JOURNAL AFRICAIN DES SCIENCES
VOL. 1, **2** (2024) 64-69

https://jafrisci.org

ISSN (online) : 3006-2306 ; *ISSN (print) : 3006-3760*

RESEARCH ARTICLE

Article Info.:
Received : 21st November 2024
Accepted : 21st December 2024
Published : 24th January 2025

PHYSICOCHEMICAL CHARACTERIZATION BY AXRF AND XRD ANALYSIS OF CLAYS SAMPLES FROM BULUNGU, KWILU PROVINCE, DEMOCRATIC REPUBLIC OF CONGO

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https://doi.org/10.70237/jafrisci.2024.v1.i2.08

Resumé

Cette étude analyse quatre échantillons d'argile prélevés à Bulungu, dans la Province du Kwilu en RDC, en utilisant la fluorescence X (XRF), la diffraction des rayons X (XRD) et l'analyse thermogravimétrique (ATG). Les résultats montrent que ces argiles sont constituées des oxydes suivants selon leurs proportions décroissantes: silice (plus de 50%), alumine (20%), oxyde de fer (10%) et oxyde de potassium (plus de 5%). Sur le plan minéralogique, elles renferment principalement l'illite (plus de 50%), la kaolinite (19%), l'albite (5%) et la microcline (10%) avec un faible pourcentage de quartz (moins de 3%) qui rend ces argiles utilisables dans l'industrie du ciment. L'analyse des éléments en traces révèlent la présence en proportions décroissantes de Rb>Zn>Cr>Ni>Cu>Th>U. L'analyse thermogravimétrique montre une perte de poids d'environ 18 % à 800°C.

Mots clés : Argiles, Kwilu, Fluorescence X, Diffraction X, caractérisation physicochimique

Abstract

This study analysed four clay samples from Bulungu, Kwilu Province, DRC, using X-ray fluorescence (XRF), X-ray diffraction (XRD) and thermo gravimetric analysis (TGA). The results show that these clays are made up of oxides regarding their decreasing proportions: silica (over 50%), alumina (20%), iron oxide (10%) and potassium oxide (over 5%). Mineralogically, they mainly contain illite (over than 50%), kaolinite (19%), albite (5%) and microcline (10%), with a low percentage of quartz (less than 3%) which makes them suitable for use in cement industrys. Trace element analysis reveals the presence of Rb>Zn>Cr>Ni>Cu>Th>U in decreasing proportions. Thermo gravimetric analysis shows a weight loss of around 18% at 800°C.

Key words : Clays, Kwilu, X-ray fluorescence, X-ray diffraction, physicochemical characterization.

I.INTRODUCTION

Clay minerals have been better understood because of technological advances, particularly in the fields of X-ray diffraction and differential thermal analysis, which enable their structures and chemical compositions to be accurately determined [1]. Due to their unique physico-chemical properties, clays find a multitude of applications [2], such as in construction for the manufacture of bricks, tiles and cement [3], in agriculture for the production of fertilizers and growing media to improve water retention [4], in textiles as adsorbents for impurities and color stabilizers [5], in the pharmaceutical industry as excipients and adsorbents [6], in ceramics because of their malleability and resistance after firing [7], in electricity as insulators and supports for printed circuits [8], in oil exploitation as additives for drilling muds [9], and even in the nuclear field for the storage of radioactive waste because of their stability [10].

Traditionally, clays have been recognized for their essential role in the ceramics, construction and geotechnical sectors due to their binding properties, water retention capacity and mechanical strength [3].

In nanotechnology, clays are used as reinforcing matrices in polymer composites, improving the strength and stability of materials while reducing their weight and cost [11].

