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L. GEREI, M. REMÉNYI *

TRANSFORMATION OF CLAY MINERALS IN Na-SALT SOLUTIONS

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Abstract. The effect of Na_2CO_3 and Na_2SO_4 solutions on the transformation of clay substances has been investigated. It has been found that in the kaolin sample well crystallized aluminium hydroxide forms at the cost of amorphous substances. In the structure of montmorillonite, mixed layers of the hydromica type arise. In the case of clay fraction of soil, an increase in the content of minerals with mixed-layer illite/montmorillonite structures has been noted.

INTRODUCTION

Soil-forming processes occurring in a salinized, alkaline environment may involve changes in the structure of clay minerals (degradation, transformation) or their neoformation. Na-salt solutions play a significant role in those processes, and their effect on the soil clay minerals has been investigated by several authors. The formation of new minerals (Barnishel, Rich 1965; Gupta, Malik 1969), their destruction (Arnold 1960; Correns 1961), or substantial transformation of their structure (Gerei *et al.* 1966; Gerei 1965; Laatsch 1954; Michailova, Gradushov 1969) have been observed under those conditions. To have a better insight into the secondary salinization processes caused by irrigation, the present authors investigated „in vitro" the transformations of clay minerals effected by Na-salt solutions.

EXPERIMENTAL

The investigations were carried out on the following samples:

— Zettlitz kaolin (GDR),

— Füzérradvány illite (Hungary), containing 15—20% of swelling layers in its structure,

* National Institute of Agricultural Quality Testing, Budapest, Keleti Károly u. 24, Hungary.

Table 1

Chemical analyses of the samples

Component	Kaolin Zettlitz	Illite Füzérradvány	Bentonite Istenmezö
SiO_2	46.30	53.30	65.40
Al_2O_3	39.64	34.10	21.20
Fe_2O_3	0.64	3.80	4.24
CaO	0.26	0.62	0.29
MgO	0.18	2.70	5.96
Na_2O	0.10	0.24	0.20
K_2O	0.02	0.45	0.33

— Istenmezö bentonite (Hungary), containing 80% of dioctahedral montmorillonite, quartz and a small amount of cristoballite. Analyses were performed on the < 1 μm bentonite fraction separated by sedimentation.

The chemical composition of the samples is shown in Table 1.

Moreover, investigations were carried out on the clay fraction separated from the horizon *A* of two strongly salinized meadow soils.

2-g samples of clay substance were treated with 10 ml of 2N Na_2CO_3 and Na_2SO_4 solution and left for a week. Then they were dried at 105°C or frozen at −4°C, or dried and frozen alternately. After desiccation the samples were treated with such an amount of distilled water that the concentration of salt solution remained unchanged. After 70 treatments the samples were washed with distilled water. The chemical composition of the solution was determined by atomic absorption spectroscopy whereas the clay substance was subjected to X-ray examinations and thermal analysis on the derivatograph.

RESULTS

As appears from the chemical composition of the filtrate (Table 2), the treatment of samples with sodium carbonate solution is generally more effective than that with sodium sulphate since more Al_2O_3 and SiO_2 pass into the solution. Iron has been found in the filtrates obtained upon treatment of bentonite and soil clay fraction; it is missing, on the other hand, in the filtrates after kaolin or illite. During treatment with Na_2SO_4 solution more Fe is dissolved than during treatment with Na_2CO_3. The amount of soluble silica in the filtrates increases in the sequence: kaolin — illite — bentonite — clay fraction of meadow soils. In the latter, also the highest Al content has been noted. The Mg content is the lowest in sulphate-treated kaolinite and the highest in the filtrates after bentonite and soil clay fraction.

