Application of the Rietveld Method to Quantify Mineral Phases in a Kaolin Mineral

Ramiro G. Escudero ✉
Institute of Research in Metallurgy and Materials, Mexico

Javier A. Guillén
Superior Technologic Institute of Michoacán, México

Rosa Elena S. Pérez
Faculty of Chemical Pharmacobiology, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Michoacán, México

Abstract:

The applications of the mineral kaolin are varied, such as the ceramic industry, and the pharmaceutical industry, among others; although it is generally found in mining deposits accompanied by other mineral species considered contaminants. The above makes it necessary to apply qualitative and quantitative analysis techniques that determine the purity of the mineral, from its extraction, during its mechanical processing and kaolin recovery. In this work, a procedure for quantification of the majority species in the Kaolin mineral is proposed, according to the procedure proposed by Rietveld, from the diffractogram obtained by the x-ray diffraction technique, as well as the knowledge of the crystallographic characteristics of the mineral constituents. Three models are proposed based on the structural parameters of the phases present in the system: tridymite, cristobalite, and kaolinite. The experimental results show the total adjustment of the diffraction pattern in which it is observed that the weight percentage corresponds to 40.0% for tridymite, 39.5% for cristobalite, and 20.5% for kaolinite. These results were corroborated by specific semi-quantitative chemical analyses using scanning electron microscopy.

Keywords: *Kaolin, Kaolinite, Rietveld Method, Tridymite, Cristobalite, Crystal structure.*

Introduction

Kaolin is one of the most used minerals in the ceramic, refractory, cement, and fiberglass industries, and is also widely used in other industries such as paint, paper, pesticides, pharmaceuticals, and cosmetics (Murray, 2000). In this sense, the potential for its industrial application is very broad; Various kaolins from different regions of the world have been characterized (Leite et al., 2007). Minerals extracted from the Earth's surface frequently present high degrees of heterogeneity due to the presence of the impurities that accompany them, depending on the atmospheric and geological conditions of the region, as well as the degree of alteration of the environment from which the clay is extracted. Impurities such as hematite, limonite, ilmenite, pyrite, magnetite, and chromite are usually present (Maslennikova, Solodkii, & Solodkaya, 2004; Carty, & Sinton, 2000; Bundy, 1993).

Rietveld refinement is a technique to quantify mineral phases present in a solid sample, which fits a model to an experimental diffractogram. An initial model is needed where the crystallographic aspects of the material are specified, as well as the instrumental aspects (Rietveld, 1967; 1969; Young, 1995; Rodríguez-Carvajal, 1990; McCusker, & Von Dreele, 1999; O'Connor, & Raven, 1988; Plançon, & Zacharie, 1990; Raudsepp, & Pani, 1999). In this method, the crystal structure, and microstructure of the polycrystal are refined (Young, 1995). The Rietveld method was applied in this work, for the quantitative analysis of phases of a kaolin that corresponds to the Azufres region, Michoacán, Mexico. The powdercell® software was used in its free version, used in its full pattern adjustment mode with X-ray diffraction data obtained with CuK radiation. The mineral is representative of a certain area of the deposit.

Before the application of the refinement, the mineral was characterized by X-ray diffraction (XRD), and scanning electron microscopy (SEM) techniques. The images obtained by SEM show the morphology of the particles contained in the mineral that is the subject of this study,

and it can be seen that it is made up of fine agglomerate particles, and some others with regular geometries that range between 1, and 100 μm in size.

Quantitative Analysis by the Rietveld Method

Rietveld refinement is a technique in which a model is fitted to an experimental diffractogram. An initial model is needed where the crystallographic aspects of the material, as well as the instrumental aspects, are specified. In this method, the crystal structure and microstructure of the polycrystal are refined (Rodríguez-Carvajal, 1990).