Color and stability of clays depend on their mineral composition and crystalline structure. Color is influenced by the oxidation of structural cations, the charge and position of ions, and water content. Mössbauer spectroscopy techniques

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have revealed that the color of clays varies according to the oxidation state of iron: bivalent iron (Fe^{2+}) makes clays green, trivalent iron (Fe^{3+}) makes them red, and the absence of iron makes them white [12, 13]. X-ray diffraction (XRD) techniques can also show that structural ions influence color: Al^{3+} and Mg^{2+} for white clays, Fe^{3+} for yellow ones, Mn^{3+}, Co^{3+} and Ti^{4+} for red ones, and Fe^{2+}, Cr^{3+} and Ni^{2+} for green ones [12, 14]. These diverse applications illustrate the versatility of clays and their importance in many industrial sectors.

An analysis of clays from the SONGOLOLO region (Kongo Central) in the Democratic Republic of Congo had shown that they consisted mainly of Kaolinite (27-34 %) with SiO_2, Al_2O_3 and quartz contents ranging from 20 to 68 % [15]; in another study, Mubiayi et al, [16] found that clays in the Bukavu region were composed of muscovite, kaolinite, illite and quartz; those in Kinshasa contained dickite, kaolinite, montmorillonite, and those in Lubumbashi contained quartz, kaolinite, muscovite and various oxides.

No work has been found on clays from Kwilu Province, so in the present study we propose to use X-ray diffraction and X-ray fluorescence to determine the chemical and mineralogical composition of four clays samples from the Bulungu region, Kwilu Province in the DRC, with a view to exploring the possibilities of using them in cement industry, and to carry out thermogravimetric analyses to assess their heat stability.

II. MATERIALS AND METHODS

II.1 Materials

The clays samples used in this study were collected from a quarry in Bulungu, Kwilu Province. The quarry, shown in Figure 1 below, has the following geographical coordinates: 4°38'55.16412"S and 18°24'7.2024"E. These clays are used by local residents for pottery and house painting.

