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Physico-Chemical Analysis for Differents Types of Clays Soils in the Areas of Analamanga, Itasy and Vakinankaratra

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Abstract The aim of this work is to highlight the physicochemical properties of three various types of clay soils respectively collected at Bevalala (sample 1), Arivonimamo (sample 2) and Antsirabe (sample 3). The analyses obtained by x-ray fluorescence showed the variation of the composition of the major elements in each sample in particular the rates of SiO_2 (47.6%, 41.2%, 52.5%), of Al_2O_3 (16%, 23%, 25%), of MgO (0.52%, 0.39%, 1.9%) and of Fe_2O_3 (8.3%, 4.7%, 6.4%) at 500°C.. The study of the plasticity of these samples (I_p1= 29.33, I_p2=14.5, I_p3= 24.16) which are intended for the manufacture of pot, of muds or of bricks allowed to highlight that the clay soil is more plastic than its plasticity index is important. The addition of $CaCO_3$ and the heating of the sample at 500°C during five hours make it possible to increase the concentration in CaO.

Keywords Clay, X-ray Fluorescence Analysis, Plasticity

1. Introduction

In Antananarivo,yellow, gray or white clays, with different thickness, under a weak covering, offer reserves very limited on the industrial sphere because of presence of rice plantations on the surface. Only many artisanal exploitations for brickyard developed, of restricted extension.

These clays, of complex composition: kaolinite, halloysite (hydrated kaolinite, beidellite, nontronite, cook red. Their reserves (not cubed) appear important but are partly obliterated by the presence of cultures on the surface. An exploitation is designed to feed the cement factory of Antsirabe.

In the coastal area of Madagascar, the soil clays are not useful to build houses because there are a lot of sand. High-plasticity clays occur in many areas of Madagascar especially in the middle and often offer the most economical material alternative for construction of highway embankments. This study shows that in the three areas which we have chosen, the soils contain very important content of clays.

The clays minerals[1] have several physical properties and chemical which are: their faculty to aspire water especially when they dry. They can also reject this water under the action of heat (phenomenon of hydration and dehydration) [2]. When they are mixed with water, one can obtain from it a paste intended for the ceramic manufacturing of product as the bricks and the tiles. The clay fraction is used because its plasticity is easy to calculate by the method of Casagrande. Obtaining a good paste is especially subordinate to this plasticity which depends on the chemical composition of clay. Then, we will study the plasticity of the clay soil according to the method of Casagrande. For the chemical properties of the grounds, we will see the chemical composition by the method of spectrometry of Fluorescence to X-rays (FRX).

We will approach a particular study of the clay soils coming from the area of Bevalala, Arivonimamo and the area of the thermal spring of Antsirabe.

2. Theoritical Background

In general, the properties of the grounds are related to those of the minerals which constitute them.

2.1. Chemical Properties

2.1.1. Structure of the Clay

The clay minerals are presented under the aspect of the particles, crystallites or layers of very small sizes.

2.1.2. Ionic exchanges Property[3]

One of the most known properties of clays is their aptitude

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to fix some anions and especially the exchangeable cations at other cations and anions. The cations most easily exchangeable in clay materials are: Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+, Na^+ and the anions most easily, exchangeable are: SO_4^{2-}, Cl^-, PO_4^{3-} and NO_3^- One can write for example an exchange of the cations:

$$\text{Clay-Ca}^{2+} + 2\text{NaCl} \longrightarrow \text{Clay-2Na}^+ + \text{CaCl}_2$$

Here a balance was established but if one systematically renews the solution with balance (by a new solution with balance) by a new solution NaCl, one obtains after several treatments a clay – Na and the number of equivalence of fixed Na^+ is equal to that of moved Ca^{2+}. This balance also depends on the concentrations of the exchangeable ions

$$\frac{Clay - Na^+ 2}{Clay - Ca^{2+}} = K\frac{\left(Na^+\right)^2}{\left(Ca^{2+}\right)}$$

With K= the constant of balance If P is the power of absorption one a:

$$P = K\frac{\left[Na^+\right]}{\left(\frac{\left[Ca^{2+}\right]}{2}.\frac{1}{2}\right)}$$

With$[Ca^{2+}]$ and$[Na^+]$ are expressed in equivalent grams.

