

Article

Optimizing Conditions for Scandium Extraction from Bauxite Residue Using Taguchi Methodology

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Abstract: Bauxite residue is the voluminous by-product of alumina production after Bayer process. Its high alkalinity causes disposal problems and harmful environmental impacts. However, the residue contains significant amounts of valuable elements such as rare earth elements including scandium. Greek bauxite residue contains a high amount of scandium close to its main resources. Taking into account scandium limited availability coupled with its high demand in modern technology, bauxite residue could be considered as a potential resource for scandium recovery. In this study, the optimization of scandium extraction from bauxite residue with sulfuric acid is investigated using Taguchi methodology. Based on previous studies acid molarity, leaching time, solid/liquid ratio and reaction temperature were selected as control parameters for the selective Sc recovery. Method optimization targeted the highest concentration of scandium combined with the lowest concentration of iron without taking into account applications constraints. The predicted values resulted by Taguchi methodology were affirmed by a confirmation experiment conducted at optimal conditions. Regression analysis provided the respective equations to be applied on several conditions depending on different applications.

Keywords: Taguchi method; experimental design; optimization; scandium; extraction; sulfuric acid

1. Introduction

Bauxite residue (BR) or red mud (RM) is the by-product generated in alumina production after Bayer process. About 1–1.5 tons of BR are generated per ton of alumina produced [1] raising its annual output up to almost 120 million tons and its accumulation up to 2.7 billion tons globally [2]. Its disposal is problematic requiring large land areas and overloading alumina's production cost [3]. During the years, many investigations have been performed aiming to low cost and environmental friendly treatment and utilization of BR, focusing on its use as agent in building and constructing materials, adsorbent for pollutants removal, coagulant for waste and water treatment, agent for neutralizing acidic waste and raw material of low cost for the recovery of valuable elements [4–16]. All these applications could be a potential and beneficial route for BR consumption and its introduction again in the economic cycle. BR is a complex material enriched in numerous metals. Depending on bauxite origin and Bayer process conditions, it mainly consists of Fe, Al, Ca, Na, Si, Ti oxides and salts and significant amounts of minor and trace elements such as V, Cr, Zn, Ga, Nb, Zr and Ta as well as rare earths - REEs (Sc, Y, lanthanides). It was found that Greek BR –produced by Mytilineos S.A. (formerly Aluminium of Greece, the largest Greek alumina and aluminum producer) - contains ~1kg REEs/t of dry BR with a Sc content of about 120g/t of dry BR (0.02% Sc₂O₃) close to Sc main resources [17–20]. Scandium is the most important of rare earth elements and is classified from the European Commission as Critical Raw Material (CRM) due to its high economic importance

resulted from the growing market demand in advanced technologies in combination with its low availability [21,22].

Scandium extraction from its main minerals such as thorveitite, gadolinite and euxenite, is difficult due to their rarity as well as its low concentration and the presence of radioactive elements in other natural minerals. Different methods have been investigated for the recovery of REEs and Sc from BR such as hydrometallurgical treatment, ion liquids leaching, bioleaching or pyrometallurgical pretreatment of the residue before leaching process. Pyrometallurgical pretreatment requires intensive energy consumption increasing the process cost. Furthermore, leaching with ionic liquids fall short due to their cost and lower Sc recoveries, while bioleaching is not thoroughly investigated [23-25]. Among all, hydrometallurgical treatment is the most widely used technique for REEs and Sc recovery due to its simplicity and low cost [26]. Several solutions (acidic, alkaline) have been tested as solvents. Mineral acids were found to be more suitable resulting to higher Sc recovery and favoring following processes e.g. ion exchange, solvent extraction. Method yield and selectivity highly depends on the type of mineral acid used as well as the leaching parameters [27-29].

A large number of experiments are needed in order to study the effect of each parameter in addition to all possible interactions between them on the response variable. Taguchi experimental design can be employed instead. Taguchi Method uses orthogonal arrays to conduct a set of a limited number of experiments. It involves the description of the control factors in order to obtain the optimum results of the process. The relative importance of each parameter is determined with ANOVA statistical method. The results of the experiments are evaluated in order to predict the optimum outcome [30-32].

