POTENTIAL OF ILMENITE AS A SOLAR ABSORBER

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ABSTRACT

Titanium is considered the fourth most widely used material in industry worldwide. Titanium minerals are currently being applied in various branches of industry, mainly in the field of pigmentation. Ilmenite (FeTiO3) is an iron and titanium oxide of more common and abundant occurrence, with theoretical composition of Fe (36.8%), Ti (31.6%) and O (31.6%). Having regard to the potential of titanium minerals and the abundance of ilmenite, together with the importance of validating direct applications of this ore, since the processing of titanium is still complex and expensive, it is necessary to study this mineral and the knowledge of its main characteristics. This work brings thermal, chemical and mineralogical characterizations of ilmenite, in order to know the potential of application of this ore as a solar absorbing material. The characterization techniques used were: X-ray diffraction (XRD) and Rietveld refinement for phase quantification, X-ray fluorescence (XRF), optical spectroscopy in the middle infrared region with Fourier Transformation by Transmittance (FTIR) and thermogravimetric thermal analysis (TGA). The analyzed sample obtained X-ray diffractogram, ilmenite (80.6%) and rutile (19.4%) as significant phases, corroborating the FRX results that indicated greater presence of Fe and titanium oxide in the ilmenite chemical composition under study. The TGA, DTA and DSC analyses indicated good thermal stability of the material in medium and high temperatures. The integration of the obtained data shows that the application of this ore as a precursor material of absorber films for selective purposes is considerable.

Keywords*:* ilmenite; characterization; x-ray diffraction; solar absorber

NOMENCLATURE

Subscripts

FRX X-Ray Fluorescense
ICSD The Inorganic Crystal Structure Database
TGA Thermal Analyses
UV-Vis-NIR ultraviolet, visible and near infrared range of the electromagnetic spectrum

INTRODUCTION

Most of the energy used by humanity comes from fossil fuels, and the use of such energies, on a large scale, has considerably changed the environmental conditions of the planet. The study of renewable sources of energy has become extremely relevant ahead of the growing world demand for energy (Medeiros et al., 2017). Among these sources, solar energy stands out. One of its forms of exploitation is using solar collectors, which promote the conversion of solar energy into thermal energy (Cao et al., 2014). According to Kennedy (2002) the efficiency of these collectors is compromised due to a large loss from the emission of thermal radiation, resulting in operating temperatures below 100ºC and limiting their applicability. An effective method to increase the performance of a collector is incorporate a selective (spectral) wavelength surface for the absorber. The selective surfaces absorb the maximum possible radiation in the ultraviolet, visible and near infrared (UV-Vis-NIR) range of the electromagnetic spectrum, while emitting little in the medium and distant infrared region, that is, they have absorption above 85% and emission below 15% in the mentioned wavelength bands (Xiao et al., 2011).

One of the variables that must be considered, when it is intended to improve efficiency and minimize the costs of a thermal conversion system in collectors, is the choice of selective material. Ilmenite ($FeTiO_3$) is a common and abundant iron and titanium oxide in the world. With theoretical composition of Fe (36.8%), Ti (31.6%) and O (31.6%), ilmenite is a typically opaque mineral, characterized by conducting bands of iron and titanium oxides that extend across the spectrum (Rodbari et al., 2015). This crystalline structure was previously studied by Barth and Posnjak (1934) and gained high scientific interest over the years, both for its mineralogical importance and for its technological applications around pigmentation and photocalizers.

In view of the great abundance of the ilmenite mineral, added to the fact that the production of pure metallic titanium implies the use of sophisticated chemical processes and high cost, there is a need to develop research in order to increase the applications of minerals derivatives of that metal. The goal of this work is to evaluate the potential of ilmenite as a selective surface of solar thermal collectors on the basis of thermal, chemical and mineralogical characterizations of ilmenite.

EXPERIMENTS

Preparation of the samples

Ilmenite was supplied by an industry located on the Northeast coast of Brazil, in the city of Mataraca, where ilmenite occurs disseminated in coastal dunes. For experimental techniques, ilmenite was used in two configurations: in natura (original state of industrial processing) and after being sieved (53 microns), according to Medeiros (2018).

