The mechanical analysis of soils in general and the effect of anions on the dispersibility of lateritic soils in particular

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Summary

The conclusion drawn in DE LEENHEER and VAN HOVE's (1957) article would seem to be incorrect as regards tropical laterites. Whatever the mineral clay, it is probable that soils can always be successfully dispersed with meta- or pyrophosphate-containing agents. Pyrophosphate is to be preferred owing to the difficulty of dissolving sodium hexametaphosphate.

After the entire mechanical analysis methodology had been examined for weaknesses, an explanation was sought of the various problems that arose.

1. Introduction

The investigation described below was prompted by an article by DE LEENHEER and VAN HOVE (1957) in which they compare the effect of a number of dispersing agents used in practice for the mechanical analysis and state that the agents they tested produced identical results.

I have felt for some years that clay percentages obtained with the use of particular dispersing agents were somewhat suspect, and the obvious way of settling the matter was to check DE LEENHEER and VAN HOVE's investigation with various soil samples sent to the Laboratory for Applied Soil Science over the course of years. As may be expected at an institute of tropical agriculture, all the samples were tropical ones.

A brief preliminary examination of the dispersing agents referred to by DE LEENHEER and VAN HOVE showed, in fact, that their conclusion was incorrect, at any rate in its general form. But this discovery created a further problem, namely which dispersing agent gave the right result? On the face of it one might be inclined to dismiss this problem by selecting the dispersing agent that gives the highest clay percentages and is the best deflocculator, this being the object of the mechanical analysis.

This was, in fact, my first reaction, but since these well-dispersed clay suspensions often had glittering colours they were placed in a show-case for educational purpose where, unlike the suspensions which had not been so well dispersed, they usually showed no sign of sedimentation after being allowed to stand for weeks. There was some similarity to pseudo thixotropy.

Hence the problem was more involved than it seemed to be at first. Was the sus-

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pension in the sedimentation cylinder in a thixotropic state caused by the dispersing agent, so that the sedimentation rates derived from Stokes' Law were inapplicable? This led to the further question. What dispersibility state of the soil in the cylinder is the correct one? It is possible that every dispersibility state found may be taken as reflecting a given state of the soil under given conditions. If this is the case it is important to ascertain what degree of dispersion is best suited to the entire system of soil analysis employed.

At the beginning of the investigation it only appeared to be important to determine which types of soil could show variations during sedimentation, so that soon after the first preliminary examination, which was confined to two samples from Tanganyika, the work was extended by including a large number of samples of widely different origin. It became abundantly clear that the curious behaviour found in one laterite (Tanganyika 71) was shared by all the lateritic soil samples I examined. It may be imagined that I gradually became curious as to why certain soils, or, in fact, this clay mineral, exhibited such a strange behaviour. I also began to suspect the soils with a non-constant degree of dispersibility might possibly be the normal ones, and the soils which always gave the same clay percentage irrespective of the dispersing agent added were actually abnormal.

In the initial stage of examining all these various problems each result obtained brought a fresh problem in its train. Is was found, moreover, that certain steps in the mechanical analysis procedure were rather delicate and that a really satisfactory duplicate could only be obtained provided the same work was always carried out by the same person. Consequently neither my assistant nor myself was able to make use of pupils.

It is owing to lack of time, erroneous conclusions and an occasional lack of inspiration that this investigation has dragged on for so many years. It will be clear that it is not progressive to keep to a constant mechanical analysis technique, so that my aim was to standardise it in such a way as to reduce as much as possible any errors resulting from faulty methods.

2. Procedure for the mechanical analysis

20 g of air-dry fine earth were well mixed in an ordinary 400 cc beaker with 100 cc of 3 % H_2O_2 and heated with periodical stirring over a vigorously boiling water bath until the soil was clearly seen to be separated from the supernatant liquid. The H_2O_2 employed was then entirely decomposed and there was usually complete oxidation of the organic material present in the soil. However, if the supernatant liquid turned out to be dark coloured, another 10 cc of 30 % H_2O_2 were added and the suspension again heated over the water bath with periodical stirring. But this repeated addition of H_2O_2 is not often required for tropical samples.

50 cc of 0,5N HCl were then added, the beaker made up with water to over 300 cc and the suspension again heated over the water bath with stirring. After one hour the beaker was removed from the bath and allowed to cool for 15 minutes. The contents of the beaker were then stirred and quantitatively transferred to a Buchner funnel containing a wetted, hardened filter (Schut No. P 212) the whole being under vacuum.

After the liquid had been drawn off in a clear state the soil on the filter was washed with 300 cc of distilled water.

The soil was again well dried by suction and the funnel with filter and soil placed above the corresponding beaker until the soil on the filter was dry. The soil can

afterwards be returned to the beaker without undue loss by using a stiff brush and distilled water.

After the beaker had been made up to about 300 cc with distilled water it was heated over the water bath until the soil disintegrated. The necessary amount of dispersing agent was then added by pipetting and the beaker heated for a further 15 minutes with periodical stirring of the suspension.

After cooling the suspension, it was transferred to a sedimentation cylinder via a 200 μ bronze sieve. Material remaining on the sieve after thorough washing was dried, weighed and taken as the coarse sand fraction. The contents of the cylinder were made up to 1 litre with distilled water, vigorously homogenised, and placed in the sedimentation room.

Next morning the cylinder was again vigorously shaken until the suspension was completely homogenised; 8 hours afterwards, calculated from this moment, 20 cc were pipetted off at the depth of insertion determined for the clay fraction.

The volume pipetted off was collected in a nickel dish and evaporated to dryness over the water bath, dried at 105°, and after cooling weighed and taken as the clay fraction.

Corrections for the various dispersing agents used were calculated from the composition and checked with the residual weight obtained by evaporating and drying at 105° a certain volume of this dispersing agent.

