

Optimization of rare earth elements recovery from Kızıldag (Karaman-Türkiye) shale ore using response surface methodology

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Abstract: In this study, the usability of bauxite-related shale ore, rich in Rare Earth Elements (REEs), to produce REEs, which have high added value and critical importance, was investigated. In this context, Kızıldag (Karaman-Türkiye) shale ore, was prepared for tests through size reduction and sampling processes. HCl leaching was performed at different acid concentrations, leaching times, leaching temperatures, and liquid/solid ratios to determine the optimum leaching conditions for the milled ore. The modeling and optimization parameters related to leaching recovery were investigated using the response surface method (RSM). The results were evaluated using analysis of variance, three-dimensional graphs were drawn, and the accuracy of the models was discussed. Accordingly, optimum values were found, and the REE leaching recovery corresponding to these optimum values was 49.13%. It was concluded that the optimization results were compatible with the experimental results, and the average error rate (6.35%) was low.

Keywords: shale, rare earth element, acid leaching, optimization, response surface methodology

1. Introduction

Considering the global supply and demand for commodities, the European Commission has identified 34 critical raw materials for 2023, with REEs ranking at the top of the list (European Commission, 2023). REEs consist of 17 elements, including the lanthanide group, scandium, and yttrium, all of which exhibit similar chemical properties. These elements, with an ionic valence of +3, are categorized as light and heavy REEs based on their atomic numbers and frequency of occurrence in nature. REEs are widely used in the production of many high-tech devices and equipment, such as electric/hybrid vehicles, wind turbines, solar panels, aircraft, and electronic devices, including cell phones, computers, rechargeable batteries, and modern medical devices, such as MRI devices (Krishnamurthy and Gupta, 2016; Erust et al., 2023). With the widespread use of electric vehicles, wind turbines, and solar panels, demand for REEs has increased.

The literature contains numerous studies on the recovery of REEs from shales and clays. This section presents a selection of these studies. Voßenkaul et al. (2015) investigated the recovery of REE from shales with an average concentration of approximately 1100 ppm REE. They employed an alternative methodology involving leaching with combinations of acid solutions (HCl, HNO₃, and H₂SO₄) alongside ion-exchange reactions using sulphate, chloride, or nitrate salt solutions (Na₂SO₄, NaCl, and NaNO₃) to facilitate the release of adsorptive ligation. The optimal recovery was achieved with a combination of 0.5 M (NH₄)₂SO₄ and 0.1 M H₂SO₄, resulting in a 20% increase in REE recovery, attaining an recovery exceeding 90%. This enhancement is attributed to the dissolution of REE minerals in both the colloidal and mineral phases, as well as the exchangeable phase of REE. Ji and Zhang (2021) examined the impact of thermal activation on REE recovery from kaolinite containing 245 ppm REE. Their acid leaching results indicated that while the REE leaching recovery of the untreated ore in 1.2 M HCl was below 20%, post-heat treatment at 600 °C, a recovery rate exceeding 80% was achieved in 0.01

M HCl. In a separate study, Ji et al. (2022) explored the effect of thermal activation on REE recovery from two natural kaolinite samples. The leaching recovery of untreated samples was 10% and 56% in 1.2 M HCl, whereas the recovery of samples calcined between 500 °C and 900 °C increased significantly, reaching 93%. SEM-EDX analysis revealed that some REEs were encapsulated within kaolinite aggregates, while others were present as free particles.

