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AN ATTEMPT TO MINIMIZE THE COST OF EXTRACTING LITHIUM FROM BORON CLAYS THROUGH ROBUST PROCESS DESIGN

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Abstract—In this study a robust design method is developed for extracting Li from boron (B) clays with the aim of minimizing cost and maximizing productivity. Lithium is commercially extracted from brines and certain minerals. Its extraction from clays has previously been found to be expensive, a major part of the extraction cost being attributed to the raw materials used. In this study, raw materials from lower-cost resources are used without applying any standardization to them and this might increase variation in the results. To minimize the variation, and achieve high extraction levels, robust design, statistical design and analysis of experiments, and response surface methodologies are utilized. As a result, consistently higher extraction levels have been achieved compared to previous studies. The experiments were conducted using the Bigadiç boron clay fields in Turkey. However, the method is generally applicable to other cases also.

Key Words—Boron Clays, Design Optimization, Extraction, Lithium, Statistical Design of Experiments, Response Surface Methodology, Robust Design.

INTRODUCTION

Lithium is an important element with many applications, *e.g.* ceramics, glasses, aluminum smelting, batteries and lubricants (Fishwick, 1974). The past decade has witnessed a significant increase in the demand for Li batteries. The market for Li-ion cells is expected to exceed 1.1 billion units valued at >$4 billion by 2005 (Abraham, 2002). Saller and O'Driscoll (2000) forecast an average annual increases of 16% for Li batteries up to 2008. Moreover, it has been the intent of Mitsubishi Chemical to commence production of electrolytic solutions for Li ion batteries in June 2004, believing that the growth of the Li ion battery sector will be maintained (Light Metals, 2004). The world's largest Li producer, Sociedad Quimica y Minera de Chile, has also declared that the Li battery market grew by 30% in 2003 and was expected to grow a further 30% in 2004 (Lithium battery market set to grow again, 2004).

Lithium is found in brines, minerals and clays, hectorite being a well known clay that contains Li. Hectorite, a Mg silicate, forms by precipitation from Mg-rich, Li-bearing hydrothermal solutions, and is associated with travertine deposits in areas of basaltic volcanic activity. It belongs to the smectite family, but is distinguished from other smectite species by its high Mg and F and low Al contents. The term hectorite is used for trioctahedral smectite clays containing 1% or more Li_2O or 4% or more F (F substitutes for OH). The chemical comparison of smectites is shown in Table 1 (Fitzgerald and Kendall, 1996).

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It is known that Li exists in the Bigadiç clays, but there is no evidence of the clear occurrence of hectorite. Ataman and Baysal (1978) completed a study of the clay fraction of Bigadiç clay and claimed that the dominant clay minerals are montmorillonite and vermiculite. As montmorillonite is defined as hectorite when it contains at least 1% Li_2O, and as the Li_2O content of Bigadiç clays is at most 7000 ppm, we refer to the Bigadiç clays as Li-containing montmorillonite. Commercial production of Li from clays has not yet been performed. This is mainly because extracting Li from clays is not economic compared to extracting it from brines and other minerals (Lien, 1985; Crocker and Lien, 1988; Beşkardeş *et al.*, 1992; Mordoğan *et al.*, 1995). Lien (1985) and Crocker and Lien (1988) reported the major cost components of Li extraction from clays as raw material, preparation and roasting. Crocker and Lien (1988) considered reducing the amounts of raw materials, but still did not find the results economically viable.

We attempt in this study to use raw materials from lower-cost resources such as industrial waste and naturally occurring limestone. This, of course, is expected to increase the variability in the raw materials and hence extraction results. Therefore, we developed a method to find optimal process-parameter levels that minimize sensitivity of the extraction results to variation in the raw materials. The method utilizes robust design, statistical design and analysis of experiments, and response surface methodologies with modifications for the extraction problem. In order to demonstrate how the process of Li extraction from clays can be designed, we have used the Bigadiç boron fields in Turkey, the waste from a boric acid production facility as a source of gypsum, and limestone directly from a site near the boron fields. However, the methodology of this study

Table 1. Chemical comparison of smectites.