3. Composition of the dispersing agents used in the preliminary investigation

a. Dissolve 13,4 g sodium oxalate and 2,1 g anhydrous sodium carbonate in distilled water to 1 litre. Per litre of suspension 50 cc = 12 meq per 20 g soil. Correction 15,5 mg.

b. Dissolve 44,6 g sodium pyrophosphate 10 aq = 26,6 g anhydrous sodium pyrophosphate in distilled water to 1 litre. Per litre of suspension 20 cc = 8 meq per 20 g soil. Correction 10,6 mg.

c. Dissolve 35,7 g sodium hexametaphosphate and 7,95 g anhydrous sodium carbonate in distilled water to 1 litre. Per litre of suspension 20 cc = 10 meq per 20 g soil. Correction 17,5 mg.

d. Dissolve 53,52 g sodium pyrophosphate 10 aq = 31,92 g anhydrous sodium pyrophosphate and 4,24 g anhydrous sodium carbonate in distilled water to 1 litre. Per litre of suspension 25 cc = 14 meq per 20 g soil. Correction 18,1 mg.

e. Dissolve 53,52 g of sodium pyrophosphate 10 aq = 31,92 g anhydrous sodium pyrophosphate and 12,72 g anhydrous sodium carbonate to 1 litre. Per litre of suspension 25 cc = 18 meq per 20 g soil. Correction 22,3 mg.

f. Dissolve 15,9 g anhydrous sodium carbonate to 1 litre in distilled water. Per litre of suspension 50 cc = 15 meq per 20 g soil. Correction 15,9 mg.

Dispersing agents a, b and c are taken from DE LEENHEER and VAN HOVE's article. Dispersing agent a has also been in use for a considerable time at the North-East Polder Laboratory, Kampen. Dispersing agent d is in use at the Oosterbeek Laboratory, while e is a variant of the latter, used for determining the effect of soda increase. Peptisation agent f is used for determining how this salt, which is found in a number of dispersing agents, behaves when used separately.

4. Results of the preliminary investigation with these dispersing agents

The examination of the deflocculating action of the various dispersing agents was undertaken in the first instance with two Tanganyika soils:

sample 71: Munsell classification 2½ YR 4/7 (laterite)
Cation-exchange capacity at pH 8,3: 4,0 meq/100 g soil
at pH 4,8: 2,65 meq/100 g soil
p.p.m. nitrogen 476
pH-H_2O 5,1 ; pH-KCl 4,7

sample 76: Munsell classification 5 Y 4/1
Cation-exchange capacity at pH 8,3: 23,8 meq/100 g soil
at pH 4,8: 19,8 meq/100 g soil
p.p.m. nitrogen 448
pH-H_2O 6,5 ; pH-KCl 5,4

TABLE 1. Results obtained with soil sample 71

Code No.		Disp. agent (cc)	Fraction $> 200\ \mu$	Clay fraction after 8 hrs	Same depth of insertion after	
					30 hrs	1 week
71a	1	50	23,0	20,2	1,1	—
	2		22,9	13,8	1,6	—
	3		24,5	13,3	4,1	—
	4	20	26,3	31,8	32,0	
	5		26,5	36,0	33,6	5,8
	6	10	25,9	20,4	21,5	
	7		26,2	20,9	20,4	—
71b	1	20	22,6	55,0	52,7	?
	2		22,5	54,8	53,7	50,0
	3	20(1)	24,6	53,4	53,5	49,4
	4	(1)	25,9	53,2	53,2	48,6
	5	10	25,9	51,6	51,8	47,5
	6		23,9	51,5	51,3	
	7	20	22,8	56,1(2)	55,3(3)	
	8		21,1	55,3(2)	54,6(3)	
	9	40	22,2	53,9	53,1	49,2
	10		22,4	55,5	52,0	49,3
71c	1	20	22,5	55,5	53,7	50,7
	2		22,8	55,6	53,4	49,2
71d	1	25	21,6	56,4	53,3	50,0
	2		24,1	54,3	51,3	49,0
71e	1	25	23,3	53,7	53,1	48,4
	2		24,6	54,3	51,9	49,4
71f	1	50	24,0	17,2	15,4	11,8
	2		23,6	16,2	17,2	13,6

(1): amount of soil weighed 10 g
(2): after 3 hours sedimentation at 60°
(3): after 8 hours sedimentation at 60°
— : entirely or almost entirely sedimented
? : failure

At each fresh sedimentation period the suspension was first shaken up again but not made up again to 1 liter. The depths of insertion for 30 hrs and 1 week are the same as the depths of insertion for 8 hrs at the average temperature.

TABLE 2 Results obtained with soil sample 76

Code No.		Disp. agent (cc)	Fraction $> 200\ \mu$	Clay fraction after 8 hrs	Same depth of insertion after	
					30 hrs	1 week
76a	1	50	19,2	49,2	45,9	43,4
	2		19,6	51,9	47,3	44,2
	3	20	19,5	45,9	44,1	
	4		21,0	45,7	43,3	41,9
	5	10	20,0	43,3	42,5	
	6		21,5	42,8	42,8	40,6
76b	1	20	18,7	47,9	46,8	44,8
	2		18,5	49,0	46,5	46,0
	3	20(1)	21,0	46,8	46,6	44,6
	4	(1)	21,6	48,0	45,4	44,8
	5	10	20,9	45,7	44,8	43,1
	6		19,5	46,6	45,9	
	7	20	19,6	48,5(2)	48,4(3)	
	8		19,7	48,5(2)	48,3(3)	
	9	40	20,5	49,0	48,0	45,5
	10		20,1	47,9	46,8	44,4
76c	1	20	19,8	48,9	46,3	46,3
	2		18,7	45,8	46,3	46,3
76d	1	25	17,8	46,5	45,5	44,1
	2		19,5	47,8	46,5	42,9
76e	1	25	18,2	47,5	47,7	44,4
	2		19,7	49,2	44,9	43,8
76f	1	50	20,6	46,6	46,3	43,3
	2		20,9	46,8	45,9	43,3

(1) : amount of soil weighed 10 g
(2) : after 3 hours sedimentation at 60°
(3) : after 8 hours sedimentation at 60°

At each fresh sedimentation period the suspension was first shaken up again but not made up again to 1 liter. The depths of insertion for 30 hrs and 1 week are the same as the depths of insertion for 8 hrs at the average temperature.

