

Dissolution kinetics of Amazonian metakaolin in nitric acid

(Cinética de dissolução de um metacaulim amazônico em ácido nítrico)

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Abstract

The kinetic study of Amazon metakaolin dissolution was performed with the application of the shrinking core model for spherical and 'flat plate' particles with constant size. The Amazon kaolin was calcinated at 700 °C in order to produce metakaolin. This metakaolin was leached with 5% excess nitric acid at 70, 80 and 95±3 °C for 3 h. Samples were collected every 15 min and subjected to aluminum analysis. The acid leaching was a chemically controlled process. The spherical morphology showed better fit than the flat plate particles when taking into account the regression coefficients. 91.58 kJ/mol of activation energy was found as well as an aluminum leaching reaction of the first order. The results found in this work using 5% excess acid and Amazon kaolin were consistent with previous research results using excess acid above 50% and standard kaolin.

Keywords: kaolin, metakaolin, leaching, kinetic study.

Resumo

O estudo cinético da dissolução de um metacaulim amazônico foi realizado com a aplicação do modelo 'shrinking core model' para partículas esféricas e 'placas planas' com tamanho constante. O caulim amazônico foi calcinado a 700 °C para promover a formação do metacaulim. O metacaulim foi lixiviado utilizando ácido nítrico com excesso de 5% a 70, 80 e 95±3 °C por 3 h. Amostras foram coletadas a cada 15 min e submetidas à análise de alumínio. A lixiviação ácida realizada foi um processo quimicamente controlado. A morfologia esférica mostrou melhor ajuste matemático do que a morfologia de placa plana levando-se em consideração os coeficientes de regressão obtidos. Foi encontrada uma energia de ativação equivalente a 91,58 kJ/mol, assim como reação de lixiviação de primeira ordem em relação ao alumínio do metacaulim. Os resultados encontrados com a utilização de excesso ácido de apenas 5% e caulim amazônico foram consistentes com trabalhos realizados anteriormente, cuja metodologia utilizou excesso ácido acima de 50% e amostra padrão de caulim.

Palavras-chave: caulim, metacaulim, lixiviação, estudo cinético.

INTRODUCTION

There are kaolin mines located in the Amazon region of northern Brazil, specifically in the states of Amapá (Rio Jari) and Pará (Rio Capim). Kaolin is mainly used in the paper industry as a filler and cover. However, it is also a possible source of metallic aluminum, porous silica, aluminum sulfate, chloride and nitrate [1-9]. Currently, bauxite is used for metallic aluminum production, but the limited availability of bauxite in the world makes researchers look for other available resources. Kaolin is a possible alternative to bauxite because it contains high alumina concentrations and is abundant in the Amazon region. The aluminum production process using kaolin can also produce silica with high specific area [10-13].

The aluminum extraction from kaolin is carried out by first performing the calcination and then the leaching process. The calcination of the kaolin promotes metakaolin production ($\text{Al}_2\text{Si}_2\text{O}_7$) through the dehydroxylation process [14-17]. The metakaolin produced from calcination can then

be subjected to an acid leaching process which promotes aluminum dissolution [18]. The main acids used in this process are: hydrochloric, sulfuric and nitric acid [10, 13]. The following reaction represents the nitric acid leaching of metakaolin:



The kinetic study of this process has already been examined by many researchers. Hulbert and Huff [10] carried out a kinetic study of calcinated kaolin dissolution with three different acids: sulfuric, hydrochloric and nitric. Ajemba and Onukwuli [12] studied the dissolution kinetics and reaction mechanisms of Udi clay with an excess of nitric acid above 50% of the required stoichiometry. Phillips and Wills [19], Olsen *et al.* [20], and others studied the aluminum dissolution process of kaolinitic clays. However, previous work found in the literature dealing with kinetic studies of metakaolin aluminum dissolution with nitric acid did not use Amazon metakaolin and used acid excess above 50%.

The high excess of acid which is recommended by literature for this kinetic study is not industrially viable. Therefore, the aim of this paper is to carry out a kinetic study of the metakaolin aluminum dissolution process using Amazon kaolin as starting material and then leaching it with nitric acid at 5% excess. The shrinking core model (SCM) is then applied for spherical and 'flat plate' particles with constant size.