Filtrate analyses have revealed that salt solutions of relatively low concentration affect visibly the structure of clay minerals only after a longer period of time. Kaolinite is the most resistant to treatment, illite is less so, whereas the most profound chemical and structural changes have been noted in bentonite and soil clay fraction. Yet, it must be taken into account that the number of cations ascertained by analysis in the filtrate does not fully reflect the effect of alkali solutions on clay substances because both the fixation of dissolved components by these substances and the formation of new compounds are possible. As appears from investigations, amorphous and weakly crystallized oxides are presumably the first to dissolve, and only then does the crystal lattice of minerals slowly collapse. This is evidenced by a change in the dissolved Si : Al

Table 2

Chemical analyses of filtrates after treatment of samples 70 times with Na-salt solutions

Sample		Treatments with Na_2SO_4 solutions				Treatments with Na_2CO_3 solutions			
		Fe_2O_3	Al_2O_3	MgO	SiO_2	Fe_2O_3	Al_2O_3	MgO	SiO_2
		mg/100 ml solution							
Kaolinite	D	—	0.39	0.76	0.92	—	3.55	1.00	7.5
	F	—	0.59	0.49	1.48	—	1.92	0.64	6.2
	D—F	—	0.43	0.49	0.98	—	3.24	0.64	2.33
Illite	D	—	1.96	2.26	6.03	—	5.73	1.98	8.30
	F	—	1.31	2.03	7.78	—	6.06	1.60	6.71
	D—F	—	1.82	2.31	7.59	—	10.88	1.58	7.55
Bentonite	D	0.05	0.57	4.63	5.99	0.1	0.77	0.69	25.50
	F	0.3	4.78	5.75	17.5	0.25	2.88	3.23	16.0
	D—F	0.4	0.39	5.24	8.56	0.1	0.43	0.54	23.1
Soil 1	D	0.25	3.87	5.47	32.3				
	F	0.75	5.77	4.48	31.9	0.1	8.91	2.74	26.7
	D—F	0.65	6.17	2.74	25.00	0.05	9.95	1.58	9.09
Soil 2	D	0.25	3.55	1.89	9.63	—	2.58	1.08	20.99
	F	0.55	1.38	1.93	24.8	0.12	7.46	1.45	16.7
	D—F	0.32	5.41	2.32	28.0	0.10	23.18	2.64	22.25

D — dried, F — frozen, D—F — dried-frozen.

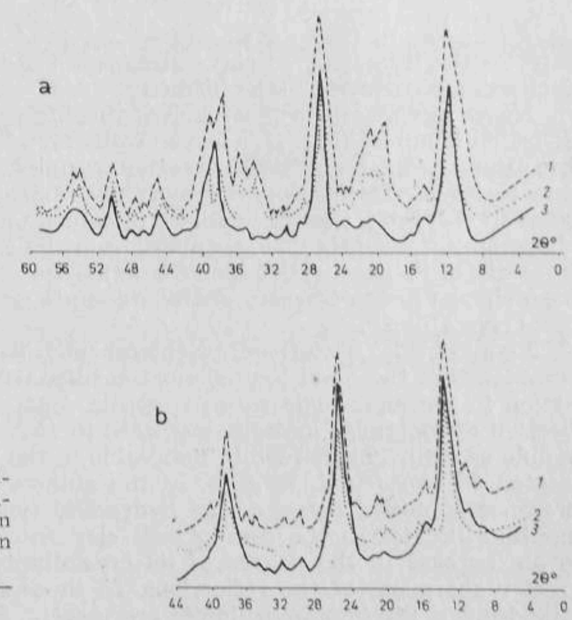

Fig. 1. X-ray diffraction patterns of kaolinite after 70-times treatment with: *a* — 2n Na_2SO_4-solution, *b* — 2n Na_2CO_3-solution

