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## Microstructural Study of Some Kaolin by Warren-Averbach and Williamson-Hall Methods

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### Abstract

In this work, we have studied two kaolins from different origins. The first one denoted M1 consists of two main phases (kaolinite and halloysite) and the other M2 whose main constituents are kaolinite, quartz and mica. Using the diffraction of X rays technique, our choice was set on the component of Kaolinite because of the existence of the latter in both kaolins. Lorentz-Polarization correction was carried out on the diffraction data, which has been achieved using LWL program. The corrected profile was extracted using this program. The methods used for the micro structural analysis of the constituents in the two kaolins are those of Warren-Averbach and Williamson-Hall. Scherrer's relationship has been applied in cases where the compound is devoid of strains.

The study revealed that the Kaolinite of M1 is devoid of micro constraints, while similar analysis has shown that the Kaolinite in M2 incorporates the strains. This was confirmed by the Williamson-Hall method as well as Fourier analysis. The evaluation of strains in the kaolinite of M2 has been done by the method of Warren-Averbach and the Williamson-Hall diagram. The average value of this constraint found by the first method gave us 0.15 and 0.21 by the second method. The average size of crystallites of the Kaolinite in M1 was found to be in the range 115-145 Å using the method of Warren-Averbach and about 118 Å by the method of Williamson-Hall, while the size of crystallites in M2 was respectively 98 Å and 130 Å using the two methods. The study of the size distribution showed that the dominant size of kaolinite in M1 and M2 is about 40 Å (42%) and 58 Å (32%) respectively.

*Key words: XRD, LWL method, crystallites size, micro constraint, Williamson-Hall method, Warren-Averbach method.*

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### 1. Introduction

Ideally, the X-ray diffraction by a crystal shows diffraction peaks at corresponding angles. In reality, these peaks undergo enlargement due to crystal and diffractometer defects, namely the fine size of crystallites, constraints, etc.

By studying the widths of diffraction lines, we could derive information about the grain size and the micro strains induced. There are several methods to calculate them. We include the method of Warren-Averbach and Williamson-Hall [1-15].

Kaolins are part of the family of clays with montmorillonites, vermiculites, palygostites, etc. The main phase constituting the kaolin is kaolinite  $Al_2O_3SiO_2 \cdot 2H_2O$  or Halloysite  $Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$  with  $n \geq 4$ . Often these are ancient rocks, originally rich in Felds path; which under the influence of reducing agents such as carbon dioxide, break down into kaolin and clays.

All kaolin, formed by primary deposit contain beside hydro-silicate of alumina, kaolinite or halloysite, important debris of under composed rock and the remaining residues of the decomposition that are substantially free of quartz, mica, magnetite, titanium ores and other impurities hardly destructible.

Quality of kaolin depends on many compounds other than kaolinite which contains as well the nature and concentration of these impurities.

Often, the crude kaolin can be used directly without further processing (such as the kaolin-Djebbel Debbagh, East Algeria), but they may also be enriched with kaolinite by elimination of all or part of the impurities by granulometric methods (case of kaolin Tamazert, Eastern Algeria).

## 2. Analysis methods

There are several methods to determine the microstructural parameters from the analysis of the peaks of X-ray diffraction. The methods based on the analysis of a single diffraction peak are constructed on fairly restrictive assumptions about the shape of the peaks and the contribution of the effects of size and shape. The Warren-Averbach method requires no assumption about the shape of the diffraction peaks, and it remains the most rigorous. However, it is very sensitive to the phenomenon of truncation profile and an overestimation of background noise. This method can lead to an error of 20-30% on the determination of the Fourier coefficients and hence the microstructural parameters [13]. We have used this method in addition to one that is the Williamson-Hall [6] which is used in case of presence of microstrain in the crystallites.

### Evaluation of size

To evaluate the average crystallite size in the case of micro-strains absence in the samples, several methods are used.

Scherrer has shown that the crystallite size in the sample (where the latter does not contain micro-strains) varies inversely with the width of the diffraction line. The relationship between these two variables is given by:

$$D^f = \frac{C\lambda}{\beta \cos \theta} \quad [1] \quad \text{Widths expressed in } 2\theta$$

$C$  is a coefficient which depends on the shape of the crystallites [12] and can assume values between 0.8 and 1.39. For spherical particles, it is generally equal to 1.