During the fixing of the Na^+ ions, one can also define solutions used, the capacity of exchange of sodium (sodium adsorption ratio) noted:

$$S.R.A = \frac{\left[Na^+\right]}{\sqrt{\frac{\left[Ca^{2+}\right]+\left[Mg^{2+}\right]}{2}}}$$

S.A.R is expressed in milliequivalents-gram for clay 100g. Values of the capacities of exchange of the cations and anions are given in the following table:

Table 1. Value of exchange capacity of cations and anions[4]

MINERAL	Average exchange capacity in (meg)	
	CATIONS	ANIONS
Kaolin	3 à 15	
Halloysite	5 à 10	7 à 20
Montmorillonite	80 à 150	
Hectorite	44	23 à 30
Attapulgite	20	
Illite	10 à 40	
Vermiculite	100 à 150	
Chlorite	10 à 40	4
Sépiolite	20 à 30	

2.1.3. Colloidal Property of the Clay Matter[2]

According to the colloidal property of the clay matter, the constituent micelles of a clay paste can slip the ones on the others. This property is supported by the presence of free water in the paste which plays to some extent a part of lubricant allowing the deformation and thus returning plasticity.

In a perfectly purified clay i.e. not containing those ions H^+ and OH^-, we find the colloidal property of clay.

Let us suppose that the load of the clay matter is due to the dissociation of clay micelle in micro anion (clay-OH) $^-$ and H^+ or by adsorption of ions OH^- of the aqueous medium on the side breaks of the crystal. The positively charged H^+ ions revolve around micelles and are attracted by the negative charge of the surface of the core.

2.2. Physical Properties

2.2.1. Plastic Property of Clay

The plastic clay soils are very resistant to heat and are composed of fine particles of kaolin, quartz, illite and mica. One especially employs them in the manufacturing of pottery, dishes, tiles for walls, medical parts[5,6] (i.e.bathrooms). They are also used as agent of filling in rubbers, the plastics, paintings and the adhesives.

B.2 Classification of a ground following its degree of plasticity With the index of plasticity, one can classify a soil according to his degree of plasticity.

Table 2. degree of soil plasticity

Ip	degree of soil plasticity
0 à 5	Nonplastic soil
5 à 15	Light plastic soil
15 à 40	Plastic soil
> 40	Mostly plastic soil

Limit of magnitude:
- Clay Ip> 30
- Muddy clay 20< Ip<30
- Silt 10<Ip<20
- Clayey sand 5<Ip<20
- Muddy sand 5<Ip<15

3. Methods and Experiments

3.1. Determination of the Plasticity of Clay

We determine in experiments the plasticity of clays with the box of Casagrande. The limits of Atterberg make it possible to evaluate the plasticity of a clay soil and in particular the water content in the grounds. Indeed, water has a capital influence on the behavior of the clay soils and their cohesion. Casagrande began again and developed standardized tests making it possible to determine the water contents for which the transition is carried out

To determine Wl according to the formula:

$$W_l = W\left(\frac{N}{25}\right)^{0,121}$$

Wl: liquid limit

NR: Many blows

To calculate Wp (plastic limit). We take a sample of ground and one lets it dry (A). We add a little water and we rolls on a surface punt, a small glass plate for example. We try to form wire a 3 mm thickness and 10 cm length, without it breaking (B). We repeat this experiment by adding each time a little water until you can form a wire. The water content will correspond then to the plastic limit and could be expressed as a percentage weight of the sample.