In the present work, 3 model structures were used for the crystalline phases to be investigated (cristobalite, tridymite, and kaolinite), and computer simulation of their respective diffraction patterns. Figure 1 shows the simulation of the cristobalite structure and its respective diffraction pattern using the powdercell® software.
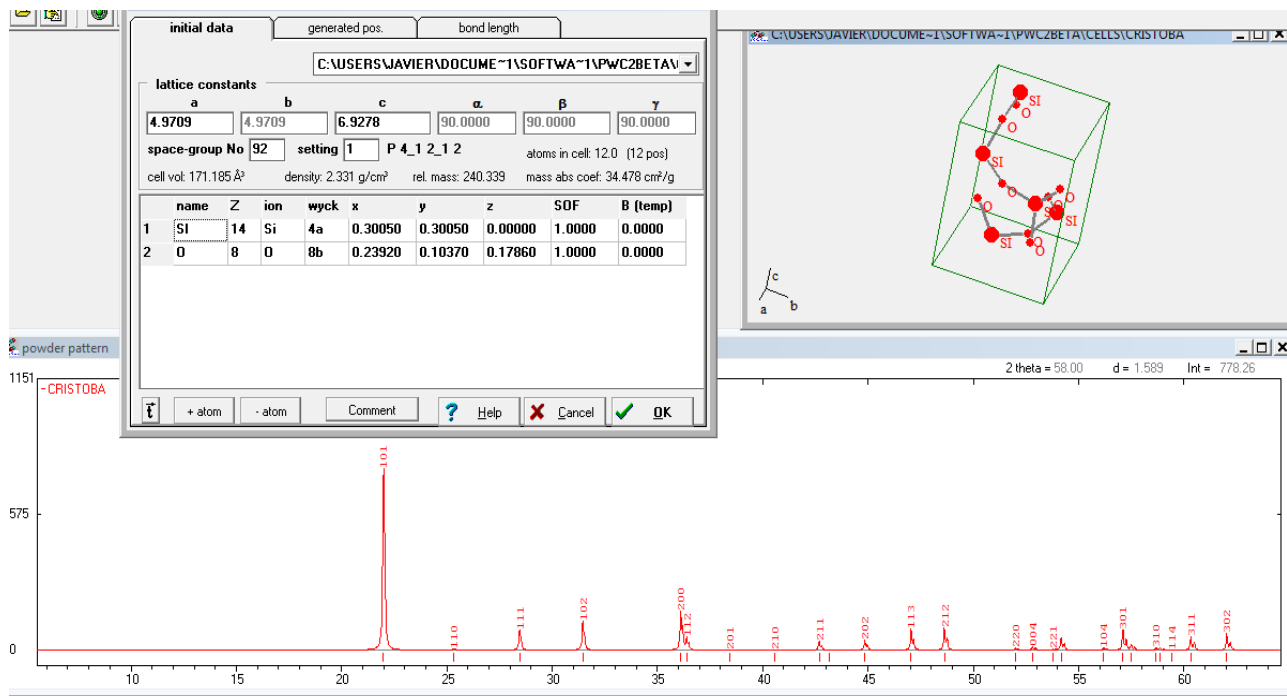

Figure 1. The Structure of Cristobalite was Simulated Using Powdercell® Software

The Rietveld Refinement, developed in 1967 by Hugo Rietveld, is a method of adjusting the diffraction pattern of a polycrystal. This refinement requires measuring the experimental intensity (Y_i) that is obtained from point-to-point measurements where the increments between said points depend on the type of diffraction experiment performed, such as time of flight, angular dependence, and energy parameters (McCusker, & Von Dreele, 1999; O'Connor, & Raven, 1988; Plançon, & Zacharie, 1990; Raudsepp, & Pani, 1999). The refinement or approximation, by least squares, is carried out once the best fit between experimental, and calculated data is obtained. The minimized quantity is defined by the following expression (Plançon, & Zacharie, 1990; Raudsepp, & Pani, 1999):

$$S_{y=\sum_i w_i}(Y_i - Y_{ci})^2 \qquad (1)$$

Where S_y is the so-called "residue"; Y_i is the experimental intensity of the diffraction pattern; Y_{ci} is the intensity calculated according to a model of the polycrystal and involving parameters of the diffraction experiment; W_i is a weight factor in the minimization, which is considered equal to $1/Y_i$.

The calculated intensity is obtained by adding the contributions of the Bragg reflections, for all phases j, plus the background Y_{bi}, based on the formula for the intensity in the powder method:

$$y_{ci} = s \sum_K L_k |F_k|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_{bi} \qquad (2)$$

Where S is the scale factor; K represents Miller indices; L_K contains Lorentz factors, polarization, and multiplicity; f is the reflection profile function; P_K is the Preference Orientation Model; A is the Absorption Factor; F_k the structure factor; Y_{bi} is the Intensity of the background at the ith point.

