

KINETIC STUDY UNDER NON-ISOTHERMAL CONDITION FOR SILICON PURIFICATION

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Abstract

This study aims to evaluate the process of acid leaching, in HCl, for purification of silicon metal, obtained by magnesiothermic reduction of silica and promote greater removal of impurities. The reaction product formed is a powder which is physically and/or chemically bound, with approximately 75% of MgO and approximately 25% of silicon metal, among other elements. Acid leaching is a technique used in the solubilization of oxides by an acid solvent. The silicon metal with purities up to 94% can be obtained in one step. Thus, it has been tested the effect of the following concentration of hydrochloric acid HCl (1, 2, and 3 M), temperature (50, 65, and 80° C) and time (60, 90 and 120 min). The leaching kinetics was studied under non-isothermal condition. After the treatments, it was shown that concentration is the main effect of leaching. In some analyses, it was possible to convert up to 76%, i.e., 99.66% of MgO has been extracted.

Keywords: Kinetics; Non-isothermal condition; Magnesiothermic; Silicon.

ESTUDO CINÉTICO EM CONDIÇÕES NÃO ISOTÉRMICAS PARA PURIFICAÇÃO DE SILÍCIO

Resumo

Este trabalho teve como objetivo avaliar o processo de lixiviação ácida em HCl para remoção de impurezas e purificação de silício metálico obtido por redução magnesiotérmica de sílica. O produto de reação formado é um pó que está fisicamente e/ou quimicamente ligado, com cerca de 75% de MgO e aproximadamente 25% de silício metálico, entre outros elementos. A lixiviação ácida é uma técnica utilizada na solubilização de óxidos por um solvente ácido. O silício metálico com purezas até 94% pode ser obtido em uma etapa. Assim, foi testado o efeito da seguinte concentração de ácido clorídrico HCl (1, 2 e 3 M), temperatura (50, 65 e 80° C) e tempo (60, 90 e 120 min). A cinética de lixiviação foi estudada sob condições não-isotérmicas. Após os tratamentos, foi demonstrado que a concentração é o principal efeito da lixiviação. Em algumas análises, foi possível converter até 76%, isto é, 99,66% de MgO foram extraídos.

Palavras-Chave: Cinética; Condições não-isotermicas; Silício; Magnesiotérmica.

1 INTRODUCTION

Estimated that the consumption of silicon until 2019 may reach up to 3.6 million metric tons of raw material [1]. Silicon is used in the form of quartz sand, clay, metal alloys, composites, semiconductors and silicones, among others.

Carbothermal reduction of silica is the main way of obtaining silicon, and it is held in submerged-arc electric

furnaces, reaching 99.5% of purity. However, there are other forms of reduction for obtaining silicon [2], e.g., magnesiothermic reduction, forming silicon and MgO through reduction of quartz by gaseous magnesium [3,4].

The result of the reaction is a powder that is physically and/or chemically bound, with approximately 75% of magnesium oxide (MgO), approximately 25% of silicon

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metal, among other chemical species formed, according to the conditions of the reduction process [3,4].

The silicon metal purification technique, obtained by magnesiothermic reduction, is well grounded in the literature for the solubilization of oxides via an acid solvent, promoting acid leaching [3,5-8]. Through acid leaching, solubilization can be performed for Si purification.

Understanding the mechanisms of chemical dissolution of oxides in aqueous acidic solutions is crucial for a wide variety of processes, including, for example, geochemical and environmental, hydrometallurgical, corrosive, catalyst processes, as well as drug delivery. The many events involved in the leaching process require an extensive series of multidisciplinary knowledge beyond the scope of this study.

Raschman, Fedoročková [9,10] in their work they performed dissolution of MgO under isothermal conditions. However, the literature lacks studies, in the non-isothermal system, to purification of reaction products obtained by magnesiothermic reduction of silica.

Thus, this research was conducted with the objective of evaluating the process of acid leaching for purification of silicon metal by the magnesiothermic reduction of silica, in order to achieve the greatest recovery (yield) of silicon metal at a given concentration, temperature and time, in a single step. In this way, the experiment used a factorial design with 2^3 factors + 3 center points, in order to investigate the possible effects and/or combinations of effects resulting from the variation of concentration, temperature and time. Based on the results of each treatment, a kinetic study was performed on leaching under non-isothermal conditions.

2 MATERIALS AND METHODS

The powder, the reaction product of the magnesiothermic reduction of silica, was obtained in batches in a pit furnace with 7.0 kW of power at the Nuclear and Energy Research Institute of the Federal University of São Paulo (IPEN-USP).