The Kızıldağ and Kemiklitepe bauxite mineralizations in Türkiye are in the Bolkar Mountain Bauxite Province. The protolith, the source rocks of the Bolkar Mountain bauxite mineralization, was defined as shale by Hanilçi (2013). Heavy REEs enrichment is typical in these deposits, and bauxite deposits and their source rocks and shales contain high amounts of REEs that can be potential sources. Researchers (Hanilçi et al., 2013; Hepvidinli, 2019; Öztürk et al., 2019) have studied the formation of REEs in bauxite-related deposits in the Bolkar mountain region and found that clay minerals formed during the lateritic weathering process balance the lack of electrostatic charge on their outer edges with ions, such as Ca^{2+} , Na^+ , and REE^{3+} . Thus, REEs were enriched by adsorption on the outer surface of the clay. These REE-rich clays were formed by the addition of bauxite. It is necessary to investigate the recoverability of REEs from these bauxites with REE potential in the Bolkar Mountain region using a sustainable method. This study investigated and optimized the recovery of REEs from shales which is considered unproductive because of their high silica and iron contents.

2. Materials and methods

2.1. Materials

Shale samples were obtained from bauxite mines in the Ayrancı district of Karaman (Türkiye), operated by Demireller Mining Inc. Analysis by X-ray diffractometer (Fig. 1) revealed that the ore primarily comprises paragonite, muscovite, quartz, pyrophyllite, kaolinite, and hematite. The chemical composition of the shales is presented in Table 1, which demonstrates strong concordance with the XRD results.

Table 1. Major oxide content of Kızıldağ shale ore, %

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI
42.70	28.80	4.29	5.69	0.56	3.04	3.04	1.41	0.03	0.05	9.49

Table 2. REE content of Kızıldağ shale ore, ppm

Ce	La	Y	Nd	Sc	Pr	Dy	Er	Gd	Sm	Yb
115.70	82.80	83.80	59.20	28.00	15.70	11.65	7.46	10.42	10.75	7.06
Ho	Lu	Eu	Tb	Tm	ΣREE	Rb	Th	U	Nb	
2.52	1.04	1.88	1.73	1.09	473.00	112.00	21.70	4.39	31.60	

2.2. Methods

2.2.1. Mineral processing

Shale ore was systematically crushed to a length of -4.75 mm with a Pulverisette I model (Fritsch) jaw crusher with an adjustable exit opening. Half of the crushed samples were separated into reference samples using a riffle sample splitter. The other half was crushed by jaw crusher to a length of -2 mm. Later, the samples were crushed to ~2 mm in size and divided into small batches using a rotary sample divider. Then the samples were dried at 105 °C for 60 min before the leaching experiments.

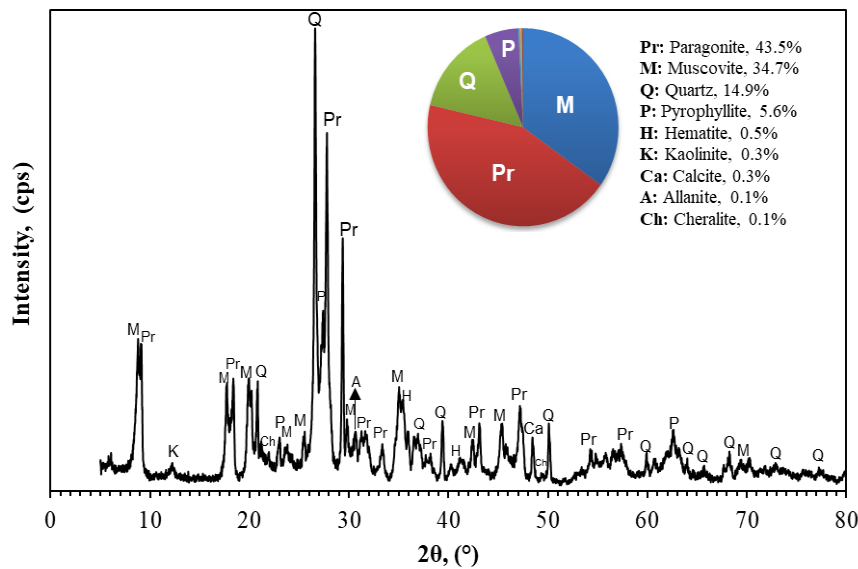


Fig. 1. XRD pattern of Kızıldağ shale ore and its contents determined by Rietveld analysis (Uysal, et al., 2024)