We have used the relationship  $D^f = \frac{1}{\beta^*}$  for widths expressed as reciprocal units, where:

$\theta$ : Bragg angle,

$D^f$ : mean size grains,

$\lambda$  : Wave length

$\beta^*$ : is the integral width characterizing enlargement, expressed as the reciprocal lattice.

The method of Williamson-Hall is to plot a graph showing the change of  $\beta^*$  as a function of the reciprocal variable  $d^*$ . This graph, being a straight line, gives indications of the presence or absence of micro-strains in the sample. The slope of the line indicates the presence of the latter (Figure 1) [2-6].

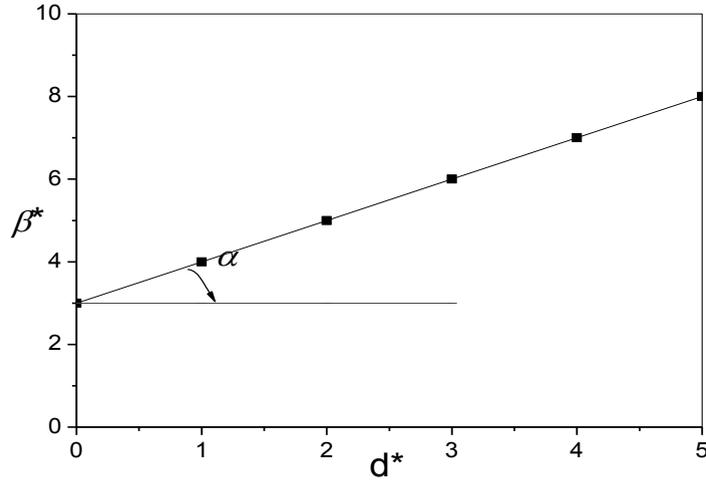


Figure 1 : *Williamson & Hall Diagram.*

$$\beta^* = D^f + d^* \quad \text{where } D^f = \beta^* \cdot d^* \text{ giving mean size grains}$$

#### Warren-Averbach Method

If the sample does not include micro-strains, their effects on the Fourier coefficient is zero, and so  $A^D(l, s) = 1$ , so  $A(l, s_n) = A^s(l)$ . The initial slope of the curve giving  $A(l, s_n)$  as function of the length  $L$  of the columns is inversely proportional to the apparent size of the crystallites in a direction perpendicular to the (hkl) considered plane (see Figure 2). This apparent size is given by B. Marinkovic et al. [3] by the following equation:

$$D_f = \left| \frac{d A(l, s_n)}{dL} \right|_{L \rightarrow 0} \quad \text{where } L = l \Delta s \text{ with } \Delta s = \lambda/2 (\sin \theta_2 - \sin \theta_1) \quad \theta_1 \text{ and } \theta_2 \text{ are the values of}$$

the limit angles that define the profile.

From Figure 2 below, the point of intersection of the initial slope of the curve with the x-axis ( $L$ ) provides the size  $D_f$ .

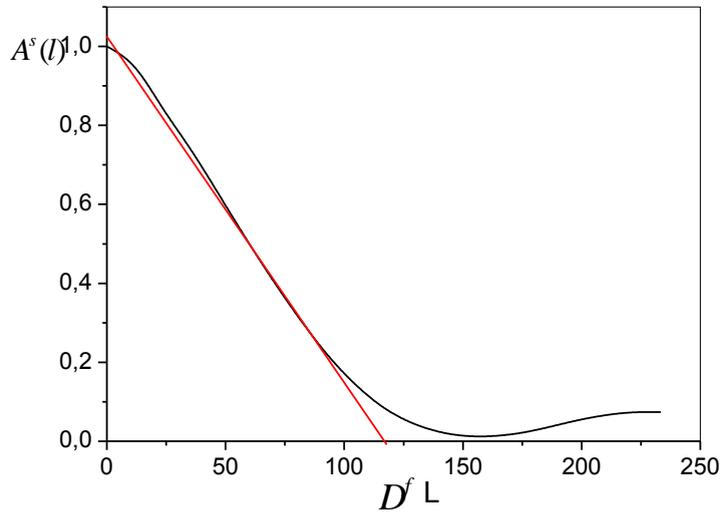


Figure 2: Fourier Coefficients of  $A^s(l)$  as function of  $L$ .

