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CHEMICAL TREATMENT OF KAOLIN. CASE STUDY OF KAOLIN FROM THE TAMAZERT– JIJEL MINE

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Abstract: The Tamazert-Jijel kaolin deposit is located in eastern Algeria, It was formed during a process of hydrothermal alteration of feldspars rich in potassium. Kaolin, obtained at the mine, mainly contains varying amounts of impurities such as iron oxide (Fe_2O_3) and anatase (TiO_2). These components negatively affect the quality of the commercial product. This research was performed to improve the quality of kaolin to be used in the paper industry with the goal of reducing the impurities of iron and titanium oxides. Different sized fractions of the original sample were analyzed by XRD. The results obtained showed that the mineralogical composition is: quartz, muscovite, kaolinite, dolomite, albite and orthoclase. Kaolin, like all clays, has a thin dissemination of minerals throughout it. After processing kaolin, the particle size fraction of less than 45µm, corresponding to the liberation mesh size, was retained for purification by chemical treatment with different acids of different concentrations (hydrochloric acid, sulfuric acid, acetic acid), heated to boiling point temperatures. The kaolin samples treated with the various acids above were analyzed by X-ray fluorescence and by XRD. The results obtained from the sample treated with hydrochloric acid show that the iron oxide content of acid is reduced by 1.65% to 0.88%. Meanwhile, the brightness of the sample reached 90% under the effect of the treatment with hydrochloric acid at concentration of 2 mole/dm^3.

Keywords: kaolin, hydrochloric acid,sulfuric acid, acetic acide

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INTRODUCTION

Kaolin is used as a white filler and pigment in paper industry, ceramics, pharmaceuticals, etc. However, to meet the requirements of these industries, kaolin must first be purified. The objective of this study is to reduce the content of colouring impurities (iron and titanium oxides). Cambier and Picot (1988) and Shi (1986) presented a method of treatment of kaolin by reductive lixiviation and bleaching with acids. The brightness of kaolin, based on the work of the latter, was improved up to the value of 90.6%. Eze et al. (2012) have recently considered the treatment of kaolin by hydrochloric acid. The results obtained show that HCl is a good reagent for removal of impurities contained in kaolin.

Carroll and Starkey (1971) have reviewed a variety of clays (montmorillonite, metabentonite, illite, kaolinite and halloysite) and a plurality of solvents suitable for their treatments. The objective of this study was to select the most suitable solvent. The results obtained showed that treatment with dilute acids has no detrimental effect on the preparation of the clay to the X-ray diffraction. By contrast, acetic acid was preferred to hydrochloric acid but the latter did not change the iron oxide surfaces of clay minerals, which makes it ineffective in the processing of kaolin.

Newns and Pascoe (2002), Cieśla (2012), and Asmatulu (2002) have carried out tests whose purpose was to extract iron and titanium oxides to obtain brightness greater than 90%.

Also research has been conducted on kaolin treatment processes by selective flocculation. Among the authors of this research were Larroyd et al. (2002), Franklin, (1984), Ravishankar et al. (1995), and (Pradip et al., 1991).

Regarding the processing of kaolin by flotation, Koster et al. (1992), Sharad (2002), Yoon et al. (1992), Murray (1980) (abd Elkhalek et al., 1996) were able to improve the whiteness of kaolin for the paper industry.

TAMAZERT KAOLIN ORE CHARACTERIZATION

CHARACTERIZATION BY X-RAY FLUORESCENCE (FX).

The analysis of the original sample by x-ray fluorescence yielded the following results: 68.13 Sio_2, 19.72 Al_2o_3, 1.65 Fe_2o_3, 0.14 Cao, 0.38 Mgo, 0.01 So_3, 4.34, K_2o, 0.43 Na_2o, 0.08 P_2o_5, 0.35 Tio_2 and 9.29% as loss on ignition. Other chemical analyses were performed for differently sized for 9 samples. The results gave Fe_2o_3 content ranging from 1.27% to 3.00%.

The mineralogical distribution curve over different size fractions, given in Fig. 1, shows that the SiO_2 content increases gradually from 53.90% for the fraction of 0.045 mm to 77.34% for the fraction of 2 mm thickness. This confirms that the Tamazert

kaolin is siliceous. From Fig. 2, we see that the TiO_2 content is not more than 0.48% for the sample of 0.045mm in size. By contrast, the Fe_2O_3 content reached 3.00% in that fraction. It results from the chemical analysis that the initial sample of Tamazert kaolin have a grade of 1.65% Fe_2O_3.

