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POTASSIUM FIXATION IN SMECTITES BY WETTING AND DRYING IN NaCl SOLUTION

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Abstract: Wetting and drying experiments performed at 60 °C were used to examine the effect of various concentrations of NaCl solutions on the degree of K-fixation. Cheto and Texas montmorillonites were used as a starting material for experiments. K-saturated samples were put through up to 100 cycles in 0.05–5 M NaCl solutions. The expandability values, measured by XRD peak position method, indicate a higher degree of K-fixation in the most diluted NaCl solution at a given number of cycles in comparison with smectites wet by distilled water. However, the effect of NaCl solutions of higher molarity on the degree of K-fixation is not straightforward. Smectites wet by moderately concentrated NaCl solutions approach the K-fixation pattern of water-wet smectites. K-fixation in the smectites in the most concentrated NaCl environment was clearly retarded. The effect of NaCl on K-fixation was much less visible when a buried altered volcanoclastic sample was used.

Key words: wetting and drying cycles, NaCl environment, K-fixation, smectites.

Introduction

Many papers are devoted to the problem of potassium fixation in smectites and to the related change of expandable layers into non-expandable. This reaction, which occurs in a variety of environments became one of the most extensively studied clay mineral reactions. The most frequently studied reactions are diagenetic K-fixation in shales, illite formation in sandstones as well as hydrothermal illitization. Significantly less attention has been paid to potassium fixation (diagenetic and non-diagenetic) in saline environments. Some studies focus on potassium fixation within limited depth intervals in the sediments of saline lakes (Singer & Stoffers 1980; Deconinck et al. 1988; Hay et al. 1991; Turner & Fishman 1991). The common conclusion of these studies is that a high degree of potassium fixation is not caused by diagenetic change (i.e. burial related temperature), but is associated with specific chemical compositions of lake water. The observed clays were affected by alkaline-hypersaline environment and did not experience deep burial. Moreover, Šucha (unpublished data) observed a higher degree of potassium fixation in the buried bentonites from the saline environments compared to bentonites from non-saline environments in the East Slovak Basin, even though these bentonites experienced the same diagenetic temperature.

In the laboratory, potassium fixation can be achieved by two ways. K is rendered non-exchangeable by hydrothermal heating of K-smectites (Eberl & Hower 1976) and/or K-fixation occurs when K-smectites are exposed to repeated wetting and drying (WD) cycles (Gaultier & Mamy 1979; Eberl et al. 1986; Šucha & Širáňová 1991; Mikloš & Číčel 1993). Wetting and drying lead to irreversible fixation of K and subsequent layer collapse. This transformation is not accompanied by a significant change in the chemistry of the 2 : 1 layers as is the case during hydrothermal smectite alteration. The number of the layers collapsed at the end of the WD experiment is proportional to the layer charge of the original sample (Eberl et al. 1986; Šucha & Širáňová 1991).

Most of the WD K-fixation experiments were performed in distilled water. Eberl et al. (1986) observed that WD in KOH solutions led to a higher proportion of collapsed layers than WD cycles of K-saturated samples in distilled water. Later experiments (Eberl et al. 1993) showed that heating smectites at 60 °C in 0.1–1 M KOH promoted layer collapse. The same experiment with 3 M KOH initially led to a drastic reduction in expanded layers finally leaving an amorphous product. Heller-Kallai & Eberl (1997) performed WD experiments at 60 °C in the presence of K_2CO_3, $KHCO_3$, $K_2C_2O_4$, KCO_2CH_3 and KCl. Samples cycled with K_2CO_3 or $KHCO_3$ contained more collapsed layers than those treated with acetate or chloride. Oxalate appeared to attack the clay layers. In addition, smectites exposed to WD cycles at high pH using K_2CO_3 or $KHCO_3$ solutions underwent partial deprotonation.

