreover, it has yielded an optimum value that has been higher than the previous results of the experimental region. However; this optimum point could not be treated as the global optimum as the algorithm suggests that it is a local optimum. Furthermore, this optimum point has a drawback that the roasting temperature is very high at this point.

An economic off-set should be calculated for other factors. As the roasting process is a reversible process, less time is needed for completion of converting process for higher temperatures than for lower temperatures. So for

deciding on optimal settings, this study has presented two solutions. If lower roasting temperature will be more suitable, then the result obtained from modelling of the mean by adding optimum points to the experimental region should be used. The settings for this optimum are 1.5, 915°C, 120 minutes, 0.26, 120 minutes and 1.5 for gypsum, roasting temperature, roasting time, leaching solid to liquid ratio, leaching time and limestone, respectively. If less time of roasting time will be seen more adequate for extraction, the results obtained from Ridge Analysis, should be used. The settings for the parameters are 3.178, 986°C, 67 minutes, 0.187, 33 minutes, 2.6 for the same order of factors.

Extraction of lithium from boron clays has had a solid waste at the end of the leaching process. The raw materials other than the lithium containing clay must be chosen for evaluation of this solid waste. This study is unique in the sense that natural limestone has been used as $CaCO_3$ source and waste product of boric acid is used as gypsum source. These two raw materials will not bring any additional cost to the extraction process as they are owned by Eti Holding, Inc. Moreover, using these wastes will decrease the need hence cost for storing them. Therefore, an important parameter to consider here is the amount of limestone and gypsum used in lithium extraction. As another solid waste has obtained during the extraction process, the optimal settings for raw materials can be modified in a way to utilise that solid waste. For this purpose, pelletizing can be introduced to the process. The author's opinion is that it will be crucial to make a study for utilising the solid waste of lithium extraction in order to decrease the economy of the process significantly.

In this study, experiments have been made based on clay amount. 40 grams of clay have been used and gypsum and limestone ratio have been chosen with respect to that value. For example, at the optimal settings, gypsum/clay ratio and limestone/clay ratio are both 1.5/5 meaning that 12 grams of gypsum and limestone have been used. This will add to totally 64 grams. After the leaching process, about 45 grams of solid waste are left. This means that at the optimal settings about 30% reduction can be achieved for the wastes. Moreover, by just using natural raw materials, about 78% cost reduction for extraction have

been gained compared with the study made by Crocket et. al. (1988). To add up, this study not only extracts lithium in an economic way but also attempts to decrease the solid wastes of Eti Holding, Inc.

The results of the cost analysis show that if import price of lithium increases more than 50%, if we find enough clays that contain about 3500 ppm lithium and if fuel and electricity prices decrease, then it is economically feasible and more advantageous for Turkey to produce its own lithium (and export the excess) by using the proposed extraction process. Apart from the cost considerations, this proposed process has a social benefit to the society in the manner that the solid wastes to the nature are decreased by significantly.

Another important research that should follow this study is the precipitation of lithium. Lithium carbonate is the most widely used compound of lithium and the studies in literature (Lien, 1985, Beşkardeş, 1992) have been concentrated on it. The optimal settings for the precipitation of lithium can be found by following a similar approach.

It has been well known to the researchers of robust design that tolerance design should have been performed after robust design. This study needs to be followed by a tolerance design study as the raw materials used in extracting lithium are all solid wastes and they show great variability (especially limestone) in their beneficial portion for extraction of lithium. In such a study, the allowable variation for lithium content of clay, limestone's $CaCO_3$ content and gypsum's $CaSO_4.2H_2O$ content or lower limits of lithium content of the clays, calcium carbonate ($CaCO_3$) content of limestone and calcium sulphate dihydrate content ($CaSO_4.2H_2O$) of gypsum can be defined for optimum extraction of lithium from boron clays with much smaller variation than the variation obtained in this study. This will further reduce variation of the results. As a part of the tolerance design, a detailed cost analysis should be conducted for producing lithium carbonate or any other lithium compound. In order to make the cost analysis more accurately, the grade and reserves of lithium content of boron clays should have been determined.

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APPENDICES

APPENDIX 4A

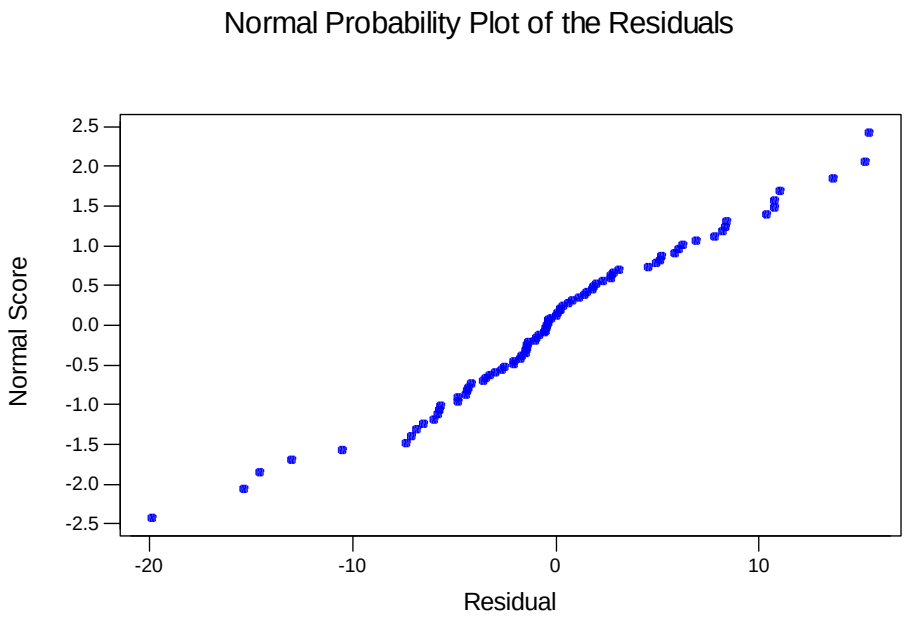
Appendix 4A.1. L27 (313) Orthogonal Array