The results of the examination are presented in TABLES 1 and 2. The figures therein may be elucidated as follows:

I. the determinations carried out under (1), (2) and (3) served to ascertain the extent to which thixotropy ocuurred in the highly dispersed suspension obtained with the highly dispersing agents b, c, d and e. But the results disprove any suggestion that this phenomenon might be present.

II. the determinations carried out on the clay insertion depth calculated for a sedimentation time of 8 hours, but in which the suspension was pipetted off after a considerably longer interval, served, for example, to ascertain the extent to which the clay fraction consists of colloidal particles, *i.e.* particles smaller than 0,5 μ. It can, in fact, be seen from the results that the clay largely consists of non-sedimenting particles, *i.e.* particles smaller than 0,5 μ, which is only to be expected in tropical soils and readily explained.

III. the determinations carried out with amounts of dispersing agent differing from those specified served to vary the soil/dispersing ion ratio at the time these preliminary tests were made, in order to detect any thixotropy.

The figures given in the TABLES 1 and 2 clearly show that in the case of sample 71 it is a matter of some importance which dispersing agent is used in the mechanical analysis. It may be interesting to establish whether a particular fraction between 200 and 2 μ or all intermediate fractions are affected by the clay differences due to the dispersing agent employed, but since this investigation was mainly undertaken for practical reasons (*i.e.* for the purpose of giving reliable advice) such by-paths, for all their attractiveness, have not been explored.

5. Do all lateritic soils show such a difference in dispersibility when different dispersing agents are used?

After it had been shown by the preliminary investigation that the red Tanganyika soil No. 71 did not act conform to DE LEENHEER and VAN HOVE's conclusion, the first task was to ascertain whether the same was true of lateritic soils in general. For this purpose a number of soil samples were pretreated according to the prescription and their behaviour examined with regard to dispersing agents a and b. The results are presented in TABLE 3.

TABLE 3. Results obtained with soil samples of different origin

Code No.	Colour	Fraction $>200\ \mu$	Dispersing agent a after			Fraction $>200\ \mu$	Dispersing agent b after		
			8 hrs	30 hrs	1 week		8 hrs	30 hrs	1 week
25NG	2½YR4/6	6,0	0,6	0,3	—	5,5	10,4	9,2	8,0
		6,0	0,7	0,3	—	5,3	10,7	9,2	7,5
26NG	2½YR5/6	7,7	1,9	0,5	—	8,3	6,2	5,2	4,3
		7,9	3,1	0,6	—	7,5	6,9	5,4	4,3
27NG	7½YR5/6	40,6	3,0	2,3	—	34,6	12,3	11,5	9,4
		40,6	3,1	2,7	—	35,3	10,7	9,1	7,4
34Ke	2½YR3/2	4,6	8,4	7,1	6,1	4,9	11,9	9,1	8,4
		4,4	10,1	7,9	7,4	4,4	14,4	12,4	10,1
37WA	7YR5/4	10,8	24,1	20,3	15,4	12,6	28,6	24,7	21,7
		13,9	22,5	18,4	14,3	11,5	29,5	24,7	21,9
69Ta	2½YR5/4	33,8	16,6	15,6	2,0	31,4	36,5	35,4	32,6
		33,2	17,1	16,3	2,1	32,9	35,3	34,9	31,7
93Is	5YR3½/4	48,8	13,2	11,6	10,6	52,6	12,4	11,8	11,3
		48,3	13,0	12,3	11,4	53,9	13,0	11,9	11,4
153J	10YR4/4	2,1	77,5	76,4	75,3	1,6	76,4	76,0	74,2
		2,0	75,7	75,1	73,2	1,8	75,0	73,2	72,5
369SA	YR4/6	15,0	9,8	3,6	0,8	14,4	40,5	37,9	34,6
		15,0	9,9	2,9	0,7	15,6	40,9	37,9	34,4
370SA	2½YR3/4	17,5	13,4	9,9	1,9	19,1	38,0	37,2	34,9
		15,2	14,5	11,9	2,5	17,2	38,6	36,6	34,6

Explanation:
NG = New Guinea; Ke = Kenya; WA = Western Australia; Ta = Tanganyika; Is = Israel; J = Jamaica; SA = Republic of South Africa.
Sample 37WA is a degrading terra rossa.
Sample 93Is is a terra rossa-like salty soil.
Sample 153J is yellowish-brown and certainly not a laterite, as is also shown by the pH.
The other samples are lateritic, so that the facts ascertained with Tanganyika 71 are also confirmed by the analyses made with these samples.

6. Examination of the procedure employed for the mechanical analysis

As stated above, the study was originally undertaken with the intention of settling

the problem in a few weeks, but assumed the proportions of an extensive investigation in which success alternated with failure. On several occasions the work had to be postponed for months owing to more urgent problems. When it was resumed again the figures found for identical experiments sometimes differed from previous results by over 5 %. To prevent differences in procedure from having more than a minimal effect on the figures all work required for the analyses was invariably undertaken by one and the same person. Despite this precaution it was found that after a time interval of some weeks or months it was possible for the analyst to vary the special features of his method in such a way that the differences in results were often impossible to keep below 5 %. Hence the procedure to be followed in the mechanical analysis is somewhat delicate, and in the present instance in particular it was necessary to discover and where possible standardise the most vulnerable parts of the method.

At first it was found that despite every precaution and the fact that the fine earth was well mixed before each weighing, the last residues in particular in the vessel were apt to show greater deviations. It was necessary to make up the vessel in good time from the stock container.