1 — dried-frozen, *2* — dried, *3* — untreated

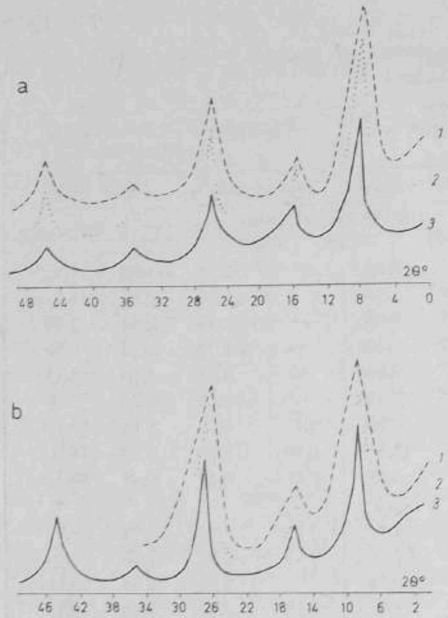

Fig. 2. X-ray diffraction patterns of illite after 70-times treatment with: *a* — 2n Na_2SO_4-solution, *b* — 2n Na_2CO_3-solution
1 — dried-frozen, 2 — dried, 3 — untreated

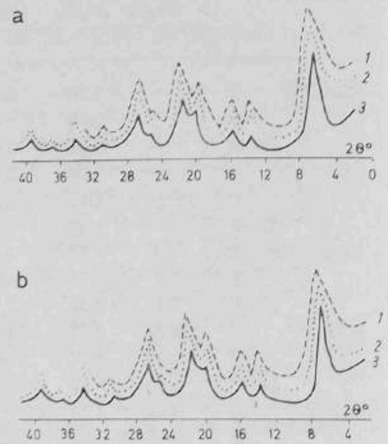

Fig. 3. X-ray diffraction patterns of montmorillonite after 70-times treatment with: *a* — 2n Na_2SO_4-solution, *b* — 2n Na_2CO_3-solution
1 — dried-frozen, 2 — dried, 3 — untreated

ratio as the treatment of clay substances is prolonged, as well as by an increasing Mg content in the filtrates.

X-ray examinations have shown that Na_2CO_3 solution has no visible effect on kaolinite (Fig. 1), whereas well crystallized aluminium hydroxide has been recorded in Na_2SO_4-treated samples. Its presence seems to be due to the crystallization of amorphous substances occurring in kaolin since the crystal lattice of kaolinite remained unchanged. Neither has illite shown any significant changes apart from slight broadening and increased intensity of its basal reflections (Fig. 2). These facts may be accounted for by a change in the fineness of this mineral and an increase in the degree of its crystallinity.

X-ray powder patterns of oriented bentonite preparations (Fig. 3) have revealed that the basal line of montmorillonite is asymmetrical. Its inclination in the high-angle range is gentle. Upon glyceration, the basal reflection of montmorillonite is displaced to 16 Å, the reflection 10 Å being visible as well. This is readily noticeable in the case of samples that were treated 70 times with Na_2CO_3. In the authors' opinion, it points to the presence of mixed layers of the hydromica type in the crystal lattice of montmorillonite. In the case of soil clay fraction, 70 treatments result in an increase in the degree of its crystallinity, which is evidenced by greater sharpness of the reflections. In those samples small amounts of mixed-layer illite/montmorillonite are present. From the basal reflections

on the X-ray diffraction patterns it may be inferred that treatment with Na-salt solutions results in an increase in the content of mixed-layers structures. In the samples treated with Na_2CO_3 solution and then dried and frozen alternately, products of intermediate character have been noted (Fig. 4).

To summarize, it may be stated that treatment with Na-salt solutions involves the following transformations of clay minerals:

1. The removal of weakly crystallized oxides and hydroxides is followed by slight opening of the crystal lattice of clay minerals.
2. In kaolin, well crystallized aluminium hydroxide forms at the cost of amorphous substances (Fig. 1).
3. Mixed layers of the hydromica type arise in the structure of montmorillonite.
4. In the case of soil clay fraction there is an increase in the content of minerals with mixed-layer illite/montmorillonite structure (Fig. 4).

