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EXTRACTION OF FERRUGINOUS COMPOUNDS AND GIBBSITE FROM KAOLINIC CLAY MATERIALS

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ABSTRACT. Clay samples composed of kaolinite and halloysite were subjected to either acid or base and acid treatment to remove ferruginous impurities and gibbsite. The acid treatment (12 N HCl at 85°C for 20 min) resulted in the extraction of nearly all the ferruginous compounds, while base treatment (boiling 0.5 N NaOH for 3 min) of the clay samples followed by acid treatment for 30 min, resulted in the elimination of over 80 % of the gibbsite. In both cases of treatment, over 90 % of the mineralogical clay were undestroyed.

INTRODUCTION

Natural clay materials usually contain impurities whose mineralogical nature depends on the geographical areas of the materials deposit; sometimes, these impurities lead to disadvantageous modification of the material properties for some uses. This is the case with ferruginous compounds which diminish the clay material's refractability at higher temperatures (1), or with gibbsite, which diminishes its degree of crystallinity and probably alters its plasticity (2). These two types of impurities are frequent in kaolinic clay materials which are abundant in humid tropical zones covering about half of the Cameroonian territory.

Numerous methods have been used for the extraction of iron from soil samples. Mineral (3,4) and organic and/or organomineral reagents (5,6) enable the extraction of iron, but are partially adsorbed on clay and could not be removed completely; otherwise require several extractions with longer treatment time.

Mineral acids have also been used either for studing clay solubility, extraction of aluminium and iron from clay or elucidating the kinetics of silico-alumina network attack (7-9). These acids result in the elimination of most of the iron but also contribute largely to the destruction of part of the clay network. However, among the mineral acids, it has been found that hydrochloric acid does not attack clays easily and, in particular, kaolinite and halloysite.

In the present work, we used hydrochloric acid as the extractive reagent for iron. In order to enhance its efficiency we used it at a high concentration (12 N) and moderate temperature (85°C). This has led to the search for optimum conditions in the total extraction of iron compounds from the clay materials without the substantial destruction of the clay mineral network. For the extraction of gibbsite, we have chosen among the general methods used in the dissolution of amorphous alumino-silicates, silica and free alumina (11-13), that of Hashimoto and Jackson (12), which seems more rapid and efficient.

MATERIALS AND METHODS

Materials. The samples used were crude materials from two deposits found in Cameroun and previously studied by Njopwouo (2), namely Bo_1 and Bo_4 for kaolinite, $Si_2O_5Al_2(OH)_4$, based samples and Ba_1 and Ba_2 for halloysite, $Si_2O_5Al_2(OH)_4.xH_2O$, ($x\approx 1.5$), based samples. The < 2 µm fractions of these materials, more rich in mineralogical clay (kaolinite or halloysite), respectively specified as Bo_1^{*}, Bo_4^{*}, Ba_1^{*} and Ba_2^{*} were also considered. The mineralogical compositions of these samples, calculated from both the X-ray and chemical analyses (2) are represented in Table 1 and 2. It is observed that all the samples considered contain the following ferruginous compounds: geothite (α-FeO-OH), pyrite (FeS_2), ilmenite ($FeTiO_3$) and siderite ($FeCO_3$) in the kaolinic materials; and hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3) and gibbsite [$Al(OH)_3$] in the halloysic materials.

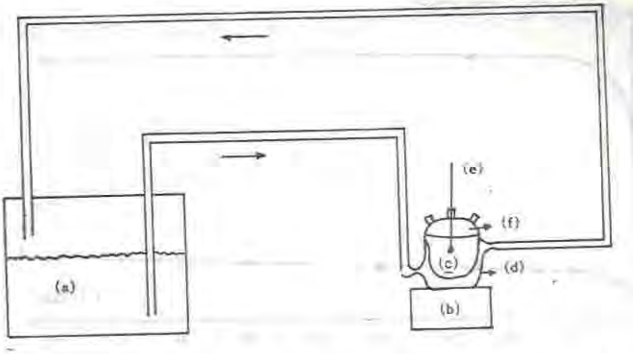
Table 1. Mineralogical composition of total materials (Ba) and fine fractions of Bomkoul deposit, before (Bo^{*}) and after (Bo^{**}) extraction of ferruginous compounds (w/w % of dried sample at 25°C).