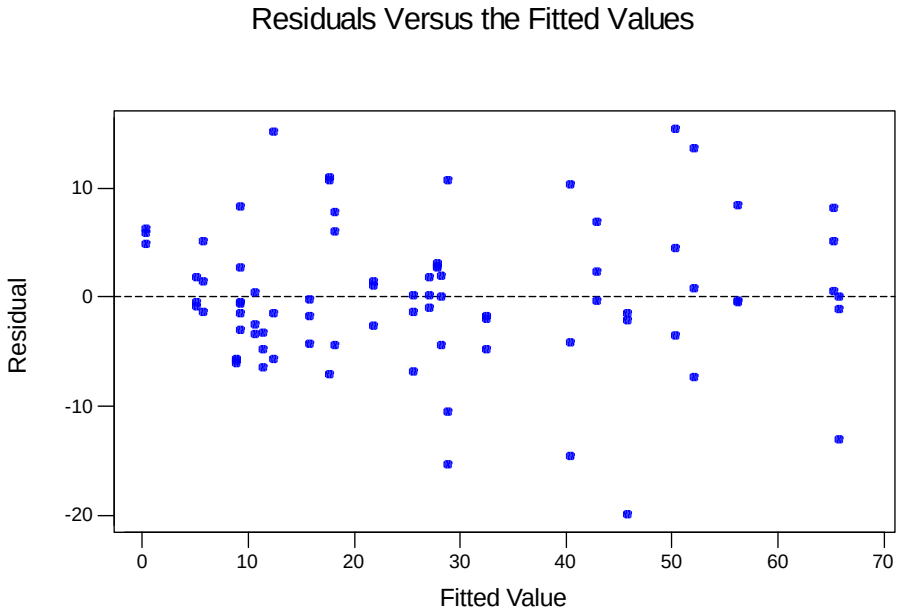
Run	Columns												
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2	2	2	2	2	2
3	1	1	1	1	3	3	3	3	3	3	3	3	3
4	1	2	2	2	1	1	1	2	2	2	3	3	3
5	1	2	2	2	2	2	2	3	3	3	1	1	1
6	1	2	2	2	3	3	3	1	1	1	2	2	2
7	1	3	3	3	1	1	1	3	3	3	2	2	2
8	1	3	3	3	2	2	2	1	1	1	3	3	3
9	1	3	3	3	3	3	3	2	2	2	1	1	1
10	2	1	2	3	1	2	3	1	2	3	1	2	3
11	2	1	2	3	2	3	1	2	3	1	2	3	1
12	2	1	2	3	3	1	2	3	1	2	3	1	2
13	2	2	3	1	1	2	3	2	3	1	3	1	2
14	2	2	3	1	2	3	1	3	1	2	1	2	3
15	2	2	3	1	3	1	2	1	2	3	2	3	1
16	2	3	1	2	1	2	3	3	1	2	2	3	1
17	2	3	1	2	2	3	1	1	2	3	3	1	2
18	2	3	1	2	3	1	2	2	3	1	1	2	3
19	3	1	3	2	1	3	2	1	3	2	1	3	2
20	3	1	3	2	2	1	3	2	1	3	2	1	3
21	3	1	3	2	3	2	1	3	2	1	3	2	1
22	3	2	1	3	1	3	2	2	1	3	3	2	1
23	3	2	1	3	2	1	3	3	2	1	1	3	2
24	3	2	1	3	3	2	1	1	3	2	2	1	3
25	3	3	2	1	1	3	2	3	2	1	2	1	3
26	3	3	2	1	2	1	3	1	3	2	3	2	1
27	3	3	2	1	3	2	1	2	1	3	1	3	2

Appendix 4A.2. Interaction Table for L27 (313)

Column	Column												
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
1	(1)	3 4	2 4	2 3	6 7	5 7	5 6	9 10	8 10	8 9	12 13	11 13	11 12
2		(2)	1 4	1 3	8 11	9 12	10 13	5 11	6 12	7 13	5 8	6 9	7 10
3			(3)	1 2	9 13	10 11	8 12	7 12	5 13	6 11	6 10	7 8	5 9
4				(4)	10 12	8 13	9 11	6 13	7 11	5 12	7 9	5 10	6 8
5					(5)	1 7	1 6	2 11	3 13	4 12	2 8	4 10	3 9
6						(6)	1 5	4 13	2 12	3 11	3 10	2 9	4 8
7							(7)	3 12	4 11	2 13	4 9	3 8	2 10
8								(8)	1 10	1 9	2 5	3 7	4 6
9									(9)	1 8	4 7	2 6	3 5
10										(10)	3 6	4 5	2 7
11											(11)	1 13	1 12
12												(12)	1 11
13													(13)

Appendix 4A.3. Residual Plots for the model of mean





Appendix 4A.4. Level Averages For Mean

Gypsum			**Ro.Te. °C**		
1.5	*3*	*4.5*	*850*	*950*	*1050*
25.71	25.67	30.27	11.20	37.16	33.29
Ro.Ti. min			**Leach S/L**		
30	*60*	*120*	*0.1*	*0.2*	*0.4*
20.72	25.35	35.59	22.15	35.47	24.04
Le.Ti. min			**Limestone**		
30	*60*	*120*	*1.5*	*3*	*4.5*
28.42	18.20	35.03	31.98	31.19	18.48
Ro. Te. x Ro. Ti.			**Ro. Te. x Leach S/L**		
850 x 30	4.74		*850 x 0.1*	13.13	
850 x 60	11.77		*850 x 0.2*	13.29	
850 x 120	17.09		*850 x 0.4*	7.19	
950 x 30	21.96		*950 x 0.1*	27.38	
950 x 60	38.60		*950 x 0.2*	43.75	
950 x 120	50.92		*950 x 0.4*	40.35	
1050 x 30	35.45		*1050 x 0.1*	25.92	
1050 x 60	25.68		*1050 x 0.2*	49.38	
1050 x 120	38.75		*1050 x 0.4*	24.57	

There are two combinations for determining the optimum levels since interaction of roasting temperature and leach solid to liquid ratio has the highest level of B_3D_2 combination. So the first combination includes the optimum levels of $A_3B_2C_3D_2E_3F_1$ and the second combination includes the optimum levels A_3B_3 $C_3D_2E_3F_1$. The estimation of the expected value of the mean is as follows:

COMBINATION 1:

$$E(y) = \overline{T} + (\overline{A}_3 - \overline{T}) + (\overline{B}_2 - \overline{T}) + (\overline{C}_3 - \overline{T}) + (\overline{D}_2 - \overline{T}) + (\overline{E}_3 - \overline{T}) + (\overline{F}_1 - \overline{T}) + (\overline{B_2 x C_3} - \overline{T}) + (\overline{B_2 x D_2} - \overline{T}) \quad [1]$$

From the level averages table;

E(y) = 27.22 + (30.27-27.22) + (37.16-27.22) + (35.59-27.22) + (35.47-27.22) + (35.03-27.22) + (31.98-27.22) + (32.61-27.22) + (25.56-27.22)

E(y) = 27.22 + 3.05 + 9.94 + 8.37 + 8.25 + 7.81 + 4.76 + 5.39 – 1.66
= 73.13

COMBINATION 2:

$$E(y) = \overline{T} + (\overline{A}_3 - \overline{T}) + (\overline{B}_3 - \overline{T}) + (\overline{C}_3 - \overline{T}) + (\overline{D}_2 - \overline{T}) + (\overline{E}_3 - \overline{T}) + (\overline{F}_1 - \overline{T}) + (\overline{B_3 x C_3} - \overline{T}) + (\overline{B_3 x D_2} - \overline{T}) \quad [2]$$

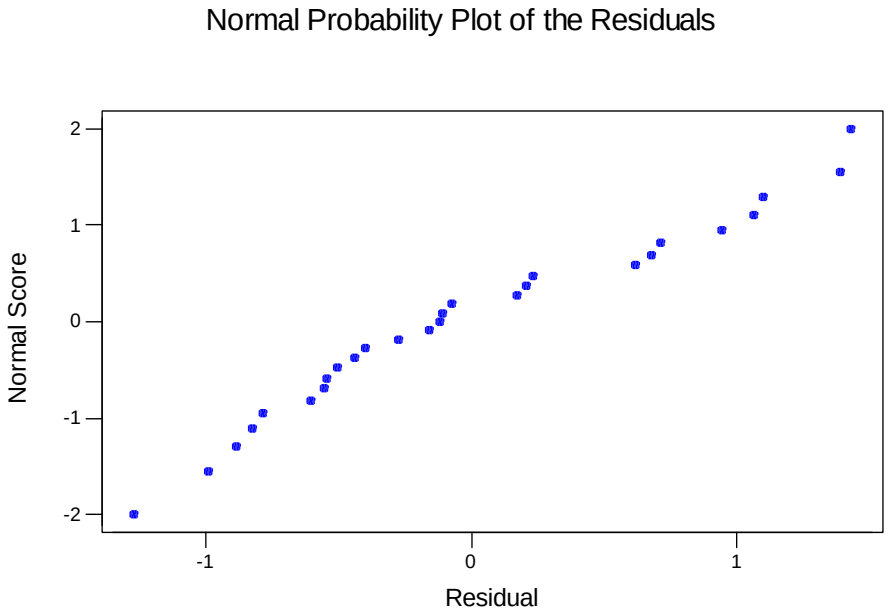
From the level averages table;