The weighed soil sample was oxidised with H_2O_2. Since I employed ordinary commercial peroxide which is negatively catalysed by addition of phosphoric acid, the amount of which may vary considerably from one flask to another, a number of analyses were made with increasing amounts of free phosphoric acid during the oxidation in order to determine the possible effect of this phosphoric acid on the further course of the mechanical analysis. But in the case of the amounts added, which were far in excess of the usual additions of H_2O_2, there was nothing to indicate that the deflocculation was in any way affected. (Subsequent experiments revealed that the orthophosphate ions were the poor dispersers).

The oxidation time, *viz.* the time during which the soil was in contact with H_2O_2, was also examined within reasonable limits. Provided oxidation was complete no influence could be detected.

The acid reaction time and concentration did appear to affect the results of the mechanical analysis as regards the clay content. As regards the concentration of the acid, the safety margin was found to be very wide; one hour over a thoroughly boiling water bath, *i.e.* at about 95° with 38 % HCl, still gave reasonably good results. In the case of soil 71 they may even be termed good; in the case of soil 76 the clay percentage was rather lower. These results were to be expected and are readily explained. It is not until the evaporation stage that the particles of both red and grey soil in the beaker can be seen to undergo a sudden discoloration. A substantial reduction is found in the clay percentage, *viz.* 71a : 2,3—3 % ; 71b : 2,9—3,4 % ; 76a : 1,1—3,0 % ; 76b : 7,7—10,5 % (TABLE 1). The safety margin for the reaction time was also found to be fairly wide provided the acid used was of the specified concentration and, as prescribed, it was diluted by making up the contents of the beaker to 300 cc with water. The red soils were most affected by an increase in the reaction time and generally speaking there was a slight increase in clay percentage with an increasing reaction time.

Since a great deal of time could be saved if it were possible to combine the oxidation with the acid action by applying both simultaneously, several series of analyses were carried out in order to test this possibility. The usual method in which oxidation was followed by heating with acid was compared with the reverse method of first heating with acid and then oxidising, and with a method in which H_2O_2 and HCl

were simultaneously added. Under normal conditions the acid reaction time is one hour; in the reverse method the soil is contacted with the hydrochloric acid for 4 hours, while with simultaneous addition the reaction time is at least 3 hours. The results obtained with the various methods are presented in TABLE 4.

TABLE 4. Results obtained with variation in pre-treatment sequence

Code No.	Colour	Method								
		normal			reverse			simultaneous		
		$>200\ \mu$	$<2\ \mu$	pH	$>200\ \mu$	$<2\ \mu$	pH	$>200\ \mu$	$<2\ \mu$	pH
Dispersing agent a										
71	2½YR4/7	23,8	18,6		24,9	33,1		24,2	35,2	
			23,4	9,1		42,1	9,1		43,4	9,1
76	5Y4/1	20,8	49,2		20,7	48,9		21,0	47,9	
			49,6	7,3		48,5	7,2		48,2	7,2
26NG	2½YR5/6	7,0	3,5	7,2	6,7	1,1	7,7	7,1	0,8	7,8
			4,7	8,4		1,4	8,2		2,1	8,3
28NG	Y5/6	13,9	20,4		14,2	22,4		14,1	21,4	
			20,5	7,7		24,0	7,9		23,9	8,0
29NG	10YR3½/4	—	42,8		—	50,3		—	50,1	
			48,6	7,3		51,8	7,5		52,2	7,5
449US	5YR5/6	6,3	18,4	6,8				4,8	34,7	6,7
			26,7	6,7					40,6	9,0
Dispersing agent b										
71		23,4	52,8		24,9	54,1		22,7	56,2	
			53,4	9,1		54,4	9,2		56,3	9,2
76		20,5	48,9		19,7	47,7		20,9	47,7	
			49,5	7,6		48,9	7,4		49,0	7,5
26NG		6,9	18,8	9,5	7,1	33,6	9,6	7,1	25,1	9,5
			19,3	8,9		36,8	9,0		28,2	9,0
28NG		13,8	21,1		14,2	21,2		14,3	21,1	
			22,4	8,2		21,7	8,2		21,5	8,3
29NG		—	46,2		—	49,4		—	49,2	
			48,0	7,1		50,4	7,2		50,3	7,4
449US		5,8	29,0	8,5				5,6	41,8	8,2
			35,0	8,9					43,3	8,7

Explanation:
NG = New Guinea; US = United States.
Sample 28NG is of swamp provenience.
Sample 29NG has a pH of 7,5 and is not red enough to be a terra rossa.

Whenever possible the pH of the suspension in the cylinder during pipetting is mentioned in the above table and below. With the use of the dispersing agents hitherto specified the suspensions have a natural pH of from 7 to 8. Higher pH's were obtained by adding dropwise to the suspension some caustic soda solution before shaking; a lower pH was obtained by adding a little of the acid corresponding to the dispersing agent used.

It can be seen from the figures in the above table that it are the crumbs of the red soils that are most intensely inorganically cemented; longer action of the hydrochloric acid results in an overall increase in the clay percentage.

We are therefore quite justified in saying that in addition to the effect of the dispersing agent on the result of the analysis, the effect of the reaction time of the acid is a factor of some importance in the clay determination of red soils. The figures

create the impression that the reaction time of one hour, as specified in the procedure, is not long enough to soak and separate all the cemented clay particles, but on the other hand it may be objected that the mechanical composition of the soil as found in the analysis should correspond to the entire context of the soil analysis and that one should not proceed too far in soaking and separating pseudo sand aggregates, thereby releasing particles which have actually nothing in common with the real texture of the soil. This question is very important, not only in the present context, but in connection with the problem, discussed below, as to whether any pseudo sand aggregates occurring in the coarse sand fraction are chafed through or not.

In order to demonstrate clearly what has been discussed above I carried out a number of experiments in which the normal method was contrasted with a pretreatment minus the acid treatment.