Minerals	Kaolinite	Quartz	Palygorskite	Microcline + Illite	Montmorillonite	Geothite	Anatase	Pyrite	Ilmenite	Siderite	Manganocalcite	Indetermined
Bo_1	65.3	14.1	2.0	3.3	0.2	7.9	2.2	0.1	0.4	-	-	4.3
Bo_1^{*}	82.1	1.0	0.9	2.2	0.5	8.3	1.4	-	-	-	-	3.3
Bo_1^{**}	86.2	4.6	-	0.4	1.9	-	1.1	-	-	-	-	5.2
Bo_4	55.4	13.6	5.9	8.1	1.1	-	1.9	1.0	0.2	6.3	0.3	5.4
Bo_4^{*}	69.4	6.1	5.1	4.5	1.1	-	1.3	6.3	-	-	0.4	5.6
Bo_4^{**}	83.9	3.3	1.4	0.7	3.8	-	1.0	1.2	-	-	-	5.0

Table 2. Mineralogical composition of total materials (Ba) and fine fractions of Balengou deposit, before (Ba^{*}) and after (Ba^{**}) extraction of ferruginous compounds and gibbsite (w/w % of sample at 25°C).

Minerals Samples	Halloysite	Quartz	Gibbsite	Feldspath	Hematite (Maghemite)	Anatase	Indetermined
Ba_1	70.4	18.4	4.9	0.5	4.1	0.4	1.8
Ba_1^{*}	89.7	0.3	3.6	0.5	4.5	0.3	1.1
Ba_1^{**}	83.3	7.8	0.6	4.5	-	0.2	3.2
Ba_2	80.0	13.7	1.4	0.8	3.2	0.4	0.5
Ba_2^{*}	94.0	0.9	0.3	0.6	3.2	0.3	0.2
Ba_2^{**}	86.3	6.5	-	5.1	-	0.2	2.5

Extraction of ferruginous compounds. The search for optimum extraction conditions in the total removal of iron compounds without the destruction of the structure of the clay mineral was carried out on two samples: Bo_1 (kaolinite) and Ba_2 (halloysite), crushed and passed through a 100 µm sieve. The apparatus used for the extraction of iron compounds is shown in Fig. 1.



(a) thermostated bath, (b) magnetic stirer, (c) magnetic stirring bar,
(d) reactor chamber, (e) thermometer, (f) reactor cover.

Fig. 1. Apparatus used for extraction of iron compounds.

HCl (100 ml, 12 N) was placed in a reactor (d). Three small refrigerating columns are placed at three exits of the cover (f). After stabilizing the temperature at 85 ± 1°C, a weighed amount of the clay materials was introduced into the reactor at time $t_o = 0$ min. At time t, a 0.5 ml of the acid solution was withdrawn with the aid of a precision pipette. The lower extremity of the pipette was blocked with cotton, so as to prevent clay particles from passing through it. The withdrawn acid solution was transferred to a 50 ml volumetric flask and diluted to volume with distilled water. The amount of iron in this solution was determined colorimetically using 1,10-phenanthroline at 508 nm.

To determine extraction conditions, we have examined successively: (i) the effect of stirring, and (ii) the influence of clay material concentration in the reaction medium.

Extraction of gibbsite. The extraction of gibbsite consisted of treating 10 g of the clay material with 100 ml of boiling 0.5 N NaOH for about 3 min (12). Trials made with gibbsitic material previously treated with 12 N HCl at 85°C showed a very weak attack on the gibbsite. On the other hand, by treating the material at first with boiling 0.5 N NaOH before using a 12 N HCl at 80°C, the attack on gibbsite was almost complete. Thus, for gibbsitic materials, the elimination of gibbsite was done before extraction of ferruginous compounds.

After extraction of iron compounds or gibbsite, the mineralogical control of the extractive residue was made by X-rays and differential thermal analyses. The results obtained on Bo_1 and Ba_2 samples were applied on fine fractions $B\overset{*}{o}_1$, $B\overset{*}{o}_4$, $B\overset{*}{a}_1$ and $B\overset{*}{a}_2$.

RESULTS AND DISCUSSION

Extraction of ferruginous compounds.

Effect of stirring. Figures 2 and 3 show that stirring of the reaction mixture during the extraction is an important factor. This reaction condition is particularly essential in the extraction of an optimum quantity of Fe_2O_3 within an adequate period of time. With stirring, the initial rate of attack is very high. This result enabled us to use stirring in the sequel of this study.