Clay	Formula
Dioctahedral smectites	
Montmorillonite	$M^{+}(Al_{2y}(FeMg)_y)Si_4O_{10}(OH)_2.nH_2O$
Beidellite	$M^{+}Al_2(Si_{4-x}Al_x)O_{10}(OH)_2.nH_2O$
Nontronite	$M^{+}Fe^{3+}(Si_{4-x}Al_x)O_{10}(OH)_2.nH_2O$
Trioctahedral smectites	
Saponite	$M^{+}(Mg_{3-y}AlFe_y)(Si_{4-x}Al_x)O_{10}(OH)_2.nH_2O$
Hectorite	$M^{+}(Mg_{3-y}Li_y)Si_4O_{10}(OH,F)_2.nH_2O$

can easily be applied to other clays, and other cheap sources of gypsum and limestone.

In the following sections some background information on robust design methodology and Li extraction is provided. Then, Li extraction process parameters and operations are described. Statistical design of the experiments is explained and response surface models are presented. The search for and confirmation of optimal process-parameter levels are presented. Further improvement of the parameter levels using the feedback from confirmation experiments is explained. Finally, a comparison of this study to the relevant literature, a discussion of the process cost and the other results, and concluding remarks are provided.

ROBUST DESIGN

The fundamental principle of robust design (or parameter design or design optimization) is to improve the quality of a product or a process by minimizing the effect of the causes of variation without eliminating the causes (Phadke, 1989). The causes (sources) of variation, commonly referred to as 'noise', may arise from variation in properties of raw materials and manufacturing conditions. Many noise factors are difficult to identify and control. Robust design is based on the belief that one can find such product or process-parameter settings that yield consistently high performance irrespective of the 'noise' levels. Hence, if such parameter settings can be found, there will be no (or minimum) need to spend money or time controlling the sources of variation.

Robust design was originally developed by Taguchi (1986) as an innovative idea and a simple application of statistical design and analysis of experiments. Later some drawbacks of the Taguchi method were identified (Nair, 1992) and various statistics and optimization-based approaches were developed for solving robust-design problems. These include use of response surface methodology (Vining and Myers, 1990; Myers *et al.*, 1992) and nonlinear programming (Fathi, 1991; Del Castillo and Montgomery, 1993). Robust design has been applied in many engineering fields and business applications. However, we have focused on a small number of attempts, described in the literature, to use robust design in the field of metal or mineral processing (Srinivasan and Chaudhary, 1990; Koolen, 1998; Khoei *et al.*, 2002) where it is common to seek to control the sources of variation or to limit them, rather than seeking process designs that can cope with the variation.

For the Li-extraction problem, we have adapted various robust design approaches such as ANOVA, response surface modeling, ridge regression, and nonlinear optimization (Büyükburç and Köksal, 2004). However, in this paper we present only our contribution to the experimentation and analysis strategy, and optimization based on the response surface models.

Li EXTRACTION

Lithium carbonate (Li_2CO_3) is the most widely used compound of Li that is produced from brines and minerals. The production of Li_2CO_3 from clays generally comprises raw material preparation, roasting, leaching, evaporation and precipitation. Various methods have been developed to extract Li: water disaggregating, hydrothermal treatment, sulfuric acid leaching, acid pug-water leach, acid baking-water leaching, alkaline roasting-water leaching, sulfate roasting-water leaching, chloride roasting-water leaching, multiple reagent roasting-water leaching (May *et al.*, 1980), selective chlorination (Davidson, 1981) and lime-gypsum roasting-water leaching (Lien, 1985; Edlund, 1983). Water disaggregation and hydrothermal treatment techniques have the drawbacks of low extraction yields, *e.g.* 1–2%. Using acid for extraction purposes gave high yields, but was not commercially feasible because of the use of excessive amounts of acid and contamination of the leach solution with Mg, K and Fe. Alkaline, sulfate, chloride and multiple-reagent roasting-water leach methods had been found unsuitable for our purpose as pure (chemical-grade) reagents, which were difficult to find in nature, were required. Moreover, significant amounts of Li were lost due to volatilization leading to additional cost and effort to recover the Li. Of all the methods, lime-gypsum roasting-water leach is the most promising as no acid is required and there was little contamination of the leach solution with undesired species. This method requires use of the following raw materials: Li-bearing clay, gypsum ($CaSO_4.2H_2O$) and limestone ($CaCO_3$). Preparation includes crushing, grinding and pelletizing of the raw materials. Then, the pellets are roasted at elevated temperatures of ~1000ºC. The main reactions that occur during roasting are given in equations 1 and 2:

$$CaSO_4.2H_2O + SiO_2 \rightarrow CaSiO_3 + SO_2 + \tfrac{1}{2}\,O_2 + 2H_2O \quad (1)$$

$$Li_2Si_2O_5 + SO_2 + \tfrac{1}{2}\,O_2 \rightarrow Li_2SO_4 + 2SiO_2 \quad (2)$$