TABLE 5. Results obtained with incomplete pre-treatment

	Dispersing agent											
	b						d					
	sample 71			sample 76			sample 71			sample 76		
	$>200\,\mu$	$<2\,\mu$	pH	$>200\,\mu$	$<2\,\mu$	pH	$>200\,\mu$	$<2\,\mu$	pH	$>200\,\mu$	$<2\,\mu$	pH
Normal	23,8	53,2	7,2	19,9	48,0	6,7	23,9	51,9	8,4	19,9	47,9	5,6
Without acid	23,5	43,9	8,8	20,4	47,9	8,3	24,0	43,2	8,8	20,7	48,1	9,3

The figures of TABLE 5 confirm expectations, so that we are obliged to adhere to one method and carefully follow the prescription as regards the acid treatment. Since the subsequent aim of the investigation is to determine the effect of different dispersing agents, throughout the remainer of the work I adhered to a hydrochloric acid treatment of one hour over a thoroughly boiling water bath, as stated in the prescribed procedure. But the fact that even this brief reaction time resulted in changes in the clay fraction is demonstrated by the following.

Several series of experiments were performed on samples 71 and 76. One series was dried by suction after oxidation, 10 g being percolated with 0,5 N ammonium acetate after mixing with 60 g fine quartz sand, and again percolated with 0,05 N HCl after washing with 70 % alcohol. A second series was oxidised and treated with hydrochloric acid for one hour, according to prescribed procedure and then dried by suction and percolated as described above. The results are presented in TABLE 6.

TABLE 6. Some data obtained by percolation of pre-treated samples

meq/100 g soil	K	Na	Ca	Cation-exchange capacity	Morgan
71 H_2O_2	0,115	0,410	0,65	4,50	
	0,130	0,510	0,65	4,50	
71 HCl	0,160	0,198	1,25	4,40	Al high; Fe moderate
	0,175	0,198	1,25	4,70	
76 H_2O_2	0,105	1,06	8,75	22,60	
	0,105	1,05	8,75	22,60	
76 HCl	0,175	0,385	2,87	17,30	Al very high; Fe very high
	0,145	0,310	1,98	20,70	

It will be noticed that only soil 76 was affected by the hydrochloric acid treatment following oxidation, resulting in a decrease in cation-exchange capacity.

7. Further investigation of the methods prescribed

The separation of soil from electrolite-containing liquid following the pretreatment of the soil did not afford much possibility of varying the method. It may be asked why I preferred separation by suction to siphoning. Readers will be familiar with the fact that the clay in tropical soils largely consists of colloidal particles which only exhibit a reasonably rapid degree of flocculation in an electrolite-rich liquid, so that there is a rapid reduction in the sedimentation rate during the repeated siphoning operations required. Since the procedure we prescribe is also meant for the least favourable conditions of equipment and staff we invariably adopted the least delicate method. This proved to be the filtering-off method, especially when the work had to be performed by unskilful or less reliable staff. So long as there is a vacuum below the filter there is no question of any cloudy suspension passing through and hence any loss of clay.

After the electrolite-containing liquid has been removed by suction the soil remaining on the filter has to be washed free of acid, as fluctuating amounts of electrolite residues in the soil would have an unequal effect on the pH of the suspension obtained from this soil, which could result in secondary phenomena, especially when use is made of less buffered dispersing agents. The prescribed amount of 300 cc of distilled water was invariably found sufficient for washing the soil free of acid, although it is important that after the electrolite-rich liquid has been removed by suction the soil should not be left dry on the filter for so long that the disc of soil begins to show shrinkage cracks (this may even happen immediately after the electrolite-containing liquid is removed). In this case the wash water will percolate through the cracks instead of through the disc of soil, thus impairing the washing effect.

After the soil has been washed free of electrolites, dried and transferred to the beaker, the next step is the deflocculation. This proceeds very rapidly, although it can be seen that after the suspension has been left to stand for some weeks and then again homogenised and pipetted off, the clay percentage in the same cylinder is often somewhat higher than before. This is illustrated by the figures in TABLE 7.

TABLE 7. Influence of reaction time on the dispersibility of the suspension

Code No.	Colour	Dispersing agent							
		a				b			
		$>200\ \mu$	$<2\ \mu$			$>200\ \mu$	$<2\ \mu$		
			immediately	1 wk.	1 month		immediately	1 wk.	1 month
26NG	2½YR5/6	6,7	1,9	2,8	6,6	6,4	18,3	19,3	22,3
28NG	Y5/6	12,9	19,5	20,4	21,2	13,7	21,3	21,8	22,9
29NG	10YR3½/4	—	36,6	39,6	47,3	—	47,7	49,9	52,1
67Ta	7½YR5/4	33,3	32,3	33,3	34,3	34,4	36,6	36,8	37,5
437NSW	2½YR4½/6	—	4,6	4,7	5,6				
441TS	2½YR4/4	—	8,0	10,3	12,3				
449US	5YR5/6	5,0	23,1	26,0	39,0	5,8	29,0	35,0	
503Is	2½YR4/5	5,4	30,5	35,3	41,4				

Explanation: NSW = New South Wales; TS = Tasmania.

Thus on the first occasion material was pipetted off from the suspension as in the specified procedure. The results are listed under "immediately". The cylinder was then covered over and left to stand for a week without being made up. It was then shaken again and pipetted off after 8 hours; the results are listed under "1 wk." I then left the cylinder to stand for a further 3 weeks, shook it again, and pipetted after 8 hours. These figures are shown under "1 month". Thus in each pipetting operation the total amount of clay present was reduced by 1/50th.

A more considerable difference can be obtained by pouring the dispersed liquid into the cylinder through the 200 μ-sieve. Generally speaking there will not be a good separation between coarse sand and particles smaller than 200 μ when the only step taken is to spray the soil on the sieve with distilled water. Even in the case of Dutch soils a substantial amount of clay still remains on the sieve, the cylinder already being full up with suspension.