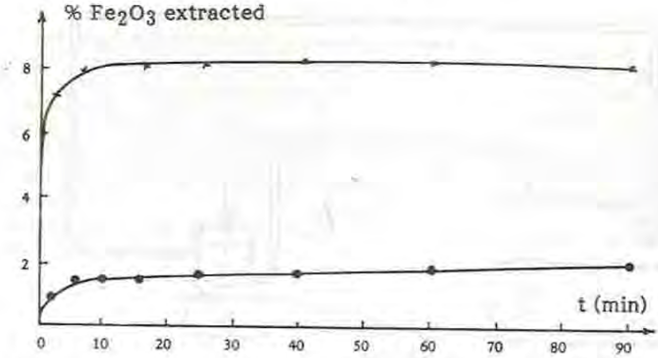


Fig. 2. Percentage of Fe_2O_3 extracted as a function of time (Sample Bo_1)
(x with stirring, ● with out stirring).

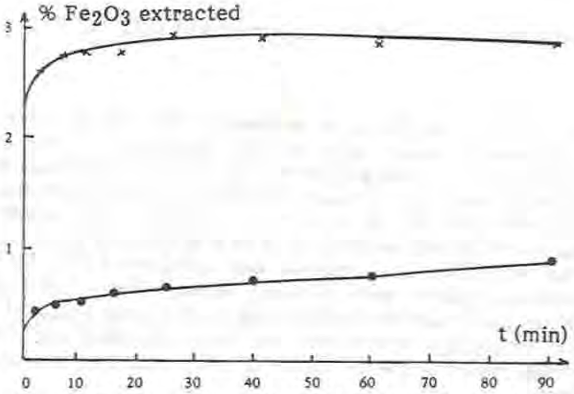


Fig. 3. Percentage of Fe_2O_3 extracted as a function of time (Sample Ba_2)
(x with stirring, ● without stirring).

Effect of clay material concentration. A great deal of care was taken to maintain the volume of the acid at 100 ml during the extraction period. By varying the amount of the clay material from 2 to 10 g, the results obtained are presented in Fig. 4 and 5, where the concentration P of clay material is expressed as grams per milliliter of hydrochloric acid. Figure 4 is representative of the extraction of ferruginous compounds from Bo sample; the extraction curves present a sort of segregation depending on P values from 0 to 45 min of treatment. The extraction curves for Ba sample (Fig. 5) also present a sort of segregation depending on P values from 0 to 70 min of treatment. In both cases, it is noted that for the times of treatment considered, the extraction rates are less influenced by the concentration P; however, the extraction rate is more important for P = 0.1 g/ml. At this concentration, it is observed that all of the iron compounds in the clay material are extracted after 20 min of attack for the Bo sample and 30 min for the Ba sample. If 10 g of material are to be used for 100 ml portions of acid, calculations indicate that for Ba sample, whose density is 2.5 g cm^{-3}, the real volume would be 104 ml instead of 100 ml; that is, there is a relative error of 4 % in determining P. Otherwise, for P > 0.1 g/ml, the withdrawal of aliquots from the reaction vessel become difficult, because clay particles agregate and progressively obstruct the cotton filter.

This has led us not to consider the study of concentrations greater that 0.1 g/ml.

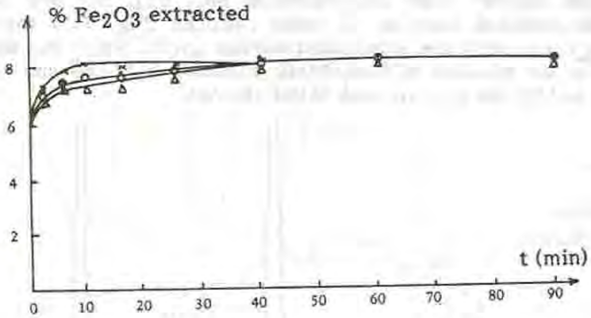


Fig. 4. Percentage of Fe_2O_3 extracted as a function of time (Bo_1)
(x: P = 0.1 g/ml, ●: P = 0.06 g/ml, o: P = 0.04 g/ml, Δ : P = 0.02 g/ml).

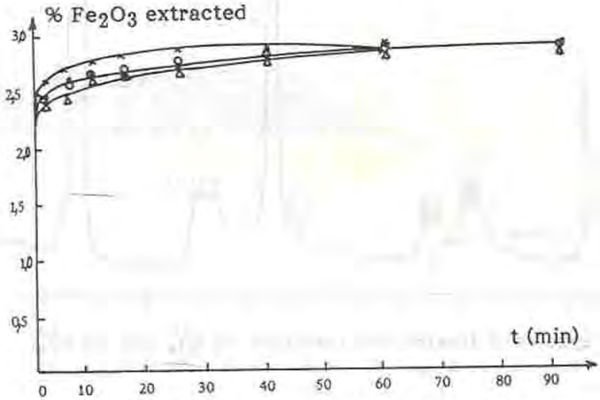


Fig. 5. Percentage of Fe_2O_3 extracted as a function of time (Ba_2)
(x: P = 0.1 g/ml, ●: P = 0.06 g/ml, 0: P = 0.04 g/ml, Δ : P = 0.02 g/ml).