The fit of the model for the calculation of the observed data is expressed numerically according to the indices or R values. The R_{wp} value of the weighted profile is defined as:

$$R_{wp} = 100 \sqrt{\frac{\sum_i w_i(y_i^{obs} - y_i^{cal})^2}{\sum_i w_i(y_i^{obs})^2}} \qquad (3)$$

For good refinement, the final R_{wp} should be similar to the expected R_{exp} value:

$$R_{exp} = 100 \sqrt{\frac{(N-P+C)}{\sum_i w_i(y_i^{obs})^2}} \qquad (4)$$

Where N is the total number of points used, P is the number of refined parameters, and C is the number of constraints. Typical R_{wp} values range from very good percentages of 15-30%, depending on the data collection time count used, the degree of targeting preferred, and the number of parameters refined. The weight fraction W_i of each phase can be calculated with the scale factor, according to the following expression:

$$W_i = \frac{S_i(ZMV)_i/\tau_i}{\sum_i S_i(ZMV)_i/\tau_i} \qquad (5)$$

Where W_i is the overall sum of the phases, S_i is the scale factor, Z_i is the number of molecules per unit cell, M_i is the molecular weight, V_i cell is the unit volume, and Brindley is the particle absorption contrast (Raudsepp, & Pani, 1999).

Methodology

The mineral samples obtained from different points of the deposit, covering an average of 10,000 m², were analyzed using XRD. The samples were characterized in a SIEMENS D5000 Diffractometer, in continuous analysis

mode using Cu Kα radiation, with an increment of 0.02°, and a counting time of 2 s/step, and an angular range of 10 to 75 in the position 2θ. Three structure models were used for the crystalline phases to be investigated (cristobalite, tridymite, and kaolinite), and computer simulation of their respective diffraction patterns. Observations with scanning electron microscopy (SEM) were carried out on a JEOL JSM-6400 equipment, equipped with a microanalysis system (EDS). Which was used for microanalysis in kaolin samples. 40 mappings were carried out in various fields of the sample, taking care of good distribution, and homogeneity of the particles. The samples were prepared at different concentrations: 0.5, 0.75 and 1%, of deionized water, and sodium silicate, to guarantee the dispersion of the particles. A drop of the suspension was taken from each solution and placed in a brass sample holder, subsequently dried and metalized.

Results and discussion

R-ray Diffraction (XRD)

The XRD spectra of the head mineral exhibit the presence of three crystalline phases for the mineral: cristobalite (SiO_2, tetragonal crystal system), kaolinite ($Al_2Si_2O_5(OH)_4$), and tridymite (SiO_2, triclinic crystal system). The indexed phases belong to cristobalite with the card number (JCPDS 01-0750923), tridymite (JCPDS 01-0860681), and in smaller proportions to kaolinite (JCPDS 01-010782110).
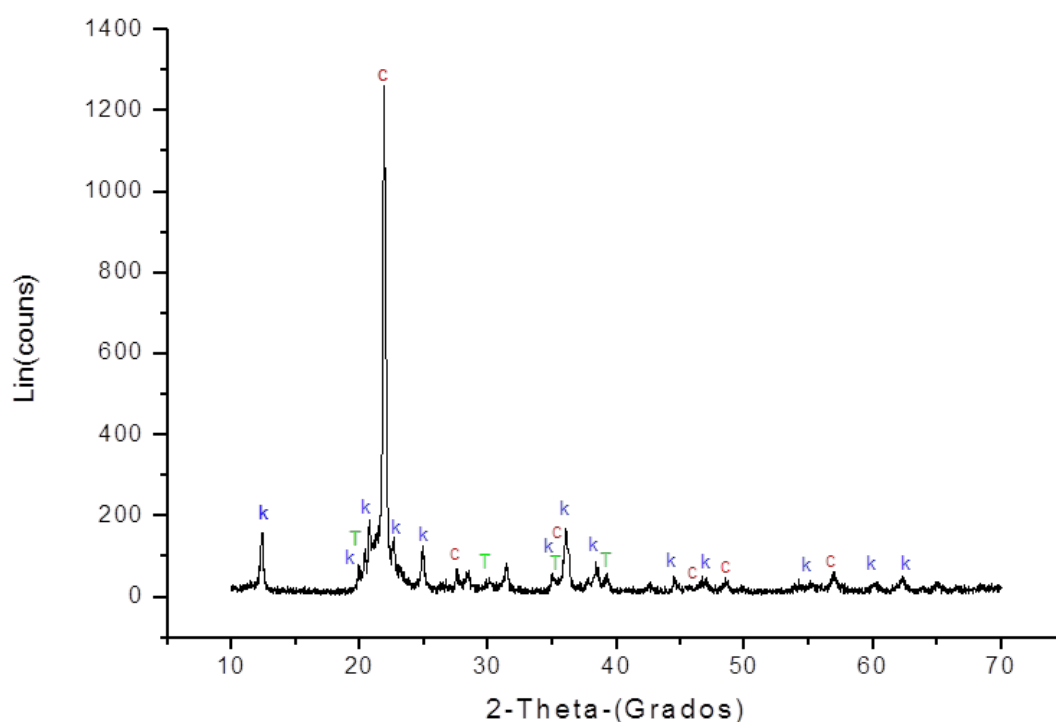