The present study examines the effect of various concentrations of NaCl solutions on the degree of potassium fixation by WD at 60 °C. Whereas high alkalinities of saturated KOH solutions are geologically rare, NaCl solutions of different concentrations may play a significant role in the diagenesis of sediments taking place in the playas and sabkhas of arid regions. In the case of the buried sediments, they may affect the reaction as brines circulating along the faults and in the pore spaces.

Materials and methods

The starting material were two smectites from the Source Clay Mineral Repository: Cheto (SAz-1), Texas (STx-1) and smectite from the buried bentonite of borehole Bánovce 4 (Ban 4/1) in the East Slovak Basin having an expandability of

~90 %. The <2 μm size fraction was obtained using sedimentation for all samples. Sample Ban 4/1 was treated prior to the size separation as described by Jackson (1975) to remove carbonates, Fe-Mn oxyhydroxides and organic matter. Removal of the interference phases makes the identification of I-S peaks easier. The smectites were converted into K-form using 1 M KCl solution (the samples were treated 3 times overnight and then washed with distilled water). Two grams of clay were then put into 20 ml of sodium chloride solutions of the following concentrations: 0.05, 0.1, 1, 2 and 5 M. A gentle ultrasonic treatment, not exceeding 1 minute, was applied for better sample disintegration. The samples were dried at 60 °C with occasional stirring. 20 ml of distilled water was added to the dry sample for each subsequent WD cycle. When a certain number of cycles (5, 20, 50 and 100) was completed, aliquots of the samples were taken for XRD investigation. Exchangeable cations (K^+ or Na^+) were replaced by treating the samples with 0.05 M $SrCl_2$ solution overnight (Eberl et al. 1986), washed with deionized water and dialyzed to remove the excess salts. Oriented specimens were prepared by settling water suspensions on glass slides. The XRD of air-dried and ethylene-glycolated specimens were carried out using a Philips 1075 diffractometer with Ni filter and Cu-Kα radiation.

Results and interpretations

The degree of the K-fixation, in other words the percentage of smectite layers collapsed, was determined by the peak position method described by Środoń (1980, 1981). The experimental XRD data were also compared to simulated patterns using the NEWMOD computing program (Reynolds 1985). The thickness of the ethylene-glycol complex for each sample was determined to avoid the possible error in the expandability measurement as documented by Środoń (1980). The glycol complex thickness of the studied samples varied between 1.64–1.73 nm. The percentages of smectite layers in mixed-layer I-S (expandability) were determined in Sr exchanged, glycolated samples after 5, 20, 50 and 100 WD cycles. The XRD patterns of starting samples (K-smectites) are shown in Fig. 1. The effect of K-fixation is also reflected in the thickness of the coherent scattering domains. Fig. 2 shows how samples with the highest degree of K-fixation affect the sharpness of the XRD peaks. All measured data for NaCl environments of various concentrations are summarized in Table 1. Generally, a trend of increasing the smectite layer collapse with the number of WD cycles is observed, as has been documented in several papers (Eberl et al. 1986; Šucha & Širáňová 1991; Mikloš & Číčel 1993 etc.). The effect of NaCl concentration on the number of collapsed layers is significant, and shows consistent evolution (Figs. 3, 4, 5). Low starting NaCl

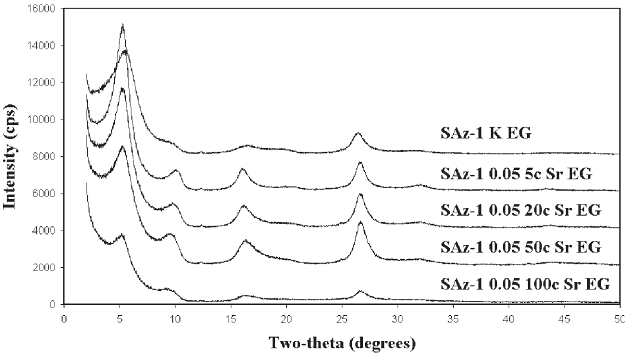

Fig. 2. The evolution of XRD patterns of the sample SAz-1 in the course of WD cycles in 0.05 M NaCl solution. The uppermost pattern represents the original K-smectite, the lower patterns are Sr-saturated and ethylene-glycolated samples after 5, 20, 50 and 100 WD cycles.