During spraying the fingers should rub the soil over the sieve. Particles of very heavy montmorillonite soils of the type forwarded to me from Mozambique cohere again below the sieve when rubbed through it, so that the cylinder contains well-divided particles as well as conglomerates which are very difficult to homogenise. Consequently there are also some disadvantages in rubbing the clay while spraying it, but in any case it is quite impossible to work this type of soil through the sieve without rubbing and to limit the total volume of suspension to 1 litre (Since these soils are not otherwise included in the investigation I will only remark in passing that such very heavy clays are better to work from the filter immediately when still wet). Another problem connected with this necessary rubbing occurs during the processing of laterites having a large amount of pseudo sand aggregates, such as the samples sent to me from the Argentine. In this case the coarse sand fraction has to be separated from the other fractions by spraying and careful rubbing, spraying alone being insufficient. During this rubbing the aggregates continually lose finer particles, so that after the volume of 1 litre has been reached in the cylinder the parts remaining on the sieve still produce a turbid washing water. Should the aggregates have been rubbed harder? And how long should rubbing continue? The entire "coarse sand" fraction of these soils can often be rubbed through the sieve if only the operation is continued long enough.

Thus one of these soils gave a coarse sand fraction of 7,3 % after vigorous rubbing and one of 18,7 % with more careful rubbing. Other figures are 7,1 % and 22,2 %; 11,4 % and 23,8 %; 8,4 % and 21,6 %. But the presence or absence of rubbing did not result in any appreciable increase in the clay content of the material I used. This was confirmed visually, since when the pseudo granules are rubbed they disintegrate into black, rapidly settling Fe_3O_4-particles. Buth the intermediate fractions are undoubtedly considerably affected, so that the question arises once again. What does one expect to achieve by means of a mechanical investigation?

8. Effect of the concentration of dispersing agent in the suspension

In view of the very low exchange capacity of the lateritic soils it is quite conceivable that the addition of the dispersing agent, *i.e.* electrolite, will cause flocculation of the colloidal clay more readily than in the case of the highly adsorbent soil 76.

In order to determine this, soils 71 and 76 were treated with increasing amounts of dispersing agents, 3½ cc, or one equivalent of the cation-exchange capacity of this soil at a pH of 8,3, being added to No. 71, this being the smallest amount of agent

a which causes difficulties with this soil. The dispersing agent used in addition to a was d, which for this purpose was diluted in a 1 : 1 ratio. Hence, like a, it should be used in an amount of 50 cc (the normal amount prescribed being 25 cc). An analysis was also carried out with 200 cc of d as an extreme amount. The results are presented in TABLE 8.

TABLE 8. Results obtained with increasing amounts of dispersing agents

	Disp. agent	Amount of dispersing agent (cc)						
		3½	10	20	30	40	50	200
Sample 71	a	6,6	6,5	9,0	13,7	16,5	19,7	
pH		8,1	8,0	8,1	8,8	8,7	8,5	
Sample 76			49,1	48,8	49,1	49,5	49,6	
pH			6,8	6,5	7,0	7,1	7,3	
Sample 71	d		26,5	49,4	50,8	50,8	50,6	
pH			8,4	8,6	9,0	8,7	8,5	
Sample 76			48,0	48,5	47,7	47,0	47,2	47,4
pH			6,6	6,1	6,8	7,3	7,6	7,8

It may be concluded from the figures in TABLE 8 that within reasonable limits there is no question of flocculation due to the addition of excess dispersing agent with respect to the cation-exchange capacity.

9. Effect of the anion on the degree of dispersibility

Thus we are still faced with the fact that when lateritic soils are deflocculated they are extremely sensitive to the anion accompanying the dispersing sodium. Since there is fairly limited variation in the anions of the dispersing agents hitherto tested, the obvious course was to increase the number of dispersing agents by a number of sodium compounds having very divergent anions. There was, in fact a possibility that the lyotropic series of anions is the key to the problem of differences in dispersibility.
A very large number of mechanical analyses were carried out with twelve sodium compounds selected from this series, each agent being tested at different pH's. Not to trouble the reader with an uninteresting summary of the results, and to cut a long story short, I will merely state that the investigation gave the following conclusion:
Although there is some anion influence it was also found that soil 76 is little affected by the anion so long as the pH in the cylinder is higher than about 4 during sedimentation. As regards the dispersing action on soil 71 of the 12 newcomers, it must be stated that despite some variation in the figures the general tendency is in complete agreement with what we found with the use of agent a. Hence the low dispersing action of agent a on lateritic soils is the normal state of affairs for most sodium compounds. Only one of the new agents employed was capable of reaching a degree of dispersibility equal to that of agents b, c, d and e, this exception being sodium hydroxide solution!

10. Effect of the pH on the degree of dispersibility

One may be readily inclined to lay the blame on the pH, but perhaps unjustifiably because the figures obtained with the anions P_2O_7 and PO_3 occurring in dispersing

agents b, c, d and e did not show that manipulation of the pH of the suspensions caused the pH to have such a predominant effect. Moreover even at a pH increasing to beyond 10 there was no single newcomer with which a comparable degree of dispersibility could be obtained with dispersing agents b, c, d and e. There is a possibility that comparable figures may be produced with a still higher pH, but in this case it is not the anion of the dispersing agent but the added OH ions that are the determining factor. And we already know from the positive results obtained with caustic soda solution as dispersing agent that the OH ion is an excellent deflocculator.

It is therefore of greater interest to ascertain the pH effects of agents which already have an excellent effect in a neutral medium. Agents b, c, d and e came under this category. Our choice fell on b, the results being presented in TABLE 9.