2.2.2. Acid leaching

The leaching process was carried out in a 500 cm³ glass flask placed in a flask heater device (Weightlab) with a bed volume of 500 cm³, using a 200±10 cm³ solution that could be mixed with a magnetic stirrer under reflux, with a mechanism set up in a fume hood, where the solution temperature was constantly monitored. Because the balloon heater also has magnetic stirring, an external stirrer was not required for the mixing process. At the end of the leaching period, the heating and mixing mechanisms were stopped immediately, and solid-liquid separation was performed by vacuum filtration of the loaded leaching solution. After recording volume of the liquid samples, they were placed in lidded plastic containers and stored in a refrigerated cabinet, whereas solid samples were placed in another lidded plastic container after weighing.

Before the leaching optimization experiments, leaching was carried out with different solvents to determine the solvent type. The leaching parameters used in the solvent-type determination study were 2 M concentration, 100 °C leaching temperature, 3 h leaching time, and 10 l/kg solution-ore ratio. The chemical analysis results of the leaching residue obtained from this study are given in Table 3.

Table 3. Chemical content of leaching waste obtained by leaching with different solvent types

%	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	LOI	Total
Raw ore	42.70	28.80	4.29	5.69	0.56	3.04	3.04	1.41	9.49	99.14
(NH₄)₂SO₄	43.50	27.60	4.23	2.97	0.55	2.98	3.06	1.38	9.68	96.08
H₂SO₄	38.10	23.60	0.78	2.82	0.29	2.66	2.69	1.22	19.75	92.00
HCl	51.40	32.10	1.21	0.13	0.39	3.50	3.55	1.60	6.29	100.30

LOI: Loss of ignition (1000 °C)

Table 3 indicates that the solubility is significantly low following (NH₄)₂SO₄ leaching, whereas all cations are evidently dissolved as a result of H₂SO₄ leaching. In the case of HCl, it was determined that iron, calcium, and magnesium are dissolved, while silicon and aluminum are concentrated in the residue. The loss on ignition due to H₂SO₄ leaching is 19.75%, which is notably high. Consequently, XRD analysis of the leaching residue was conducted to ascertain the formation of sulfate species in the leaching waste, as depicted in Fig. 2.

The total REE recoveries for leaching with NH₄SO₄, H₂SO₄, and HCl were 11.9%, 27.7%, and 26.8%, respectively. Although the recovery rate of H₂SO₄ (27.7%) was slightly higher than that of HCl (26.8%), it was concluded that HCl was more appropriate for use. This conclusion is based on the formation of

sulfates with H_2SO_4 , the higher decomposition roasting temperature required compared with HCl , and the operational challenges posed by H_2SO_4 , such as its corrosive effect.