MATERIALS AND METHODS

Materials: the starting materials were kaolin (a final product used for paper coating) from the Capim region in the state of Pará and nitric acid (65% purity). The nitric acid was used in concentrations to produce aluminum/acid rates similar to the reaction stoichiometry with 5% excess. The leachings were carried out in a reactor with a heating mantle capacity of 1000 mL, under constant stirring and refluxing, and coupled with a thermometer and a thermostat.

Methods: the kaolin was dried at 110 °C and calcinated in a muffle furnace at 700 °C for 2 h. The calcinated kaolin was named MK700. The non-calcinated kaolin and MK700 were leached with nitric acid at 5% excess. Leaching tests were carried out for 3 h with 50 g of sample. The non-calcinated kaolin was leached at 95±3 °C and MK700 at 95, 80 and 70±3 °C. Samples were collected every 15 min, filtered and subjected to aluminum analysis using EDTA titrimetric method. Leachings were carried out in duplicate and the solid residue was named MKA700. The mathematical adjustments were carried out in Microsoft Excel using the Solver tool with the hyperbole equation.

The materials were characterized before and after the calcination and leaching processes according to the following techniques: 1) X-ray diffraction analysis (XRD), using an X'PERT PRO MPD (PW 3040/60) from Panalytical, CuK α (K α_1 = 1.54060 Å) radiation, Ni β filter, 4°-75° (2 θ), step size of 0.017° (2 θ), time/step of 20 s, voltage of 40 kV and slit width of 1/4°; 2) chemical analysis by X-ray fluorescence spectrometry (XRF) using an Axios Minerals WDS, Panalytical spectrometer; 3) particle size distribution (PSD) using an Analysette 22 MicroTec Plus, from Fritsch; and 4) scanning electron microscopy (SEM) analysis in an LEO 1430 Zeiss equipment.

Table I - Final equations of the shrinking core model for spherical and flat plate particles with constant size.

[Tabela I - Equações finais do modelo 'shrinking core model' para partículas esféricas e placa plana.]

Morphology	Equations ^a
Flat plate	$\frac{t}{\tau} = X_B$; $\tau = \frac{\rho_B L}{bk_s C_{Af}}$
Sphere	$\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$; $\tau = \frac{\rho_B R}{bk_s C_{Af}}$

^a - (t) time, (τ) time for complete conversion, (X) conversion, (ρ) molar density, (R) particle radius, (b) alumina stoichiometric, (k) rate constant, (C) reagent concentration, (L) length of the largest particle.

The shrinking core model (SCM) was used in the kinetic study for spherical and flat plate particles with constant size (heterogeneous reaction). The activation energy was calculated using the Arrhenius equation [13, 21-23]. Table I shows the equations used.

RESULTS AND DISCUSSION

Material characterization: Fig. 1 shows the XRD patterns of kaolin for MK700 and MKA700. Kaolinite was predominant in kaolin, but small amounts of anatase were observed. MK700 and MKA700 were both shown to be in amorphous phase. Table II shows the chemical composition of these materials. The micromorphological analysis showed that the kaolin was composed of pseudo-hexagonal plates, which is typical of kaolinite. This micromorphological aspect remained even after the calcination and leaching processes which can be seen in Fig. 2 [24]. Concerning the PSD analysis (Fig. 3), the kaolin showed an average particle size (D_{50}) of 3 μ m. Calcination and leaching did not promote significant changes in the particle size, with D_{50} of 4.1 μ m and 4.9 μ m for MK700 and MKA700, respectively.