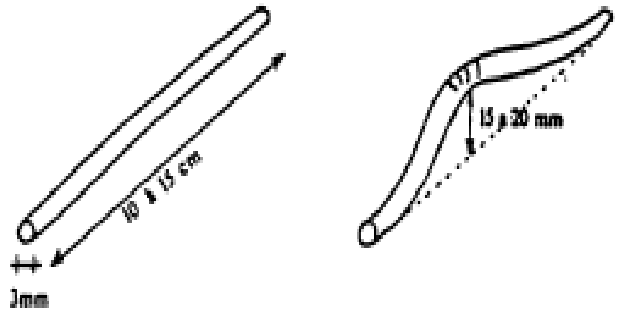

Figure 1. test of plasticity

Research of the limit of plasticity Ip:
The calculation of the index of plasticity I_P is determined by the formula:

$$Ip = W_l - W_p$$

W_l and Wp being liquid limit and plastic limit

3.2. X-ray Fluorescence Spectrometry

The fluorescence-X spectrometry is a chemical method of analysis using a physical property of the matter, the fluorescence of X-rays. When one bombards matter with X rays, the matter emits energy in the form. The spectrum of the X-rays emitted by the matter is characteristic of the composition of the sample by analyzing this spectrum, we can determine the elementary composition from it and the mass concentrations in elements. We use this method to analyze our samples.

4. Results and Discussion

4.1. Results

4.1.1. Determination of the Plastic limit of the Samples

The aim of this study is to determine the plasticity of the samples in Bevalala, Antsirabe and Arivonimamo. We use the box of Casagrande to determine the different plastic limits of those samples.

➢ **Sample of Bevalala**

1. Liquid limit W_l:

Table 3. Determination of the liquid limit of the sample of Bevalala

Many blows: N	20		24	
Tare N°	1	2	3	4
Tare weight (1)	9.5196	9.4750	9.4976	9.4732
Wet total weight (2)	11.3693	11.2910	10.8554	10.7590
Dry total weight (3)	10.6111	10.5494	10.3057	10.2398
Weight of water (4) = (2) – (3)	0.7582	0.7416	0.5497	0.5192
Dry material weight (5) = (3) – (1)	1.0915	1.0744	0.8081	0.7666
Water content W % (4) / (5)	0.6946	0.6902	0.6802	0.6773
Average Water content %	69.46	69.02	68.02	67.73

2. Plasticity limit WP:

Table 4. To Determine plasticity limit of the sample of Bevalala

Tare N°	5	6	7	8
Tare weight (1)	1.7133	1.7097	1.7007	1.6990
Wet total weight (2)	2.4555	2.3387	2.2820	2.2086
Dry total weight (3)	2.2598	2.1700	2.1133	2.0636
Weight of water (4) = (2) – (3)	0.1957	0.1687	0.1687	0.1450
Dry material weight (5) = (3) – (1)	0.5465	0.4603	0.4126	0.3646
Water content W % (4) / (5)	0,3580	0,3665	0.4088	0.3976
Average Water content %	35.80	36.65	40.88	39.76

3. Plasticity index Ip:

Liquid limit: W_l= 67.59
Plasticity limit : W_P = 38.27
Plasticity index: I_P =29.33

➢ **Sample of Arivonimamo**

1. Liquid limit WL

Table 5. Determination liquid limit of the sample of Arivonimamo

Many blows : N	26		22	
Tare N°	1	2	3	4
Tare weight (1)	1.7005	1.7048	1.6972	1.7013
Wet total weight (2)	5.6238	5.0966	6.9030	4.9350
Dry total weight (3)	4.2931	3.9328	5.1115	3.8220
Weight of water (4) = (2) – (3)	1.3307	1.1638	11.7915	1.1130
Dry material weight (5) = (3) – (1)	2.5926	2.2280	3.4143	2.1207
Water content W % (4) / (5)	0.5133	0.5224	0.5247	0.5248
Average Water content %	55.33	52.24	52.47	52.48