The samples were sintered in two methodologies: A (The samples were submitted to a temperature of 900ºC at a rate of 5ºC per minute) and B (The samples reached a temperature of 500ºC at a rate of 20ºC per minute and then reached the level of 900ºC at a rate of 10ºC per minute). Table 1 presents the sample nomenclature.

Table 1. Nomenclature of the samples.

Samples	Processing	Sinter
Sample 1	Sieve - 53μm	B
Sample 2	Sieve - 53μm	A
Sample 3	*In natura*	A
Sample 4	*In natura*	B

Characterization of ilmenite

To validate a new material in a specific application, a better understanding of the physical, chemical and mineralogical properties of this material is required. Chemical investigation by FRX made it possible to determine the chemical elements present in the ore as well as its most stable oxides using the Sequential X-Ray Fluorescense Spectrometer, Shimadzu XRF-1800 model.

The crystalline structure and identity of phases of ilmenite were studied by X-Ray diffraction using a diffractometer D2 Phaser Bruker, Cu – Kα radiation, with tension and current of 30 kV and 10 mA, respectively. The tests were performed with a 2θ scan between 10˚ and 75˚ with a 0.02˚/s pitch and a 1 mm gap, in accordance with recommendations by Rodbari et al. (2015). The diffractograms generated in the test and the quantitative analysis of the crystalline phases were analyzed using Bruker AXS software.

Transmittance analyzed in the infrared region were performed with a Shimadzu spectrophotometer IR Prestige-21 model for microstructural characterization of the ilmenite, highlighting its main vibrational bands in the suggested wavelength range. The experiments were carried out in the range between 4000 and 400 cm-1, with a resolution of 4 cm-1 and 20 accumulations.

Thermal analyses were performed on the samples *in natura* and sieve. Given the importance of predicting the behaviour of the selective surface as a function of temperature, the purpose of this test is to determine the loss of mass and the thermal stability of the ilmenite. The equipment used was a TA Instruments SDT 650, performing the analysis of Thermogravimetric Analysis (TGA). The analysis was up to 1000ºC with heating rate of 20ºC/min in argon atmosphere (100 $ml.min^{-1}$) using Platinum crucible.

RESULTS AND DISCUSSION

Table 2 shows composition of the most stable oxides present in the ilmenite under study, found in the X-ray fluorescence analyzes. Most of the iron and titanium oxides is noted. The differences between the compounds in the sample and the impurities contained in the mineral itself are related to the mineral origin of the ilmenite.

Table 2. Most stable oxides found in ilmenite.

Oxides	% atomic weight
TiO_2	49,92
Fe_2O_3	42,08
Al_2O_3	2,90
SiO_2	2,38
ZrO_2	0,31
Na_2O	0,30
NbO	0,17
Others	0,47

The analysis by X-ray diffraction show that is in mineral chemical constitution, the main phases found in the compound are ilmenite ($FeTiO_3$), followed by some peaks of Rutile (TiO_2). Using Bruker AXS software, it was possible to perform the refinement to estimate in percentage terms the quantification of the phases in the analyzed sample. Promptly, the highest concentration in this sample is 86.4% ilmenite and 13.6% rutile. The ICSD code of the letters found in the software for the ilmenite and rutile phases were 029209 and 039167, respectively. The refined X-ray diffractometry spectrum of the ilmenite sample, with $FeTiO_3$ structural formula is shown in Figure 1.