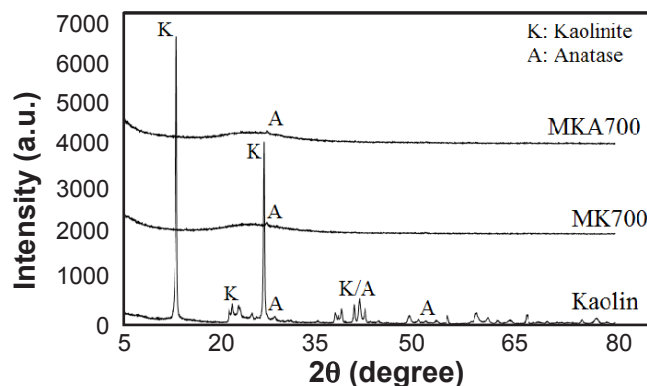


Figure 1: X-ray diffraction patterns of kaolin, MK700 and MKA700.

[Figura 1: Difratogramas de raios X do caulim, MK700 e MKA700.]

Acid leaching: the fractional conversions obtained from the leachings are shown in Fig. 4. The final conversion values obtained were as follow: 95.9% at 95 °C, 79.9% at 80 °C and 44.6% at 70 °C for MK700 and 4.5% at 95 °C for non-calcinated kaolin.

Kinetic study: the shrinking core model (SCM) was applied for spherical and flat plate particles with constant size with the chemical reaction as a determining step. The results found were similar (Fig. 5, Table III). Differences between the rate constant can be attributed to the changes in the reaction area considered. The reaction was of the first-order with respect to aluminum from metakaolin and had an activation energy of 91.58 and 91.78 kJ/mol for spherical and flat plate particles, respectively. The spherical morphology showed a better fit with regression coefficients very close to 1. Therefore, the results obtained for spherical particles were considered for the final analysis of this study.

Some authors carried out metakaolin leachings with nitric

Table II - Chemical composition of samples - major oxides (mass %).

[Tabela II - Composição química das amostras - principais óxidos (% em massa).]

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	TiO ₂	LOI ^a
Kaolin	45.96	38.50	0.53	0.22	0.42	14.29
MK700	52.99	44.63	0.56	0.34	0.50	0.98
MKA700	78.52	1.92	0.41	0.02	0.81	18.30

^a - loss on ignition.

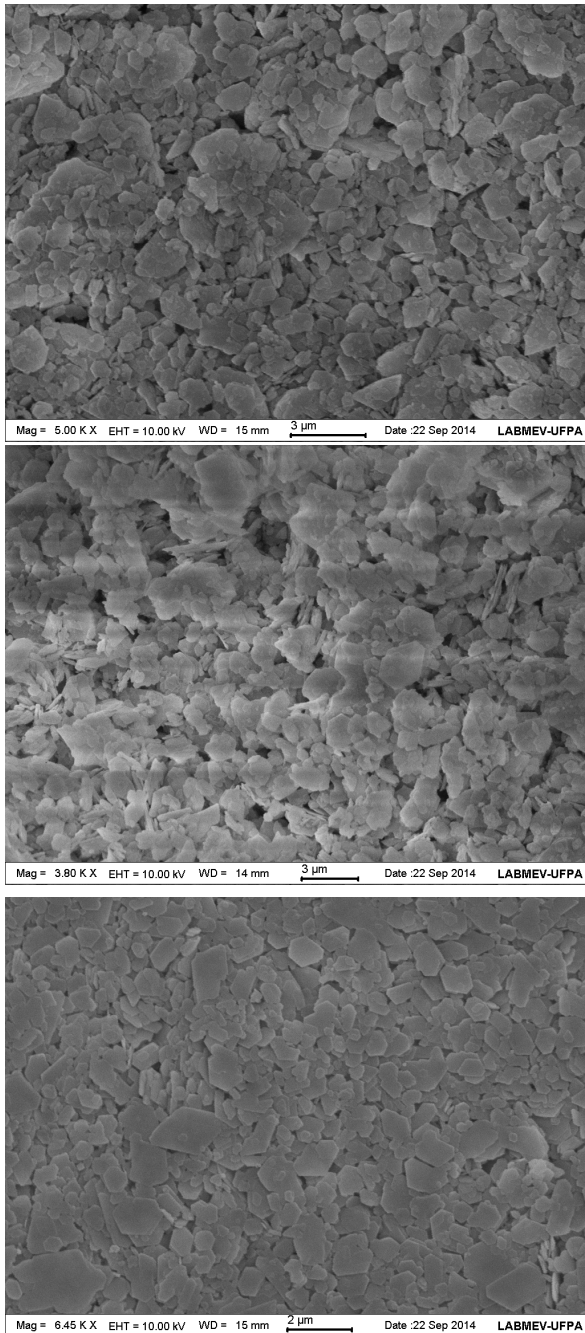


Figure 2: SEM micrographs of kaolin (A), MK700 (B), and MKA700 (C).