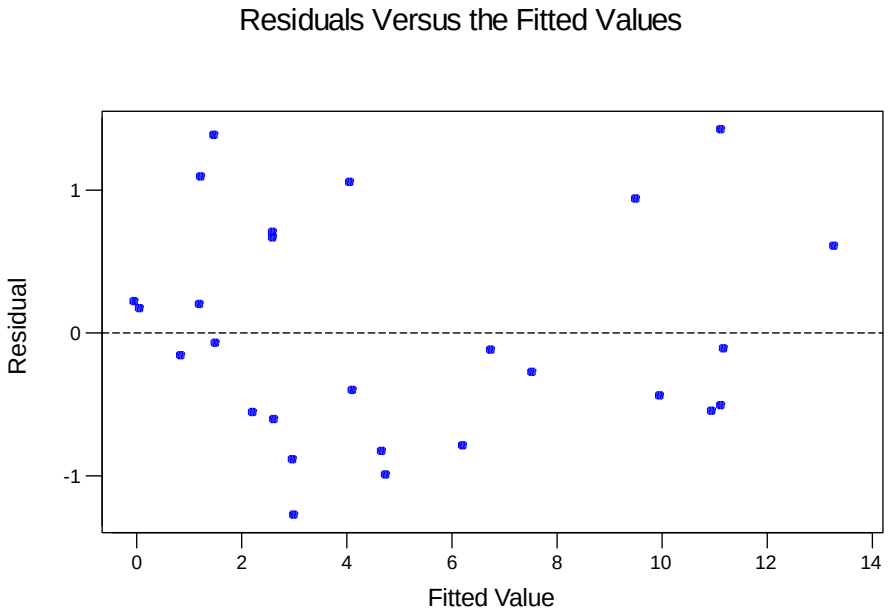
E(y) = 27.22 + (30.27-27.22) + (33.29-27.22) + (35.59-27.22) + (35.47-27.22) + (35.03-27.22) + (31.98-27.22) + (24.31-27.22) + (35.06-27.22)

E(y) = 27.22 + 3.05 + 6.07 + 8.37 + 8.25 + 7.81 + 4.76 – 2.91 + 7.84
= 70.46

As the first combination predicts higher extraction value, it is better to use this. Moreover, as roasting temperature is lower in the first combination, it will be economical to treat this combination as the optimum for mean.

Appendix 4A.5. Residual plots for the model of standard deviation





Appendix 4A.6. Level Averages for Standard Deviation

Gypsum			**Ro.Te. °C**		
1.5	*3*	*4.5*	*850*	*950*	*1050*
5.115	6.678	3.420	3.339	4.564	7.310
Ro.Ti. min			**Leach S/L**		
30	*60*	*120*	*0.1*	*0.2*	*0.4*
5.138	3.911	6.165	3.589	5.986	5.639
Le.Ti. min			**Limestone**		
30	*60*	*120*	*1.5*	*3*	*4.5*
6.317	4.480	4.416	4.076	7.180	3.957
Ro. Te. x Ro. Ti.			**Ro. Te. x Leach S/L**		
850 x 30	0.746		*850 x 0.1*	5.942	
850 x 60	3.828		*850 x 0.2*	1.854	
850 x 120	5.444		*850 x 0.4*	2.222	
950 x 30	6.498		*950 x 0.1*	1.401	
950 x 60	2.734		*950 x 0.2*	5.920	
950 x 120	4.459		*950 x 0.4*	6.369	
1050 x 30	8.170		*1050 x 0.1*	3.423	
1050 x 60	5.170		*1050 x 0.2*	10.184	
1050 x 120	8.591		*1050 x 0.4*	8.324	

Computation of the predicted standard deviation based on the optimum points of S/N Analysis:

$$E(\sigma) = \overline{T} + (\overline{A}_3 - \overline{T}) + (\overline{B}_2 - \overline{T}) + (\overline{C}_3 - \overline{T}) + (\overline{D}_2 - \overline{T}) + (\overline{E}_3 - \overline{T}) + (\overline{F}_1 - \overline{T}) + (\overline{B_2 x C_3} - \overline{T}) + (\overline{B_2 x D_2} - \overline{T})$$

From the level averages table;

E(σ) = 5.071 + (3.420-5.071) + (4.564–5.071) + (6.165-5.071) + (5.986-5.071) + (4.416-5.071) + (4.076-5.071) + (3.872-5.071) + (5.512-5.071)

E(σ) = 5.071 – 1.651 – 0.507 + 1.094 + 0.915 – 0.655 - 0.995 - 1.199 + 0.441
= 2.514

Appendix 4A.7. The regression model with only main factors

The regression equation is
Mean = - 87.0 + 1.52*A + 0.110*B + 0.166*C - 2.8*D + 0.103*E - 4.50*F

Predictor	Coef	SE Coef	T	P
Constant	-86.95	39.30	-2.21	0.039
A	1.519	2.546	0.60	0.557
B	0.11044	0.03819	2.89	0.009
C	0.16603	0.08333	1.99	0.060
D	-2.76	25.00	-0.11	0.913
E	0.10307	0.08333	1.24	0.230
F	-4.499	2.546	-1.77	0.092

S = 16.20 R-Sq = 46.5% R-Sq(adj) = 30.4%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	6	4555.3	759.2	2.89	0.034
Residual Error	20	5249.3	262.5		
Total	26	9804.6			

Source	DF	Seq SS
A	1	93.4
B	1	2195.5
C	1	1042.0
D	1	3.2
E	1	401.5
F	1	819.7

Unusual Observations

Obs	A	Mean	Fit	SE Fit	Residual	St Resid
18	3.00	22.92	52.65	8.25	-29.73	-2.13R
25	4.50	13.68	44.14	8.50	-30.46	-2.21R

R denotes an observation with a large standardized residual

Durbin-Watson statistic = 2.44

Appendix 4A.8. The regression of the quadratic model

A*E is highly correlated with other X variables
A*E has been removed from the equation

C*E is highly correlated with other X variables
C*E has been removed from the equation

D*E is highly correlated with other X variables
D*E has been removed from the equation

C*C is highly correlated with other X variables
C*C has been removed from the equation

D*D is highly correlated with other X variables
D*D has been removed from the equation

E*E is highly correlated with other X variables
E*E has been removed from the equation

The regression equation is

Mean = - 1332 + 17.2*A + 2.89*B - 0.105*C - 98.5*D + 0.631*E - 50.2*F + 0.0189*AB + 0.195*AC - 1.49*AD + 5.20*AF - 0.00121*BC - 0.142*BD -0.000631*BE + 0.0545*BF + 3.75*CD - 0.0134*CF - 2.97*DF - 9.80*A^2 -0.00149*B^2 - 3.49*F^2

Predictor	Coef	SE Coef	T	P
Contant	-1332.1	129.5	-10.29	0.000
A	17.17	17.08	1.01	0.354
B	2.8857	0.2644	10.91	0.000
C	-0.1051	0.3143	-0.33	0.749
D	-98.52	95.90	-1.03	0.344
E	0.6312	0.4228	1.49	0.186
F	-50.18	10.84	-4.63	0.004
A*B	0.018944	0.007003	2.71	0.035
A*C	0.19532	0.02154	9.07	0.000
A*D	-1.491	6.461	-0.23	0.825
A*F	5.2019	0.4669	11.14	0.000
B*C	-0.0012118	0.0002335	-5.19	0.002
B*D	-0.14162	0.06711	-2.11	0.079
B*E	-0.0006306	0.0003968	-1.59	0.163
B*F	0.05452	0.01212	4.50	0.004
C*D	3.7501	0.8618	4.35	0.005