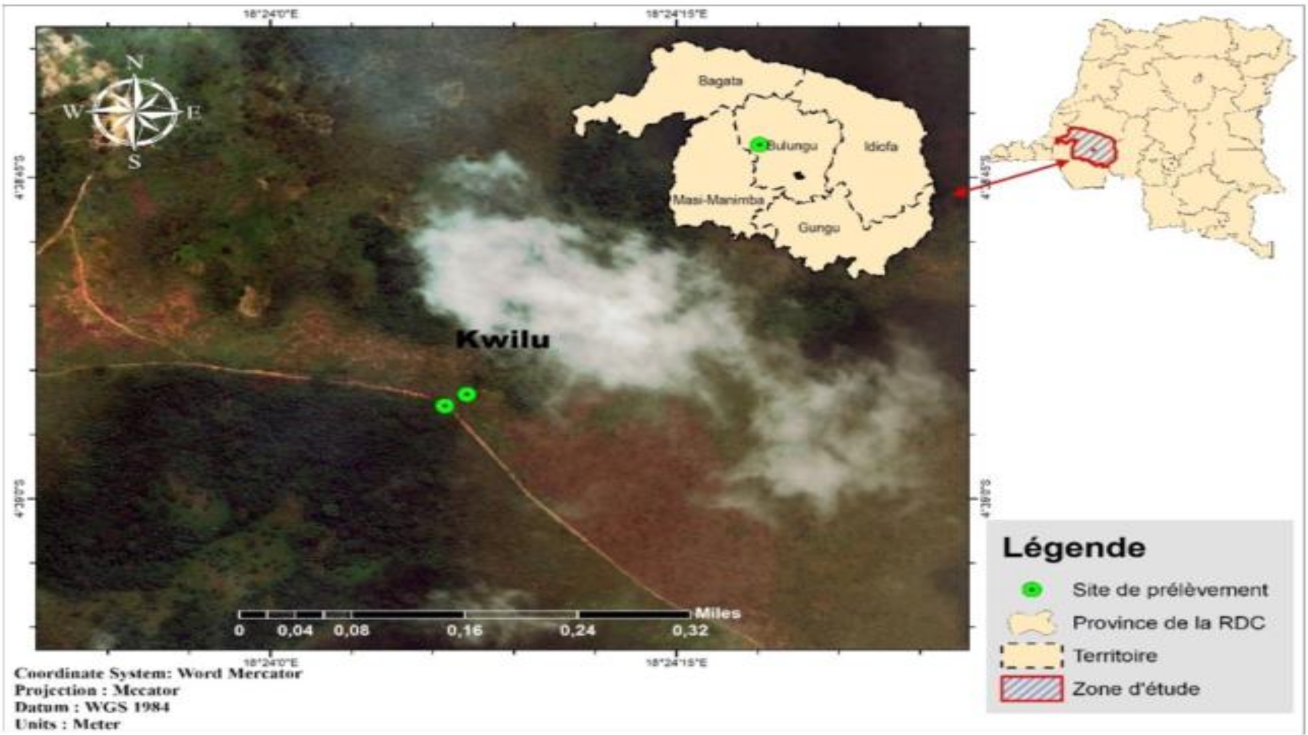

Figure 1: *Clay sampling site.*

The clays were collected from depths of around 5 m and they were sun-dried in the open air for 14 days before being crushed and sieved using a 63µm RETSCH sieve shaker and were referenced ARG-1, ARG-2, ARG-3, ARG-4 as shown in the following photo 1:

ARG-1 ARG-2 ARG-3 ARG-4

Figure 2. *The four clays used*

II.2 Methods

II.2.1. Thermo gravimetric analysis

Each clay sample was weighed and subjected for 1 hour successively to 200, 400, 600 and 800°C in a NABERTHERM muffle furnace. The difference in weight before and after calcination is used to deduce the loss on ignition, expressed as a percentage [17].

II.2.2. X-ray fluorescence analysis

A 5 g test sample was mixed with 1 g Fluxana binder, homogenized, placed in a mold and pelletized with a 1000 kg SPECAC hydraulic press.
Analyses were carried out using an XEPOS III energy-dispersive X-ray fluorescence spectrometer (ED-XRF), using the "FP-Pellets CGEA" and "TQ-Pellets Fast" methods. Standards ISE870, ISE890, ISE919, ISE961 and SOIL-7 containing certain elements of interest were used as references [18].

II.2.3. X-ray diffraction analysis

Clay samples were analyzed by X-ray diffraction (XRD) using a BRUKER D2 PHASER spectrometer equipped with a cobalt anode source. Crystalline phase identification was performed with BRUKER's DIFFRAC EVA software, using data from the International Center for X-ray Diffraction (ICDD) PDF2 database [18].

III. RESULTS AND DISCUSSION

III.1. Thermogravimetric analysis

Results of thermogravimetric analysis are given in Table 1. They show an increase in loss on ignition as temperature rises. This trend suggests that calcination induces decomposition of clay minerals such as kaolinite and chlorite by dehydration and dehydroxylation. This decomposition may be partial or total at high temperatures, as suggested by Lucas and Jehl [19]. The presence of carbonate minerals ($CaCO_3$ and $CaMg(CO_3)_2$), which can decompose into metal oxides by releasing carbon dioxide under the effect of heat, also explains the loss on ignition recorded for the four clay samples [17].

Table 1: Percentage weight loss after calcination of clays

T (ºC)	ARG-1 (%)	ARG-2 (%)	ARG-3 (%)	ARG-4 (%)
25°C	0		0	0
200	12.8	8.6	9.6	9.5
400	13.8	10.0	10.5	10.4
600	18.2	15.4	16.7	15.4
800	19.2	16.2	16.9	16.7

III.2. Chemical composition of various clays

The clay samples were analyzed for major elements. The chemical composition is expressed in terms of oxides for major elements, as shown in figure 3. The content of minor elements in the clays is given in Table 2 in mg/kg. Trace elements analysis shows the presence of rare-earth elements in mg/kg such as La (171-176), Ce (135-347), Pr(77-219), Nd (54-198), U (27-38) and Th (19-47). As it could be seen in table 2, the minor elements proportion decrease as follow: Rb>Zn>Cr>Ni>Cu>Th>U.