The solid reagents used in the reduction were the following: high purity silica and magnesium flakes, which have received heat treatment (700-830°C), required to promote the reaction between reagents.

The powder was leached with hydrochloric acid (HCl) (Vetec), with a concentration of 37%, in a 500 mL jacketed batch reactor. According to the factorial design of the experiment, the effect of variation of the following factors was investigated: concentration (hydrochloric acid - HCl at concentrations of 1, 2 and 3 M), temperature (50, 65, and 80°C) and time (60, 90 and 120 min). In addition to a statistical study, pH was monitored in real time to evaluate in a complementary fashion the kinetic behavior of leaching under non-isothermal conditions in all runs.

The experiments were carried out in a reactor with useful volume of 500 mL, a mechanical shaker with speed set at 600 RPM (with a PTFE-coated stir bar), thermostatic bath for temperature control and pH monitoring.

Dilutions were performed containing 1, 2 and 3M, considering 1M of MgO, as well as the other chemical species, to ensure the molar ratio of 1:1, 2:1 and 3:1 HCl:MgO. The thermostatic bath was calibrated at temperatures of 50, 65 and 80 °C. The solid reagent was the first to be introduced into the reactor, Shaking speed was calibrated with a digital tachograph and HCl was then quickly added. The data were read by the electrode and sent to the microcomputer.

In this study, the experiment used a complete factorial design with 3 factors at 2 levels + 3 center points, to determine which variables are the most influential on the results. The experiments were conducted at random. The factors chosen were concentration, temperature and time. The analysis of the responses obtained from the planning will show the best concentration, temperature and time for obtaining the highest percentage of Si, the lowest percentage of MgO and the greatest leached fraction. The table containing the experimental design, levels and answers will be presented in the results and discussions.

After the completion of the leaching procedure, the solution containing solids and liquids was filtered using ultrapure water in and a vacuum pump.

Characterization of the samples was performed through the following tests: X-ray diffraction (XRD) in an X-ray diffractometer (Shimadzu, LABX XRD-6000) with copper $K\alpha$ ($\lambda = 1.5405980 \text{ \AA}$) radiation source, power of 30 kV and 30 mA, for determination of mineralogical phases. To the interpretation and quantification of the results was used the software FullProf Suite Toolbar (I450), with the free database COD - Crystallography Open Database - and quantitative method of Rietveld. The BET method enabled the determination of the surface area and pore size distribution of solids. The equipment used in the test was Autosorb I (Quantachrome Instruments) for Windows 1.54. ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) to identify the elements in the powder sample.

3 RESULTS AND DISCUSSION.

In the results calculated (Figure 1a) by the software FullProf using the refinement of Rietveld from the diffractogram of the XRD of the original sample, it was possible to verify that the powder is composed of, approximately, 76.2% of MgO, 22.8% of Si and about 1% of W. From the knowledge of the elementary percentages it was possible to perform the balance of the mass.

XRD analyses were performed in all samples, however, only the diffractogram of the most revealing result will be shown. The Figure 1b is related to the run (7), according to the experimental design (3M, 80 oC and 120 min). It is observed that peaks of MgO and W have been reduced drastically. The Si has acute and high peaks, very similar to the standard texture of the element.