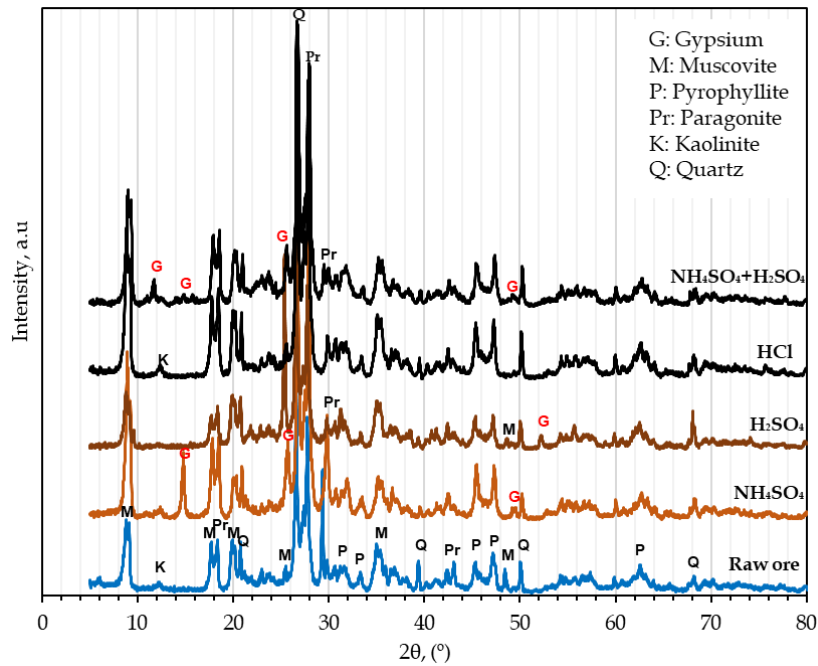


Fig. 2. XRD analysis of cakes resulting from leaching with various solvents

As shown in Fig. 2, gypsum formation was observed in the cake at 2θ : 12.24° , 14.98° , and 49.6° in the leaching results with H_2SO_4 and NH_4SO_4 , indicating a weight increase leaching. The peak at 2θ : 12.58° , associated with the kaolinite mineral in the ore, was dissolved in sulfuric acid, while it remained undissolved in other solvents. Additionally, the peak at 2θ : 48.68° , corresponding to muscovite, was dissolved in the HCl medium. It was determined that quartz was generally insoluble and enriched in the cake. In the NH_4SO_4 medium, peak intensities similar to those of the raw ore were observed, with some peaks even exhibiting increased intensities.

2.2.3. Experimental design

A set of leaching tests was carried out to simulate the leaching process of REEs and determine the optimal conditions for producing a pregnant solution with the highest rare earth ion concentration. RSM is a correlation-based experimental design and statistical modelling method that reveals trial patterns that aim to reach the point where the response variable takes its maximum value on the response surface with the least possible number of observation values (Mead and Pike, 1975). The effects of these parameters on the leaching recovery were examined using the BBD, and mathematical models were developed. This method provides an experimental study and repetition opportunity, excluding the main points. With this design, the change and interaction of all the variables can be examined using the same process. Statistical analyses were performed using the Minitab 22 (Version 22.1.0) software. The results were statistically tested with a 95% reliability rate using Analysis Of Variance (ANOVA). A total of 27 experiments were performed for the four factors according to the BBD method. When the response data were obtained from the experimental studies, regression analysis was performed to determine the coefficients, standard deviations, and magnitudes of the response model. The second-degree polynomial equation used to explain the dependent variables is given in Eq. 1.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i < j}^k \beta_{ij} X_i X_j + \sum_{i=1}^k \beta_{ii} X_i^2 + \dots \quad (1)$$

In Eq. 1, y is the dependent variable (leaching recovery) and is a function of the independent variables coded in terms of x_1 , x_2 and x_3 . β_0 is the regression coefficient, ε is the error, β_i is the linear coefficient, β_{ii} is the quadratic coefficients and β_{ij} are the pairwise interaction coefficients.

In this study, in order to optimize the leach parameters to enhance the leach recovery, HCl concentration (0.5-4.0 M), leaching temperature (25-100 °C), leaching time (3-24 h), and solid concentration (5.0-20 l/kg) were selected as independent variables, while the leach recovery was chosen as the response. Accordingly, the experimental design parameter ranges are presented in Table 4.

Table 4. Leaching experiment design parameter ranges

Factor	Parameters, Unit	Low (-1)	Medium (0)	High (+1)
A	HCl concentration, M	0.5	2.75	4
B	Leaching temperature, °C	25	62.5	100
C	Leaching time, hour	3	13.5	24
D	Solution-ore ratio, l/kg	5	12.5	20
Response	Leach recovery, %	0-100		

2.2.4. Characterization techniques

The inductively coupled plasma atomic emission spectrometry (ICP-AES) for major oxides and inductively coupled plasma mass spectroscopy (ICP-MS) for REEs used to determine the chemical composition in ALS Global Analytical Laboratories (İzmir, Türkiye). X-ray diffractometer (XRD) analysis was used to determine which minerals the calcined and over-ground products in Kızıldağ shale ore consist of and to monitor the change in the crystal properties of these minerals with calcination and grinding. XRD patterns were obtained with Rigaku MiniFlex 600 model XRD device (Munzur University) at CuK α ($\lambda=1.5405$ Å) irradiation, at a scanning speed of 2°/minute and at diffraction angles ranging from 5-80°. The International Center for Diffraction Data Powder Diffraction File (ICDD-PDF) database was used for mineral identification.