The differences in the extraction rates of the iron compounds from both the Bo and the Ba samples could be attributed to the nature of the ferruginous compounds, notably to the differences in their structures and their particles morphologies and sizes (14-16).

Extraction of ferruginous compounds and gibbsite from the fine fractions of the clay materials.

Taking into account the preceding results, the following scheme was used.

For clay materials without gibbsite (B$\overset{*}{o}_1$ and B$\overset{*}{o}_4$). The scheme involved elimination of ferruginous compounds by treatment of 10 g of material in 100 ml of a 12 N HCl at 85°C for 20 min, followed by submerging in distilled water, filtration, washing of the residue with distilled water and drying in air (25°C).

For gibbsitic clay materials (B$\overset{*}{a}_1$ and B$\overset{*}{a}_2$). The scheme involved elimination of gibbsite by treatment of 10 g of material in 100 ml of boiling 0.5 N NaOH for about 3 min, filtration, followed by washing and drying of the residue; and elimination of ferruginous compounds by treating the preceding residue in the same conditions as for clay materials without gibbsite but for 30 min.

The extraction residues were designated as Bo_1^{**}, Bo_4^{**}, Ba_1^{**} and Ba_2^{**}. X-rays and differential thermal analyses of these residues (Fig. 6-9) show that: (a) all ferruginous compounds are eliminated except pyrite which remains in trace amounts in Bo_4^{**}; (b) gibbsite is completely eliminated in Ba_2^{**} and some traces remain in Ba_1^{**}; and (c) the clay network is not altered.

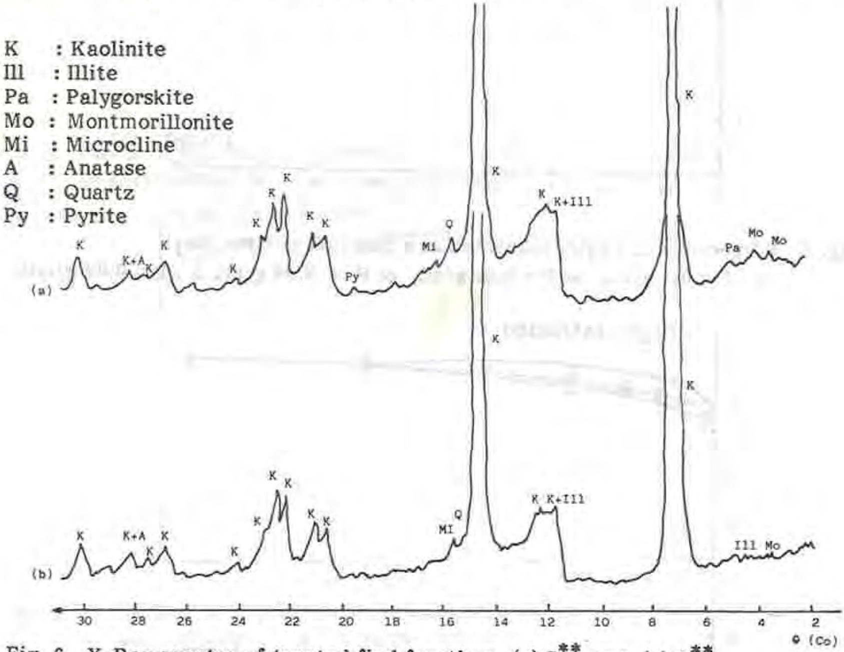


Fig. 6. X-Ray spectra of treated find fractions (a) Bo_4^{**} and (b) Bo_1^{**}.

