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EXPERIMENTAL STUDIES OF THE FERROLYSIS PROCESS PRODUCTION OF EXCHANGE ACIDITY AND DEMONSTRATION OF THE CATALYTIC ROLE OF THE CLAY MINERALS

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In soils where seasonal successions of wet and dry periods create an alternance of anaerobic (hydromorphic) and aerobic conditions, the state of iron goes through reduction and oxydation cycles. The change from reduced to oxydized iron is combined with hydrolysis and production of protons according to this scheme (3) :

$$2\,Fe^{2+} + 1/2\,O_2 \rightleftharpoons 2\,Fe^{3+} + O^{2-}$$

$$2\,Fe^{3+} + 6\,H_2O \rightleftharpoons 2\,Fe(OH)_3 + 6\,H^+$$

$$O^{2-} + 2\,H^+ \rightleftharpoons H_2O$$

$$2\,Fe^{2+} + 1/2\,O_2 + 5\,H_2O \rightleftharpoons 2\,Fe(OH)_3 + 4\,H^+$$

The action of protons on the clay minerals end up with production of exchangeable Al. This weathering process has been describe by Brinkman (1970) as ferrolysis.

The present study has been done in order to test the efficiency of this process in the formation of exchange acidity. The experiment consisted in alternate treatments of clay samples with a reduce iron reagent (iron (II) lactate 10^{-3}M) and with drying. The test was done on natural montmorillonite (Wyoming), calcie montmorillonite (Wyoming) and calcie kaolinite (Caroline). In this experiment, only the second phase, oxydation of reduced iron has been reproduced (Table I).

The amount of Ca liberated is lower than that of Fe retained. Protons and Al^{3+} ions appear progressively in the series of exchangeable cations.

The results (Tables II, V and VI) show the catalytic effect of clay mineral wich is more acuite for montmorillonite than for kaolinite. Together, the production of exchange acidity occur with smectite and kaolinite but is more important with smectite.

This indicated that catalysis is not only restricted to interlayer surface. The exchangeable form represents a small portion of the retained iron, almost half of it went in a higly polymerised and hardly extractable form.

In the ferrolysis process, in order to reproduced reduction-oxydation cycles, it is necessary that the alternance of the two phases be maintained. In particular, the conditions for reduction seem only possible through biochemical process.

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(3) It is a model that does not take into account the mineral reality.

Table I : General presentation of experiments.

Minerals	Ca^{++}-Montmorillonite	Ca^{++}-Montmorillonite	natural Montmorillonite	Ca^{++}-Kaolinite
Reactant	Water	Iron (II) lactate (pH 4,8 - 4,9)		
Treatment	Alternative procedure	Contact with reactant : 1 to 2 days Air drying for 12 days.		

Table II : Evolution of the controled parameters during the various treatments. For each clay category, results are the mean of replicates.

	Ca^{++}-Montmorillonite					Ca^{++}-Kaolinite				
	pH	"retained" Fe^{2+} (méq./100 g)		liberated Ca^{++} (méq./100 g)		pH	"retained" Fe^{2+} (méq./100 g)		liberated Ca^{++} (méq./100 g)	
		individual treatment	cumulated treatment	individual treatment	cumulated treatment		individual treatment	cumulated treatment	individual treatment	cumulated treatment
1	6,66	5,00		2,00		5,47	4,56		1,97	
2	5,88	4,98	9,98	1,68	3,68	4,88	3,53	8,09	1,33	3,30
3	5,42	4,87	14,85	1,85	5,53	4,76	2,79	10,88	0,93	4,23
4	5,49	4,81	19,66	1,75	7,28	4,81	3,06	13,94	0,50	4,73
5	5,58	4,88	24,54			4,85	3,10	17,04	0,27	4,90
6	5,71	4,88	29,42	1,45	8,73	4,73	2,75	19,79	0,23	5,13
7	5,46	4,91	34,33	0,35	9,08	4,60	2,97	22,76	0,04	5,17
8	-	4,95	39,28	0,13	9,21	4,64	2,84	25,60	0,03	5,20
9	5,66	4,98	44,26	0,07	9,28	4,60	3,20	28,80	0,04	5,24
10	6,19	4,98	49,24	0,30	9,58	4,64	3,10	31,90	0,04	5,28
11	5,45	4,98	54,22	0,20	9,78	4,55	3,40	35,30	0,04	5,32
12	5,77	4,97	59,19	0,22	10,00	4,56	3,00	38,30	0,02	5,36
13	5,64	5,00	64,19	0,33	10,33	4,53	2,88	41,18	0,04	5,40
14	5,02	4,70	68,89	1,50	11,83	4,48	2,90	44,08	0,12	5,52
15	6,09	5,00	73,89	0,50	12,33	4,54	2,70	46,78	0,03	5,55
16	5,70	4,95	78,84	0,39	12,72	4,60	2,50	49,28	0,04	5,59
17	5,72	4,89	83,73	0,74	13,46	4,55	2,49	41,77	0,01	5,60
18	5,44	4,83	88,56	0,72	14,18	4,50	2,69	44,46	0,01	5,61

Table V : Determinations made on KCl extract exchangeable cations (results expressed in méq./100 g).

	Ca^{++}-Montmorillonite		Natural Montmorillonite		Ca^{++}-Kaolinite	
	14 treatments	18 treatments	14 treatments	18 treatments	14 treatments	18 treatments
pH	4,26	4,15	3,98	3,99	4,45	4,38
H^{+}	0,88	1,42	1,94	1,86	0,60	0,92
Al^{+3}	1,68	1,91	2,05	2,30	1,30	1,43
Fe^{+2}	8,79	11,38		17,24		1,55
Fe^{+3}	1,65	3,42		1,56		0,20
Ca^{+2}	75,15	65		13,10		0,75
ΣM^{+x}	88,15	83,13				4,25