The function of gypsum as a source of sulfate is to convert Li silicate to Li sulfate. Limestone is used to minimize the back reaction of equation 2. Free SiO_2 tends to react with Li sulfate and converts it back to Li

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silicate. Lithium sulfate is highly soluble in water even at low temperatures. Therefore, after roasting, water leaching is applied in order to extract Li from the solution. In this study, the Li-extraction process continues until the end of leaching to maximize the amount of Li that can be taken into the solution at the end of the leaching process.

Lien (1985) extracted 78–82% of Li from a hectorite-type clay containing 6000 ppm of Li by using a limestone-gypsum roast-water leach process. The production cost was estimated to be 1.4 times the market price of Li_2CO_3 at the time of the study. Crocker and Lien (1988) modified the study of Lien (1985) in order to decrease the processing cost by decreasing the raw materials. However, they reported nearly the same cost of extraction as estimated by Lien (1985). Extracting Li from boron clays was the subject of work by Beşkardeş *et al.* (1992) and Mordoğan *et al.* (1995). According to the latter, 77% of Li can be extracted from Kırka boron fields containing 2800 ppm Li. Beşkardeş *et al.* (1992) were largely concerned with the direct application of Bigadiç boron clays (Li content of 2000 ppm) in industry, and with the economy of extracting Li. They estimated the production cost to be about three times the market price of Li_2CO_3 at the time of the study.

PLANNING OF THE Li-EXTRACTION PROCESS AND ROBUST DESIGN EXPERIMENTS

The literature reveals that it is not economical to extract Li from clays, as explained in the previous section. Hence, this study focuses on some cost-reduction alternatives. The most important cost-reducing step we took was to use natural raw materials instead of reagent-grade materials. For this purpose, limestone-rich clay, found in the Bigadiç boron fields, was dried and crushed for direct use in the Li-extraction process as a source of $CaCO_3$. Similarly, the waste of a boric acid production plant was dried and crushed for direct use in the process as a source of gypsum. (The Bigadiç boron fields contain limestone-rich areas with a minimum of 70% limestone content, and the gypsum content of the boric acid production waste is at least 85%.) It is observed that significant variability exists in the composition of these raw materials, especially the limestone. Another cost-reducing step in this study was to omit pelletizing during preparation of the raw material. The process eventually applied requires grinding of crushed limestone, gypsum and boron clay (initially wet screened and dried) together to get a homogeneous raw material mixture. Then, this mixture is roasted at a certain temperature for a certain time, and finally leached with distilled water. At the end of leaching the slurry is filtered to separate the solution from it. Finally, the Li content of the solution is chemically analyzed by using atomic absorption spectrophotometry which has a Li detection limit of 0.02 ppm.

There are several parameters that affect the extraction of Li from boron clays. Some of these parameters have been treated as control factors, and some as noise factors. Control factors are identified as gypsum:clay ratio, limestone:clay ratio, roasting temperature, roasting time, leach solid:liquid ratio, and leaching time. The amount of gypsum is important, as it will be used as a source of sulfate in order to convert Li silicate to Li sulfate. Roasting time and temperature are important as the conversion process occurs at high temperatures and it is reversible. Moreover, high-temperature roasting consumes large amounts of fuel (in the real production environment), hence it significantly affects the cost of the process. Leaching time and leach solid/liquid ratio are important as dissolution of Li sulfate must be achieved without dissolution of some impurities such as Fe, Al and Mg. These impurities cause some problems later during precipitation. A smaller solid:liquid ratio means that there is more water to evaporate, and thus a higher cost. The sulfate solubility equilibrium of the leaching process is important, hence leaching time should be monitored closely. Levels of these control factors to be used in experimentation are summarized in Table 2 based on the literature and previous experience with these factors.