### Williamson-Hall Method

In the case of the presence of micro-strains, the following equation (Williamson-Hall) is used. It provides the average crystallite size and estimation of micro-constraints [4]:

$$\beta(\cos \theta / \lambda) = (1 / D^f) + e_l (\sin \theta / \lambda) \quad e_l \text{ is the value associated to the constraint.}$$

The diagram corresponding to this relationship (giving  $\beta^*$  depending on  $d^*$ ) is a straight line whose slope represents the average value of micro-constraints and whose intersection with the horizontal axis give the average crystallite size.

The most appropriate method for the separation of the size effect and the effect of constraint is that of Warren-Averbach. Remember that this method is based on the use of data in the form not of a single line, but several lines of the same family of planes corresponding to different levels of reflection. The profile data are expressed in terms of real coefficients of Fourier  $A(l, s)$ , and the relationship between the average value of micro-constraints and different coefficients are:

$$\ln A(l, s) = \ln A^s(l) - 2\pi^2 l^2 s^2 \langle e_l^2 \rangle \quad \text{This means: } \langle e_l^2 \rangle = \frac{\ln A(l, s_2) - \ln A(l, s_1)}{2\pi^2 (s_1 - s_2)^2 l^2}$$

The coefficients  $A^s(l)$  which result from this relationship, allow to have the average size of the crystallites. The quantity  $s$  is equal to the reciprocal variable.

### **3. EXPERIMENTAL**

We have performed X-ray diffraction recordings on kaolin using a diffractometer Siemens Advanced D8. For this, we have followed different steps. First, a grinding of the powder was made to have homogeneous grains. The powder is then deposited on the sample holder and pressed by a glass slide of plane surface avoiding to press too much on the powder in order to avoid preferential directions.

It should be noted that the sample preparation is a critical parameter for obtaining quality results because the main information obtained from diffraction data are influenced by the sample. Those are the position, intensity and shape of the lines, and the continuous background.

Data recording is carried out on a predefined angular range with a step of  $0.02^\circ$  ( $2\theta$ ) and a counting time of three seconds.

Qualitative analysis by X-ray diffraction allowed from diffracting planes, to highlight the presence in kaolin M1 of main crystal phases shown in Table 1.

Phase	(hkl)	$2\theta$
Halloysite	(010)	12.36
	(020)	29.28
Kaolinite	(200)	19.90
	(300)	35.02
	(011)	36.06
	(201)	38.54

Table 1: *Diffraction planes of the two main phases of M1.*

The same way as kaolin M1, qualitative analysis by X-ray diffraction has highlighted the presence in the kaolin M2, crystalline phases as follows (Table 2):

Phase	(hkl)	$2\theta$
Kaolinite	(100)	12.40
	(010)	19.88
	(200)	24.94
	(001)	38.52
Quartz	(201)	20.88
Quartz+Mica	(101)	26.66
Mica+kaolinite	(011)	35.00

Table 2 : *Diffraction planes de des phases présentes dans M2*

#### 4. Results and Discussion

To exploit the results, we wanted to see the effect of the application of Lorentz-polarization correction; we have chosen to make the correction on a dozen peaks of kaolins M1 and M2. We have noticed that the peaks remain almost unchanged after Lorentz-polarization correction, except for the first peak of each diffractogram which shows differences in a small part at the beginning of the peak.

Figure 3 shows the first peak (010) of kaolin M1 where we see the difference at the beginning of the peak, and another peak (200) where we see the good superposition of the corrected peak and uncorrected peak.

Similarly, the same figure shows the first diffraction peak of M2 (peak (100)) where the difference is visible in the early peak and a second peak (200) where we see the negligible effect of the Lorentz correction -Polarization.