TABLE 9. Influence of pH on the dispersibility of the suspension

Sample	Fraction $> 200\ \mu$	Clay $< 2\ \mu$	pH on sedimentation
71	22,9	51,7	5,8
	23,9	53,3	7,0
	23,9	51,9	8,4
	23,5	52,5	9,4
76	20,5	0,0	3,1
	20,4	47,2	4,1
	20,2	47,9	5,0
	19,9	47,9	5,6
	20,6	47,5	6,7
	20,2	48,8	7,7
	20,0	47,9	8,3
	20,7	48,1	9,3

If we consider in the light of the figures of TABLE 9 the result of the above-mentioned sodium hydroxide solution, *viz.*:

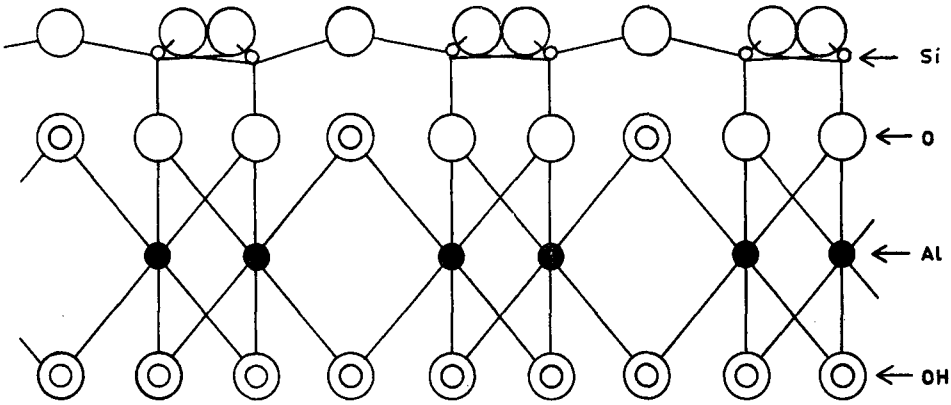
Sample	Fraction $> 200\ \mu$	Clay $< 2\ \mu$	pH on sedimentation
71	24,2	52,2	11,7
	25,5	51,8	11,5
	22,7	22,0	8,5 [1]
76	19,0	48,8	10,8

[1] Too little Na^+

we come to realise that it is not the pH as such that is the determining factor, but the concentration of OH ions when a sodium hydroxide solution is used as the dispersing agent, and that these ions may be replaced by the anions present in agents b, c, d and e. The results obtained with agent f show that the CO_3 ion is not responsible for the high degree of dispersibility. Hence it is ultimately the P_2O_7 and PO_3 ions which are capable of competing with OH-ions in dispersing effect, *viz.* of occupying the place of OH in the deflocculation of lateritic soils.

When the crystal lattice of kaolinite — *i.e.* the clay mineral of lateritic soils — is examined, its lattice parameter assumes the form shown in FIG. 1.

FIG. 1. The crystal lattice of kaolinite



The clay determinations we made in tropical soils were clear evidence that the clay fraction in these soils largely consists of particles of colloidal size, *viz.* particles smaller than 0,5 μ. Bearing this in mind we must assume that the kaolinite lattices present are only of slight extent and have approximately the appearance as shown in FIG. 2.

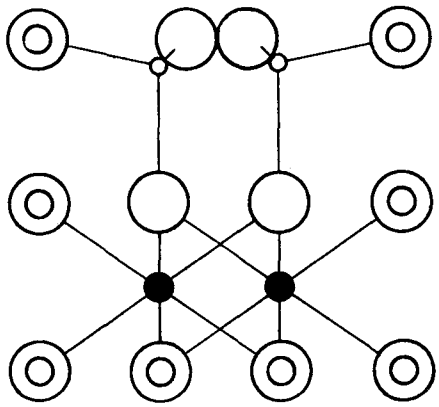
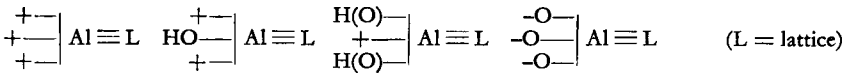


FIG. 2. The colloidal lattice of kaolinite

But a lattice of this kind with a clay percentage of about 53 %, as we found in soil 71, would cause considerably greater exchange capacity than was found in this soil. Hence the only explanation must be that many of these theoretically present OH groups are not added to the lattice structure in the soil. As a result, in addition to the negative cation-adsorbent points which are derived from the OH-groups and are characteristic of all mineral clays, an exceptionally high number of positive forces occur on the edges, these forces being due to the fact that not all OH-groups shown in the drawing form part of the lattice structure.

As the OH-ion concentration increases, *i.e.* the pH in the soil (or in the suspension) increases, the mineral clay is able to add OH to the lattice, thereby reducing the number of positive forces and increasing the number of negative points (*i.e.* the cation-exchange capacity). We see, in fact, an increase in exchange in soil 71 of 2,65 meq

per 100 g of soil at pH 4,8 to 4,0 meq at a pH of 8,3, which is an exceptionally high percentage increase compared with that of soil 76 under the same conditions, so that it cannot be solely ascribed to the mixed NH_4 - H percolation from which the exchangeability at 4,8 is calculated.
This may be shown diagrammatically by the following sketch :



Reverting now to the dispersing investigation, we can clearly see from this diagram the dispersing effect of an excess of OH-ions on a lateritic soil, since it results in a decrease in the number of positive, sodium-repellant forces and an increase in the number of negative, cation-adsorbent points to which the Na^+ must adhere in order to exert their dispersing effect.
Let us now return to the soil as such. As we have seen, with an increasing OH-ion concentration these ions are first of all added in their entirely to the lattice. But these OH-groups are then to be regarded as O^{2-}-ions which are firmly built on to the crystal lattice with H^+ adsorbed to them. Now this H^+ (or H_3O^+) is an extremely small ion, so that it will be less affected by any neighbouring positive forces than the far larger (wet) metal ions that might also be adsorbed by these O^{2-}-points. It would seem likely that there will only be regular adsorption of metal ions by these small kaolinite particles when all positive forces on the surface have been swept away by the addition of OH-groups. In other words if we percolate or shake soil 71 with a rising pH there is bound to be a sudden sharp increase in the derived cation-exchange capacity.