Apart from the control factors, there are some noise factors for the process that are difficult and costly to control. Some are listed in Table 3.

Controlling the noise factors will bring additional cost to the process. For the purposes of this study, we did not wish to control them to reduce cost, but wanted to simulate them as much as possible in order to collect data about their effects on extraction yields. This way we can find control-factor levels that are insensitive to the noise factors, if they exist. This is an important

Table 2. Control factors.

Factors	Code	Level 1	Level 2	Level 3
Gypsum ratio (units)*	A	1.5	3	4.5
Roasting temperature (°C)	B	850	950	1050
Roasting time (min)	C	60	30	120
Leach solid:liquid ratio	D	0.1	0.2	0.4
Leach time (min)	E	30	60	120
Limestone ratio (units)*	F	1.5	3	4.5

* Clay is taken as 5 units

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Table 3. Noise factors.

Operation	+Noise factors
Raw material preparation	Properties of raw materials: $CaSO_4.2H_2O$ content of gypsum $CaCO_3$ content of limestone Li content of clay Measurement error: calibration of balance
Roasting	Temperature variation in furnace
Leaching	Leaching temperature Stirring speed Leaching particle size Measurement error: Calibration of balance Accuracy of container Chemical analyses

distinction between robust-design experiments and more traditional ones.

Gypsum and limestone have not been standardized in this study; hence their properties may vary considerably. Another important noise factor that can affect the yield is temperature variation in the furnace. In a real production environment, temperature in the furnace cannot be kept consistently at desired levels, as this is technologically not possible or very costly. In this study, a furnace that shows ±10ºC variation has been used in order to partially simulate the production environment. Furthermore, measurement errors may cause variation in the results. As the capacities in a real production environment are large, the weighting errors are prone to be larger compared to laboratory measurement errors. However, in this study, real production measurement (weighting) errors are not simulated. Leaching temperature is another important factor that can affect the solubility of Li sulfate, and hence extraction. As the room temperature (RT) solubility of Li sulfate is high, it is not necessary to work at higher leaching temperatures. Moreover, leaching will be performed near room temperature in a real production environment. Hence, room temperature is used during the experiments. In addition, stirring speed is a factor that cannot be controlled accurately in the real production environment. In this study, stirring speed has been allowed to vary at 410±10 rpm so that this noise factor can be simulated as well. Leaching particle size is yet another noise factor. Leaching in the real production environment will be performed with powder particles (particle size of <200 μm). In this study, the average particle size was ~74 μm. Furthermore, no pelletizing was carried out in this study although it has been used in other studies in the literature (Lien, 1985; Crocker and Lien, 1988; Beşkardeş *et al.*, 1992; Mordoğan *et al.*, 1995). The results from this study do not show a considerable difference from those studies. However, if pelletizing is needed in the actual production environment to reduce dusting in the roasting process, then leaching particle size should be taken into consideration. Another important noise factor is the accuracy of chemical analyses. In order to increase the accuracy, a mass-balance for the chemical analysis results was set up, and if a difference of >15% occurred in mass-balance, then the analyses and/or experiments were repeated.

STATISTICAL DESIGN OF THE EXPERIMENTS

It is generally believed that roasting is the most critical step in the process, and it is suspected that interactions of roasting temperature with gypsum, roasting time, and leach solid:liquid ratio are significant. Hence the effects of these interactions should be estimated as well as the effects of the control factors themselves on the extraction results. If three levels are assumed for the control factors, the minimum number of experiments that allows estimation of all the effects was found to be 25. A suitable experimental design that can be used for this purpose is an 'orthogonal array' that has 27 rows (experimental runs) and can accommodate up to 13 factors of three levels each (referred to as L_{27} (3^{13}), given by Phadke, 1989, p. 293). The control factors are placed on the columns of this array to allow estimation of the desired effects, as shown in Table 4. In order to capture the effects of noise factors on the extraction results, it was decided to make three replications of each experimental run at random times under varying noise conditions.

RESPONSE SURFACE MODELING OF THE RESULTS

The extraction values are converted into some performance measures to find the optimal levels of design parameters (control factors) that yield maximum extraction with minimal variation. For this purpose, arithmetic mean and sample standard deviation of the results are used in this study.