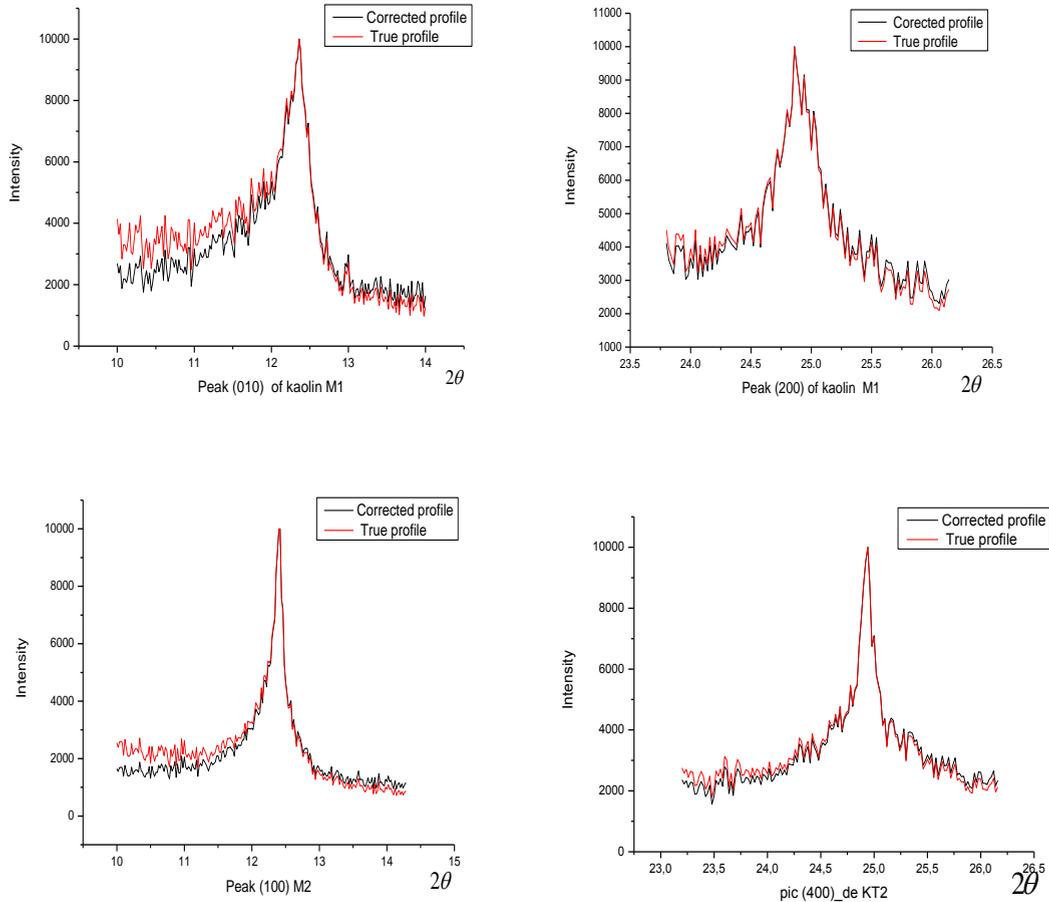


Figure 3: Lorentz-polarization correction effect on some peaks of kaolins M1 et M2

The Williamson-Hall diagram of Kaolin M1 is given in Figure 4. We represent values of  $\beta^* = \beta \cdot \cos \theta / \lambda$  as function of  $d^* = \sin \theta / \lambda$ . We note that the curve is a straight line and the slope has a value which is negative. The negative value of the slope is likely due to the accuracy of the data (obtaining diffraction data, fitting, distance from the last point on the figure 3). We infer that there are no substantial constraints in crystals of kaolinite in kaolin M1.

Figure 5 shows Williamson-Hall diagram of Kaolin M2. We notice that the curve is a straight non-zero slope indicating the existence of micro-constraints in the sample.