In this study, the optimization of scandium selective leaching process from BR with sulfuric acid is investigated using Taguchi methodology. Sulfuric acid was preferred for its mild environmental impact. Method performance was assessed by Sc concentration in the leachate solution. Method selectivity was estimated in respect to iron content since it is the major element of BR. Taguchi experimental design was used in order to evaluate the contribution of each parameter and define the optimal conditions for maximization of concentration. Application limitations such as scale-up of the process and feed requirements of a subsequent ion exchange procedure for scandium purification were not taken into account in this study. Previous investigation [33] indicated acid molarity, leaching time, solid to liquid ratio and reaction temperature as control parameters for Sc concentration in the leachate solution and its selective recovery in respect to iron. Signal to noise (S/N) ratio and analysis of variance (ANOVA) statistical approach was employed for the calculation of percentage contribution of each parameter and optimization of leaching conditions. Equations for Sc and iron concentration were produced by applying regression analysis. A confirmation experiment was conducted under the optimal conditions and the results were in good agreement with the predicated values.

2. Materials and Methods

2.1 Sample collection and characterization

Bauxite residue used in this study was obtained from Mytilineos S.A. former of Aluminium of Greece, in the form of ferroalumina. Ferroalumina is the cake with 26% humidity produced from BR slurry, which is washed and filtered under pressure. The BR sample was very fine having a particle size $D_{80}=25\mu\text{m}$. The initial pH of the BR slurry was 11.3 (5 g of BR stirred with 100 mL of deionized water for 30 min). The sample used in all tests was dried at 105 °C and crushed prior to leaching.

As mentioned elsewhere (Ochsenkuehn-Petropoulou et al, 2018) the chemical composition of BR is Fe_2O_3 (43.5%), Al_2O_3 (19%), SiO_2 (7.3%), TiO_2 (5.6%), Na_2O (3%), and CaO (9.4%). Mineralogical analysis of BR revealed phases of iron (hematite, goethite), alumina (gibbsite, diaspore, aluminium oxide) titania (rutile), silica (quartz), calcium (calcite), aluminosilicates (kaolinite, anorthite, cancrinite, montmorillonite). Scandium arises up to an average of 100 mg/kg almost constant over 20 years.

2.2 Preliminary tests

Several different acids had been tested previously [17,18,34]. It was proven that the type of acid used in the leaching procedure was critical for the recovery of all metals studied. Extraction of Sc though, is mainly influenced by the protons produced by the acids. The acid counter ion severely influences iron with HCl resulting to the highest recovery [17]. Chloride ions compared to sulfate replace more easily the hydroxyl groups of hematite and iron is readily released in the solution [27]. Thorough studying of the processes and mechanisms taking place is beyond the scope of this study.

The “one-factor-at-a-time” approach was used in order to evaluate the effect of several parameters such as solid to liquid ratio (S/L), acid concentration (M), time, temperature, final pH and type of agitation[33].

The results obtained, indicated four parameters being the most important control factors for Sc recovery and concentration: Acid (H₂SO₄) molarity, Temperature, Solids to Liquid ratio (S/L) and Leaching time. In order to study the effect of these parameters on the proposed process, and identify their optimized values, a matrix experiment is set up by appropriately changing their values over a specified range [35,36]. According to the findings of the previous phase and following a symmetric as well as a rational resources’ use approach, each parameter is chosen to vary among three values: minimum, middle and maximum, as shown in Table 1.

Table 1. Parameters and their values at each level to be set and studied in experiments.

Factor	Parameter	Unit	Level		
			1 (minimum)	2 (middle)	3 (maximum)
A	H ₂ SO ₄ molarity	M	2	4	6
B	Temperature	°C	25	55	85
C	Solids to Liquid ratio	%	10	20	30
D	Leaching time	hrs	1	4	7

2.3 Experimental procedure

The experimental procedure as well as instrumentation and reagents used are reported in details elsewhere [33]. All experiments investigated in this study were conducted using sulfuric acid at three different acid concentrations (2, 4 and 6 M) as designed by Taguchi’s experimental methodology (Table 1). The different solid to liquid ratios were obtained by mixing a specific amount of BR with 200 mL of sulfuric acid of a certain molarity.

The solution was magnetically stirred at 600 rpm in all cases on a magnetic stirring plate. Agitation rate was not involved in the parameters tested since it is of lesser importance [33].

The leaching process was allowed to proceed for the different time intervals (1, 4 and 7 hours). After each experimental run, pH of slurry was measured. Temperature leaching tests were performed under reflux in a pre-heated water bath using pre-heated acids with magnetic agitation. Temperatures tested are also listed in Table 1.