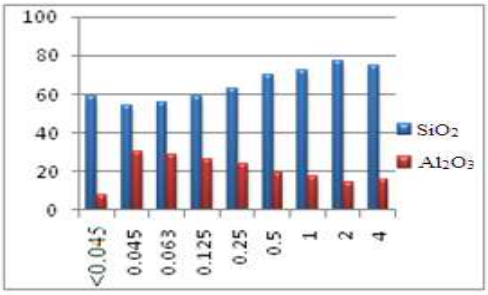

Fig. 1. Chemical analysis distribution of SiO_2 and Al_2O_3 against different size fractions

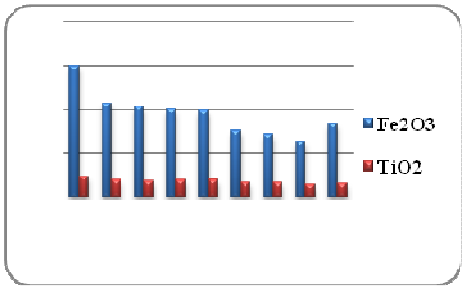

Fig. 2. Chemical analysis distribution of TiO_2 and Fe_2O_3 against different size fractions

Table 1. The results of statistical analysis for the Fe_2O_3 contents

Parameters	Symboles	Formulas	Values	Unit
Number of Fe_2O_3 content	n	-	9.0000	-
Mean content of Fe_2O_3	$\overline{T}_{Fe_2O_3}$	$\frac{\sum_{i=1}^{n} T_i}{n}$	1.8900	%
Standard deviation	S	$\sqrt{\frac{\sum_{i=1}^{n} (\overline{T}_i - T_i)^2}{n}}$	0.4841	%
Confidence interval level	$\propto$	-	0.1000	-
Probability associated with the confidence interval	P	$1-\propto$	0.9000	-
Deviation characterizing the confidence interval	E_{ic}	$\frac{st_s}{\sqrt{n-1}}$	0.2367	%
Mean content of Fe_2O_3 (major Eic)	$\overline{T}^{maj}_{Fe_2O_3}$	$\overline{T}_{Fe_2O_3} + E_{1c}$	2.1267	%
Mean content of Fe_2O_3 (minor of Eic)	$\overline{T}^{min}_{Fe_2O_3}$	$\overline{T}_{Fe_2O_3} - E_{ic}$	1.6533	%
Average coefficient of variation	K_{var}	$\frac{s}{\overline{T}_{Fe_2O_3}} \cdot 100$	12.5200	%
Relative error	ε	$\frac{E_{ic}}{\overline{T}_{Fe_2O_3}} \cdot 100$	12.5200	%

Number of tests required	N	$\left[t_s \frac{K_{var}}{\varepsilon} \right]^2$	8.0030	tests

In order to verify and confirm the reliability of the Fe_2O_3 content results shown in Fig. 2 with respect to the content of Fe_2O_3 obtained in the initial sample statistical processing was applied. The results are presented in Table 1.

In Table 1, the mean contents are:

- major by the deviation characterizing the interval

$$\overline{T}_{Fe_2O_3} + E_{ic} = 1.8900 + 0.2367 = 2.1267\ \%$$

- minor by the deviation characterizing the confidence interval:

$$\overline{T}_{Fe_2O_3} - E_{ic} = 1.8900 - 0.2367 = 1.6533\ \%$$

The statistical analysis of the 9 samples size fraction confirms the mean grade of 1.65% Fe_2O_3 in the initial sample.

MINERALOGICAL CHARACTERIZATION

The samples were finely ground and then analyzed by the X-ray diffraction (XRD). The obtained spectra are composed of several peaks. The results, related to the diffraction X-ray spectra of the initial sample, are shown in Fig. 3.