3. Results and discussion

3.1. Analysis of variance

The multiple determination coefficients and standard deviation values for the dependent variables of the REE recovery are listed in Table 5.

Table 5. Summary statistical values provided by BBD

Factor	S	R-sq	R-sq (adj)	R-sq (pred)
REE	3.49	91.32%	81.18%	56.76%

S: Std. Deviation R-sq: Determination coefficient -R², R-sq (adj): Adjustable R², R-sq (pred): Estimated R²

As shown in Table 5, the multiple determination coefficient of the second-degree regression equation R² was calculated to be 91.98%. The fact that these values approach each other and Eq. 1 indicates the success of the model. In addition, the R² and adjusted R² values were compatible with each other. This indicated that the model fit was high. The regression results showed that R² values greater than 80% were obtained for the responses, and based on this the RSM model has the ability to correctly determine the effect on the leach recovery responses. In addition to RSM a variance analysis (ANOVA) was applied to determine whether there was a significant difference between the means of the factors. The ANOVA results are given in Table 6.

The most important criteria to consider in the ANOVA table were the F-value and P-value. A larger F value indicated more effective factor. The F-statistic is used together with the P-value when deciding whether the overall results are significant. The P-value is determined by the F statistic and expresses the probability that the results occur by chance. For a factor to influence the response, the P-value must be less than 0.05 (Box and Hunter, 1957; Obeng, Morrell, and Napier, 2005; Hirotsu, 2017). P-values greater than 0.05 mean that the parameter is insignificant or has no effect on the response. Table 6 shows that the leaching recovery values had a significant effect on the response in linear terms. It was determined that the leaching temperature and leaching time P-values were less than 0.05, and the F

value was high; therefore, they were the most effective parameters. It was also concluded that the temperature is more effective than the leaching time because of the higher F-value and lower P-value. In addition, when the binary interactions were examined, it was determined that the concentration×temperature, concentration×solution/ore, temperature×solution/ore, and time×solution/ore values were lower than 0.05 and that they were effective together. The estimated second-degree polynomial model equation suggested by the software program for the leaching recovery response value is given by Eq. 2. An estimate can be made using this equation and the experimental results can be compared with the model estimate.

Table 6. ANOVA for REE leaching recovery

Source	Degree of freedom	Adj SS	Adj MS	F-Value	P-Value
Model	14	1538.80	109.914	9.01	0.000
Linear	4	579.93	144.983	11.89	0.000
HCl concentration, M	1	11.12	11.121	0.91	0.358
Temperature, °C	1	322.83	322.828	26.47	0.000
Leaching time, h	1	257.29	257.291	21.10	0.001
Solution-Ore ratio, l/kg	1	2.19	2.192	0.18	0.679
Squares	4	186.20	46.549	3.82	0.032
Concentration*Concentration	1	18.38	18.379	1.51	0.243
Temperature*Temperature	1	27.34	27.336	2.24	0.160
Time*Time	1	54.24	54.238	4.45	0.057
Sol/Ore*Sol/Ore	1	66.24	66.241	5.43	0.038
2-Way Interaction	6	1120.75	186.791	15.32	0.000
Concentration*Temperature	1	78.85	78.848	6.47	0.026
Concentration*Time	1	31.51	31.508	2.58	0.134
Concentration*Sol/Ore	1	210.66	210.655	17.27	0.001
Temperature*Time	1	14.49	14.487	1.19	0.297
Temperature*Sol/Ore	1	511.99	511.987	41.98	0.000
Time*Sol/Ore	1	368.89	368.892	30.25	0.000
Error	12	146.34	12.195	-	-
Lack-of-Fit	7	74.38	10.626	0.74	0.656
Pure Error	5	71.96	14.392	-	-
Total	26	1685.14	-	-	-