Collected data are analyzed using response surface methodology to develop empirical models of the relationships between the performance measures (mean, variance) and the control factors. These relationships can then be used to find the optimal values of the control factors within the experimental region.

Collected data were in the range 0−100 (percentage values). We find it appropriate to apply logit transformation to the data before developing the empirical models. The logit transformation formula is given in equation 3:

$$\theta = \log\left[\frac{p}{100 - p}\right] \qquad (3)$$

where p is the extraction value, and θ is the logit transformed value.

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Table 4. The experimental design used and the results of the replications.

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

Ro. Te.: roasting temperature; Ro. Ti.: roasting time; Leach S/L: leach solid:liquid ratio; Le. Ti.: leaching time

Mean, $\bar{y}_L$, and standard deviation, s_L, of the logit-transformed data were modeled by using a least-squares regression method (Box and Draper, 1987) and the *MINITAB* (2000) statistical package program.

The regression equation developed for the mean is given as:

$$\bar{y}_L = -38.0 + 0.314\,A + 0.0802\,B + 0.00800\,C - 4.78\,D - 1.24\,F + 0.000464\,AB + 0.00405\,AC + 0.110\,AF - 0.000036\,BC - 0.00141\,BD + 0.00116\,BF + 0.0797\,CD + 0.276\,DF - 0.210\,A^2 - 0.000042\,B^2 - 0.0630\,F^2 \quad (4)$$

The model in equation 4 has $R^2 = 99.7\%$ and $R^2_{(adj)} = 99.3\%$, indicating that the model explains 99.7% of the variation in the data, and the terms in the model are significant. Residual analysis of the model shows that the assumptions about independent and normal distribution of errors with constant variance are valid. Hence, the model is adequate.

The standard deviation, s_L, itself cannot be modeled adequately, hence a $\log(s_L^2)$ transformation has been made. The regression equation developed for the $\log(s_L^2)$ is given as:

$$\log(s_L^2) = 47.2 + 0.849\,A - 0.111\,B - 0.0142\,C + 2.45\,D - 0.00197\,E + 1.17\,F + 0.00597\,AC - 0.248\,A^2 + 0.000059\,B^2 - 0.182\,F^2 \quad (5)$$

The model in equation 5 is not as adequate as the mean model ($R^2 = 68.4\%$, $R^2_{(adj)} = 48.7\%$, the error assumptions are satisfied). However, it can still be used to represent the relationship between the variance of the data and the control factors.

DESIGN OPTIMIZATION BASED ON THE RESPONSE SURFACE MODELS

The process-design problem can be formulated as a nonlinear constrained optimization problem:

$$\begin{aligned} &\text{Maximize } \bar{y}_L \\ &\quad \text{subject to} \\ &\quad\quad \log(s_L^2) < a \\ &\quad\quad\quad A,B,C,D,E,F \in R \end{aligned} \quad (6)$$

where a is an upper limit on $\log(s_L^2)$ values, which can be determined by the process designer, and R is the region in which control factors A–F can take values. This region can be taken as the region of experimentation used before.

Problem 6 can be solved for optimal values of A,B,C,D,E,F using several algorithms. A general review of such algorithms was given by Luenberger (1989). Many of these algorithms start at a point and apply an intelligent search to converge to an optimum. However, these algorithms are sensitive to the starting points, and

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may converge to a local optimum rather than a global one. Consequently, several attempts are made starting at different points to search for the global optimum. *MINITAB* (2000) response optimizer can be used to perform such a search. Using this program, and setting a to 1 and R to the experiment region used before, 50 trials were performed each time starting at a different point. The resulting best ten points from these runs are given in Table 5. As observed from Table 5, point 1 predicts the best mean; though the roasting temperature (B) and time (C) are so high that the process will not be economical at the corresponding parameter levels. Points 3 and 4 have also been eliminated for the same reason. Points 2 and 10 predict about the same mean and variance, but as point 10 is better for both performance measures, point 2 is eliminated. Points 9 and 10 seem to yield low mean-extraction values, though the variances and the associated roasting temperatures are low. As a result, points 5–10 are selected for testing in the laboratory.