2 Plasticity limit WP:

Table 6. To determine plasticity limit of the sample of Arivonimamo

Tare N°	5	6	7	8
Tare Weight (1)	1.6913	1.7039	1.7012	1.6993
Tare weight (1)	2.4423	2.3996	2.3927	2.3074
Wet total weight (2)	2.2366	2.2121	2.2020	2.1437
Dry total weight (3)	0.2057	0.1875	0.1907	0.1637
Weight of water (4) = (2) – (3)	0.5453	0.5082	0.5008	0.4444
Dry material weight (5) = (3) – (1)	0.3772	0.3689	0.3808	0.3683
Water content W % (4) / (5)	37.72	36.89	38.08	36.83

3. Plasticity index Ip:

Liquid limit: W_l = 51.88
Plasticity limit : W_P =37.38
Plasticity index: I_P = 14.5

➢ **Sample for the thermal source of Antsirabe**

1. Liquid limit W l:

Table 7. Determination liquid limit of the sample for the thermal source of Antsirabe

Many blows : N	32		34	
Tare N°	1	2	3	4
Tare weight (1)	1.6998	1.7048	1.6960	1.7008
Wet total weight (2)	4.9824	5.0101	6.2724	6.4510
Dry total weight (3)	3.6604	3.6775	4.4342	4.5476
Weight of water (4) = (2) – (3)	1.3220	1.3326	1.8382	1.9034
Dry material weight (5) = (3) – (1)	1.9606	1.9727	2.7382	2.8468
Water content W % (4) / (5)	0.6743	0.6755	0.6713	0.6686
Average water content %	67.43	67.55	67.13	66.86

2. Plasticity limit WP:

Table 8. Determination plasticity limit of the sample for the thermal source of Antsirabe

Tare N°	5	6	7	8
Tare weight (1)	1.6913	1.7036	1.7000	1.6985
Wet total weight (2)	2.3741	2.2776	2.4738	2.5826
Dry total weight (3)	2.1533	2.0968	2.2555	2.3317
Weight of water (4) = (2) – (3)	0.2208	0.1808	0.2183	0.2509
Dry material weight (5) = (3) – (1)	0.4620	0.3932	0.5555	0.6332
Water content W % (4) / (5)	0.4779	0.4598	0.3930	0.3925
Average Water content %	47.79	45.98	39.30	39.25
	43.08			

3. Plasticity index Ip:

Liquid limit: W_l= 67.24
Plasticity limit : W_P = 43.08
Plasticity index: I_P = 24.16.

4.1.2. Chemical Analyses of Clays by X-rays Fluorescence[7,8]

The elements detected by X-ray fluorescence spectrometry of our samples are gathered in the following table:

Table 9. Results of the analyses by the method of X-ray fluorescence spectrometry

N° atom (Z)	Name	Corresponding oxide (%)	Percentage		
			Sample of Bevalala	Sample of Arivonimamo	Sample for the thermal source of Antsirabe
			500°C	500°C	1150°C
14	Silicium	SiO_2	47.569	41.189	52.548
13	Aluminium	Al_2O_3	14.649	23.463	25.184
26	Iron	Fe_2O_3	8.372	4.736	6.360
20	Calcium	CaO	3.224	1.334	12.259
12	Magnesium	MgO	0.525	0.390	1.922
19	Potassium	K_2O	0.701	0.883	1.605
11	Sodium	Na_2O	0.085	-0.049	0.887
16	Sulphur	SO_3	0.090	0.082	0.188
22	Titanium	TiO_2	1.066	2.234	2.002
15	Phosphorus	P_2O_5	0.068	0.123	0.173
25	Manganese	MnO	0.039	0.030	0.085
24	Chrome	Cr_2O_3	0.031	0.077	0.056
		LI	9.770	13.26	0.000
		Total	**86.189**	**87.752**	**103.269**

4.1.3. Improvement of the Content of CaO

We take the clay sample of Arivonimamo for this stage of improvement because this clay has a low plasticity among the three samples. The goal of handling[9, 10] is to increase the percentage of calcium CaO oxide which is an oxide very much used for the clay plasticity.