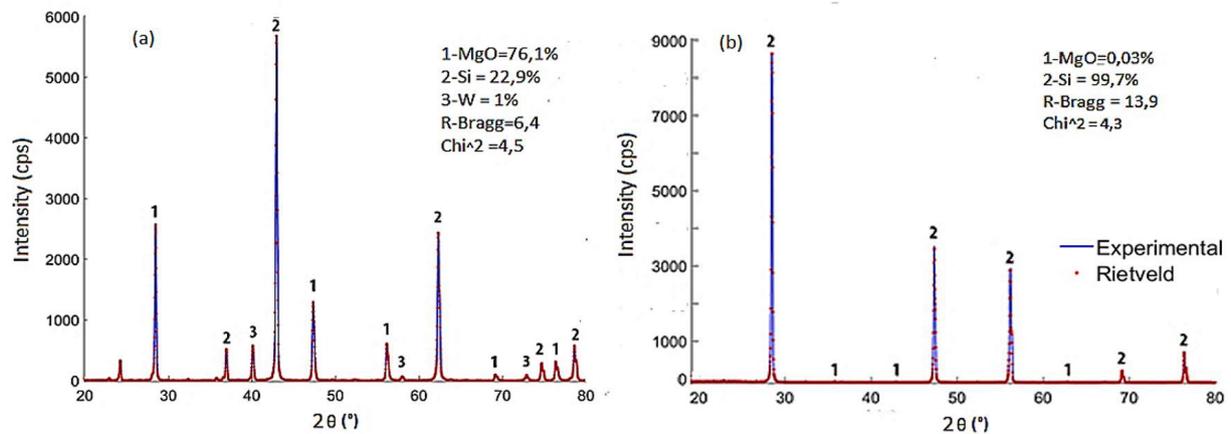


Figure 1. X-ray diffractogram of the (a) original powder and (b) run 7 (3M, 80°C and 120 min) with Rietveld refinement.

The result percentage of phase calculated by the refinement of Rietveld from diffractogram (Figure 1b), presented, approximately, 99.3% of Si and 0.7% of MgO.

Figure 2 shows the isotherm adsorption/desorption of nitrogen in the original sample. The slight concavity observed is relative to the relative pressure (P/P_0) axis, referring to the formation of the monolayer of N_2 gas on the surface of the sample. After multilayers are filled on the surface of powder, the inflection in the initiation of the convexity of the curve, in relation to the P/P_0 axis, occurs. The red line represents a small amount of hysteresis in the desorption of N_2 . Based on data collected by multipoint BET test and through supplementary estimates of the analysis BJH (Barret, Joyner and Halenda), it can be concluded that the isotherm is type II with hysteresis H_3 . The surface area of the material has pores of $1.5061 \text{ m}_2/\text{g}$. Regarding the diameter of the pores, it is concluded that about 78% of the pores have a diameter of 22 to 156 \AA , which is within the limits of the mesopore diameter according to the definition of IUPAC (International Union of Pure and Applied Chemistry). It can be suggested that the powder is at its highest “mesoporous” fraction. The percentage of remaining diameters correspond to approximately 21% of micropores and 1% of macro-pores contained in the sample. As for the pore volume, it can be said that 81% corresponds to mesopores, $\sim 15.5\%$ to macropores and the remaining $\sim 3.5\%$ to micropores.

Table 1 shows the chemical analysis obtained by the ICP-AES technique of leached Si in run 7 (experimental design) (described in Table 4). The data were compared with the commercial percentage commonly found in metallurgical grade silicon (MGS) [2]. It is concluded that, with the exception of boron, the values are well below the high and low concentration levels of reference. To reduce the concentration of boron, additional treatments should be performed, including: multiple leachates (with formation of complexes), directional solidification, plasma, among others.

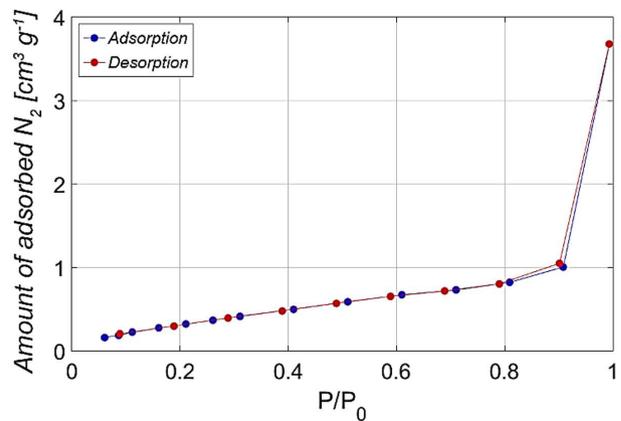


Figure 2. Isotherm adsorption/desorption of the original powder.

According to the results shown in Table 1, the powder leachate in run 7 (experimental design) (described in Table 4) can be used in the market of metal alloys and silicones.

The chemical dissolution of MgO in hydrochloric acid is a liquid-solid reaction in that no solid product is formed. For non-porous MgO, the overall process can be controlled by the chemical reaction on surface [3,6,9,10] (Equation 1). When the particles of MgO are dissolved in HCl in a batch reactor, the consumption of their respective mass fractions can be related (Eq. 2) (where m^0_{MgO} is the initial amount of MgO in mass unit, V_R is the reaction volume and $d\alpha$ is the fraction of dissolved MgO). Equation 2 integrated within the limits of $[\text{H}^+\text{A} \text{ to } \text{H}^+]$ and $[\alpha_0 \text{ to } \alpha]$ results in Equation 3 (Where $[\text{H}^+\text{i}] = 10^{-\text{pHi}}$, pH at instant i) [9,10]. When rearranged, Equation 3 results in leached fraction α (Equation 4), which will be used in the non-isothermal kinetic model. In general, it represents the mass loss rate for a decomposition reaction using Equation 5, often used in thermal analyses (where $d\alpha/dt$ is reaction speed, $f(\alpha)$ the function of the decomposed fraction and $k(T)$ the specific