Separation of liquid from solid residue was performed after completion of each test, via centrifugation (3000 rpm for 10 min, Eppendorf 5702 centrifuge). All liquid samples were filtered under vacuum with 0.45 µm cellulose nitrate membranes supplied by Whatman plc (GE Healthcare Life Sciences, Little Chalfont, UK) prior to storage and analysis.

All solutions were analyzed with an Optima 7000 DV, Perkin Elmer Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) instrument. External calibration method was applied using multi-element stock solutions (High Purity Standards, Charleston, USA). The wavelengths used (nm) were Sc (361.383 nm) and Fe (259.939 nm) while method accuracy and precision was checked using BX-N Certified Reference Material as reported elsewhere [20].

2.4 Taguchi Method

In case of four parameters with values of three different levels, a traditional experimental design -to satisfy all possible combinations (3^4)- would require the realization of 81 individual experiments. Considering that each experiment has to be repeated 2-3 times (requirements of repeatability), a significant analytical measurements load arises both lasting a long time as also having a high cost due to the extensive consumption of resources and man-hours. To avoid this fully combinatorial pattern, a fractional experimental plan is proposed based on Taguchi method [37].

Taguchi method sets the norms to perform experiments in order to test the sensitivity of a set of response variables (dependent variables) under the effect of a set of control parameters (independent variables) by considering experiments in 'orthogonal array' thus aiming to attain the optimum setting of the control parameters [38]. The fundamental advantage of Taguchi method lies in using 'orthogonal array' distribution. It allows a much-reduced set of experiments to be done in order to find the optimum settings of involved control factors, at minimum cost of resources but in a robust way achieving high rates of reproducibility [32,39,40].

The Taguchi method applies through a) the designing phase of the experiment, b) the calculation of factor effects, c) the selection of optimum factor levels, and finally at d) the validation of experimental results stage [39].

In our study (four factors at three levels), the appropriate orthogonal array $L_9(B^C)$ which distributes the factors (parameters) in a balanced manner, is $L_9(3^4)$. $A=9$ is the requisite number of experiments to be conducted, indicating the significant economy made in experimental procedure (materials and man-hours) under Taguchi design, as the traditional design of 81 experiments is reduced by a square root. $B=3$ denotes the number of levels and $C=4$ corresponds to the factors involved in the experiment. Table 2 presents the L_9 orthogonal matrix experiment plan with the resulting combinations among factors and their levels to be considered in order to study the effect of Sc leaching parameters.

Table 2. $L_9(3^4)$ orthogonal matrix experimental plan.

Experiment No.	Factors/Parameters			
	A (H_2SO_4 Molarity)	B (Temperature)	C (Solid/Liquid)	D (Time)
1	2	25	10	1
2	2	55	20	4
3	2	85	30	7
4	4	25	20	7
5	4	55	30	1
6	4	85	10	4
7	6	25	30	4
8	6	55	10	7
9	6	85	20	1

As reported above, iron concentration in leachate was chosen to be monitored as selectivity assessment since it is the major element of BR. The focus is on Sc aiming to maximum concentration possible in contrary to Fe where the lowest content is considered as optimum. Both element concentrations act as response variables under the Taguchi method. Table 3 shows the results for Sc and Fe throughout all nine experiments, where each measurement was repeated thrice, accompanied with the arithmetic average of each triplet of experiments. It has to be noted that in Taguchi method, the experiment corresponding to optimum conditions for Sc extraction from BR might not exist within the designed orthogonal matrix experimental plan [41]

Table 3. Measurements of Sc and Fe concentrations for the corresponding factor combinations of the $L_9(3^4)$ experimental plan.

Exp. No.	Factors Combination	Concentration (mg/L)							
		Sc				Fe			
		C^{Sc_1}	C^{Sc_2}	C^{Sc_3}	$C^{Sc_{avg}}$	C^{Fe_1}	C^{Fe_2}	C^{Fe_3}	$C^{Fe_{avg}}$
1	A ₁ B ₁ C ₁ D ₁	3.72	3.57	3.69	3.66	1263	1255	1294	1271
2	A ₁ B ₂ C ₂ D ₂	9.36	8.89	8.96	9.07	22806	21815	22698	22440
3	A ₁ B ₃ C ₃ D ₃	13.77	14.58	14.31	14.22	50260	51389	52072	51240
4	A ₂ B ₁ C ₂ D ₃	7.80	7.65	7.68	7.71	15075	15133	14855	15021
5	A ₂ B ₂ C ₃ D ₁	13.16	13.94	13.48	13.53	25684	25594	25459	25579
6	A ₂ B ₃ C ₁ D ₂	8.90	9.66	9.41	9.32	36225	39154	37358	37579
7	A ₃ B ₁ C ₃ D ₂	11.88	10.93	12.71	11.84	19588	19111	20814	19838
8	A ₃ B ₂ C ₁ D ₃	8.14	7.99	8.91	8.34	31388	32697	32685	32257
9	A ₃ B ₃ C ₂ D ₁	12.57	14.29	13.22	13.36	43741	41526	41370	42212