Adj SS = Adjusted sum of squares; Adj MS = Adjusted mean squares

$$\begin{aligned} \text{REE Recovery, \%} = & -58.1 + 31.33*A + 0.921*B - 6.08*C + 9.65*D - \\ & -1.093*A^2 + 0.00294*B^2 + 0.0528*C^2 - 0.15*D^2 - 0.1745*A*B + 0.385*A*C - 1.531*A*D + \\ & + 0.0113*B*C - 0.0917*B*D + 0.2755*C*D \end{aligned} \quad (2)$$

Pareto analysis is a bar chart used to separate important leaching parameters from relatively less important parameters. The Pareto chart is shown in Fig. 3, and the contour maps showing the interdependent interactions of the parameters are shown in Fig. 4.

In the Pareto chart, the factors to the left of the dashed red line are ineffective for the response while those to the right have a significant effect on the response. Accordingly, it can be observed that the leaching temperature and leaching time are effective for both responses. The standardized effect value was 2.179 for both the responses. When the 2-way interaction and squared interaction are examined, it is seen that the values solution/ore², temperature×time, temperature×solution/ore, time×solution/ore, concentration×temperature, and concentration×solution/ore are effective for the response.

Contour maps show the regions with low and high recovery, their boundaries, and the operating parameters of these regions using color scales. The parameters kept constant in the contour maps were the optimum leaching parameters. For example, for an REE recovery value between 25-50%, it is necessary to work in the green areas, that is, above 1 M HCl concentration and approximately above

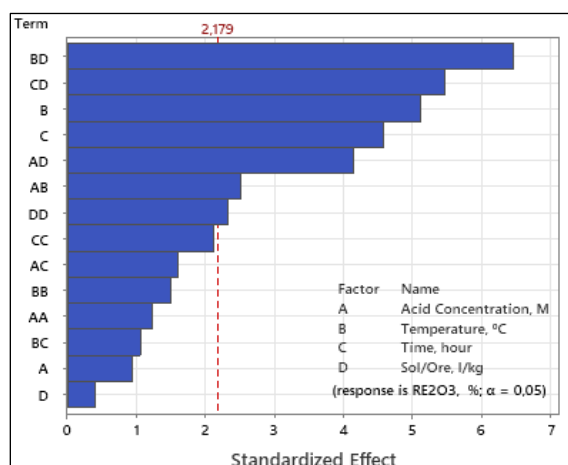
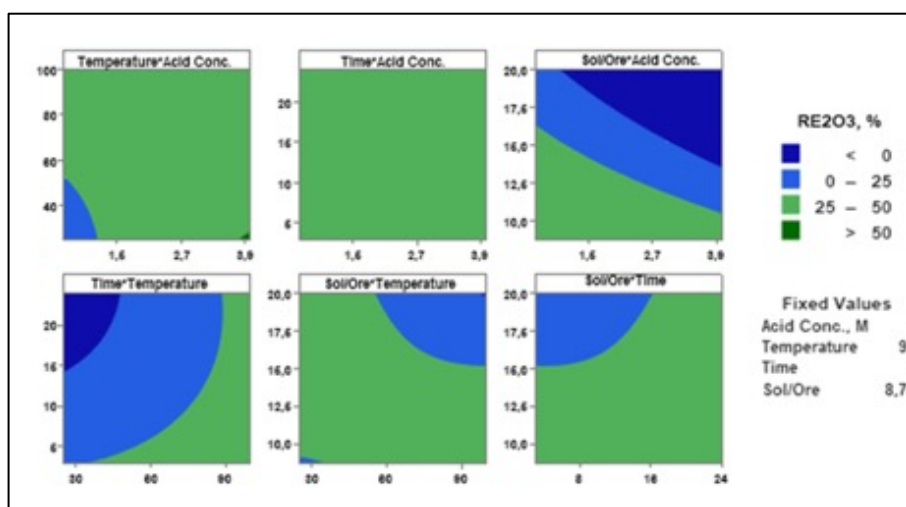
Fig. 3. Pareto plot of standardized effects (α : 0.05)