Figure 2. X-Ray Diffraction Diffractogram of Kaolin Head Mineral. Kaolinite is Represented by the Letter (k), Tridymite by (t), and Cristobalite by (c)

Quantitative Analysis of the Present Phases

The total fit of the diffraction pattern is shown in Figure 3; it is observed that the percentage by weight (w/w) corresponds to 40% for tridymite, 39.5% for cristobalite, and 20.5% for kaolinite.

Morphology and Distribution of Elements Using SEM

Figure 4 shows the images obtained by Scanning Electron Microscopy, showing the morphology of the particles contained in the kaolin mineral.

It is observed that the mineral is made up of fine agglomerate particles, with irregular geometries that range between 1, and 100 μm. In Figures 4a, and 4b the crystalline phases cristobalite, and tridymite are identified; while Figures 4c, and 4d show the fine agglomerates containing the clay mineral kaolinite and the corresponding point analysis that identifies Al, Si, and O.
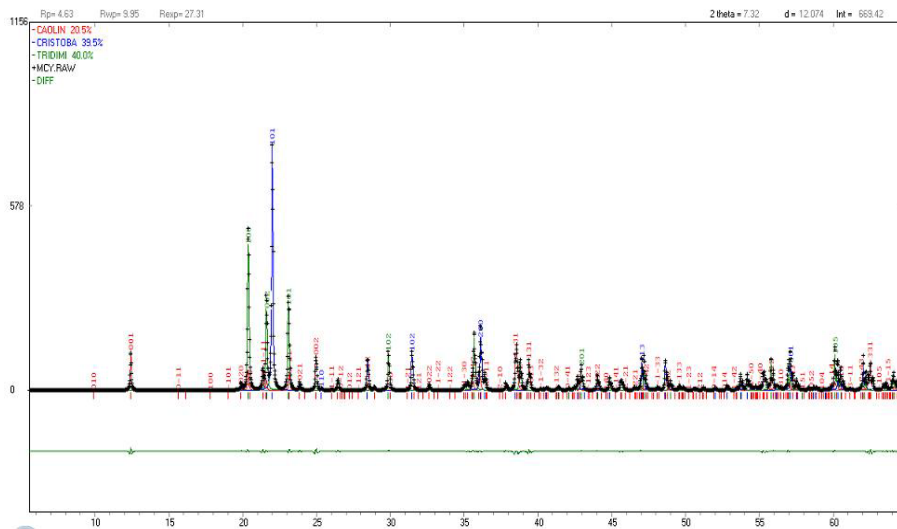

Figure 3. Rietveld Refinement Graph. Experimental (Dotted Line) and Calculated (Solid Line) Diffraction Pattern, (Rwp = 9.95, Rexp = 27.31).
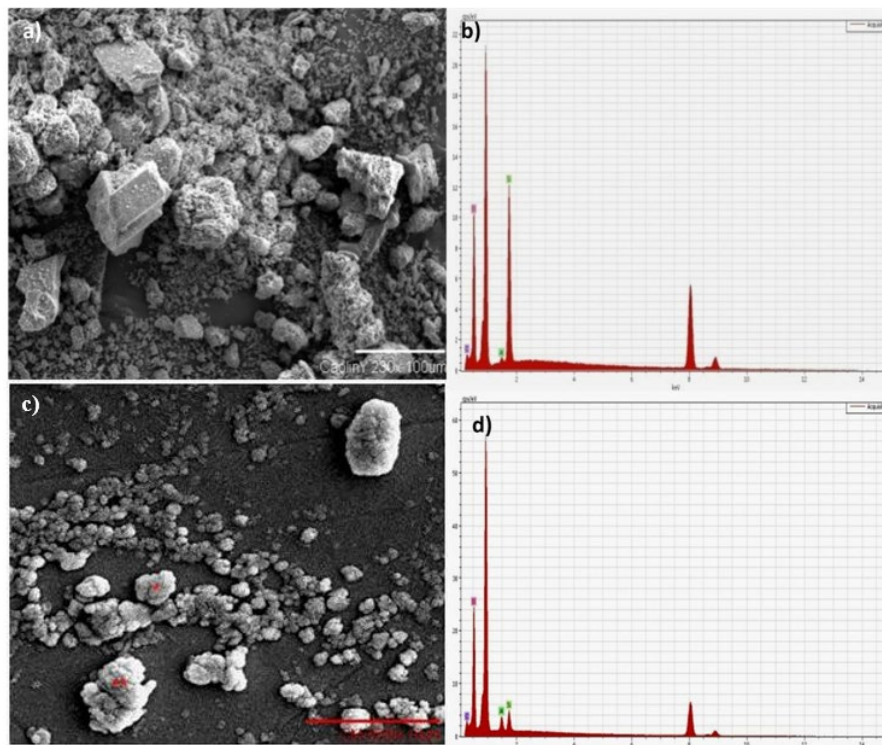