According to the Taguchi method, the metric of signal-to-noise (S/N) ratio is employed to find the optimum conditions of BR's H₂SO₄ leaching process. Sc and Fe concentrations follow exactly the opposite direction for this particular expression of 'objective function' to be optimized, meaning that for Sc the higher the concentration, the better are the performance characteristics, while for Fe it applies exactly the opposite -the smaller the concentration, the better is- [32,36,42,43]. As for the case of Sc (the larger-the-better type), the form of S/N ratio is expressed as:

$$\left(\frac{S}{N}\right)_{C^{Sc}_{avg}} = -10 \cdot \log \left(\frac{1}{n} \cdot \sum_{i=1}^n \frac{1}{|C^{Sc}_{avg}|_i^2} \right) \quad (1)$$

While for the case of main elements, in specific Fe (the smaller-the-better type), the form of S/N ratio is as follows:

$$\left(\frac{S}{N}\right)_{C^{Fe}_{avg}} = -10 \cdot \log \left(\frac{1}{n} \cdot \sum_{i=1}^n |C^{Fe}_{avg}|_i^2 \right) \quad (2)$$

In both cases $n=9$, meaning the number of experiments done for an experimental combination and C^{Sc}_i or C^{Fe}_i is the performance value for the corresponding i^{th} experiment.

$$Y_i = \mu + X_i + e_i \quad (3)$$

where μ is the overall mean of performance value, X_i the fixed effect of the parameter level combination used in i^{th} experiment and e_i the random error in i^{th} experiment [41,42,44].

2.5 Analysis of experimental data

Analysis of Variance (ANOVA) is used to evaluate the experimental data of Table 3, and to identify the relative influence of each factor on the variation of results of Sc and Fe concentrations respectively. Furthermore, a regression analysis is performed in order to extract an equation correlating the four independent variables with the dependent variable of Sc and Fe concentrations. This step will provide the necessary tool to predict the response in Sc/Fe concentrations for a larger variety of the four factors combinations outside the norms of the orthogonal array distribution and their set levels. As in designing of the experimental plan, Minitab Statistical Software is used to calculate the effects of leaching process parameters with a 95% confidence level as well as the regression model and its coefficients.

3. Results and Discussion

According to ANOVA results, for Sc, the prioritization of four factors' contribution is as shown in Table 4. The most significant factor is S/L with a contribution of 58.95% followed by Temperature with 33.32% while the other two factors have a much lower contribution to BR leaching process thus to Sc concentration. H₂SO₄ molarity presents a percentage of 7.71% while Leaching time seems to have an almost negligible effect at 0.02%.

Table 4. ANOVA results for Sc.

Factor	Degree of Freedom	Sequential sums of squares	Contribution (%)	Adjusted sums of squares	Adjusted Mean Squares	F-Value	P-Value
A	2	2.2742	7.71	7.2742	3.6371	*	*
B	2	31.4224	33.32	31.4224	15.7112	*	*
C	2	55.5981	58.95	55.5981	27.7991	*	*
D	2	0.0187	0.02	0.0187	0.0094	*	*
Error	0	*	*	*	*		
Total	8	94.3135	100.00				

Regression analysis for Sc concentration produced the following best-fit equation with an R² = 1 (Equation 4):

$$C_{Sc} = -3.017 - 0.758 \cdot A + 0.112 \cdot B + 0.262 \cdot C - 0.067 \cdot D - 0.026 \cdot A^2 - 0.328 \cdot 10^{-3} \cdot B^2 + 1.066 \cdot 10^{-3} \cdot C^2 + 6.469 \cdot 10^{-3} \cdot D^2 \quad (4)$$

As for Fe concentration, the corresponding findings of ANOVA are emphatically different compared to those for Sc. As reported in Table 5, the largest contribution by far belongs to Temperature with 81.89%. This result is very reasonable as Fe is fully coupled with temperature meaning that increased temperatures favor Fe dissolution. Unlike Sc, S/L effect is significantly lower for Fe with a 6.14% weight. Leaching time has a contribution share of 8.06% while H₂SO₄ molarity keeps at the same order of magnitude at 3.90% as Sc's one.