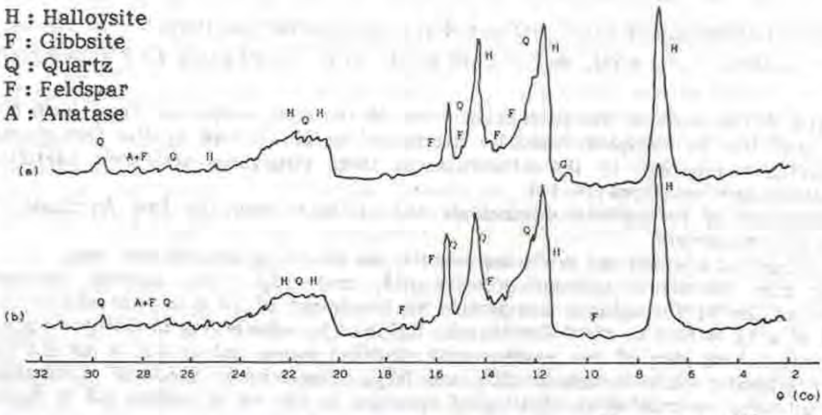


Fig. 7. X-Ray spectra of residues after treatment (a) Ba_1^{**} and (b) Ba_2^{**}.

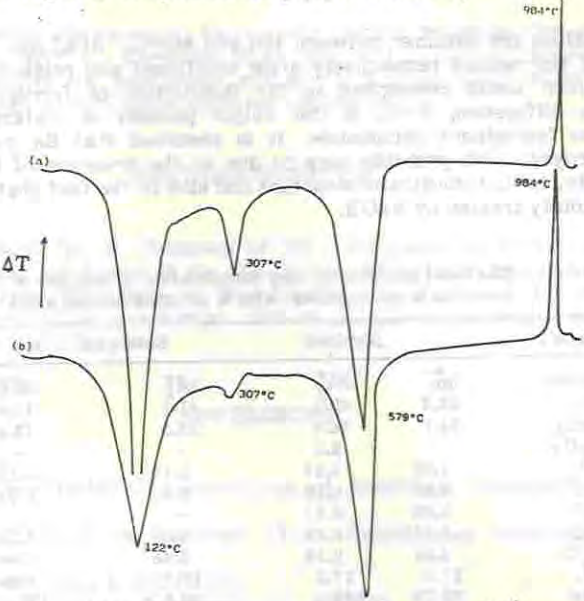


Fig. 8. D.T.A. thermograms (a) $\overset{*}{Ba}_1$ fine fraction and (b) $\overset{**}{Ba}_1$ fine fraction treated successively by NaOH and HCl.

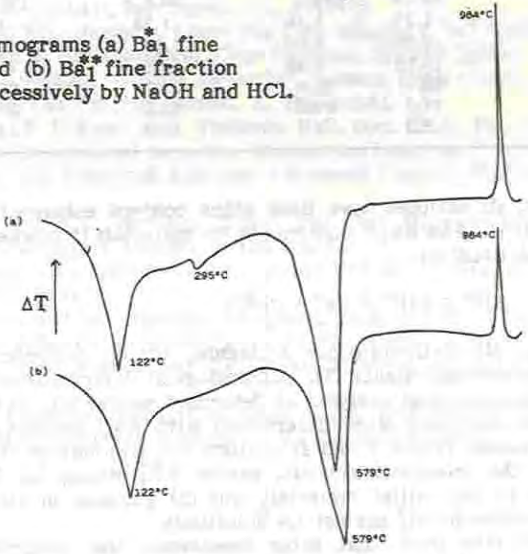


Fig. 9. D.T.A. thermograms (a) $\overset{*}{Ba}_2$ fine fraction and (b) $\overset{**}{Ba}_2$ fine fraction treated successively by NaOH and HCl.

Chemical analysis of the residues after the attack (10) is shown in Table 3. Here, ΔP_1 values, which indicate loss of weight, are obtained by thermogravimetric analysis; ΔP_1 values are obtained between 25 and 180°C and ΔP_3 values are obtained between 380 and 850°C. R(%) and R'(%) are weight percent of the residue respectively after treatment and related to a hypothetic residue which would correspond to the destruction of ferruginous compounds only. The difference, R'-R, is the weight percent of material destroyed in addition to ferruginous compounds. It is observed that Ba materials are the most destroyed. This probably may be due to the presence of interlayer water in halloysite, to its turbostratic structure and also to the fact that those materials were previously treated by NaOH.

Table 3. Chemical analyses of clay sample after extraction of ferruginous compounds and gibbsite (w/w % of dried sample at 25°C).