C*F	-0.01341	0.01557	-0.86	0.422
D*F	-2.967	4.474	-0.66	0.532
A^2	-9.804	2.563	-3.82	0.009
B^2	-0.0014914	0.0001375	-10.85	0.000
F^2	-3.4884	0.8082	-4.32	0.005

S = 3.367 R-Sq = 99.3% R-Sq(adj) = 97.0%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	20	9736.54	486.83	42.94	0.000
Residual Error	6	68.02	11.34		
Total	26	9804.56			

Source	DF	Seq SS
A	1	93.42
B	1	2195.49
C	1	1041.97
D	1	3.20
E	1	401.55
F	1	819.68
A*B	1	70.78
A*C	1	657.35
A*D	1	280.31
A*F	1	1090.42
B*C	1	293.39
B*D	1	42.70
B*E	1	170.07
B*F	1	622.66
C*D	1	103.84
C*F	1	7.60
D*F	1	4.99
A^2	1	291.40
B^2	1	1334.51
F^2	1	211.22

Unusual Observations

Obs	Gypsum	Mean	Fit	SE Fit	Residual	St Resid
8	1.50	37.947	38.320	3.356	-0.374	-1.39 X
18	3.00	22.917	22.842	3.367	0.075	1.39 X
25	4.50	13.677	13.378	3.360	0.299	1.39 X

X denotes an observation whose X value gives it large influence.

Durbin-Watson statistic = 1.96

Appendix 4A.9. Regression Analysis for Improved Quadratic Model:

The regression equation is

Mean = -1332 +18.2*A +2.89*B -0.121*C -108*D +0.629*E -50.2*F
+0.0189*AB+0.195*AC +5.20*AF - 0.00121*BC-0.142*BD-
0.000631*BE + 0.0545*BF+ 3.82*CD-0.0134*CF-2.97*DF-10.0*A^2-
0.00149*B^2- 3.49*F^2

Predictor	Coef	SE Coef	T	P
Constant	-1331.6	120.4	-11.06	0.000
A	18.19	15.34	1.19	0.275
B	2.8857	0.2459	11.73	0.000
C	-0.1209	0.2853	-0.42	0.684
D	-108.21	80.18	-1.35	0.219
E	0.6288	0.3930	1.60	0.154
F	-50.18	10.08	-4.98	0.002
A*B	0.018944	0.006512	2.91	0.023
A*C	0.19532	0.02003	9.75	0.000
A*F	5.2019	0.4341	11.98	0.000
B*C	-0.0012118	0.0002172	-5.58	0.001
B*D	-0.14162	0.06241	-2.27	0.058
B*E	-0.0006306	0.0003690	-1.71	0.131
B*F	0.05452	0.01127	4.84	0.002
C*D	3.8247	0.7430	5.15	0.001
C*F	-0.01341	0.01448	-0.93	0.385
D*F	-2.967	4.160	-0.71	0.499
A^2	-10.020	2.220	-4.51	0.003
B^2	-0.0014914	0.0001278	-11.67	0.000
F^2	-3.4884	0.7515	-4.64	0.002

S = 3.131 R-Sq = 99.3% R-Sq(adj) = 97.4%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	19	9735.94	512.42	52.27	0.000
Residual Error	7	68.62	9.80		
Total	26	9804.56			

Source	DF	Seq SS
A	1	93.42
B	1	2195.49
C	1	1041.97
D	1	3.20
E	1	401.55
F	1	819.68
A*B	1	70.78
A*C	1	657.35
A*F	1	1090.42
B*C	1	293.39
B*D	1	42.70
B*E	1	170.07
B*F	1	824.40
C*D	1	122.09
C*F	1	7.60
D*F	1	4.99
A^2	1	351.11
B^2	1	1334.51
F^2	1	211.22

Unusual Observations

Obs	Jips	Ort.	Fit	SE Fit	Residual	St Resid
18	3.00	22.917	22.773	3.118	0.144	0.51 X

X denotes an observation whose X value gives it large influence.

Durbin-Watson statistic = 1.99

Appendix 4A.10. Regression Analysis for Mean with no factor having p-value greater than 10%.

The regression equation is

Mean = -1319+30.9*A+2.88*B-0.330*C-170*D-0.0334*E- 43.9*F+0.0162*AB +0.195*AC+5.15*AF-0.00117*BC-0.125*BD+0.0419*BF+4.37*CD- 11.6*A^2 -0.00149*B^2- 2.65*F^2

Predictor	Coef	SE Coef	T	P
Constant	-1318.7	127.3	-10.36	0.000
A	30.86	14.81	2.08	0.064
B	2.8807	0.2603	11.07	0.000
C	-0.3298	0.2807	-1.17	0.267
D	-170.38	78.33	-2.18	0.055
E	-0.03342	0.06971	-0.48	0.642
F	-43.885	9.413	-4.66	0.001
A*B	0.016191	0.006378	2.54	0.029
A*C	0.19532	0.02120	9.21	0.000
A*F	5.1540	0.4569	11.28	0.000
B*C	-0.0011670	0.0002213	-5.27	0.000
B*D	-0.12538	0.06360	-1.97	0.077
B*F	0.041905	0.009020	4.65	0.001
C*D	4.3652	0.7116	6.13	0.000
A^2	-11.581	2.142	-5.41	0.000
B^2	-0.0014914	0.0001353	-11.02	0.000
F^2	-2.6476	0.6014	-4.40	0.001

S = 3.314 R-Sq = 98.9% R-Sq(adj) = 97.1%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	16	9694.71	605.92	55.16	0.000
Residual Error	10	109.85	10.98		
Total	26	9804.56			

Source	DF	Seq SS
A	1	93.42
B	1	2195.49
C	1	1041.97
D	1	3.20
E	1	401.55
F	1	819.68
A*B	1	70.78
A*C	1	657.35
A*F	1	1090.42
B*C	1	293.39
B*D	1	42.70
B*F	1	991.83
C*D	1	124.40
A^2	1	321.12
B^2	1	1334.51
F^2	1	212.92

Durbin-Watson statistic = 1.38

Appendix 4A.11. The Best Regression Model for s.

The regression equation is
s = - 1.53 - 79.6*D + 6.42*F + 0.0380*AC - 6.64*AD + 0.659*AF-
0.000113*BC + 0.115*BD - 0.619*A^2 - 1.41*F^2 C6C6

Predictor	Coef	SE Coef	T	P
Constant	-1.525	5.034	-0.30	0.766
D	-79.61	27.37	-2.91	0.010
F	6.420	3.366	1.91	0.074
A*C	0.03805	0.01361	2.80	0.012
A*D	-6.639	4.249	-1.56	0.137
A*F	0.6591	0.3541	1.86	0.080
B*C	-0.00011261	0.00004762	-2.36	0.030
B*D	0.11453	0.02821	4.06	0.001
A^2	-0.6188	0.2371	-2.61	0.018
F^2	-1.4062	0.5268	-2.67	0.016

S = 2.904 R-Sq = 67.7% R-Sq(adj) = 50.6%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	9	300.633	33.404	3.96	0.007
Residual Error	17	143.330	8.431		
Total	26	443.963			

Source	DF	Seq SS
D	1	13.215
F	1	0.063
A*C	1	2.783
A*D	1	32.281
A*F	1	4.337
B*C	1	0.497
B*D	1	129.973
A^2	1	57.423
F^2	1	60.060

Unusual Observations

Obs	D	s	Fit	SE Fit	Residual	St Resid
2	0.200	0 .664	7.051	1.518	-6.386	-2.58R

R denotes an observation with a large standardized residual

Durbin-Watson statistic = 2.70

Appendix 4A.12. The Values of Log s^2:

Run No	**s**	**log s^2**
1	6.6044	1.6397
2	0.6643	-0.3553
3	1.9970	0.6008
4	1.6983	0.4600
5	5.4060	1.4658
6	3.8339	1.1673
7	2.8498	0.9096
8	10.4453	2.0378
9	12.5324	2.1961
10	1.6251	0.4218
11	1.4144	0.3011
12	11.0631	2.0878
13	5.1102	1.4169
14	13.8822	2.2849
15	2.2984	0.7228
16	10.5982	2.0505
17	10.3786	2.0323
18	3.7331	1.1441
19	3.2547	1.0250
20	0.1582	-1.60148
21	3.2723	1.0297
22	1.3922	0.2874
23	0.2066	-1.3696
24	7.2443	1.7200
25	2.0619	0.6285
26	3.6848	1.1328
27	9.5077	1.9562

Appendix 4A.13. The regression model for log s^2

* A*E is highly correlated with other X variables
* A*E has been removed from the equation

* C*E is highly correlated with other X variables
* C*E has been removed from the equation

* D*E is highly correlated with other X variables
* D*E has been removed from the equation

* C^2 is highly correlated with other X variables
* C^2 has been removed from the equation

* D^2 is highly correlated with other X variables
* D^2 has been removed from the equation

* E^2 is highly correlated with other X variables
* E^2 has been removed from the equation

The regression equation is

$$\text{Log } s^2 = 9.1 + 1.81*A - 0.0249*B + 0.0583*C - 8.2*D - 0.058*E + 0.17*F - 0.00003*AB + 0.00824*AC + 0.35*AD + 0.145*AF - 0.000099*BC + 0.0026*BD + 0.000054*BE + 0.00051*BF + 0.087*CD - 0.00035*CF + 0.33*DF - 0.499\ A^2 + 0.000016*B^2 - 0.185*F^2$$

Predictor	Coef	SE Coef	T	P
Constant	9.10	34.96	0.26	0.803
A	1.815	4.611	0.39	0.708
B	-0.02486	0.07139	-0.35	0.740
C	0.05833	0.08486	0.69	0.518
D	-8.19	25.89	-0.32	0.762
E	-0.0577	0.1141	-0.51	0.631
F	0.167	2.925	0.06	0.956
A*B	-0.000025	0.001891	-0.01	0.990
A*C	0.008236	0.005814	1.42	0.206
A*D	0.348	1.744	0.20	0.848
A*F	0.1453	0.1260	1.15	0.293
B*C	-0.00009883	0.00006305	-1.57	0.168
B*D	0.00260	0.01812	0.14	0.891
B*E	0.0000543	0.0001071	0.51	0.630
B*F	0.000507	0.003273	0.15	0.882
C*D	0.0873	0.2327	0.38	0.720

C*F	-0.000353	0.004203	-0.08	0.936
D*F	0.325	1.208	0.27	0.797
A^2	-0.4990	0.6921	-0.72	0.498
B^2	0.00001626	0.00003711	0.44	0.677
F^2	-0.1847	0.2182	-0.85	0.430

S = 0.9090 R-Sq = 81.0% R-Sq(adj) = 17.5%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	20	21.0721	1.0536	1.28	0.408
Residual Error	6	4.9576	0.8263		
Total	26	26.0297			

Source	DF	Seq SS
A	1	1.5683
B	1	4.4391
C	1	2.4724
D	1	1.0978
E	1	2.1192
F	1	0.0801
A*B	1	0.0000
A*C	1	1.4998
A*D	1	0.0062
A*F	1	0.4114
B*C	1	2.4293
B*D	1	0.0234
B*E	1	1.9276
B*F	1	0.0165
C*D	1	1.3937
C*F	1	0.0086
D*F	1	0.0599
A^2	1	0.7683
B^2	1	0.1585
F^2	1	0.5919

Unusual Observations

Obs	Gypsum	Log s2	Fit	SE Fit	Residual	St Resid
8	1.50	2.038	2.027	0.906	0.011	0.15 X
18	3.00	1.144	1.146	0.909	-0.002	-0.15 X
25	4.50	0.629	0.637	0.907	-0.009	-0.15 X

X denotes an observation whose X value gives it large influence.
Durbin-Watson statistic = 2.12

Appendix 4A.14. Regression Analysis for improved quadratic model of log s^2

The regression equation is

Log s2 = - 4.00 + 0.0905*C + 0.00632*AC + 0.670*AD + 0.158*AF -
0.000106*BC + 0.00117*BF - 0.212 A^2 +0.000005*B^2 -0.271*F^2

Predictor	Coef	SE Coef	T	P
Constant	-4.005	1.499	-2.67	0.016
C	0.09051	0.03739	2.42	0.027
A*C	0.006320	0.002397	2.64	0.017
A*D	0.6700	0.2775	2.41	0.027
A*F	0.15803	0.07296	2.17	0.045
B*C	-0.00010596	0.00003840	-2.76	0.013
B*F	0.0011689	0.0006075	1.92	0.071
A^2	-0.21231	0.04785	-4.44	0.000
B^2	0.00000468	0.00000191	2.45	0.025
F^2	-0.27120	0.09254	-2.93	0.009

S = 0.5817 R-Sq = 77.9% R-Sq(adj) = 66.2%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	9	20.2778	2.2531	6.66	0.000
Residual Error	17	5.7519	0.3383		
Total	26	26.0297			

Source	DF	Seq SS
C	1	2.4724
A*C	1	0.1371
A*D	1	0.3631
A*F	1	0.8135
B*C	1	1.7253
B*F	1	2.3838
A^2	1	3.7372
B^2	1	5.7395
F^2	1	2.9059

Unusual Observations

Obs	Ro.Ti.	Log s2	Fit	SEFit	Residual	St Resid
2	30	-0.355	0.650	0.336	-1.006	-2.12R
5	30	1.466	0.496	0.357	0.970	2.11R

R denotes an observation with a large standardized residual

Durbin-Watson statistic = 2.43

Appendix 4A.15. Regression Analysis for log s^2 with cubic terms

The regression equation is

Log s2 = - 2.58 + 0.0592*C + 0.00858*AC -0.000081*BC +0.000873*BF -
0.0273*A^3 +0.000000*B^3 + 10.6*D^3 - 0.0298*F^3

Predictor	Coef	SE Coef	T	P
Constant	-2.579	1.094	-2.36	0.030
C	0.05921	0.03772	1.57	0.134
A*C	0.008584	0.002529	3.39	0.003
B*C	-0.00008092	0.00003874	-2.09	0.051
B*F	0.0008730	0.0003786	2.31	0.033
A^3	-0.027280	0.006500	-4.20	0.001
B^3	0.00000000	0.00000000	2.46	0.024
D^3	10.609	4.543	2.34	0.031
F^3	-0.02979	0.01192	-2.50	0.022

S = 0.6189 R-Sq = 73.5% R-Sq(adj) = 61.7%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	8	19.1354	2.3919	6.24	0.001
Residual Error	18	6.8943	0.3830		
Total	26	26.0297			

Source	DF	Seq SS
C	1	2.4724
A*C	1	0.1371
B*C	1	1.5948
B*F	1	0.0021
A^3	1	5.6569
B^3	1	4.6278
D^3	1	2.2535
F^3	1	2.3907

Unusual Observations

Obs	Ro.Ti.	Log s2	Fit	SE Fit	Residual	St Resid
1	60	1.640	0.367	0.283	1.273	2.31R
2	30	-0.355	0.751	0.342	-1.107	-2.15R

R denotes an observation with a large standardized residual
Durbin-Watson statistic = 2.09