Table 1: Percent of smectite layers in mixed layered I-S.

Sample	WD cycle	distilled water	0.05 M NaCl	0.1 M NaCl	1 M NaCl	2 M NaCl	5 M NaCl
SAz-1	0	100	100	100	100	100	100
	5	78	67	72	68	80	93
	20	75	58	71	65	72	90
	50	70	48	59	62	72	90
	100	64	40	53	58	72	85
STx-1	0	100	100	100	100	100	100
	5	95	80	87	97	98	98
	20	90	76	77	85	90	98
	50	80	70	75	80	88	95
	100	75	59	68	70	85	95
Ban 4/1	0	90	90	90	90	90	90
	5	68	68	60	63	70	65
	20	65	63	55	60	60	65
	50	58	60	52	62	60	63
	100	54	56	50	62	60	62

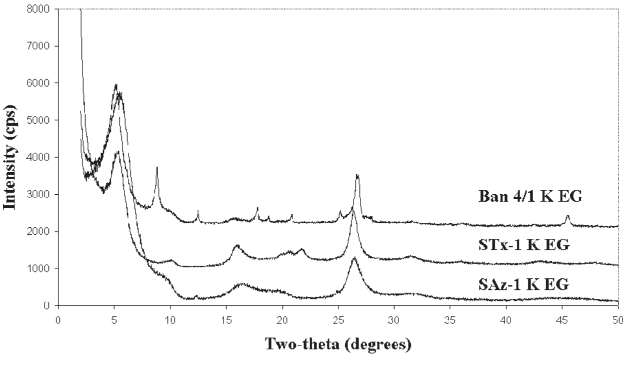

Fig. 1. XRD patterns of starting smectites (K-form, ethylene-glycolated, Cu-Kα radiation).

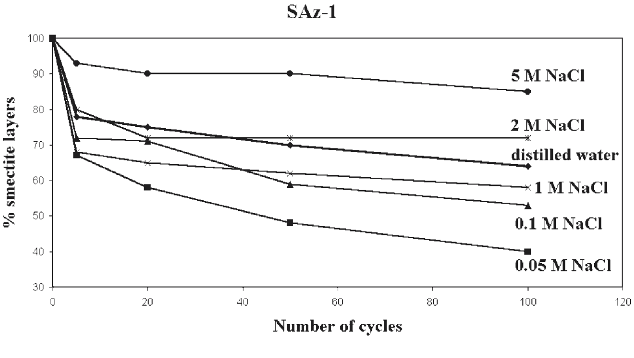

Fig. 3. The number of WD cycles with the percentage of smectite layers in the variously concentrated NaCl solutions for the sample SAz-1.

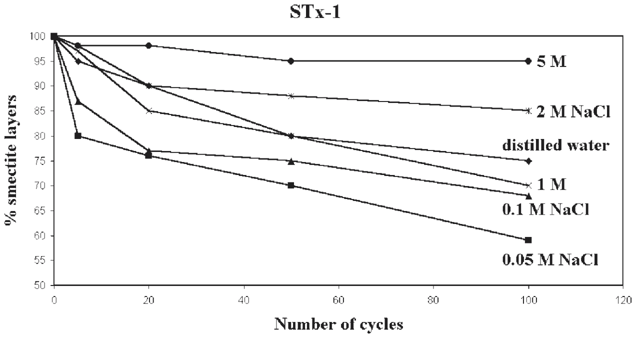

Fig. 4. The number of WD cycles with the percentage of smectite layers in the variously concentrated NaCl solutions for the sample STx-1. Note the different scale of the ordinate.

