Statistical Design and Optimization of Leaching Tests for Iron Removal from Pyrophyllite Ore

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ABSTRACT: As an impurity in pyrophyllite deposits, iron affects ceramics quality. Therefore, it should be removed before the end use. In this study, it was aimed to compare and estimate the effects of different factors on the removal of iron from ore by statistically designed experiments and to find optimum experimental parameters in such a way that the iron removal will be maximised. Effect of each factor was determined by Yates Method. Which effects had significance on the recovery was determined by the analysis of variance. After insignificant effects were removed, adequacy of new model was tested. Based on these effects, the multiple regression equation was derived as a function of four parameters. These were organic acid concentration, sulphuric acid concentration, time and temperature. Given that the objective was to maximise the iron removal which was response variable, the regression model was accepted as an optimisation problem and solved by the steepest ascend (SA). The results showed that the method combining the multiple regression analysis and the SA could be used to find optimum experimental parameters qualitatively and quantitatively.

I INTRODUCTION

The presence of iron in many industrial minerals such as quartz sand, kaolin, talk and pyrophyllite can prevent their use mainly in the ceramic industry. The red to yellow pigmentation in many clay deposits are mainly due to the associated oxides, hydroxides and hydrated oxides of Fe(III) such as hematite, maghemite, goctite, lepidocrocite, etc (Ambikadevi and Lalithambika, 2000). These oxides and hydroxides can present either as coatings on particles or as discrete fines in the clay body.

The iron content of clays can be reduced by a number physical, physicoehemical and chemical methods. The appropriate method for the removal of iron from a clay ore depends on the mineralogical forms and the distribution of iron in the particular ore. Chemical methods involve leaching of the ore with organic and inorganic acids. The most commonly used organic acids are oxalic, citric, ascorbic, acetic, fu marie and tartaric (Panias et al., 1996), and inorganic acids are hydrochloric, hydrofluoric, sulfuric and perchloric (Ubaldini et al, 1996). Of the above organic acids, oxalic, citric and ascorbic are the most used carboxilic acids, due to their effectiveness as solvent reagents (Panias et al, 1996).

The present work aims to study the main factors that are involved in the removal of iron from pyrophyllite ore by leaching with various organic-acids. Consecutive series of the tests were performed, in each of which all the factors were simultaneously varied according to rules of statistical design of experiments in order to determine the main effects and the interactions among the investigated factors.

2 MATERIAL AND METHOD

2./ *Mineral sample*

Pyrophyllite used for leaching studies was obtained from the Piitiirge-Malatya region of Turkey. The chemical composition of the original pyrophyllite sample is given in Table 1. Depending on the XRD analysis, it consists of mainly pyrophyllite and quartz with small quantities of kaolinite, muscovite and feldspar. The sample was crushed by jaw and impact crusher and was ground in a ceramic ball mill to produce desired particle size fractions. The sample with a particle size of less than 0.150 mm was chosen to carry out the leaching experiments.

2.2 *Experimental procedure*

Prior to leaching experiments, the sample was subjected to dry magnetic separation to remove the iron particles contaminated during the crushing.

Batch-leaching experiments were conducted in 250-mL mechanically agitated spherical glass reactor submerged in a thermostatically controlled water bath. Analytical grade oxalic, tannic, citric and sulphuric acids were used to prepare desired leach solutions. After the given time was consumed agitation was stopped and pulp was filtered to remove the solid phase. Total iron was determined in aqueous phase using Philips PU9100X model flame atomic absorption spectrometer and the degree of iron removal (i.e. % of iron removed) was calculated using the iron content of pyrophyllite sample

Table I. The chemical analysis of original pyrophyllite sample as determined by XRF

Ma|or consument	wt %
A1;0,	31 98
SiO,	61.76
He,C)ₜ	0.21
CaO	0.18
MgO	0.26
Na.O	0.07
K*0	0.14
MnO	-
Loss on ignition at 1000° C	3.24