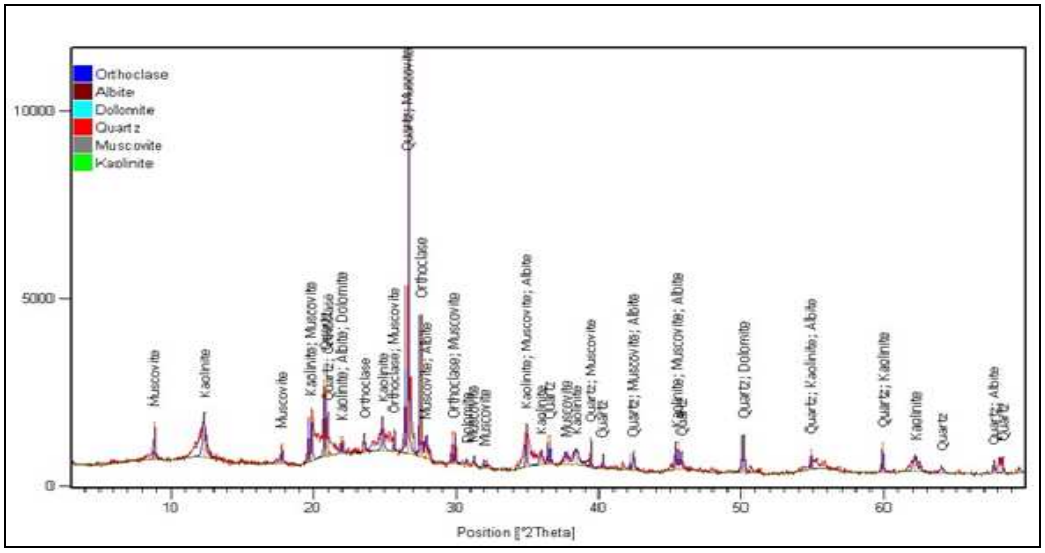

Fig. 3. X- ray diffraction spectrum of the initial sample (Tamazert case study)

From Fig. 3, we see that the mineralogical composition of the original sample contains the following minerals: kaolinite, muscovite, quartz, dolomite, albite and orthoclase. However, we note:

a) peaks of quartz and muscovite have a high intensity and are well pronounced, making their identification easier.

b) peaks of quartz and kaolinite are superimposed with muscovite or aggregate form (quartz, muscovite and kaolinite).

Further analyses by XRD were performed on different particle size ranges of: - 0.125 + 0.063 mm and - 0.063 + 0.045 mm.

The mineralogical composition of these samples was the same. From this, we note the absence of dolomite and muscovite, and the presence of illite.

OBSERVATION BY SEM

To complete the mineralogical characterization of the Tamazert kaolin sample with a particle size <45 µm, a scanning electron microscope (SEM).

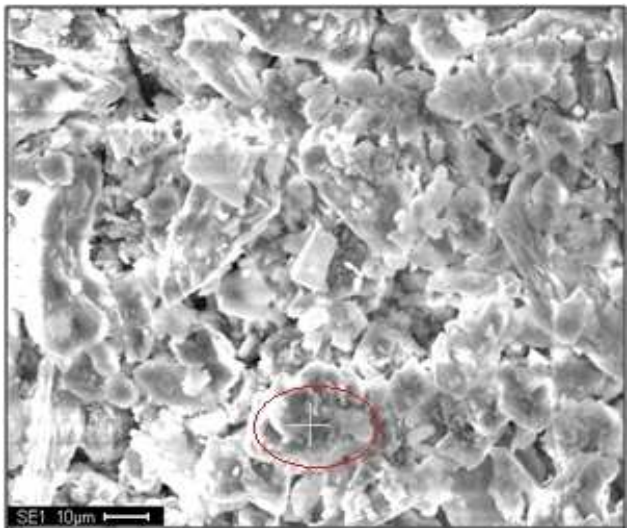

Fig. 4. Observation by electron microscopy

Most clay minerals are monoclinic, kaolinite however is triclinic. These minerals have the form of hexagonal tablets and basal cleavage (001) of mica, but these characteristics are very rarely observed in thin mica.

PARTICLE SIZE ANALYSIS

The particle size distribution curve after particle size analysis of the initial sample of Tamazert kaolin, is presented in Fig. 5.

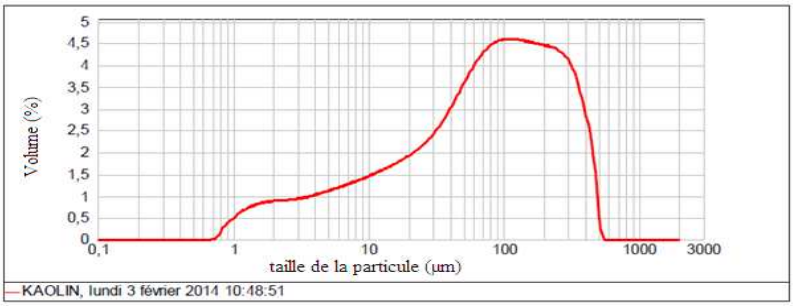

Fig. 5. The particle size distribution curve

MATERIALS AND METHODS

Particles> 45 µm in the initial sample are removed by sieving as they represent impurities of silica and mica. Three samples of 20 g of kaolin of particle size <45 micrometers were poured into three beakers of equal volume of 500 ml. Each beaker contained 200 ml of one acid: either HCl, H_2SO_4 or CH_3COOH of concentration 2 mol / l with a very acidic pH. Suspension sample N° 1 was stirred for 20 minutes and was then heated to the boiling temperature for each acid for 4 hours (with intermittent stirring for 15 seconds). The procedure was repeated with samples N°2 and N° 3 which were also treated with HCl, H_2SO_4 and CH_3COOH, but with concentrations of 4 mol/l and 6 mol/l, and heating times of 6 to 8 hours respectively.