Table 5. ANOVA results for Fe.

Factor	Degree of Freedom	Sequential sums of squares	Contribution (%)	Adjusted sums of squares	Adjusted Mean Squares	F-Value	P-Value
A	2	7.169·10 ⁷	3.90	7.169·10 ⁷	3.584·10 ⁷	*	*
B	2	150.350·10 ⁷	81.89	150.350·10 ⁷	75.175·10 ⁷	*	*
C	2	11.274·10 ⁷	6.14	11.274·10 ⁷	5.637·10 ⁷	*	*
D	2	14.805·10 ⁷	8.06	14.805·10 ⁷	7.403·10 ⁷	*	*
Error	0	*	*	*	*		
Total	8	183.597·10 ⁷	100.00%				

Regression analysis for Fe concentration produced the following best-fit equation with an R² = 1 (Equation 5):

$$C_{Fe} = -6751 - 2687 \cdot A + 392.5 \cdot B - 135.3 \cdot C + 470.9 \cdot D + 537.5 \cdot A^2 + 1.224 \cdot B^2 + 14.03 \cdot C^2 + 145.7 \cdot D^2 \quad (5)$$

The effects of each parameter associated with their levels on Sc and Fe concentration are graphically presented in Figures 1 & 3.

Since higher S/N ratio is better for obtaining higher Sc concentration, the optimum leaching conditions for Sc can be drawn from Figure 2 where the numerical value of the maximum point at each factor corresponds to the optimized value of Sc concentration according to experimental design [32]. Concerning factor A (Acid molarity), the maximum S/N ratio (20.80) is obtained at 6 M (level 3), similarly, for Temperature (Factor B) and S/L ratio (Factor C) the maximum values of S/N ratio appear also at level 3, meaning 21.65 corresponding to 85 °C and 22.38 corresponding to 30%, respectively. The maximum S/N ratio output for Leaching time (Factor D) appears at level 2 with 20.00, being related to 4 hours. Therefore, the parametrization giving the optimum BR leaching conditions for Sc concentration is $A_3B_3C_3D_2$ (6M, 85°C, 30%, 4h).

Scandium concentration in this case is predicted to be 16.4mg/L while iron is estimated as 51472 mg/L. The optimum conditions for iron extraction can be deduced from the respective S/N plot (Figure 4), although in this case maximum S/N values depict the minimum concentration of iron as defined by the smaller the better model. The optimum BR leaching conditions for Fe are $A_1B_1C_1D_1$ corresponding to leaching for 1 hour at 25 °C using 2M sulfuric acid and 10% solid to liquid ratio. Iron concentration in this case is identical to the measured value for experiment. No.1 (see Table 3) being 1271 mg/L and scandium is 3.66 mg/L.

It should be noted that the proposed optimal conditions refer only to the maximization of Sc concentration. Any application parameters such as cost analysis for large-scale extraction or restrictions resulting from subsequent purification process were not included in the design of the present study. Instead, regression analysis equations are suggested for any recommended application conditions. In any case, the leaching behavior highly depends on the chemical and mineralogical composition of the bauxite residue utilized.