[Figura 2: Micrografias obtidas por microscopia eletrônica de varredura do caulim (A), MK700 (B) e MKA700 (C).]

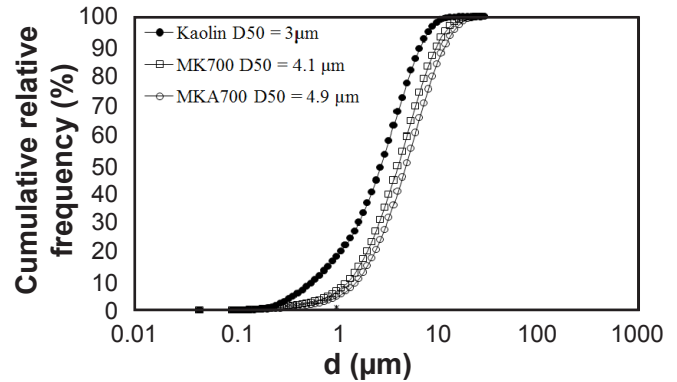


Figure 3: PSD curves of kaolin (non-calcinated), MK700 and MKA700 (d: particle size, D50: average particle size).

[Figura 3: Curvas de distribuição de tamanho de partícula do caulim (não calcinado), MK700 e MKA700 (d: diâmetro de partícula, D50: diâmetro médio de partícula).]

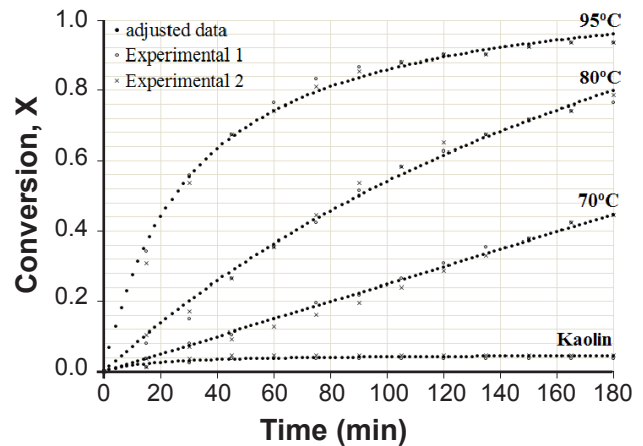


Figure 4: Fractional conversions (X) of leachings with HNO₃ at 95, 80 and 70 °C for MK700 and at 95 °C for kaolin (non-calcinated).

[Figura 4: Conversão fracional (X) das lixiviações com HNO₃ a 95, 80 e 70 °C para o MK700 e a 95 °C para o caulim (não calcinado).]

acid. Hulbert and Huff [10] studied the kinetics of alumina removal from a calcinated kaolin with nitric, sulphuric and hydrochloric acids (excess above 90%). A nucleation model was applied and concluded that the reaction with respect to aluminum was of the first order and had an activation energy of 108.68 kJ/mol. Ajemba and Onukwuli [12] investigated the dissolution kinetics and mechanisms of reaction of Udi clay in a nitric acid solution (excess above 90%). The clay was calcinated at 700 °C and showed extractable alumina concentrations of 26.5% with a high concentration of Fe₂O₃ (18.45%) and the presence of interferents such as K₂O, SO₃, MgO and others. The leachings were carried out at temperatures between 30-70 °C with maximum extraction being less than 70% at 70 °C. They concluded that it was a chemically controlled process with reaction order and activation energy of 0.31 and 21.79 kJ/mol, respectively. The activation energy found in this study (91.58 kJ/mol), carried out in nitric acid with 5% excess, was consistent with the first paper, but had a significant difference with the second