Deposit	Bomkoul		Balengou	
Samples	Bo_1^{**}	Bo_4^{**}	Ba_1^{**}	Ba_2^{**}
SiO_2	46.3	46.3	47.1	47.4
Al_2O_3	34.7	34.3	32.3	32.8
Fe_2O_3	-	0.8	-	-
TiO_2	1.05	0.99	0.16	0.18
CaO	0.03	0.16	0.07	0.04
MgO	0.09	0.32	-	-
K_2O	0.05	0.09	0.04	0.03
Na_2O	0.07	0.14	0.46^*	0.56^*
P.F.	17.5	17.2	19.5	19.6
Total	99.79	100.3	99.63	100.61
Si/Al	1.13	1.15	1.24	1.23
ΔP_1	3.55	5.00	5.47	6.01
ΔP_3	10.99	9.89	10.86	11.20
R	88.7	90.9	82.7	85.5
R'	92.0	95.8	95.5	96.8
R'- R	3.3	4.9	12.8	11.3

Furthermore, all samples have their silica content enhanced as shown by the atomic ratio Si/Al. The Na_2O contents in Ba materials (* marked) were calulated by using the relationship:

$$Al^{3+} \equiv 3\,(K^+ + Na^+ + Ca^{2+})$$

verified in an Na-K-Ca-feldspar molecule, where cationic proportions are expressed in gram-equivalents (7). Mineralogical compositions were caluclated from X-rays and chemical analyses as described earlier (2). In the present study both microcline and illite were determined with K_2O content in Bo materials. The results obtained (Table 1 and 2) confirm the elimination of : (a) ferruginous compounds in the treated materials, except Bo_4^{**} where 1.2 % pyrite remain against 6.3 % in the initial material; and (b) gibbsite in gibbsitic materials, where 0.5 % remains in Ba_1^{**} against 3.6 % initially.

These results also show that after treatment, the mineralogical clay was partially destroyed in Ba materials (destruction of 7-8 % of halloysite), and that on the contrary, the mineralogical clay contents were enhanced in Bo materials (increase of 5-20 % for the kaolinite). These results thus confirm chemical data presented in Table 3 where R'-R values were more important for Ba samples than for Bo materials.

In conclusion, the treatment applied to the clay materials studied in this work seemed efficient enough since it led to the elimination of over 80 % of pyrite, of the totality of the other ferruginous compounds and/or over 80 % of gibbsite, while maintaining over 90 % of mineralogical clay undestroyed. Otherwise, the method is rapid compared to those using organic reagents; the extractive reagent, HCl, is easy to eliminate from clay and could be regenerated by distillation, to obtain the azeotropic mixture, $HCl.nH_2O$, (with about 20% of HCl) (18), which can be used again for other applications.

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REFERENCES

1. C.A. Jouenne, "Traite de Ceramiques et Materiaux Mineraux", Septima, Paris (1984).
2. D. Njopwouo, These de Doctorat d'Etat, Faculte des Sciences, Yaounde (1984).
3. B.C. Deb, J. Soil Sci., **1**, 212 (1950).
4. P. Segalen, Cah. Orstom, Ser. Pedol., IX, 3 (1971).
5. O.P. Mehra and M.L. Jackson, Clays and Clay Miner., **7**, 317 (1960).
6. R.M. Taylor and U. Schwertmann, Clay Minerals, **10**, 289 (1974).
7. A. Michel et J. Benard, "Chimie Minerale", Masson, Paris (1964).
8. P. Segalen, Cah. Orstom, Ser. Pedol., X, 105 (1968).
9. M.C. Gastuche, B. Delmon et L. Vielvoye, Bull. Soc. Chim. Fr., **1**, 60 (1960).
10. S. Kong, These de Doctorat de cycle, Faculte des Sciences, Yaounde (1989).
11. M.L. Jackson, "Soil Chemical Analysis: Advanced Course", Madison, Wisconsin (1956).
12. I. Hashimoto and M.L. Jackson, "Clays and Clay Minerrls Proceedings 7th Conference," Pergamon, Oxford, p. 102 (1960).
13. S.S. Jorgensen, A.C. Birnie, B.F.L. Smith and B.D. Mitchel, J. Therm. Analys., **2**, 277 (1970).
14. E.T. Karapetyan and L.P. Petrova, Obogasch. Rud., **17**, 34 (1972).
15. K. Norrish and R.M. Taylor, J. Soil Sci., **12**, 294 (1961).
16. R.M. Cornell, A.M. Posner and J.P. Quirk, J. Inorg. Nucl. Chem., **36**, 1937 (1974).
17. D. Njopwouo, These de Doctorat 3e cycle, U.P.S. Toulouse (1976).
18. R. Gout, These de Doctorat 3e cycle, U.P.S. Toulouse (1971).