The suspension was filtered and the residue obtained washed three times with potable water, followed by washing with distilled water. These samples were dried at a temperature of 150 ° C for 5 hours.

Samples N°1, N°2 and N°3, treated by chemical treatment with HCl, H_2SO_4, CH_3COOH, were analyzed by energy dispersive x-ray fluorescence (FX).

RESULTS AND DISCUSSIONS

The chemical analysis of the main impurities of Tamazert kaolin, is presented in Table 2.

Table 2. Results of chemical analysis of the main impurities Fe_2O_3 and TiO_2

Samples N°	Testing	Acids	Heating time, Hour	Concentration, mol/l							
				1		2		4		6	
				Contents, %							
				Fe_2O_3	TiO_2	Fe_2O_3	TiO_2	Fe_2O_3	TiO_2	Fe_2O_3	TiO_2
1	1	HCl	04	1.15	0.35	0.98	0.35	0.93	0.34	0.90	0.33
	2	H_2SO_4		0.98	0.35	0.80	0.34	0.65	0.33	0.56	0.32
	3	$0H_3$–cooH		1.58	0.35	1.49	0.35	1.38	0.35	1.30	0.35
2	4	HCl	06	–	–	0.88	0.33	–	–	–	–
	5	H_2SO_4		–	–	0.54	0.33	–	–	–	–
	6	$0H_3$–cooH		–	–	1.30	0.35	–	–	–	–
3	7	HCl	08	–	–	0.85	0.33	–	–	–	–
	8	H_2SO_4		–	–	0.50	0.32	–	–	–	–
	9	$0H_3$–cooH		–	–	1.25	0.35	–	–	–	–

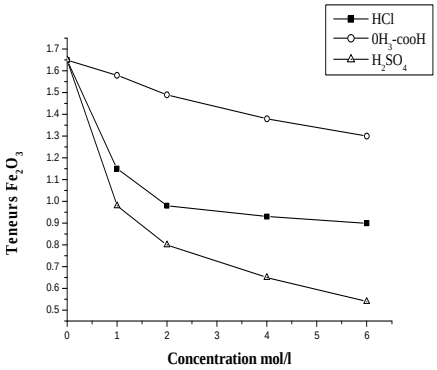

Fig. 6. Content of Fe_2O_3versus acid concentration (4 hours)

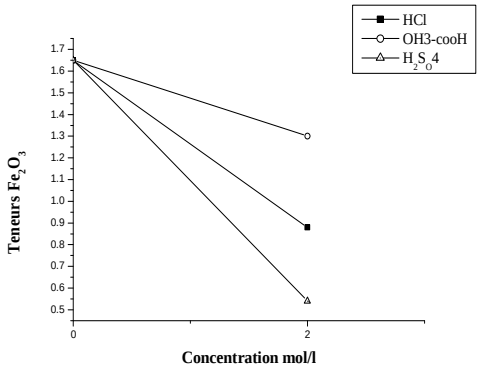

Fig. 7. Contents of Fe_2O_3versus acid concentration (6 hours).

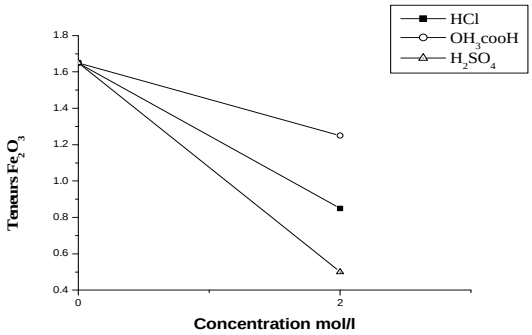

Fig. 8. Content of Fe_2O_3versus acid concentration (8 hours)

The results obtained as shown in Fig. 6, 7 and 8 confirm the influence of the preparation time on the sample processing by acids. The content of Fe_2O_3 is reduced from 1.65% at the start to 0.90% for HCl, 0.56% for H_2SO_4 and 1.30% for CH_3COOH, for a time heating 4 hours, as shown in Fig. 6.

From Fig. 7, the Fe_2O_3 content is reduced from 1.65% to 0.88% for HCl, 0.54% for H_2SO_4 and 1.30% for CH_3COOH for the time of heating equal to 6 hours.