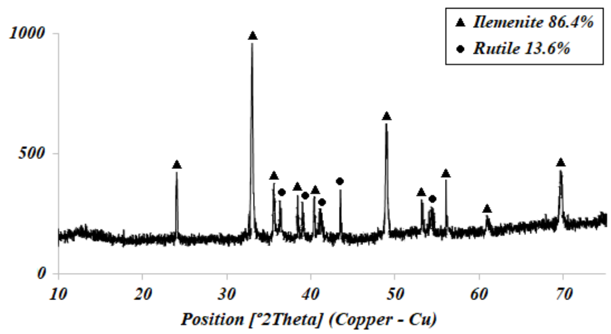

Figure 1. X-ray diffractometry spectrum refined by Bruker AXS software

The identification of a sample through its infrared spectrum is observed in the inspection of the vibration modes of the molecules. In this spectrum, the absorption band at 3440 cm^{-1} is related to the stretching vibration mode of the hydroxyl groups, hydrogen bonds and chemically adsorbed water. The band around 2922 cm^{-1} indicates the presence of quartz in the ilmenite ore, which is understood by the presence of silicon dioxide, SiO_2, in the chemical composition found by FRX. We can also notice the presence of a band close to 1035 cm^{-1}, which is characteristic of the O - Ti - O bond, confirming the formation of titanium oxide, TiO_2. The absorption band at 530 cm^{-1} can be attributed to the Fe-O bond in the ilmenite ($FeTiO_3$) which indicates the formation of Fe_2O_3. These bands could be seen in the Figure 2.

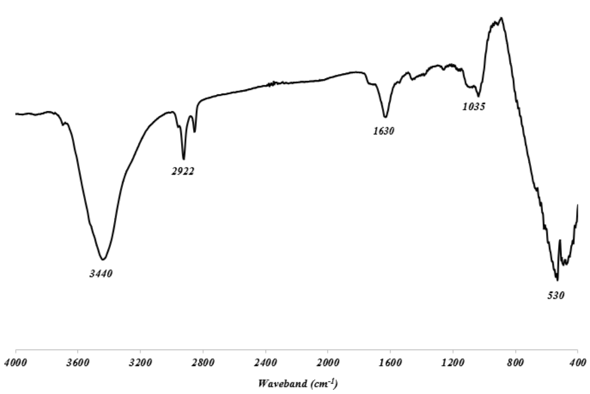

Figure 2. Ilmenite Infrared Spectrum in Transmittance Mode

The thermal analyses were performed in order to evaluate the influence of temperature on the material mass loss. Since selective surfaces are produced for high working temperatures, the thermal behavior analysis of the ilmenite can warn about the thermal stability at the collector outlet. Figure 3 shows the thermal behavior of the sample of ilmenite sieved and in natura.

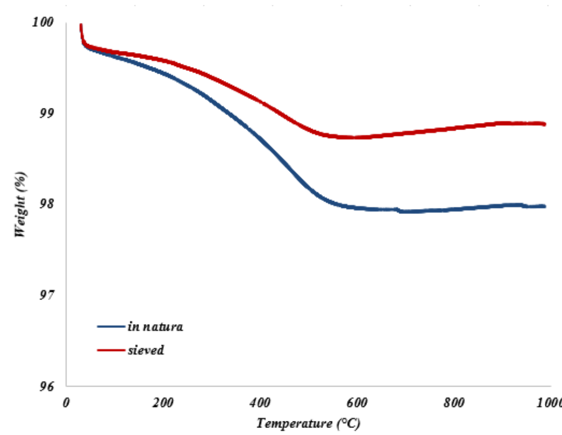

Figure 3. Thermal behaviour of ilmenite

In natura ilmenite suffered a greater loss of mass and has lower thermal stability when compared with sieved ilmenite. The loss of mass in the range of 25-50ºC is associated with the endothermic event related to the evaporation of remaining water. It is also noticeable, a mass gain (more pronounced in the sieved sample) recurrent of the iron chemical transformations.

The total mass loss, in the range of 25-1000ºC, for sieved ilmenite was 1.3%, while ilmenite *in natura*, in the same heating interval, obtained a total mass loss of 2.1%. It is noticed that a greater control of the material granulometry contributes to minimize the mass loss in medium and high temperatures, influencing the thermal stability of absorber films produced with this material.

CONCLUSIONS

The studied ilmenite presented in it composition the majority presence of iron and titanium in the solid product, which have good absorptive property.

A greater amount of the ilmenite phase and a smaller number of significant phases in the compound were observed, being 86.4% for the ilmenite phase and 13.6% for the rutile. It can be stated, then, that the compound has few recurring impurities of it mineral origin.

Greater control of the material's particle size contributed to reducing mass loss at medium and high temperatures, influencing the thermal stability of absorber films produced with this material.

The results presented in its characterization showed that ilmenite has favorable conditions for application as absorber material for solar thermal collectors.

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