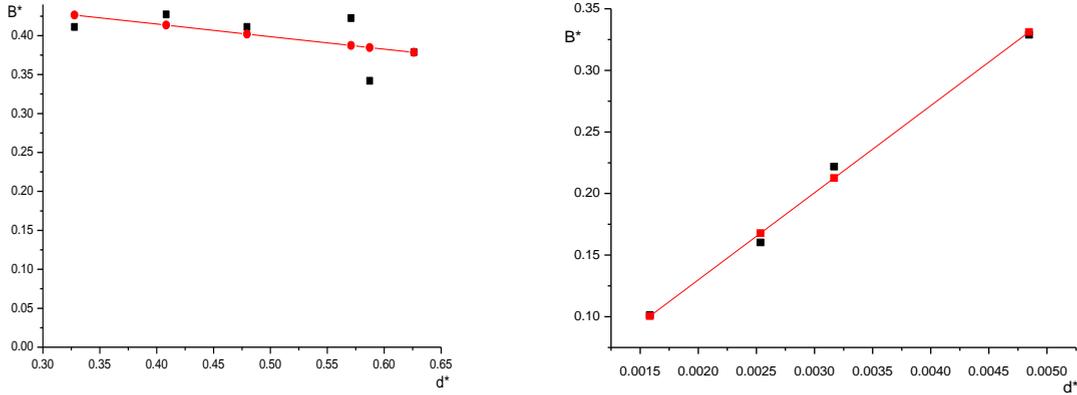


Figure 4 Williamson-Hall Diagram of kaolin M1

Figure 5 Williamson-Hall Diagram of kaolin M2

#### Size distribution in kaolinite of M1

The size distribution was estimated from the second derivative of the curve  $A^{\circ}(l)$  as a function of harmonic number L. We have used a second degree polynomial for the calculations. We give in Table 3 only the most common sizes (dominant sizes).

Peaks	Dominant size (Å)
(200)	32
(300)	35
(011)	40
(201)	42

Table 3: Dominant size of the main phase of kaolin M1.

#### Size distribution in kaolinite of M2

For Kaolin M2 and to apply Warren-Averbach method, we have used the two peaks of planes (100) and (200). These two peaks having the same orientation, only the first was used to assess the size and, therefore, to determine the size distribution. This distribution is given for the dominant size value of 52 Å.

We are also interested in the microstructure of the phase kaolinite, kaolin common component of M1 and M2.

Determining the size and micro-constraints of kaolinite was carried out by the method of Warren-Averbach and Williamson-Hall. In the case lends itself and in order to confirm the results, we have applied the simple formula of Scherrer.

The microstructural analysis of kaolinite of kaolin M1, with both Williamson-Hall method and with Fourier analysis showed the absence of constraints.

In kaolin M1 crystallite size of kaolinite phase was found between 29 and 230 Å (average size 111 Å) by the Warren-Averbach method and between 115 and 145 Å by the Scherrer relationship (average size 125 Å). The average value found from the Williamson-Hall diagram is 118 Å.

For kaolinite of kaolin M2, the Williamson-Hall method and Fourier analysis have both revealed the presence of micro-constraints. The average value of micro-constraints by the Warren-Averbach method is  $\langle e_l \rangle = 0.15$ . The value obtained from the Williamson-Hall diagram is about,  $\langle e_l \rangle = 0.21$ .

Crystallites of kaolinite M2, according to results from the Williamson-Hall diagram, have a size of 130 Å. According to Warren-Averbach, this size is an average of 92 Å.

We have calculated the size distribution of kaolinite in kaolin M1. The value found for the dominant size is 40 Å. The distribution corresponding to this dominant size is of the order of 42%.

The study of the size distribution of kaolinite in kaolin M2 gave an average value of 58 Å for the dominant size; it has a distribution of about 32% [14].

## 5. Conclusion

In this work, we have studied the Kaolin M1 and M2 by the X-ray diffraction method, and we have focused on kaolinite phase which is the main phase present in common in both products. The method of Warren-Averbach and those of Hall-Williamson were both used for determining the size of the crystallites.

The Lorentz-polarization correction was performed prior to the diffraction data. This was achieved through a program that was written in the context of this work. The effect of this correction does not affect much the shape of the diffraction peaks. The corrected profile was extracted by the program using the method LWL.

The study has shown that the kaolinite of kaolin M1 lacks micro-constraints. However, the analysis has shown that Kaolinite of M2 contains micro-constraints estimated at 0.15 and 0.21 respectively by the two methods of study.

The results give a crystallite size of the kaolin M1 between 29 and 230 Å. The dominant size is 40 Å with a distribution of 42%.

The crystallite size of M2 is 92 and 130 Å, respectively by Warren-Averbach and Williamson-Hall methods. Its dominant size is 58 Å with a distribution of approximately 32%.

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