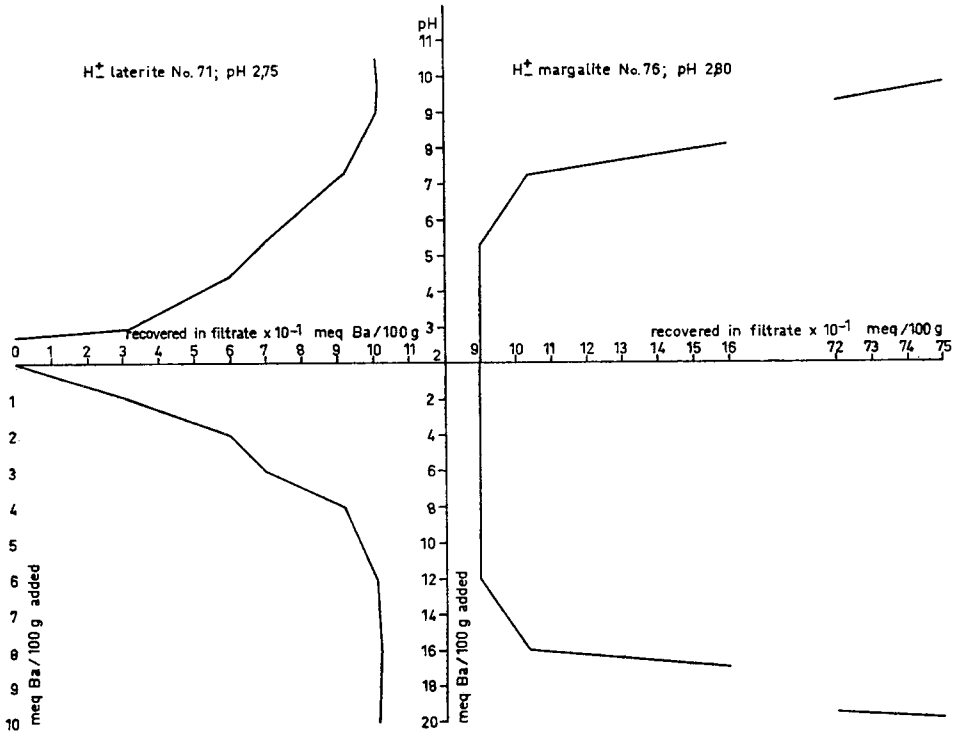
11. Proof of the theory

The following experiment was carried out in order to confirm the theory outlined above :
The soil was converted into a H^+-soil by percolation with 0,05 N HCl, followed washing until all acid was removed.
Increasing amounts of a $Ba(OH)_2$-solution of known concentration were added to equal amounts by weight of this soil in a ratio of 1 : 2½ and shaken for one hour. The pH of the suspension was then determined, as well as the amount of Ba^{2+} which had remained behind in the filtrate.
For the sake of completeness soil 76 was also included in this examination. The results are shown in the graph (FIG. 3).
It can be seen, in fact, that further increasing the amount of $Ba(OH)_2$ added to soil 71 at pH 9 does not result in an increase in the amount of Ba^{2+} recovered in the filtrate. It would appear that at pH 9 the clay mineral kaolinite is capable of adsorbing large amounts of metal ions. In the case of soil 76 it can be seen that the great increase in adsorption occurs at the low pH; after a pH of about 5,5 none of the Ba^{2+} supplied are wholly adsorbed. In the light of the theory evolved concerning soil 71, this agrees with what we found, *viz.* that soil 76 is excellently dispersed at a pH of only 4 or there-about.

12. To what extent can P_2O_7- and PO_3-ions assume the role of OH-ions?

The above is probably a reasonable explanation of the part played by the OH-ion

FIG. 3. Results of $Ba(OH)_2$-treatment



concentration. But the reason why the P_2O_7- and PO_3-ions are also good deflocculators is still obscure, even though it is clear that these ions must be capable of assuming the role of an excess of OH during dispersion.

We have seen from the above that good dispersion is only possible when the positive forces on the kaolinite surface are eliminated as far as possible and replaced by negative points adsorbing metal ions, *viz.* Na^+. This means that both these phosphate ions should be capable of bonding themselves to the positive forces, or expressed in a different way, that kaolinite is able to extend its lattice with these phosphate ions, for which it must generally employ OH-ions.

The following experiment shows that this is an acceptable explanation.

Some OH^- is added dropwise to a dilute Al^{3+}-containing solution, a positive aluminium hydroxide sol is formed; this can be checked by means of electrophoresis. An equivalent amount of dispersing agent b (pyrophosphate) or c (metaphosphate) is added to this sol and to the Al^{3+} used and electrophoresis again applied. The sol is found to have reversed its charge, but the pH does not correspond, *i.e.* it is lower than it would have been if this negative sol had been prepared with OH^-.

My attempts with the other dispersing agents were unsuccessful as the sol invariably flocculated.

I believe I have provided a satisfactory explanation of the divergent behaviour of

the lateritic sols during sedimentation, or should I have said, the divergent behaviour of the dispersing agents with the meta- or pyrophosphate ion?
I would therefore draw the following final conclusion from this investigation. One is always on the safe side as regards the degree of deflocculating of the soil suspension provided a meta- or pyrophosphate-containing dispersing agent is used for the dispersion of any type of soil.

REFERENCE

LEENHEER, L. DE, and J. VAN HOVE 1957 Vergelijkende studie over het gebruik van natriumoxalaat-carbonaat, natriumpyrofosfaat en natriumhexametafosfaat als peptisatiemiddel voor de mechanische analyse van gronden. (Comparative study on the use of Na-oxalate-carbonate, Na-pyrophosphate and Na-hexametaphosphate as dispersing agent for mechanical analysis). *Meded. Landb.hogesch. Opzoek.stations v/d Staat, Gent. 22*, 225—242. Summaries in English, French and German.