Table I. Elements obtained during the leached extract by the ICP-MS technique compared with data on MGS found in the market (concentration mg/l)

Elements	leach	SGM-CL*	Difference of levels (%)		
			high	low	high
Al	239	300	5000	0,79667	0,0478
B	897	5	70	179,400	12,814
Ca	5,6	20	2000	0,28	0,0028
Cr	2,6	5	150	0,52	0,0173
Cu	3	5	100	0,6	0,03
Fe	6	300	25000	0,02	0,00024
Mn	9,6	10	300	0,96	0,032
P	2,6	5	100	0,52	0,026
Ti	21	100	1000	0,21	0,021
V	2	1	300	2	0,00667
Zr	4	5	300	0,8	0,01333

*CL- Commercial low.

speed constant). The dependence of k on temperature is given by the Arrhenius (Equation 6) which is generally applied to limited ranges of temperature. By replacing k from Equation 6 in Equation 7, including the heating rate $\beta = dT/dt$ and integrating (where T is temperature; A , the pre-exponential factor; E , the activation energy, R the gas constant and β the heating ratio) [4,5,7,8,11,12].

The mathematical treatment of the non-isothermal equations can be carried out in accordance with the three methods proposed in the literature: Differential, approximation and integral [4,5,7,8,11,12]. For this work, we used the Coats-Redfern integral method (linearized Equation 8) in virtue of its simplicity and wide use in kinetic studies of leaching, dehydration and decomposition of different solid substances. All equations are presented in Table 2.

Figure 3 was obtained through the experimental data adjusted to the deduction of Raschman and Fedoročková [9,10], for the conversion of leaching to pH variation, the result of which presents the main conversions of the leached fraction over time. Run 7 (3M and 80°C) presented the lowest reaction time for maximum conversion (76%), i.e., in about 8 minutes it entered into steady state; in this run, silicon was obtained with purity of 99.66%. It was also evident by its curve that the energy intake accelerates the reaction. Run 6 (3M and 50°C) entered into steady state in about 13 minutes. This treatment also resulted in high conversion, with final silicon with purity of 99.7%. Run 10, on the central point (2M and 65°C), resulted in a leached fraction of 48%, even considering leaching stoichiometry, as presented by several studies in the literature. As the material was not pure and no excess amount of reagent HCl was added, it is assumed that other chemical species contained in the original powder have reacted with HCl; also, the system may have reached a new thermodynamic equilibrium that does not favor total conversion. In runs 3 (1M and 50°C) and 15 (1M and 80°C), only 38% conversion was achieved; thus, it is clear that this concentration of HCl is insufficient to react with the amount of MgO available.

Figure 4 on run 7 (3M and 80°C) shows the plot of the ratio between $1/T$ and $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$, non-isothermal

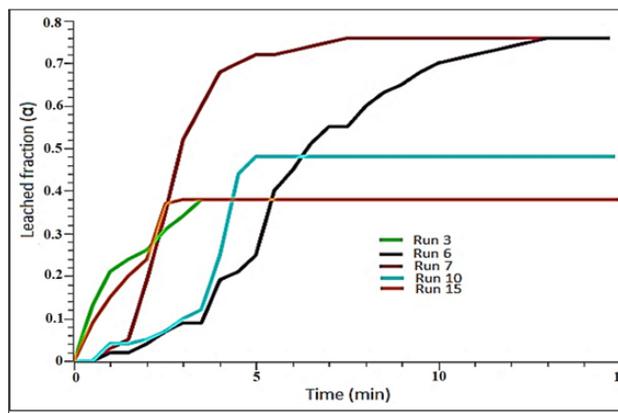


Figure 3. Conversion curves of leached α MgO at different HCl concentrations, and reaction temperatures.