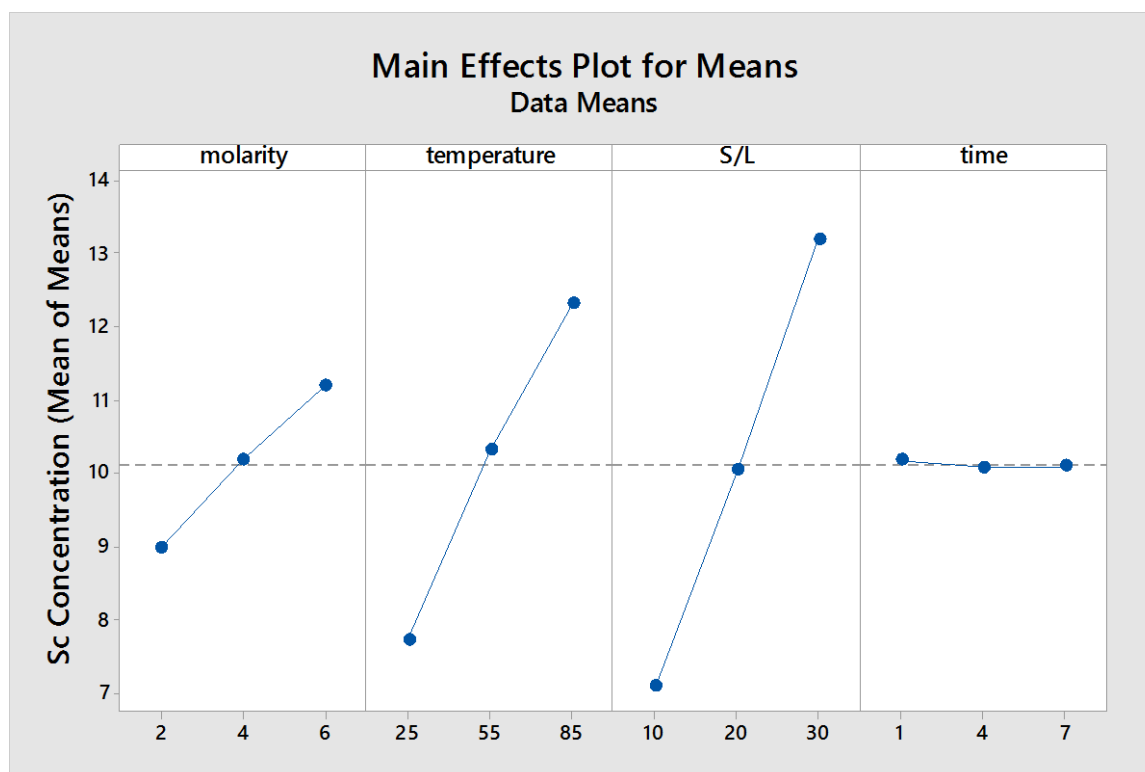


Figure 1. The effects of each parameter (A: Acid molarity, B: Temperature, C: Solid to Liquid ratio (S/L) and D: Leaching time) associated with their levels on Sc concentration.

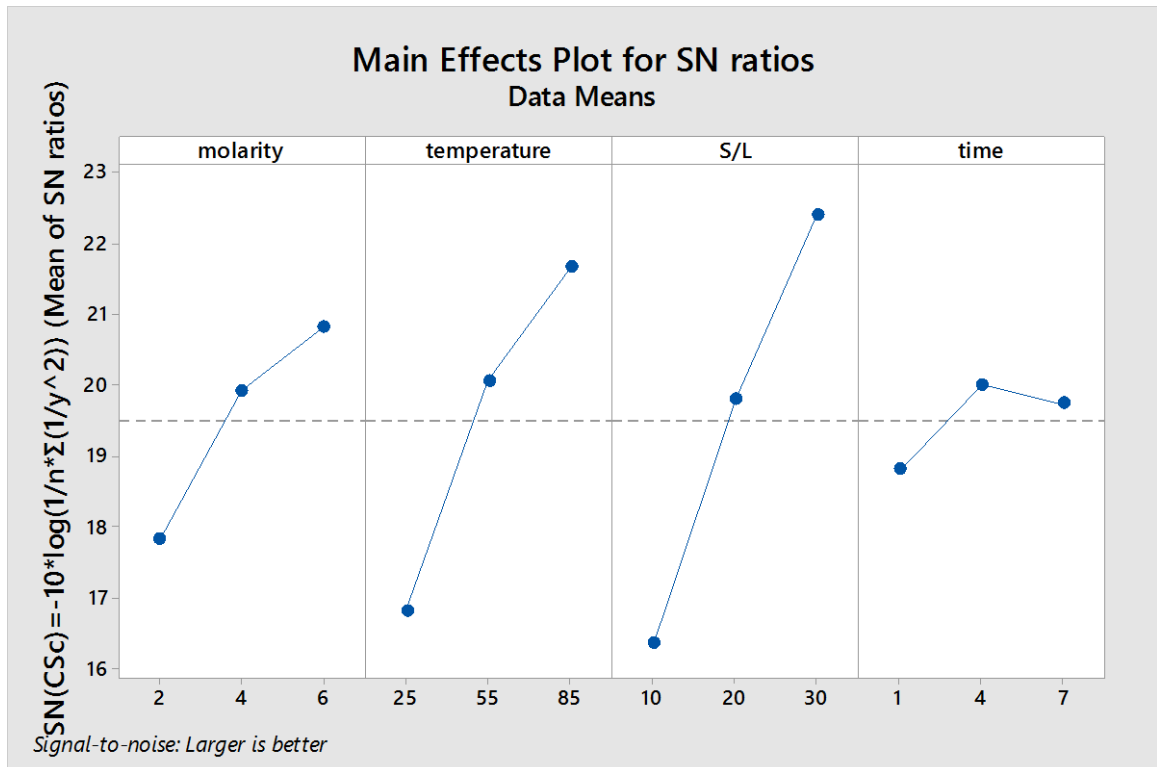


Figure 2. The effects of each parameter (A: Acid molarity, B: Temperature, C: Solid to Liquid ratio (S/L) and D: Leaching time) associated with their levels on the statistical performance of S/N ratio for Sc.