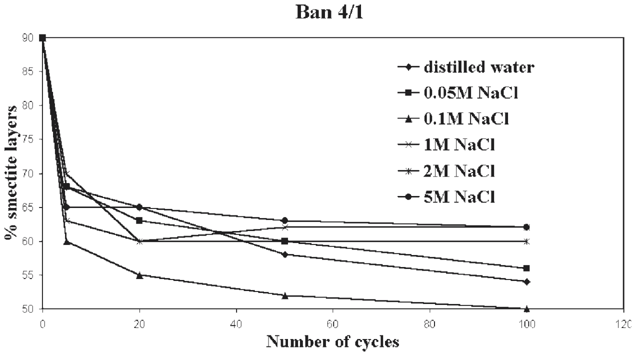

Fig. 5. The number of WD cycles with the percentage of smectite layers in the variously concentrated NaCl solutions for the sample Ban 4/1.

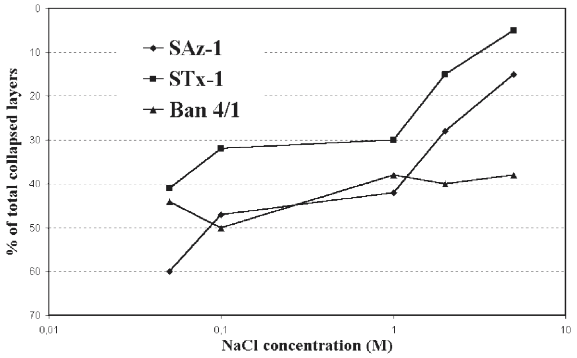

Fig. 6. The percentage of collapsed layers after 100 WD cycles in the different NaCl solutions for the 3 studied specimens.

concentrations (0.05 M, 0.1 M) lead to very fast collapse of smectite layers and high concentrations (2 M, 5 M) prevent collapse. Two bentonite samples, SAz-1 and STx-1, show very similar trends for all samples that differ only in the number of collapsed layers. The number is constantly higher for SAz-1 than for STx-1. This observation is most probably related to the higher layer charge of SAz-1 (Eberl et al. 1986; Šucha & Širáňová 1991). The maximum proportions of collapsed layers after 100 WD cycles are 60 % for SAz-1 and 41 % for STx-1 (in the presence of 0.05 M NaCl solution). On the contrary, the minimum numbers are 15 % and 5 % for the same samples when 5 M NaCl solution was added before WD experiments.

Sample Ban 4/1 (buried altered volcanoclastics) contains more mineral phases (original illite-smectite, detrital illite and chlorite), so it was much more difficult to determine the ratio between expandable and collapsed layers. The sample shows the same general trend, but behaves differently compared to pure bentonite samples. Most of the changes take place within the first 5 WD cycles, and the effect of NaCl is not the same as for the pure samples. First of all, the different concentrations have only a small impact on the collapsing process. Even so, higher NaCl concentration slows down collapse and lower NaCl concentrations enhance the process (Fig. 5), but the effect is subdued. Whereas the difference between the maximum and minimum effect of NaCl reaches 45 % and 36 %, respectively for the pure bentonite samples, it is only 12 % for the Ban 4/1 sample (Fig. 6).

Conclusions

1. A clear effect of NaCl salt on the degree of K-fixation in K-smectite during WD cycles was documented. The highest NaCl concentrations slow down the K-fixation process, and, on the contrary, low concentrations significantly enhance the process.
2. The first 5 to 20 cycles are the most important for the fixation and most of the potassium is fixed during this time.
3. The NaCl effect was much less significant when the already slightly illitized sample with admixtures of other mineral phases was used.
4. The interactions between the K-smectite collapse during the WD cycles and NaCl of different concentrations seems to be a complex process difficult to explain. Further study is needed to explain all these effects.
5. The fact of different effects of salt concentrations on the K-fixation process may have significant consequences for the use of illite-smectite as a paleotemperature indicator in geological processes as well for the use of bentonite barriers to protect the environment.

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