From Fig. 8, we see that the best results are obtained by sample N°7 during treatment with hydrochloric acid with the following parameters: HCl concentration 2 mole / l, conditioning time 8 hours, boiling point: 85 °C. This is because the iron content decreases from 1.65% to 0.85%.

As for the content of Fe_2O_3, for the sample treated with sulfuric acid, it decreases 1.65% to 0.50%, but this acid is not effective because the dissolution of Al_2O_3 in the latter. Furthermore, the influence of acetic acid on Fe_2O_3 is low.

From Table 1 we see the influence of the chemical treatment by the three acids on the TiO_2 content remains low and its content does not significantly decrease. A decrease of 35% to 33% for the sample treated with HCl 35% to 32% treated with H_2SO_4, and the content remains unchanged for the sample treated by the CH_3COOH.

When processing kaolin at different concentrations of HCl, we notice the color change towards yellow HCl and the yellow solubility product to white. By comparison, the color of samples treated with H_2SO_4 changed from yellow to white and then to gray and this was due to the dissolution of Al_2O_3 in the suspension as shown by the analysis through (FX) and XRD.

This study confirms that, if one increases the conditioning time or the concentration of acid, the content of iron oxide decreases. It was also noted that treating the sample with H_2SO_4, also decreases the Al_2O_3 content. Therefore, we can say that the treatment of kaolinite with HCl is more effective when compared to H_2SO_4 and CH_3COOH acids.

There is dissolution of metal components, mainly Fe_2O_3 in the HCl solution. The chemical reaction takes the following form:

$$Fe_2O_3(s) + 6HCl(aq) \rightarrow 2FeCl_3(aq) + 3H_2O \quad (1)$$

There are two oxidation states of iron: Fe^{2+} and Fe^{3+}. This leads us to distinguish two types of iron dichloride (II) and trichloride (III). In the case of Tamazert kaolin, iron contained in the ore is trichloride.

After leaching with hydrochloric acid at concentration of two moles per liter for a period of 8 hours, the sample of kaolin concentrate obtained was analyzed by XRD. The results obtained are shown in Fig. 9.

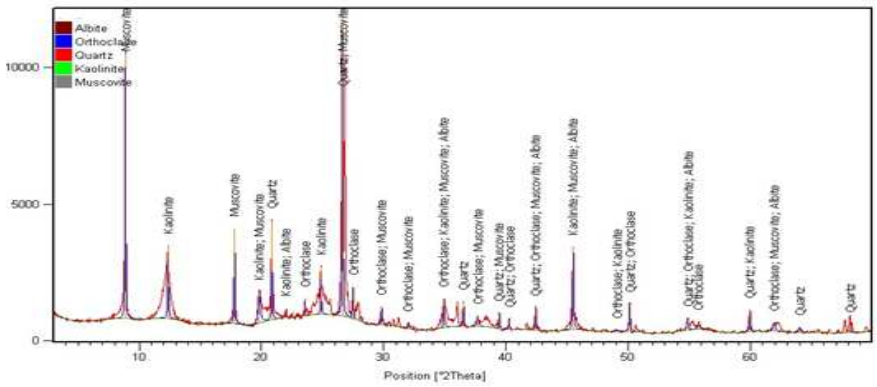

Fig. 9. X-ray diffraction spectrum of kaolin concentrate sample

From Fig. 9, it is noted that the peaks of muscovite, kaolinite and albite, with high intensity are clearly expressed relative to the peaks of the initial sample (see Fig. 3), which makes their identification easier.

CONCLUSIONS

The results of chemical analysis showed that Tamazert kaolin is siliceous because of the high silica content of up to 68.13%.

The content of the iron oxide, after the HCl acid leaching is reduced from 1.65% to 0.85% with the retained crystalline structure, and from 1.65% to 0.50% after the treatment with H_2SO_4, but with a decreases of the Al_2O_3 content. The Al_2O_3 content decreases from 30.13% to 10.80% in the treatment of kaolin sample by H_2SO_4. In the initial sample, the titanium oxide content is 0.35%. After treatment with acids, it decreased by 0.35% to 0.33% due to a weak influence of the acid on TiO_2.

When the XRD analysis of the concentrate of kaolin sample is performed, Muscovite peaks of kaolinite and feldspar are clearly expressed in relation to the initial sample. The best results are obtained when treating kaolin with HCl having two moles per liter of the acid for a period of eight hours. The results of this study confirm the existence of many structural similarities (impurities, properties, whiteness, etc.) between the treated Tamazert kaolin and kaolin used in the paper industry.

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