4.1.3.1. Method

Calcium carbonate is added ($CaCO_3$)[11,12 ,13] of various weight m to clay to be analyzed. We choose the method of X-rays Fluorescence (XRF) to follow the evolution of the contents.

4.1.3.2. Variation of the Content of $CaCO_3$

The results of the analysis by X-ray fluorescence spectrometry are presented in table 10:

Table 10. Percentage of the elements detected by the spectrometry of X-ray fluorescence

N° atom (Z)	Name	Corresponding oxide (%)	Percentage		
			Addition of 0.005g of $CaCO_3$ in 0.7g of the sample	Addition of 0.01g of $CaCO_3$ in 0.7g of the sample	Addition of 0.5g of $CaCO_3$ in 0.7g of the sample
14	Silicium	SiO_2	43.128	42.446	29.566
13	Aluminium	Al_2O_3	28.066	27.507	18.593
26	Iron	Fe_2O_3	3.274	3.068	2.409
20	Calcium	**CaO**	**4.058**	**4.611**	**19.240**
12	Magnesium	MgO	0.336	0.317	0.229
19	Potassium	K_2O	0.827	0.820	0.559
11	Sodium	Na_2O	-0.066	-0.070	0.402
16	Sulphur	SO_3	0.071	0.086	0.026
22	Titanium	TiO_2	2.492	2.431	1.524
15	Phosphorus	P_2O_5	0.130	0.124	0.079
25	Manganese	MnO	0.025	0.024	0.015
24	Chrome	Cr_2O_3	0.081	0.083	0.050
		LI	13.260	13.260	13.260
		Total	**95.682**	**94.506**	**85.951**

Loss on the ignition: LI

4.2. Discussion

Some research shows that the consistency of expansive clay soil is strongly influenced by soil water content. According to[14], plasticity index and liquid limit[14] can be used to determine the swelling characteristics of expansive clays in general.[15] stated that the only plasticity index alone[15]can be used to estimate the swelling characteristics of expansive clays in general. According[16], the higher the plastic index[16,17] an expansive clay minerals, the higher the potential for development.

The most plastic clays are called "unctuous clay" and those which are the least plastic call "meager clays"[18]. The experiments showed that samples 1 and 3 are much more plastic than sample 2 because the index of plasticity are respectively Ip1= 29.33. Ip2=14.5 and Ip3= 24.16.

The analysis by X-ray fluorescence spectrometry of our samples highlights that the major elements are: Na (Z=11), Si(Z= 14) Al(Z=13) Fe(Z= 26) Ca(Z= 20) Mg(Z=12) K(Z= 19) S (Z=16) Ti (Z=22) P (Z= 15) Mn (Z=25) Cr (Z=24). Ne (Z=10) could not be detected by the analysis by X-ray fluorescence spectrometry because Z=10, it is the limit of detection of the detector of the X-ray fluorescence spectrometer.

According to the table 10, when we increase the content of $CaCO_3$, the percentage of CaO in the sample increase. The ion Na^+ is exchangeable with Ca^{2+}[19]. So we can improve the plasticity of clays by increasing the percentage of CaO.

5. Conclusions

The present study made it possible to get fundamental results on the quantitative and qualitative characteristics of the clay soils in various places of Madagascar. Indeed, the knowledge of plasticity and the chemical components of a clay soil make it possible to determine its use well. Plasticity gave an indication on the quantity of clay in the ground. Sample 1 (I_P = 29.33) contains much more clay than the two others.

By analysis of X-ray fluorescence spectrometry, one can say that the results are in agreement with the percentages quoted in the chemical composition.

We take the clay sample of Arivonimamo for the stage of improvement because this clay has a low plasticity among the three samples. The handling consists in adding of $CaCO_3$ to sample 2 (the least plastic) made it possible to conclude that the cations (mono and bivalent) of this sample could be exchanged with of Ca^{2+} since the content of the CAO in the sample increased and those of the other actions decreased.

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