Figure 4. Kaolin Morphology of the Deposit. a) Particles of Fine Agglomerates, and Particles with Regular Geometries, b) Microanalysis of a Particle with Regular Geometry, c) Particles of Fine Agglomerates, and d) Microanalysis of the Agglomerates

Conclusions

From the study of characterization, identification, and quantification of mineral phases of a kaolin mineral by the Rietveld method, the following conclusions are derived:

The methodology applied in the preparation of kaolin effectively reveals the shape, and size of the particles of kaolinite, cristobalite, and tridymite. The quantitative analysis by the Rietveld method indicates that there are high contents of tridymite at 40%, cristobalite at 39.5%, and minor associations of kaolinite at 20%, in the mineral from the deposit which is the reason for this study.

Acknowledgments

Conflict of Interest

The authors declare that there is no conflict of interest.

References

Bundy, W.M. (1993) The diverse industrial applications of kaolin. In Murray, H.H., Bundy, W., & Harvey, C. (eds). *Kaolin Genesis and Utilization*. Clay Mineral Society, Special Publication 1, Boulder, Colorado, USA.

Carty, W.M. & Sinton, C.W. (eds.). (2000). *Science of Whitewares II*. American Ceramic Society, Westerville, Ohio.

Leite, J.Y., Veras, M., Santos, E., Souza, R., Paulo, J. & Pinheiro, M. (2007). Technological characterization of kaolin tailing from small-scale mining in RN and PB states – Brazil. *Minerals Engineering, 20,* 959-961. http://dx.doi.org/10.1016/j.mineng.2007.03.006

Maslennikova, G.M., Solodkii, N.F. & Solodkaya, M.N. (2004). Use of Kaolins from Different Deposits in the Production of Fine Ceramics. *Glass and Ceramics, 61*(7-8).

McCusker, L.B., & Von Dreele, R.B. (1999). Rietveld refinement guidelines. *Journal of Applied Crystallography, 32,* 36-50. https://doi.org/10.1107/S0021889898009856

Murray, H.H. (2000) Traditional and New Applications for Kaolin, Smectite, and Palygorskite: A General Overview. *Applied Clay Science, 17,* 207-221. http://dx.doi.org/10.1016/S0169-1317(00)00016-8

O'Connor, B.H. & Raven, M.D. (1988). Application of the Rietveld refinement procedure in assaying powder mixtures. *Powder Diffraction, 3,* 2-6. https://doi.org/10.1017/S0885715600013026

Plançon, A. & Zacharie, C. (1990). An expert system for the structural characterization of kaolinites. *Clay Minerals, 25,* 249-260. https://doi.org/10.1180/claymin.1990.025.3.01

Raudsepp, M. & Pani, E. (1999). Measuring mineral abundance in skarn. I. Rietveld method using X-ray powder-diffraction data. *Canadian Mineralogist, 37*, 1-15.

Rietveld, H.M. (1967) Line Profiles of Neutron Powder-Diffraction Peaks for Structure Refinement. *Acta Crystallographica, 22,* 151-152. http://dx.doi.org/10.1107/s03651108x67000234

Rietveld, H.M. (1969) A Profile Refinement Method for Nuclear and Magnetic Structures. *Journal of Applied Crystallography, 2,* 65-71. http://dx.doi.org/10.1107/S0021889869006558

Rodríguez-Carvajal, J. (1990). *FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis.* Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Abstracts.

Young, R.A. (ed.). (1995). The Rietveld Method. *IUCr Monographs on Crystallography,* vol. 5. Oxford University Press.