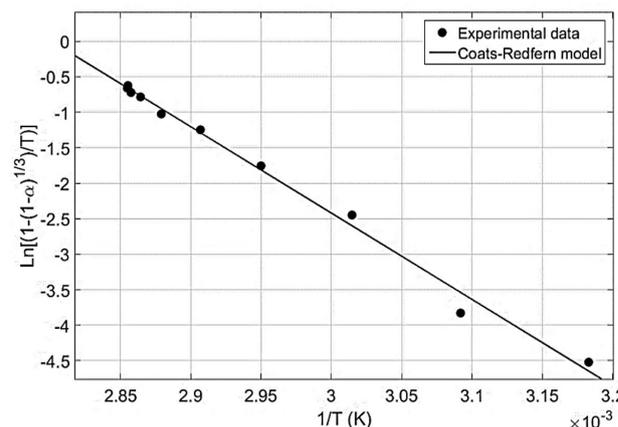


Figure 4. Ratio between $\ln\{[1-(1-\alpha)^{1/3}]/T^2\}$ and $1/T$ for determination of the activation energy, form factor and higher apparent rate constant k ; graph for run 7 (3M; 80°C).

integral Coats and Redfern [12] method (Equation 8), to obtain kinetic parameters, from which it was possible to determine the activation energy (E) with a value of 101.18 [kJ/mol]; the linear correlation coefficient (R^2) of

the data adjustment was 99.26, thus showing a great fit, indicating that HCl is a suitable solvent to promote MgO dissolution. The pre-exponential factor (A) showed a value of $3.29E+16$. Based on the values of E and using the Arrhenius equation ($\ln kc = -Ea/R * 1/T + \ln A$), we found the apparent kinetics constant (k) whose value was 21.28 min^{-1} .

Table 3 contains the conversion data for run 7, under non-isothermal condition for the first 7.5 min, at intervals of 30s, for the leached fraction, considering the temperature increase of the reaction medium.

Table 4 shows the complete matrix of experimental design, containing the factors, levels and responses obtained. As the planning was outlined in $2^3 + 3$ center points, the table contains 11 runs.

The percentages of Si and MgO ranged from 38 to 99.7% and from 0.1 to 61%, respectively. As for the leached fraction, the data show that up to 76% of impurities could be removed from the original powder, in run 7. The worst standards of silicon purity occurred in run 15, where the

levels were 1M, 80°C and 120 min. Gel was formed in this run, obstructing the passage of material through the filter.

As experiment has three responses, statistical analysis was performed separately. However, in this study, only data on the leached fraction will be presented.

This statistical analysis evaluated the extraction efficiency of all chemical species after acid treatment, in relation to the original mass contained in powder without treatment; that is, not taking into consideration only MgO, but also the other elements. Table 5 contains the analysis of variance (ANOVA), showing that the model is significant through the F-test (calculated) with a value of 246, with a small chance of any result different in relation to the F value of 0.01%. The effect of the variable concentration of HCl or (H^+) is also significant; the other variables showed no statistical significance and were withdrawn from Table 5, as well as the final equation for the process. As for the lack of adjustment and pure error, the values contained in Table 5 are adequate and the model is well adjusted.

Table 2. Mathematical equations

$MgO_{(s)} + 2H_{(aq)}^+ = Mg_{(aq)}^{2+} + H_2O_{(l)}$	(1)	$\frac{d\alpha}{dt} = k(T) f(\alpha)$	(5)
$d[H^+] = -\frac{2m_{MgO}^0}{V_R M_{MgO}} d\alpha$	(2)	$k = A \exp\left(-\frac{E}{RT}\right)$	(6)
$[H^+] - [H_0^+] = -\frac{2m_{MgO}^0}{V_R M_{MgO}} (\alpha - \alpha_0)$	(3)	$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha)$	(7)
$\alpha = \frac{(10^{-pH_0} - 10^{-pH}) V_R M_{MgO}}{2m_{MgO}^0}$	(4)	$\ln\left[\frac{1 - (1 - \alpha)^{\frac{1}{3}}}{T^2}\right] \cong \ln \frac{AR}{\beta E} - \frac{E}{RT}$	(8)

Font. Adapted [3-12].

Table 3. Data from kinetic equation for non-isothermal leaching

t(mim)	α_{MgO}	T(K)	$\text{LN}((1 - (1 - \alpha_{MgO})^{\frac{1}{3}})/T)^2$
1,0	0,03	314,20	-16,232
1,5	0,05	323,46	-15,600
2,0	0,19	331,72	-14,279
2,5	0,35	338,96	-13,648
3,0	0,52	344,02	-13,214
3,5	0,60	347,32	-13,036
4,0	0,68	349,11	-12,859
4,5	0,70	349,94	-12,816
5,0	0,72	350,20	-12,772
5,5	0,72	350,27	-12,772
6,0	0,73	350,20	-12,750
6,5	0,74	350,14	-12,728
7,0	0,75	350,07	-12,707
7,5	0,76	350,07	-12,686

The level of significance was determined at 0.1%, and the calculations resulted in an explanation of the variation of the model through $R2_{adj} = 96.64\%$. The $R2$ predicted value corresponds to 94.3% and the adequacy measure of precision is 5 times as great as the indicated value (Table 6). Final equation of terms (Equation 9).