Table 2. Design variatvles and levels

No	Variable	Low	Base	High
X,	Oxalic acid (M)	0.2	0.3	0.4
	Tannic acul (nig/L)	200	300	400
	Citric acul (M)	0.3	0.4	0.5
X;	Temperature (" C)	30	40	50
Xs	Leaching time (nun.)	10	20	30
Xj	HJSOJ concemiation (N)	0.2	0.3	0.4

Table 3. Parameters studied in coded scale and percentage of removal for each acid

	X|	X:	X,	**X₄**	Iron Removal. Y (%)		
					Oxalic Acid L.	Tannic Acut L.	Citric Acid L.
1	-	-	-	-	27.95	25.85	16.34
-)	+	-	.	-	31.58	29.12	18.56
3	-	+	-	-	32.73	30.79	17.59
4	+	+	-	-	30.53	32.11	17.98
5	-	-	+	-	30.84	30.98	19.10
6	+	-	+	-	31.76	31.52	18.06
7	-	+	+	-	31.53	30.34	19.67
8	+	+	+	.	31.19	31.75	20.29
9		-	-	+	27.60	29.43	15.44
10	+	-	-	+	28.76	29 39	16.79
II	-	+	-	+	29.53	31.52	17.79
12	+	+	-	+	30.76	31.34	17.48
n	-	-	+	+	30.68	25.85	17.21
14	+	-	+	+	28.77	25.58	15.67
15	-	+	+	+	31.30	30.96	22.91
16	+	+	+	+	^ 1.69	30.61	20.79
17	0	0	0	0	25.83	26.75	17.35
18	0	0	0	0	24.52	27.87	18.46
19	0	0	0	0	23.75	27.14	18.22
20	0	0	0	0	25.25	28.12	17.93
21	0	0	0	0	24.90	2X.53	16.62
22	0	0	0	0	25 40	27.29	17.36

3 STATISTICAL DESIGN

The leaching experiments have been conducted on the basis of the design variables. The variables and level of 2^4 factorial design are given in Table 2.

In each experiment set the variables arc one of organic acids (Oxalic, tannic and citric), the temperature, the leaching duration and the $H2SO4$ concentration. The higher level of variables is designated as "+'" and the lower level is designated as "-". Matrix in four variables varies at these two levels (Table 3). Hence, three factorial experiment sets arc obtained separately.

The regression model equation can be written as:

$$Y = bn + b,X, + b_2X_2 + h,X, + b_4X_4 + b_{t2}X,X_2 + bi.<XiX.< + b_NXiX_4 + h_2<X_2Xj + b_{24}X_2X_4 + b.»X.<X_4 + bi_2<XiX->Xt + bn_4X/X-'X_4 + bn_4XiX<X_4 + b_2<_4X->X<X_4 + b,_{2M}X,X_2X<X_4 \qquad (1)$$

where; Y is the percentage of iron removal, b is model coefficients and X's are coded factors.

The analysis of variance in the 2^4 experiments can be applied easily once the effects totals have been calculated. A systematic method for estimating the effects and performing the analysis of variance was proposed by Yates. (Chatfield. 1978; Morgan, 1997). Yates's method has been used to estimate the effects. For the leaching with each acid type, the coefficient values were computed and incorporated in Eq. (1). Then the analysis of variance has been performed and obtained which effects are significant. Adequacies of the models have been tested at %90 confidence level by the Fischer test and the obtained models have been given as follows:

For oxalic acid leaching:

$$Y = 30.45 + ().71X2 + 0.52Xr - 0.56X_4 + 0.5VXiX?X_4 \quad (2)$$

For tannic acid leaching:

$$Y = 29.H2 + l.36X_2 - 0.96X.,X_4 + 0.90X_2X.<X_4 \quad (3)$$

For citric acid leaching:
$$Y = I8.23 + U)8X_2 + 0MX., + 0.62X_2X., + 0.65X_2X_4 \quad (4)$$

As the acid type has changed, different variables are effective. In the oxalic acid leaching, the temperature and the time have a positive effect while the sulphuric acid concentration has a negative effect. In the tannic acid leaching, the concentration of organic acid and the temperature have a positive effect while the sulphuric acid concentration has a negative effect. In the citric acid leaching, the temperature and the time have a positive effect. The interactions exist in all acid types.