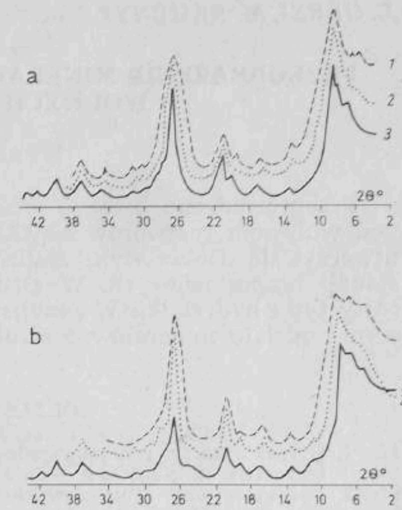

Fig. 4. X-ray diffraction patterns of clay fraction from *A*-horizon in solonized soil after 70-times treatment with: *a* — 2n Na_2SO_4-solution, *b* — 2n Na_2CO_3-solution
1 — dried-frozen, 2 — dried, 3 — untreated

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L. GEREI, M. REMÉNYI

PRZEOBRAŻENIE MINERAŁÓW ILASTYCH W ROZTWORACH WODNYCH SOLI SODOWYCH

Streszczenie

Przeprowadzono badania zmian zachodzących w minerałach ilastych pod wpływem roztworów Na_2CO_3 i Na_2SO_4. Stwierdzono, że w kaolinie utworzył się dobrze wykrystalizowany wodorotlenek glinu kosztem substancji bezpostaciowych. W strukturze montmorillonitu powstały przerosty typu hydromiki. W przypadku frakcji ilastej gleb nastąpiło zwiększenie udziału minerałów o strukturach mieszanych illit-montmorillonit.

OBJAŚNIENIA FIGUR

Fig. 1. Dyfraktogramy rentgenowskie kaolinitu po 70-krotnym traktowaniu: *a* — 2n roztworem Na_2SO_4, *b* — 2n roztworem Na_2CO_3

Fig. 2. Dyfraktogramy rentgenowskie illitu po 70-krotnym traktowaniu: *a* — 2n roztworem Na_2SO_4, *b* — 2n roztworem Na_2CO_3

Fig. 3. Dyfraktogramy rentgenowskie montmorillonitu po 70-krotnym traktowaniu: *a* — 2n roztworem Na_2SO_4, *b* — 2n roztworem Na_2CO_3

Fig. 4. Dyfraktogramy rentgenowskie frakcji ilastej z horyzontu *A* gleby zasolonej po 70-krotnym traktowaniu: *a* — 2n roztworem Na_2SO_4, *b* — 2n roztworem Na_2CO_3

Л. ГЕРЕЙ, М. РЕМЕНИ

ИЗМЕНЕНИЕ ГЛИНИСТЫХ МИНЕРАЛОВ В ВОДНЫХ РАСТВОРАХ НАТРОВЫХ СОЛЕЙ

Резюме

Проведено исследования изменений происходящих в глинистых минералах под воздействием растворов Na_2CO_3 и Na_2SO_4. Обнаружено, что в каолине из аморфного вещества хорошо кристаллизовалась гидроокись алюминия. В структуре монтмориллонита образовались включения типа гидрослюд. В случае глинистой фракции почв произошло увеличение доли минералов со смешанными иллит-монтмориллонитовыми структурами.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Рентгенограммы каолинита после 70-кратной обработки: *a* — 2n раствором Na_2SO_4, *b* — 2n раствором Na_2CO_3

Фиг. 2. Рентгенограммы иллита после 70-кратной обработки: *a* — 2n раствором Na_2SO_4, *b* — 2n раствором Na_2CO_3

Фиг. 3. Рентгенограммы монтмориллонита после 70-кратной обработки: *a* — 2n раствором Na_2SO_4, *b* — 2n раствором Na_2CO_3

Фиг. 4. Рентгенограммы глинистой фракции горизонта *A* засоленной почвы после 70-кратной обработки: *a* — 2n раствором Na_2SO_4, *b* — 2n раствором Na_2CO_3