APPENDIX 5A

Appendix 5A.1. The Starting and Optimum Points for Minitab Response Optimizer

	STARTING POINTS						OPTIMUM POINTS					
POINTS	*Gypsum Ratio*	*Roast. Temp. (°C)*	*Roasting Time (min)*	*Leach S/L Ratio*	*Leach Time (min)*	*Limestone* Ratio	*Gypsum Ratio*	*Roast. Temp. (°C)*	*Roasting Time (min)*	*Leach S/L Ratio*	*Leach Time (min)*	*Limestone Ratio*
1	1.5	987	30	0.1	120	1.5	1.5	987	30	0.1	120	1.5
2	3.23	900	120	0.4	40	2.32	3.23	900	120	0.4	40	2.32
3	4.5	900	30	0.1	120	1.5	4.5	900	30	0.1	120	1.5
4	1.5	878	120	0.36	120	1.5	1.5	878	120	0.36	120	1.5
5	3	950	60	0.2	60	3	3	950	60	0.2	60	3
6	2	1000	100	0.4	60	2	2	1000	100	0.4	60	2
7	NO STARTING POINT						4.5	850	120	0.4	120	1.5
8	3	970	30	0.2	120	3	3	970	30	0.112	120	2.41
9	4.5	900	120	0.4	30	1.5	4.5	900	120	0.4	30	1.5
10	4.5	950	60	0.3	30	4.5	4.5	950	60	0.3	30	4.5

Appendix 5A.2. GAMS Input Program

```
variable S, Z;
positive variable A, B, C, D, E, F;
EQUATIONS OB,  EQ, EQ100, EQS, A1, A2,B1, B2 ,
C1,C2,D1,D2,E1,E2,F1,F2;

OB.. Z=e= -1331.6 + 18.19*A+ 2.8857*B - 0.1209*C - 108.21*D + 0.6288*E -
50.18*F + 0.018944*A*B + 0.19532*A*C + 5.2019*A*F - 0.0012118*B*C -
0.14162*B*D -0.0006306*B*E + 0.05452*B*F + 3.8247*C*D - 0.01341*C*F -
2.967*D*F - 10.02*A*A-0.0014914*B*B - 3.4884*F*F;


EQ.. -2.579 + 0.05921*C + 0.008584*A*C - 0.00008092*B*C + 0.000873*B*F
     -0.02728*A*A*A+0.0000000015*B*B*B+10.609*D*D*D-
     0.02979*F*F*F =l=1;

EQ100..  -1331.6 + 18.19*A+ 2.8857*B - 0.1209*C - 108.21*D + 0.6288*E -
50.18*F +0.018944*A*B + 0.19532*A*C + 5.2019*A*F - 0.0012118*B*C -
0.14162*B*D -0.0006306*B*E + 0.05452*B*F + 3.8247*C*D - 0.01341*C*F
- 2.967*D*F - 10.02*A*A-0.0014914*B*B - 3.4884*F*F=l=100 ;


EQS..-2.579 + 0.05921*C + 0.008584*A*C - 0.00008092*B*C +
     0.000873*B*F    -0.02728*A*A*A + 0.0000000015*B*B*B +
     10.609*D*D*D -   0.02979*F*F*F =e=S;

A1..    A=l=4.5;
A2..    A=g=1.5;
B1..    B=l=1050;
B2..    B=g=850;
C1..    C=l=120;
C2..    C=g=30;
D1..    D=l=0.4;
D2..    D=g=0.1;
E1..    E=l=120;
E2..    E=g=30;
F1..    F=l=4.5;
F2..    F=g=1.5;

      MODEL ATIL1 /ALL/ ;
      SOLVE ATIL1 USING NLP MAXIMIZING Z;
```

Appendix 5A.3. The Starting and Optimum Points for GAMS Non-Linear Programming

	STARTING POINTS						OPTIMUM POINTS					
POINTS	*Gypsum Ratio*	*Roast. Temp. (°C)*	*Roasting Time (min)*	*Leach S/L Ratio*	*Leach Time (min)*	*Limestone* Ratio	*Gypsum Ratio*	*Roast. Temp. (°C)*	*Roasting Time (min)*	*Leach S/L Ratio*	*Leach Time (min)*	*Limestone Ratio*
1	3	950	60	0.2	60	3	2.787	989	30	0.1	120	2.512
2	2	900	75	0.1	120	2	2.787	989	30	0.1	120	2.512
3	2.9	990	31	0.11	120	2.52	2.787	989	30	0.1	120	2.512
4	3	850	30	0.3	45	2	2.876	1013	30	0.1	30	2.768
5	4.5	1000	120	0.4	120	1.5	4.02	959	120	0.4	120	1.5
6	4.5	1000	30	0.1	30	4.5	2.876	1013	30	0.1	30	2.768
7	NO STARTING POINT						2.787	989	30	0.1	120	2.512
8	1.5	875	60	0.4	120	4.5	1.5	966	120	0.4	120	4.5
9	4	900	30	0.1	90	1.5	2.787	989	30	0.1	120	2.512
10	3.75	925	100	0.25	100	2.25	3.209	980	115	0.4	120	2.12

B=

	C1	C2	C3	C4	C5	C6
C1	-10.02	0.0095	0.098	0	0	2.6
C2	0.0095	-0.0015	-0.0006	-0.071	-0.00032	0.027
C3	0.098	-0.0006	0	1.912	0	-0.0067
C4	-0.75	-0.071	1.912	0	0	-1.484
C5	0	-0.00032	0	0	0	0
C6	2.6	0.027	-0.0067	-1.484	0	-3.49

B-LI=

	C1	C2	C3	C4	C5	C6
C1	-10.02-L	0.0095	0.098	-0.75	0	2.6
C2	0.0095	-0.0015-L	-0.0006	-0.071	-0.00032	0.027
C3	0.098	-0.0006	-L	1.912	0	-0.0067
C4	-0.75	-0.071	1.912	-L	0	-1.484
C5	0	-0.00032	0	0	-L	0
C6	2.6	0.027	-0.0067	-1.484	0	-3.49-L

EIGENVALUES
-10.9511
-3.4231
-1.2753
-0.0013
0.0001
2.1392

X1	**-0.5 =**	18.19
X2		2.886
X3		-0.1209
X4		-108.21
X5		0.6288
X6		-50.18

Appendix 5A.5. Solving of Ridge Analysis for λ Inside the Region of the Experiments

```
Variable G,Z;
   positive variable A, B, C, D, E, F, L;
   EQUATIONS OB, P, Q, R, S, T, U, V, Y, X;

   OB.. Z=e=1;
   P.. (-10.02-L)*A+0.0095*B+0.098*C+2.6*F=e=-9.095;
   Q.. 0.0095*A-(0.0015+L)*B-0.0006*C-0.071*D-0.00032*E+0.027*F=e=-
       1.443;
   R.. 0.098*A-0.0006*B-L*C+1.912*D-0.0067*F=e=0.06045;
   S.. -0.071*B+1.912*C-L*D-1.484*F=e=54.105;
   T.. -0.00032*B-L*E=e=-0.3144;
   U.. 2.6*A+0.027*B-0.0067*C-1.484*D-(3.49+L)*F=e=25.09;
   V.. L=l=2.1392;
   Y.. L=g=-10.9511;
   X.. G=e=L;

         MODEL ATIL2 /ALL/ ;
         SOLVE ATIL2 USING NLP MAXIMIZING Z ;
```

SOLUTION PROPOSED BY GAMS

	LOWER	LEVEL	UPPER	MARGINAL
VAR G	-INF	.	+INF	.
VAR Z	-INF	1.000	+INF	.
VAR A	.	3.155	+INF	.
VAR B	.	982.500	+INF	.
VAR C	.	66.764	+INF	.
VAR D	.	0.187	+INF	.
VAR E	.	46.404	+INF	.
VAR F	.	2.555	+INF	.
VAR L	.	.	+INF	EPS