Fig. 4. Contour maps showing the relationship between leaching parameters

55 °C. According to the temperature $\times$ concentration maps, at the specified fixed values.

Three-dimensional graphs showing the relationship between the REE recovery and the leaching parameters are shown in Fig. 5. When Fig. 5a is examined, it is understood that to provide a high leaching recovery, it is necessary to work under either low acid concentration, high leaching temperature, or high acid concentration and low leaching temperature conditions. In other words, the two opposite extreme points of the concave shape provided the highest leaching recovery. While the leaching recovery increased as the concentration increased at relatively low temperatures (40–60 °C), the leaching recovery decreased as the concentration increased at high temperatures. It was observed that temperature was more effective at low concentrations, while the effect of temperature was weak at high concentrations. As a result of general leaching optimization, because leaching temperature is a more effective parameter than concentration, the parameter where the leaching temperature is high and concentration is low is optimized by the program as the ideal leaching condition.

In Fig. 5. b, as the leaching temperature increased. The REE recovery increased rapidly; no significant change was observed with increasing leaching time. Here, it is observed that the efficiency is high at high temperatures and short leaching times. Thus, by working with a short leaching time, the process will be more economical and the leaching selectivity will be higher. When Fig. 5.c is examined, while the REE recovery increases rapidly with temperature, the REE recovery decreases as the solution-ore ratio increases. From the ANOVA analyses, it was determined that the effect of the solution-ore ratio on leaching recovery was weak. Here, it is observed that the efficiency increases when working at a high temperature and low solution-ore ratio. When Fig. 5.d was examined, the increase in the leaching time did not significantly increase. The recovery has a significant effect on the increase in leaching time

because the amount of acid used per unit ore decreases over time, and accordingly, the significant effect of the leaching time decreases. In addition, working at a low solution-ore ratio, that is, under conditions where the amount of acid used per unit ore is low, both reduce operating costs and provide ease of operation.

Since Kızıldağ bauxite-related shale ore has undergone low-grade metamorphism, it is known that recovery efficiencies may be low due to REEs entering the crystal lattice structure of clay and mica (Chi and Tian, 2008; Öztürk et al., 2019). Therefore, in REE recovery from such ores, their solubility can be increased by the thermal activation provided by calcination before leaching and/or mechanical activation provided by excessive grinding. During thermal activation, while the crystal water in the silicate mineral structure is removed in the vapor phase (dehydroxylation), a porous, high surface area, amorphous structure, and soluble in dilute acids, that is, an activated solid, is obtained (Habashi, 1999). Preliminary studies have shown that the leach recoveries of REEs from calcined shale ore have increased significantly.