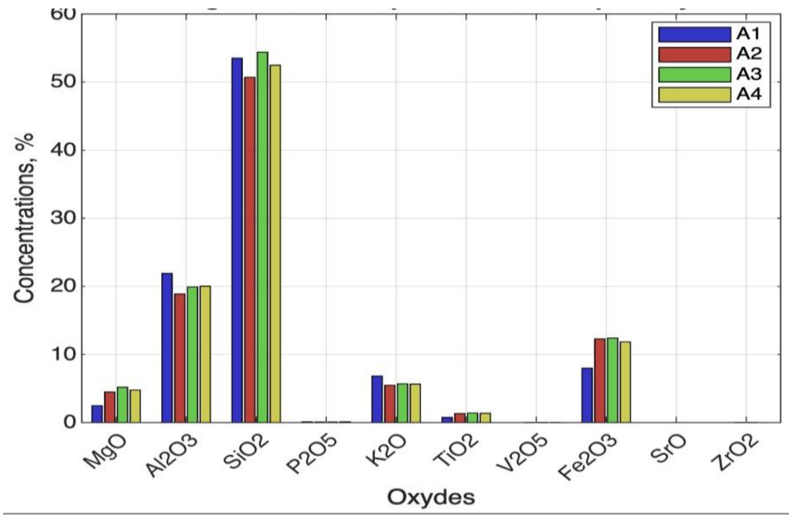

Figure 3. *Composition in percentage of oxides in the analyzed clays*

Table 2 : content of minor elements in the clays

Elements	ARG-1	ARG-2	ARG-3	ARG-4
Concentration in mg/kg				
Cr	14.8	98.4	68.4	42.1
Mn	451.1	418.3	449.4	492.6
Ni	0	41	0	50
Cu	0	41	38	49
Zn	71.7	84.4	68.3	79.8
Ga	17.4	14.5	15.7	0
As	0	0	0	0.8
Rb	108.1	0	103.7	101.6
Nb	3.4	0.016	9.5	9.8
Pd	17.0	0	0	0
Ag	20.1	0	16.3	0
Cd	3.0	1.3	10.8	0
Sn	0	0	11.8	0
Sb	3.8	0	0	0
I	28.3	8.4	0	0
Cs	0	102	0	0
Ba	285	284	174	332
La	171	0	0	176
Ce	302	135	240	347
Pr	77	179	173	219
Nd	198	62	54	0
Pb	11.0	15.6	15.5	6.3
Th	18.8	29.2	20.9	47.49
U	34.1	27.4	38.1	0

The percentage of Silica and Alumina in a clay is of great importance, as it is indicative of the presence of Kaolinite, Bentonite or Quartz. For the 4 clays analyzed, the $SiO2/Al_2O_3$ ratios are 2.44, 2.68, 2.73 and 2.62 respectively for ARG-1, ARG-2, ARG-3 and ARG-4. These ratios are lower than the values recorded when Si^{4+} substitution by Al^{3+} is maximal, i.e. 3.2. Rather, they are within the known bentonite ratio of 2.7. These ratios indicate the presence of kaolinite in the clays analyzed. The value of 3.2 reflects the presence of free quartz [18, 20-21].

III.3. X-ray diffraction results

Table 3 shows the mineralogical composition of the clays analyzed by X-ray diffraction.

Table 3: Mineralogical composition of different clays in percentage

		ARG-1	ARG-2	ARG-3	ARG-4
Mineral clays					
Ratio : Illite/Kaolinite		4.09	2.75	3.14	2.88
	illite	53.03	56,99	54	58,78
	Kaolinite	12.97	20.69	17.2	20.41
	Somme	**66**	**77.68**	**71.2**	**79.19**
Non Clay Minerals					
Feldspaths	Albite	2.8	4.56	3.97	3.65
	Microcline	24.85	10.87	12.12	10.11
	Somme	**27.65**	**15.43**	**16.09**	**13.76**
	Hematite	0	0	0.22	0