**** $\lambda=0$ is the solution for the case that $-10.391<\lambda<2.1392$

Appendix 5A.6. Solving of Ridge Analysis for λ Outside the Region of the Experiments

```
Variable G,Z;
  positive variable A, B, C, D, E, F, L;
  EQUATIONS OB, P, Q, R, S, T, U, V, Y, X;

  OB.. Z=e=1;
  P.. (-10.02-L)*A+0.0095*B+0.098*C+2.6*F=e=-9.095;
  Q.. 0.0095*A-(0.0015+L)*B-0.0006*C-0.071*D-0.00032*E+0.027*F=e=-
      1.443;
  R.. 0.098*A-0.0006*B-L*C+1.912*D-0.0067*F=e=0.06045;
  S.. -0.071*B+1.912*C-L*D-1.484*F=e=54.105;
  T.. -0.00032*B-L*E=e=-0.3144;
  U.. 2.6*A+0.027*B-0.0067*C-1.484*D-(3.49+L)*F=e=25.09;
  V.. L=g=2.1392;
  Y.. L=l=-10.9511;
  X.. G=e=L;

       MODEL ATIL2 /ALL/ ;
       SOLVE ATIL2 USING NLP MAXIMIZING Z ;
```

SOLUTION PROPOSED BY GAMS

```
SOLVER STATUS     1 NORMAL COMPLETION
**** MODEL STATUS      5 LOCALLY INFEASIBLE
**** OBJECTIVE VALUE               1.0000
** Infeasible solution. There are no superbasic variables.
```

	LOWER	LEVEL	UPPER	MARGINAL
VAR G	-INF	.	+INF	.
VAR Z	-INF	1.000	+INF	.
VAR A	.	3.155	+INF	.
VAR B	.	982.500	+INF	.
VAR C	.	66.764	+INF	.
VAR D	.	0.187	+INF	.
VAR E	.	46.404	+INF	.
VAR F	.	2.555	+INF	.
VAR L	.	.	+INF	EPS

APPENDIX 6A

Appendix 6A.1. The Starting Model for Mean Including Optimum Points

The regression equation is

Ort. = 1013+67.4*A-2.55*B-0.61*C+708*D-10.0*E+312*F
+0.0189*AB-0.313*AC+112*AD+0.261*AE+5.20*AF
-0.00121*BC-0.142*BD+0.00944*B-0.348*BF+12.3*CD+0.00611*CE-
0.0134*CF-8.39*DE-2.97*DF-0.671*EF-
$20.7*A^2+0.00153*B^2+0.00418*C^2$2322*$D^2$+0.0158*$E^2$+9.94*$F^2$

Predictor	Coef	SE Coef	T	P
Constant	1013.0	507.9	1.99	0.093
A	67.39	24.49	2.75	0.033
B	-2.552	1.309	-1.95	0.099
C	-0.608	1.431	-0.42	0.686
D	707.8	619.2	1.14	0.297
E	-10.047	1.806	-5.56	0.001
F	312.31	82.40	3.79	0.009
A*B	0.018944	0.007003	2.71	0.035
A*C	-0.3132	0.1153	-2.72	0.035
A*D	111.57	36.70	3.04	0.023
A*E	0.2606	0.4480	0.58	0.582
A*F	5.2019	0.4669	11.14	0.000
B*C	-0.0012118	0.0002335	-5.19	0.002
B*D	-0.14162	0.06711	-2.11	0.079
B*E	0.009438	0.002241	4.21	0.006
B*F	-0.34824	0.09107	-3.82	0.009
C*D	12.322	5.422	2.27	0.063
C*E	0.006107	0.009801	0.62	0.556
C*F	-0.01341	0.01557	-0.86	0.422
D*E	-8.391	7.310	-1.15	0.295
D*F	-2.967	4.474	-0.66	0.532
E*F	-0.6713	0.1587	-4.23	0.006
A^2	-20.699	5.789	-3.58	0.012
B^2	0.0015293	0.0007258	2.11	0.080
C^2	0.004180	0.004917	0.85	0.428
D^2	-2322.4	797.9	-2.91	0.027
E^2	0.015767	0.003582	4.40	0.005
F^2	9.937	3.123	3.18	0.019

S = 3.367 R-Sq = 99.6% R-Sq(adj) = 97.7%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	27	16260.81	602.25	53.12	0.000
Residual Error	6	68.02	11.34		
Total	33	16328.83			

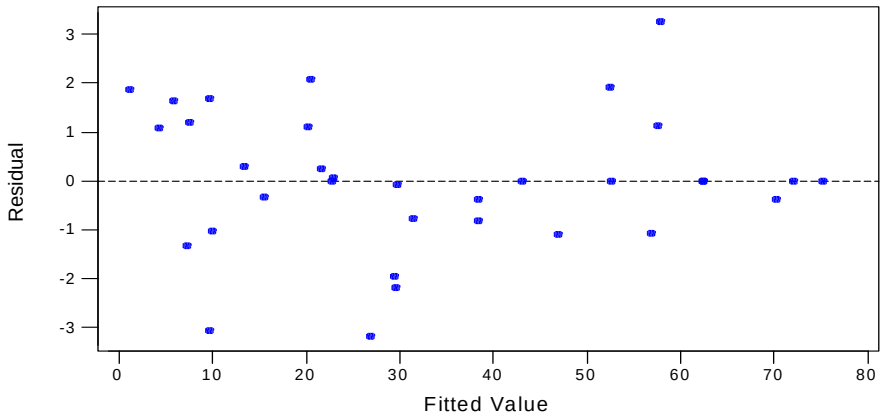
Source	DF	Seq SS
A	1	11.65
B	1	2464.23
C	1	1646.34
D	1	334.88
E	1	1238.54
F	1	1849.67
A*B	1	161.83
A*C	1	171.29
A*D	1	154.45
A*E	1	1295.18
A*F	1	976.63
B*C	1	263.47
B*D	1	17.57
B*E	1	25.98
B*F	1	463.35
C*D	1	21.84
C*E	1	2083.92
C*F	1	4.96
D*E	1	698.48
D*F	1	6.09
E*F	1	520.25
A^2	1	785.81
B^2	1	443.22
C^2	1	208.88
D^2	1	114.72
E^2	1	182.79
F^2	1	114.77

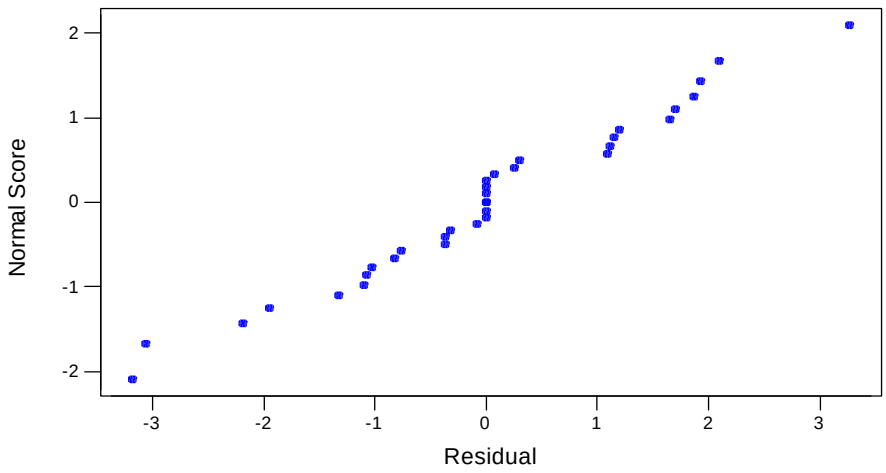
Unusual Observations

Obs	Gyp	Ort.	Fit	SE Fit	Residual	St Resid
8	1.50	37.947	38.320	3.356	-0.374	-1.39 X
18	3.00	22.917	22.842	3.367	0.075	1.39 X
25	4.50	13.677	13.378	3.360	0.299	1.39 X
28	1.50	62.355	62.355	3.367	-0.000	* X
29	1.50	72.110	72.110	3.367	-0.000	* X