After running two confirmation experiments at each selected point, it is observed that only points 6 and 10 yielded satisfactory results. Point 6 yielded 77.49% and 72.91% extraction values, the standard deviation of which is 3.24. Although point 10 predicted a very low value for the mean, it has given extraction yield values of 73.76% and 70.46%, the standard deviation of which is 2.33.

AN ATTEMPT TO IMPROVE THE OPTIMUM DESIGN POINT

The confirmation experiments show that the response surface models of the mean and the variance cannot predict results well at some points. The response surface methodology typically suggests another experiment be designed in the region of the optimum pinpointed by the results obtained so far (Box and Draper, 1987; Montgomery, 2001). Instead of designing and conducting a new set of experiments, we propose to augment the points tested so far to the experimental layout of Table 4 to improve the response surface models. This reduces the cost of experimentation and can improve modeling of the real relationships.

Logit transformation was applied to this new set of data as well, and the mean and the variance models developed. In order to have a better model for the mean, logarithm of the logit transformed values were used. Due to negative terms, a constant value of 2 was added to the mean values before taking the logarithm.

$$f_1 = \log(\bar{y}_L + 2) = -11.28 - 0.0839\,A + 0.0240\,B + 0.0145\,C + 0.419\,D - 0.0184\,E - 0.116\,F + 0.000145\,AB + 0.0276\,AF - 0.000015\,BC + 0.000012\,BE + 0.0105\,DE + 0.192\,DF - 0.000593\,EF - 0.0181\,A^2 - 0.000012\,B^2 - 3.46\,D^2 + 0.000040\,E^2 \quad (7)$$

The model in equation 7 is adequate, since R^2 = 97.3%, $R^2_{(adj)}$ = 94.4%, and the error assumptions are satisfied.

The model developed for the updated variance values is given as:

$$f_2 = \log(s_L^2) = 448.49 - 1.942\,A - 1.117\,B + 0.355\,C + 314.58\,D - 1.52\,E + 67.43\,F - 0.0798\,AC + 30.02\,AD + 0.246\,AE + 0.00186\,BE - 0.0737\,BF + 3.257\,CD - 0.0045\,CE - 3.794\,DE - 0.124\,EF - 4.34\,A^2 + 0.00062\,B^2 - 552.3\,D^2 + 0.00137\,E^2 + 2.30\,F^2 \quad (8)$$

The model in equation 8 is much better than that in the previous equation 5, as R^2 = 85.3%, $R^2_{(adj)}$ = 62.6%, and the error assumptions are satisfied.

The optimal parameter values, this time, were found simply by using grid search with the help of a computer code. The grid was specified based on previous observations about the experimental region and also on the economy of the process. As a result of this search, the point that provides the maximum f_1 value, and the point that provides the minimum f_2 value were obtained. Between these two points, B = 915, C = 110, E = 120, F = 1.5 were observed as common settings. Under these settings, the optimal values of the other parameters were searched with the help of the response surface plots of Figure 1.

According to Figure 1, the highest mean and relatively low variance occur around the point where A = 2 and D = 0.3. For these settings, the prediction

Table 5. The 'optimal' points found by *MINITAB*™ response optimizer based on problem 6.

Point no.	A	B	C	D	E	F	$\bar{y}$	s
1	4.45	1050	120	0.40	30	4.5	91.06	0.306
2	1.50	950	120	0.17	120	2.00	20.18	0.042
3	1.50	1000	60	0.40	45	1.50	28.45	0.129
4	1.76	1000	30	0.10	120	1.50	72.23	0.060
5	2.77	984	30	0.10	120	2.46	77.54	0.048
6	3.18	986	67	0.19	33	2.60	62.66	0.129
7	4.50	850	120	0.40	120	1.50	71.56	0.138
8	1.50	987	30	0.10	120	1.50	70.83	0.053
9	1.50	878	120	0.36	120	1.50	54.47	0.067
10	1.50	918	120	0.17	120	1.50	22.56	0.032