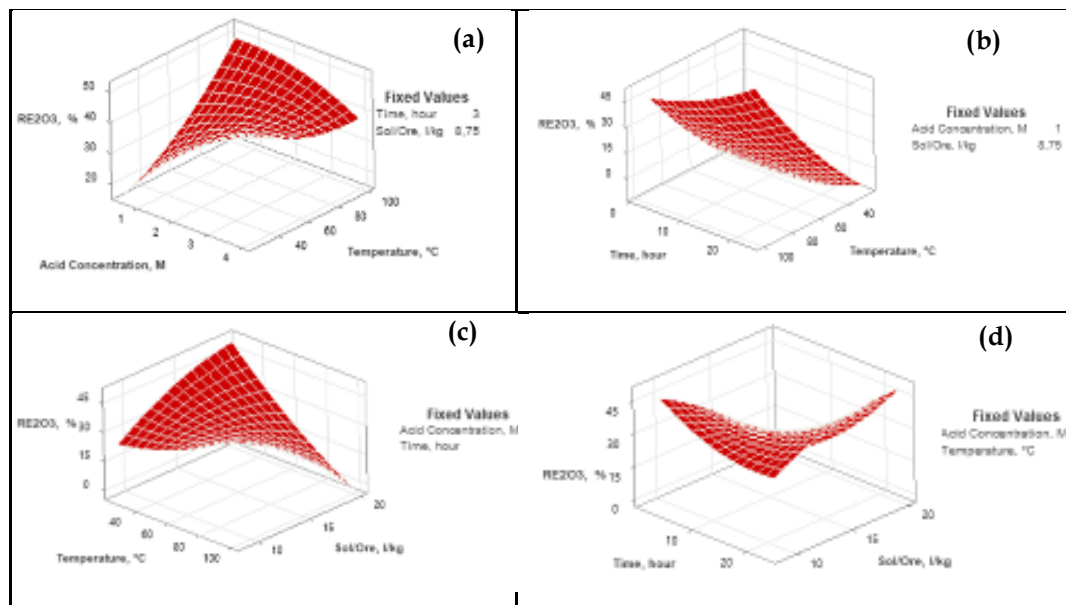


Fig. 5. Change of REE recovery value depending on different leaching parameters

3.2. Optimization and verification

The objective of optimization is to identify the optimal leaching parameters that efficiency a high leaching recovery. Consequently, a recovery value of 55.00% was set as the target. This target was preferentially established based on the highest observed recovery value of 46.00%. Upon targeting the 55.00% recovery value, the optimal leaching parameters were determined using the BBD method, and the corresponding response values are presented in Table 7.

Table 7. Optimum leaching parameters determined according to the BBD method

Parameter	HCl, M	Temperature, °C	Time, h	Solution-Ore	%REE
Optimization	1.18	98.41	3.00	8.75	48.40

The REE recovery was determined by the model as 48.40% in response to these optimum values. In addition, the estimated results obtained by the model were compared with the experimental results to verify the experimental results. The error rates in this verification study were calculated according to Eq. 3, and since the average error value was 6.35% and below 10%, it is considered that the optimization study was successful. In the optimization studies in the literature, there are studies that optimized with a similar level or higher error rate (Kumar et al., 2020; Uysal, 2023). In summary, it was determined that the values optimized by RSM were significant.

$$\text{Error, \%} = [(\text{Experimental result} - \text{Estimated result}) / \text{Experimental result}] * 100 \quad (3)$$

4. Conclusions

Leaching optimization was conducted to determine the optimal leaching parameters for recovering REEs from Kızıldag shale ore and to assess the individual significance of each factor. The optimization and modeling of the raw ore depending on different leaching parameters were investigated using the BBD method. The effects of the independent variables acid concentration, leaching temperature, leaching time and solution-ore ratio on the dependent variable leaching recovery were investigated and the optimum leaching parameters were determined. Accordingly, the optimum leaching parameters were determined as; 1 M HCl concentration, 98 °C leaching temperature, 3 hours leaching time, 8.75 l/kg solution-ore ratio. It was concluded that the experimental results were compatible with the estimated results determined by the model, the average error rate was 6.35% and was at an acceptable level. In addition, it was determined that R^2 values greater than 80% were obtained in the regression results obtained and the RSM model fit created based on these was high. In addition, the effectiveness of the leaching parameters as a result of the leaching optimization was determined as; leaching temperature > leaching time > HCl concentration > solution-ore ratio, respectively.

As the leaching optimization in this study was conducted on raw ore, the resulting leaching recoveries were observed to be low. To enhance leachability, it is recommended that the ore undergo activation through calcination and/or intensive milling prior to leaching. Preliminary investigations indicate that the leaching recovery of REEs from calcined shale ore increases significantly.

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