30	1.50	43.105	43.105	3.367	-0.000	* X
31	3.18	75.200	75.200	3.367	-0.000	* X
32	2.77	52.530	52.530	3.367	-0.000	* X
33	4.50	62.330	62.330	3.367	-0.000	* X
34	4.50	22.695	22.695	3.367	-0.000	* X

X denotes an observation whose X value gives it large influence.
Durbin-Watson statistic = 1.98





Appendix 6A.2. The Regression Model Comprising Optimum Points With No Factor Having P-Value Greater Than 10%

Regression Analysis: Mean versus Gypsum; Ro.Te.; ...
The regression equation is
Mean = 703 + 77.4*A - 1.70*B - 1.36*C + 337*D- 9.14*E + 255*F + 0.0163*AB-0.248*AC + 90.6*AD+ 5.10*AF - 0.00115*BC - 0.121*BD + 0.00792*BE -0.287*BF + 8.95*CD + 0.0116*CE - 4.09*DE - 0.567*EF - 17.0*A^2 + 0.00106*B^2 + 0.00582*C^2 – 1842*D^2 + 0.0157*E^2 + 7.87*F^2

Predictor	Coef	SE Coef	T	P
Constant	702.9	319.7	2.20	0.055
A	77.44	13.32	5.82	0.000
B	-1.7035	0.6852	-2.49	0.035
C	-1.3554	0.4839	-2.80	0.021
D	337.09	71.11	4.74	0.001
E	-9.141	1.443	-6.34	0.000
F	255.44	40.00	6.39	0.000
A*B	0.016252	0.005850	2.78	0.021
A*C	-0.24790	0.05860	-4.23	0.002
A*D	90.57	20.01	4.53	0.001
A*F	5.1048	0.4086	12.49	0.000
B*C	-0.0011496	0.0002003	-5.74	0.000
B*D	-0.12117	0.05779	-2.10	0.065
B*E	0.007921	0.001108	7.15	0.000
B*F	-0.28658	0.04403	-6.51	0.000
C*D	8.9461	0.8377	10.68	0.000
C*E	0.011551	0.001304	8.86	0.000
D*E	-4.0862	0.7136	-5.73	0.000
E*F	-0.56656	0.07959	-7.12	0.000
A^2	-16.963	2.004	-8.47	0.000
B^2	0.0010576	0.0003752	2.82	0.020
C^2	0.005822	0.003073	1.89	0.091
D^2	-1842.2	221.1	-8.33	0.000
E^2	0.015701	0.002881	5.45	0.000
F^2	7.874	1.592	4.94	0.001

S = 3.040 R-Sq = 99.5% R-Sq(adj) = 98.1%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	24	16245.64	676.90	73.23	0.000
Residual Error	9	83.19	9.24		
Total	33	16328.83			

Durbin-Watson statistic = 1.64

Appendix 6A.3. The Best Regression Model Comprising Optimum Points

Regression Analysis: Mean versus Gypsum; Ro.Te; ..

The regression equation is

$$\begin{aligned}\text{Mean} = {} & 769 + 78.2*A - 1.85*B - 1.38*C + 343*D - 9.46*E + 266*F \\ & + 0.0181*AB - 0.254*AC + 93.2*AD + 5.12*AF - 0.00115*BC \\ & - 0.135*BD + 0.00819*BE - 0.297*BF + 9.09*CD + 0.0116*CE \\ & - 0.0124*CF - 4.09*DE - 0.584*EF - 17.4*A^2 + 0.00114*B^2 + \\ & + 0.00614*C^2 - 1864*D^2 + 0.0162*E^2 + 8.23*F^2\end{aligned}$$

Predictor	Coef	SE Coef	T	P
Constant	768.8	332.8	2.31	0.050
A	78.16	13.52	5.78	0.000
B	-1.8507	0.7148	-2.59	0.032
C	-1.3787	0.4912	-2.81	0.023
D	342.71	72.37	4.74	0.001
E	-9.458	1.507	-6.28	0.000
F	266.01	42.32	6.29	0.000
A*B	0.018113	0.006303	2.87	0.021
A*C	-0.25436	0.05986	-4.25	0.003
A*D	93.18	20.50	4.55	0.002
A*F	5.1191	0.4145	12.35	0.000
B*C	-0.0011513	0.0002031	-5.67	0.000
B*D	-0.13523	0.06076	-2.23	0.057
B*E	0.008193	0.001166	7.03	0.000
B*F	-0.29740	0.04633	-6.42	0.000
C*D	9.0914	0.8654	10.51	0.000
C*E	0.011571	0.001322	8.75	0.000
C*F	-0.01238	0.01421	-0.87	0.409
D*E	-4.0865	0.7233	-5.65	0.000
E*F	-0.58447	0.08325	-7.02	0.000
A^2	-17.383	2.087	-8.33	0.000
B^2	0.0011381	0.0003914	2.91	0.020
C^2	0.006138	0.003136	1.96	0.086
D^2	-1863.7	225.5	-8.27	0.000
E^2	0.016246	0.002986	5.44	0.001
F^2	8.235	1.666	4.94	0.001

S = 3.082 R-Sq = 99.5% R-Sq(adj) = 98.1%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	25	16252.85	650.11	68.46	0.000
Residual Error	8	75.97	9.50		
Total	33	16328.83			

Source	DF	Seq SS
A	1	11.65
B	1	2464.23
C	1	1646.34
D	1	334.88
E	1	1238.54
F	1	1849.67
A*B	1	161.83
A*C	1	171.29
A*D	1	154.45
A*F	1	1815.20
B*C	1	314.76
B*D	1	15.69
B*E	1	80.25
B*F	1	271.47
C*D	1	7.86
C*E	1	50.33
C*F	1	0.22
D*E	1	580.79
E*F	1	600.13
A^2	1	1077.26
B^2	1	1052.49
C^2	1	1580.49
D^2	1	482.01
E^2	1	59.07
F^2	1	231.95

Unusual Observations

Obs	Gypsum	Mean	Fit	SE Fit	Residual	St Resid
33	4.50	62.330	62.171	3.069	0.159	0.56 X

X denotes an observation whose X value gives it large influence.

Durbin-Watson statistic = 1.96

Appendix 6A.4. The Starting and Optimum Points for Minitab Response Optimizer for maximizing extraction while minimizing variation

	STARTING POINTS						OPTIMUM POINTS					
POINTS	*Gypsum Ratio*	*Roast. Temp. (°C)*	*Roasting Time (min)*	*Leach S/L Ratio*	*Leach Time (min)*	*Limestone* Ratio	*Gypsum Ratio*	*Roast. Temp. (°C)*	*Roasting Time (min)*	*Leach S/L Ratio*	*Leach Time (min)*	*Limestone Ratio*
1	1.5	918	120	0.17	120	1.5	1.5	918	120	0.17	120	1.5
2	1.5	940	120	0.15	120	1.5	1.53	940	120	0.15	120	1.5
3	1.5	950	120	0.17	120	2	1.57	950	120	0.15	120	1.77
4	1.5	915	120	0.26	120	1.5	1.5	915	120	0.26	120	1.5
5	1.5	915	120	0.25	120	2	1.5	915	120	0.25	120	2
6	1.5	940	120	0.2	120	1.5	1.5	940	120	0.2	120	1.5
7	NO STARTING POINT						4.5	850	120	0.1	30	4.5
8	1.5	1000	60	0.4	45	1.5	4.39	1000	59	0.31	41	4.5
9	1.5	1050	30	0.1	120	1.5	1.5	1050	30	0.1	120	1.5
10	3.178	986	67	0.187	33	2.6	3.178	986	67	0.18	30	3.03