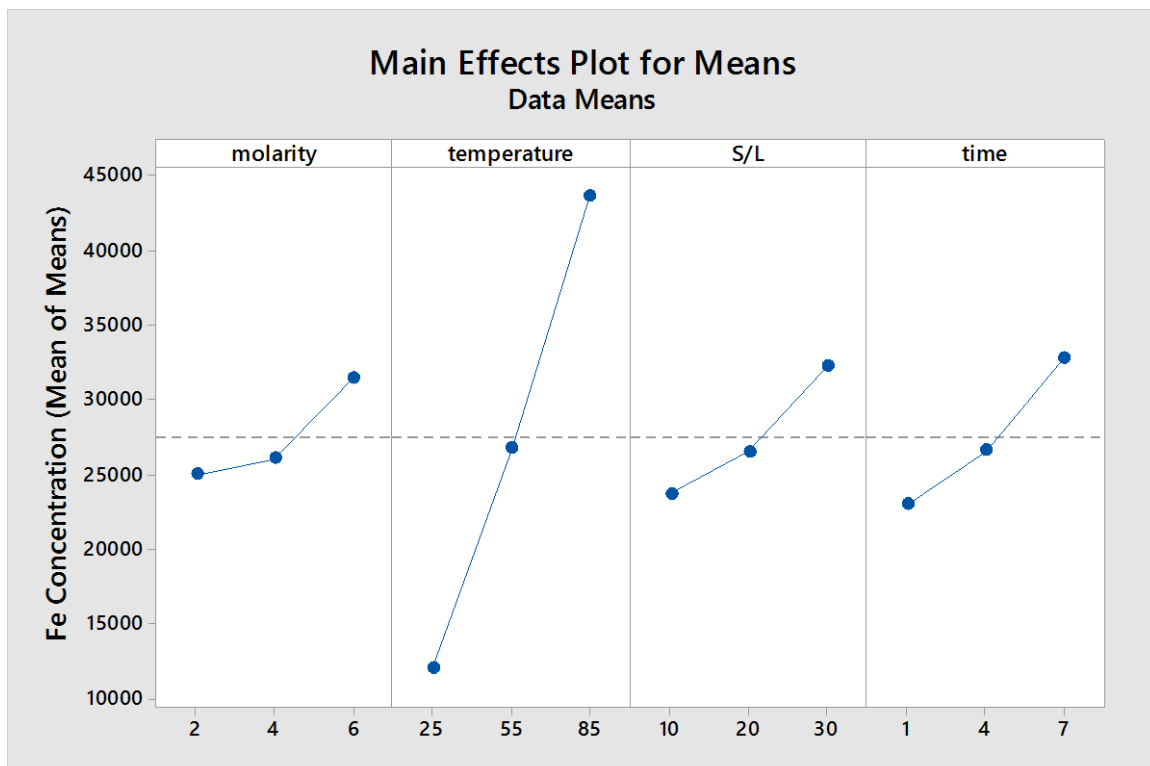


Figure 3. The effects of each parameter (A: Acid molarity, B: Temperature, C: Solid to Liquid ratio (S/L) and D: Leaching time) associated with their levels on Fe concentration.