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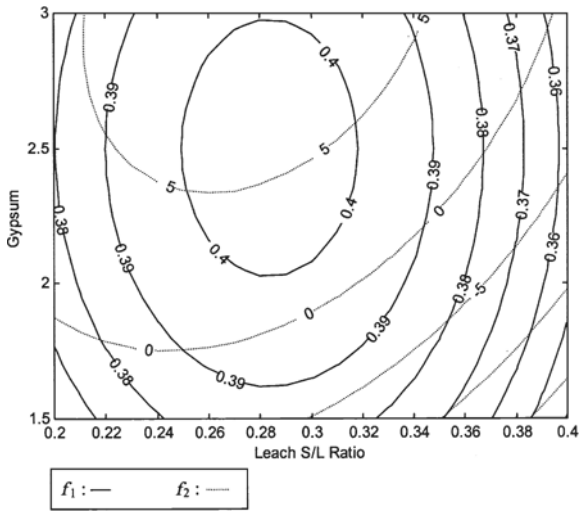

Figure 1. Contour plots of f_1 and f_2 for B = 915, C = 110, E = 120, F = 1.5.

interval that we expect to contain the mean extraction level in f_1 scale (of infinite number of experiments at the optimal point) with 95% probability is calculated as (0.301, 0.496), or in original units as (49.89, 93.10). Similarly, the 95% prediction interval calculated for the log variance in f_2 scale is (−1.657, 3.856), or in original units as (0.148, 84.723). Four confirmation experiments were conducted at these levels (A = 2, B = 915, C = 110, D = 0.3, E = 120, F = 1.5). The extraction values obtained (and the corresponding values in f_1 scale) were 93.27% (0.497), 89.80% (0.469), 88.63% (0.461), 80.94% (0.420). The mean and the standard deviation of these results are 88.16% (in f_1 scale 0.459) and 5.20 (in f_2 scale 1.432), respectively. Since the confirmation experiment results are within these intervals, we trust that the optimal settings we have found are valid.

DISCUSSION AND CONCLUSIONS

This study has been compared with relevant studies in the literature and the results are summarized in Table 6.

As can be observed from Table 6, the optimum point found in this study is different from those of the other studies. These differences are to be expected, as this study does not use standardized limestone and gypsum, pelletizing was not carried out, the noise conditions of the experiments are different, and the Li content of the clay used is small (~2000 ppm). Furthermore, none of the other studies was concerned with the variation in the results, while, in this study, the variation was also minimized, and an acceptable level of standard deviation (5.20) was achieved. The mean extraction level reached by this study, on the other hand, is the highest obtained for clays so far, and slightly greater than that of Crocker and Lien (1988).

Prediction of operating costs of the proposed process requires a detailed analysis considering the complete system. Here, only a rough cost analysis has been made. This study comprises only raw material precipitation, roasting and leaching. Calculations took into account evaporation, precipitation and crystallization, all based on the results of Crocker and Lien (1988). A proposed process flow chart with the mass balance based on Li is given in Figure 2. The mass-balance was performed for processing 1000 tons/day of clay although the experiments were conducted at a laboratory scale. Leach yield is 88.16% and the overall yield was estimated to be 78.72%. As a result, the production cost of Li_2CO_3 has been estimated as $6.36/kg. This is about four times higher than the market price of Li carbonate in 2003 reported by Ober (2003) and three times higher than that in June 2004 reported in *Prices* (2004). The cost of producing Li carbonate from clays is lowest in the case of Crocker and Lien (1988). However, this is mainly due

Table 6. Comparison of the results with those of Crocker and Lien (1988), Beşkardeş *et al.* (1992) and Mordoğan *et al.* (1995).

Field	This study Bigadiç	Crocker and Lien (1988) Nevada	Beşkardeş *et al.* (1992) Bigadiç	Mordoğan *et al.* (1995) Kırka
Li content (ppm)	2000	6000	2007	2800
Optimum points				
Clay	5	5	5	5
Gypsum	2	2	1.5	0.834
Roasting temp. (°C)	915	900	850	900
Roasting time (min)	110	120	120	120
Leaching S/L ratio	0.30	0.665	0.5	0.1
Leaching time (min)	120	5	–	60
Limestone	1.5	2	1.5	0
Performance measures				
Mean extraction (%)	88.16	84.00	72.78	77.00
Cost ($/kg Li_2CO_3)	6.36	4.45	10.65	–
Standard deviation	5.20	–	–	–