	Goethite	222	1.43	1.09	1.63
	Somme	**2.22**	**1.43**	**1.31**	**1.63**
	Quartz	0.7	0.5	2.01	1.07
	Rutile	0.95	1.97	1.66	1.1
	Anatase	0.66	0.67	1.16	1.05
Polymorph -TiO2	**Somme**	**1.61**	**2.64**	**2.82**	**2.15**
	Calcite	0.31	0.37	5.1	0.28
	Dolomite	1.28	1.45	0.91	1.4
Carbonate	**Somme**	**1.59**	**1.82**	**6.01**	**1.68**

XRD analysis showed that all samples analyzed consisted mainly of clay minerals such as illite ($K_2O,2H_2O,2Al_2(Si_3Al)O_{10}(OH)$, and kaolinite ($Al_2Si_2O_5(OH)_4$) with percentages ranging from 66 to 79%. The most abundant non-clay minerals are feldspaths (microcline and albite), with percentages ranging from 13.7% to 27%. Quartz percentages are very low in samples ARG-1 and ARG-2 (0.7 and 0.5%) and slightly higher in samples ARG-3 and ARG-4 (2.01 and 1.07%). These low quartz percentages make these clays suitable for use in the formulation of low-carbon cements; and remain very low compared with those recorded by Seke et al.[22] in their study of Central Kongo dolerite, basalt and meta-basalt at sites 2 and 3, whose quartz percentages were 7 and 25% respectively. These authors had concluded that these pozzolanic rocks could be used in the formulation of a clinker.

SiO_2 concentrations oscillate between 50.70% and 54.40%. These variations remain small, which is common for illitic clays where the SiO_2 content is generally stable due to the constancy of the layered structure. A higher SiO_2 content may indicate a higher proportion of silica in the clay minerals, which may affect the clay's plasticity and water-holding capacity [8, 23].

The proportions of Al_2O_3 vary between 18.88% and 21.90%. The fluctuations observed are also minimal, reflecting a relatively uniform aluminum composition among the samples. A higher Al_2O_3 content is characteristic of illitic clays, as aluminum is a major component of clay minerals. The presence of Al_2O_3 has an impact on the clay's ability to deform and retain water. Illites are a type of clay mineral that contains a significant amount of potassium. Potassium is often incorporated into the structure of clay minerals in the form of K_2O. In illites, potassium cations are intercalated into the sheet-like structure of clay minerals, contributing to the stability and structure of the clays [24].

The clays analyzed show a distinct mineralogical composition, with a predominance of illite over kaolinite. This dominance suggests that these clays result mainly from the alteration of rocks containing feldspaths as primary minerals.

Illite is therefore the residual product of the transformation of feldspaths under physico-chemical conditions favorable to its preservation. The persistent presence of feldspars, particularly microcline, indicates a residual influence of the source rocks. During the weathering process, feldspars are generally transformed into clay minerals such as illite or kaolinite. Variations in the proportions of feldspars within samples may reflect differences in the degree of weathering of source rocks, or in the specific processes by which clays are formed. We argue that mineralogical analysis of feldspar-bearing illite clays provides essential information on their origin and associated geological mechanisms. The predominance of illite and the residual presence of feldspars illustrate the transformations of primary minerals into clays, offering valuable clues to the geological processes that led to their formation [24].

IV. CONCLUSION

Characterization of the Bulungu clays, using XRF and XRD techniques, revealed the presence of key minerals such as illite, kaolinite, microcline, and a very low percentage of quartz. These low quartz percentages make the studied clays suitable for use in cement industry and minimize the risk of silicosis for cement industry workers. It also reduces erosion of tooth enamel in the event of geophagy. Further research into the physical properties of clays, such as their plasticity and heat resistance, is recommended to refine their industrial use. In addition, further studies could examine the benefits of their low quartz content in specific applications and assess their potential impact on health.

V. CONFLICT OF INTEREST

The authors declare no conflicts of interest regarding the publication of this paper.

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