As shown in Figure 5, as regards the response surface, for the greatest percentage of impurity removal from the original powder to occur, leaching has to be performed with the greatest concentration of HCl (3M); the temperature and time do not have significant statistical results. The results of optimization predict, with a desirability factor of 97%, that the best setting is 3M, 50° C and 60 min to get silicon with a purity of at least 98%.

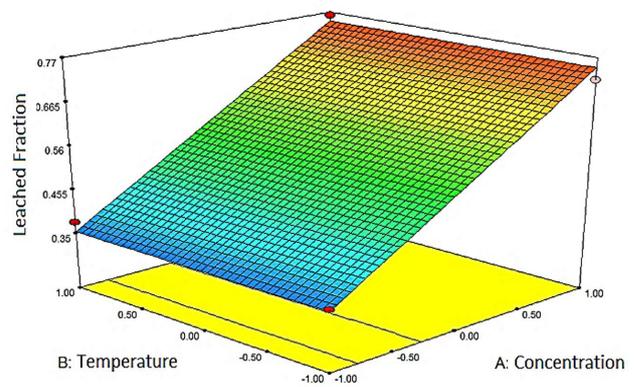


Figure 5. Fraction of response surface leached x temperature x concentration.

Table 4. Planning matrix containing levels, factors and responses

		Factor Levels 1		Factor Levels 2		Factor Levels 3	
		(-1) = 1M		(0) = 2M		(0) = 2M	
		(-1) = 55°C		(0) = 65°C		(0) = 65°C	
		(-1) = 60 min		(0) = 90 min		(0) = 90 min	
		(-1) = 120 min					
STD	Racing random	Factor 1	Factor 2	Factor 3	Resp. 1	Resp. 2	Resp. 3
		A: Concentration	B: Temperature Celsius	C: Time Min	% Fraction of Si	% Fraction of MgO	Fraction Leached
		M					
1	3	-1	-1	-1	0,421	0,548	0,356715
2	14	1	-1	-1	0,978	0,022	0,719634
3	4	-1	1	-1	0,549	0,451	0,376797
4	8	1	1	-1	0,951	0,049	0,761091
5	5	-1	-1	1	0,6	0,4	0,394358
6	6	1	-1	1	0,997	0,003	0,739256
7	15	-1	1	1	0,387	0,613	0,284536
8	7	1	1	1	0,993	0,007	0,769471
9	13	0	0	0	0,649	0,351	0,484144
10	10	0	0	0	0,652	0,348	0,470084
11	11	0	0	0	0,757	0,243	0,524501

Table 5. Analysis of variance (ANOVA) for the response of the leached fraction (red data show significant values)

SV	QS	DF	MS	F _{calculated}	p-value
Model	0,31088	1	0,31088	246,59743	< 0,0001
Concentration	0,31088	1	0,31088	246,59743	< 0,0001
Curvature	0,00716	1	0,00716	5,68669	0,0442
Residue	0,01008	8	0,00126		
Lack of fit	0,00848	6	0,00141	1,77327	0,4035
Pure error	0,00159	2	0,00079		
Total	0,32813	10			

Table 6. Model adjustment determination - leached fraction

Standard deviation	0,035506	R2	0,968578
Mean	0,534599	R2 coordinate	0,96465
C.V. %	6,641667	R2 predicted	0,943062
PRESS	0,018683	Accuracy adequacy	21,26253

Final equation of terminology

$$\text{Leached fraction} = + 0.55 + 0.20 * A$$

$$\text{That is: leached fraction} = + 0.55023 + 0.19713 * \text{concentration}$$

4 CONCLUSION

Acid leaching of the powder product obtained by magnesiothermic reduction for the concentration of silicon metal after the best treatment, it reached 99.66% purity (ICP-AES). The kinetic study under non-isothermal conditions provided outcomes for obtaining the kinetic parameters which are difficult to obtain in a single run by traditional methods.

The final powder can be considered as metallurgical grade silicon and applied in various industrial areas. All elements

contained in the sample had lower rates than the table reference for MGS, commonly found in the market, with the exception of the element boron.

The statistical analysis showed that concentration is the factor that produces a significant effect on the leaching process being studied.

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