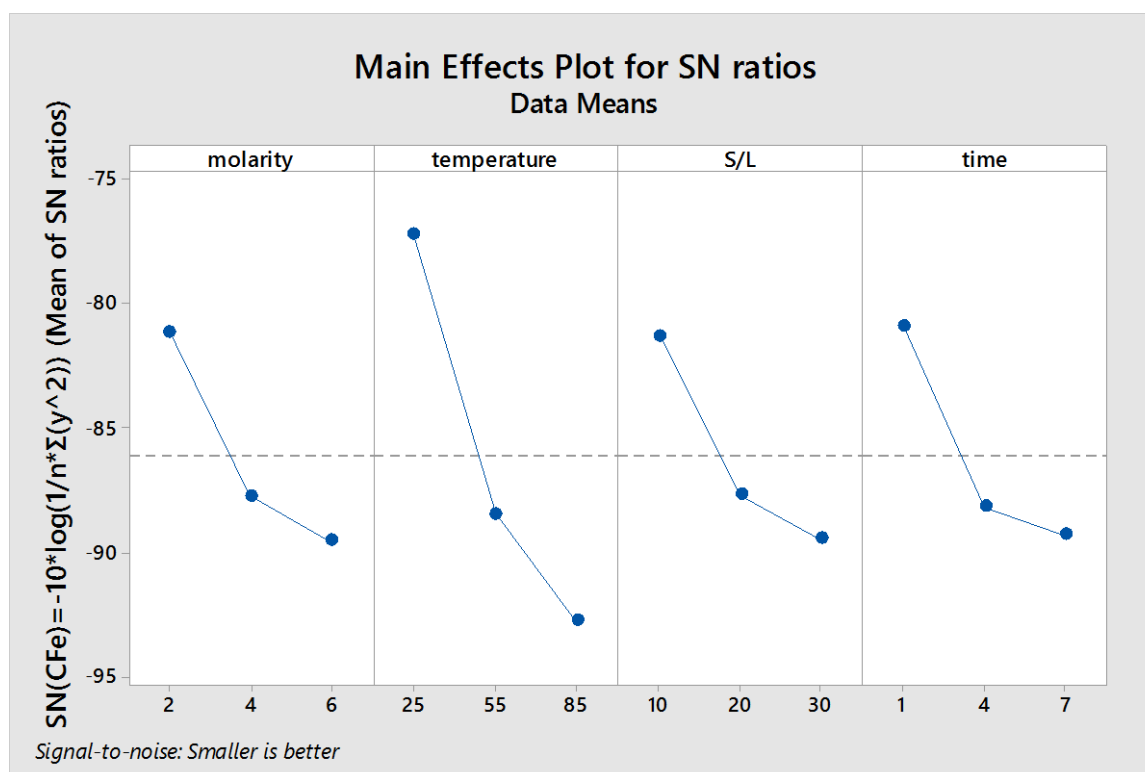


Figure 4. The effects of each parameter (A: Acid molarity, B: Temperature, C: Solid to Liquid ratio (S/L) and D: Leaching time) associated with their levels on the statistical performance of S/N ratio for Fe.

As seen from the above optimized conditions, for Sc the experiment-combination linked to the optimum leaching acid conditions is not included in the L_9 orthogonal matrix experiment plan (see Table 2) while in case of Fe the optimized conditions correspond to the experiment No.1 under the Taguchi design [32].

In order to verify that the optimal conditions resulted by Taguchi method, are indeed the best matching for the above predicted performance for Sc concentration, confirmation experiments were conducted under the specific conditions [45]. Sc concentration was predicted to be 16.4 mg/L and was measured as 16.6 mg/L while Fe concentration for the same conditions was predicted as 51472 mg/L and measured 55289 mg/L. The results are very satisfactory since the percent deviation is 1.2% for Sc and 7.4% for Fe.

4. Conclusions

Recovery of scandium and iron from bauxite residue by sulfuric acid leaching depends significantly on the conditions used. Taguchi experimental design applied clearly showed that scandium concentration in the leachate solution is enhanced with high acid concentrations, elevated reaction temperatures and high solid to liquid ratios. The most influential factor is the solid to liquid ratio (58.95%) followed by temperature (33.32%). Iron shows similar leaching behavior while being influenced mainly by temperature (81.89%) and secondarily by all the other factors. The optimal conditions predicted from Taguchi design are for Sc: 6M of H_2SO_4 , 85°C, solid/liquid 30%, 4h and for Fe: 2M of H_2SO_4 , 25°C, solid/liquid 10%, 1h. The predicted values were experimentally confirmed. Regression equations resulted from the statistical evaluation of the obtained results can be applied on leaching conditions depending on the requirements of different applications. The optimal conditions derived in this study are indicative for the leaching behavior of similar bauxite residues.

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Author Contributions: This work has been performed by the members of NTUA School of Chemical Engineering. L.-A. T., Th. L. performed the experiments and integrated ICP-OES measurements; P.G. and Th. L. evaluated the data; P.G. and Th. L. and L.-A. T. wrote the draft paper; K. H. corrected the draft paper; M. O.-P supervised the whole work, reviewed and corrected the paper.

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