4 OPTIMISATION

Each equation is an unconstrained optimisation problem to be maximised. The steepest ascend method was used to find the optimal parameters. Ascend methods are the general name of direct methods, gradients methods and Hessian methods.

The methods are first to select an initial solution that is the most likely place where optimal solution exists. Then they find a new point from the initial solution by analysing the behaviour of the objective function. This process is repeated until stopping criterion is satisfied. The steepest ascend is a useful method for moving towards the optimum in as few experimental performs as possible (Winston, 1991, Radrin, 1998, Liu. 1999).

In the oxalic, tannic and citric acid leaching the step sizes are determined on the basis of the coefficients in the Eq. 2, 3 and 4, respectively (Table 4, Table 6 and Table 8). Optimum parameters found according to the determined increments for each leaching type is given in Table 5, 7 and 9.

Table 4. Determined step size for each variable in the oxalic acid leaching

	Oxalic acid concentration (M)	Temperature (C)	Leaching time (minute)	H$_2$SO$_4$ concentration (N)
Coefficient (b)	0.18	0.71	0.52	0.56
Step size (Z)	0 1	10	10	0.1
b x Z	0.018	7.1	5.2	0.056
Normal steps	0.3	39.44	28.88	0.31

Table 5. Optimum parameters tor oxalic acid leaching.

Oxalic acid concentration (M)	Temperature (C)	Leaching time (minute)	H$_2$SO$_4$ concentration (N)	Y (Iron removal) (%)
0 3	40	20	0 3	30.45
0.4	79.44	48.88	0.61	45.46
0.5	118.88	77.76	0.92	93.60

Table 6. Determined step size for each variable in the tannic acid leaching

	Tannic acid concentration (mg/L)	Temperature (C)	Leaching time (minute)	H$_2$SO$_4$ concentration (N)
Coefficient (b)	0.36	1.36	0.12	0.49
Step size (Z)	100	10	10	0.1
b x Z	36	13.6	1.2	0.049
Normal steps	100	37.8	3.34	0.14

Table 7. Optimum parameters for tannic acid leaching.

Oxalic acid concentration (M)	Temperature (C)	Leaching time (minute)	H$_2$SO$_4$ concentration (N)	Y (Iron removal) (%)
300	40	20	0.3	29 82
400	77.8	23.34	0.44	40.87
500	115.6	26.7	0.58	84.28

Table 8. Determined step size for each variable in the citric acid leaching

	Temperature (C)	Leaching time (minute)	H$_2$SO$_4$ concentration (N)
Coefficient (b)	1.08	0.98	0 22
Step size (Z)	10	10	0 1
b x Z	10.8	9.8	0.022
Normal steps	10	9.08	0.02

Table 9. Optimum parameters lor citric acid leaching.

Temperature (C)	Leaching time (minute)	H$_2$SO$_4$ concentration (N)	Y (Iron removal) (%)
40	20	0.30	18.23
50	29.08	0.32	20.45
60	38.16	0.34	24.90
70	47.24	0.36	29.97
80	56.32	0.38	37.19
90	65.40	0.40	45.40
100	74.48	0.42	55.00
110	83.56	0.44	65.92
120	92.64	0.46	78 41
130	101.76	0.48	92.13

5 CONCLUSIONS AND PROPOSALS

This research focuses on statistical design and optimisation of leaching experiments to remove iron from pyrophyllite ore. When the acid types are compared, the oxalic and tannic acids remove almost same iron percentage. However, the iron removal with citric acid is quite low. The most important variable is temperature for all acid types. The second important factor is leaching duration. HiSO^ concentration is only significant with interactions. If complex regression models are selected for modelling, the steepest ascend had important drawbacks. In this case, modern heuristic methods such as the genetic algorithms and the simulated annealing techniques can be used easily. These

resulls may yield a background tor pilot applications.

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