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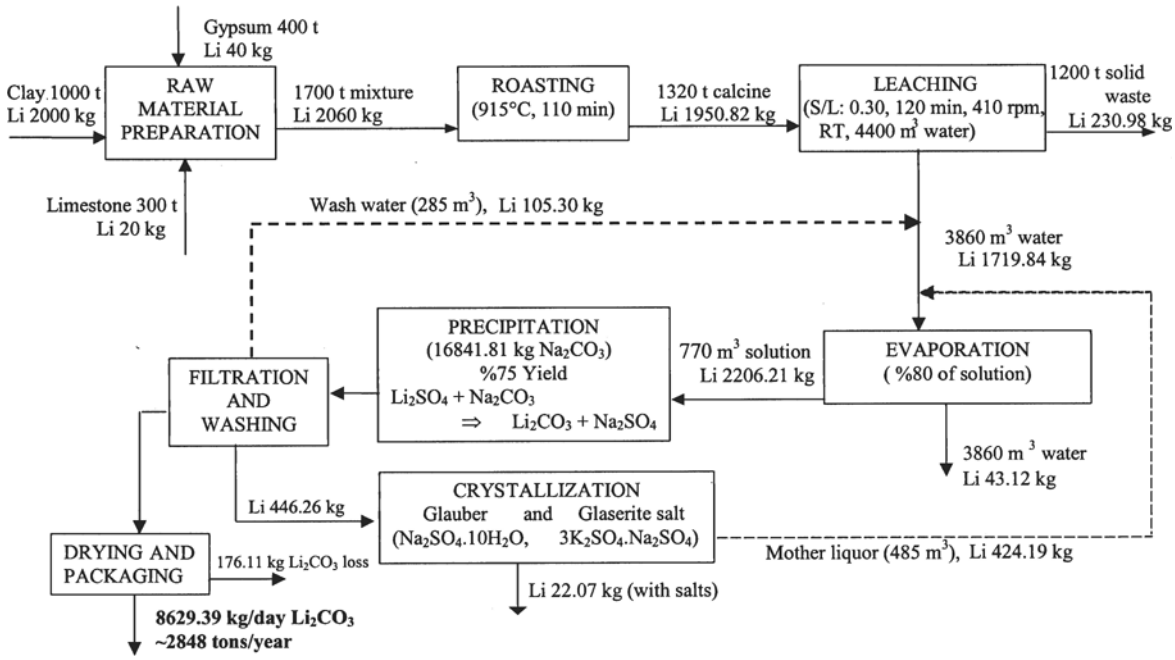

Figure 2. Process flow diagram of extracting Li from boron clays (for processing 1000 tons/day of clay).

to the higher Li content of the clay used in that study. Clays with greater Li contents could be identified at Bigadiç and thus the unit cost of production could be significantly reduced compared to previous studies.

Use of limestone directly from the field, and gypsum from boric acid production waste for Li extraction may bring about additional benefits. In the case of Bigadiç, using boric acid production waste as a source of gypsum is estimated to reduce the solid waste of the plant by ~30% at the optimal process settings. For other cases, one may choose to utilize alternative lower-cost sources of raw materials and additional benefits may accrue from this.

We believe that it is possible to fine tune the process design to reduce the production cost further using a detailed analysis of the operating costs. We observe that there is a trade-off between roasting time and roasting temperature. Even higher extraction values can be achieved at shorter roasting times when roasting temperature increases. Also the solid:liquid ratio for this study is low. This means that a large amount of water has to be evaporated, resulting in a higher cost. A detailed cost analysis may help reduce the production cost by decreasing roasting time and roasting temperature, and increasing the solid:liquid ratio. The effects of these changes on the extraction results can be predicted using the empirical models, and these effects can be balanced with the cost savings, as a future study.

Future studies can consider precipitating the Li in solution as a carbonate or as any other compound of Li. Furthermore, a study can be made to find an application for the solid residue of leaching for both economic and environmental benefits.

Lithium applications have increased significantly in the past few years. In the event that there is a substantial future increase in Li requirements due to Li batteries, the present study indicates that Li is recoverable from Bigadiç-type clays. The present study underscores the importance of using by-product gypsum and a local limestone deposit in the process instead of expensive pure reagents. Although the costs are still higher than the present-day Li carbonate produced from brines, initial results are encouraging and suggest that additional testing should be conducted to optimize the process and reduce production costs. The Bigadiç clays represent a large Li resource and may well become an additional source of Li.

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