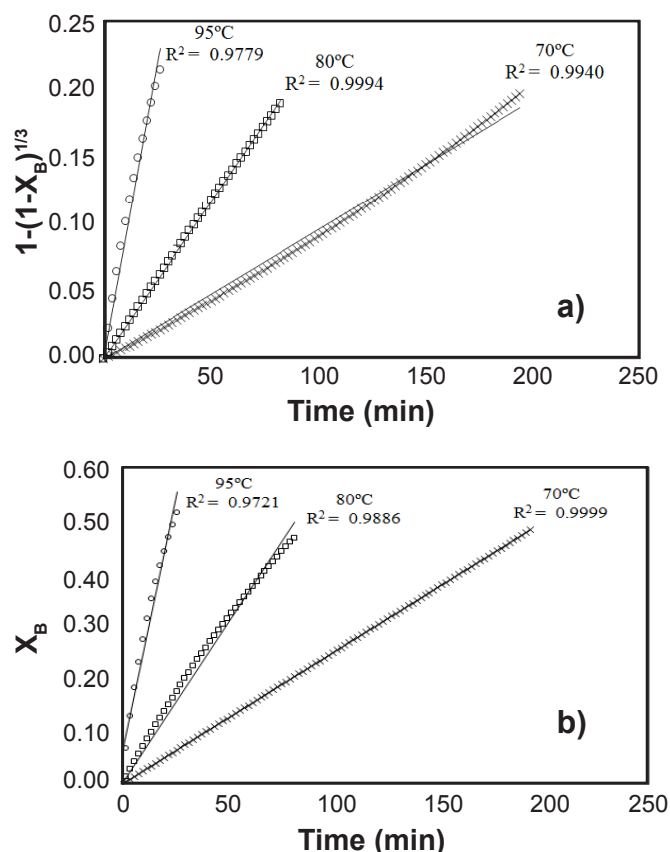


Figure 5: Regression coefficients (R^2) for: (a) spherical particle; and (b) flat plate particle (X_B : fractional conversion).

[Figura 5: Coeficientes de regressão (R^2) para: (a) partícula esférica; e (b) partícula placa plana (X_B : conversão fracional).]

paper. This difference was attributed to the starting material. The Amazon kaolin used in this work showed chemical composition not compatible with Udi clay, studied by Ajemba and Onukwuli, with low concentration of Al_2O_3 and high concentration of Fe_2O_3 . The starting material used in this study had chemical composition similar to the standard samples of kaolin (Huber CW) used in [10] (42.9% Al_2O_3 , 0.4% Fe_2O_3 and 1.8% TiO_2). In the kinetic study, the high purity gives a greater transparency because there are less errors involved. The kaolin from the Amazon region used in this study showed low concentrations of contaminants due to its sedimentary origin [8], with chemical composition close to standards samples of kaolin.

CONCLUSIONS

The results of the kinetic parameters obtained for spherical and 'flat plate' morphologies were similar. However, the regression coefficient values indicated that the spherical morphology showed a better fit. The aluminum dissolution of metakaolin in nitric acid is a chemically controlled process, is a first-order reaction with respect to aluminum and has an activation energy of 91.58 kJ/mol. The Amazon metakaolin studied in this work leached with nitric acid at 95 °C and 5% excess showed maximum aluminum extraction (95.9%). These kinetic results are consistent with studies carried out previously with compatible starting materials and acid excess above 90%.

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Table III - Results obtained with SCM for spherical and flat plate particles.^a

[Tabela III - Resultados obtidos com o SCM para partículas esférica e placa plana.^a]

T (°C)	Sphere			Flat plate		
	n	k (min ⁻¹)	Ea (kJ/mol)	n	k (min ⁻¹)	Ea (kJ/mol)
70	0.99	0.0010		1.00	0.0025	
80	1.00	0.0023	91.58	0.98	0.0060	91.78
95	0.91	0.0088		0.86	0.0222	

^a - n: reaction order; k: rate constant; Ea: activation energy.

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