

SWELLING VOLUMES OF H-MONTMORILLONITES III. NATRIFICATION

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Swelling (or sedimentation) volumes (SV) of materials prepared by treating fine fractions of bentonites from Jelšovský Potok (Czechoslovakia), Clay Spur (Wyoming, USA), and Belle Fourche (South Dakota, USA) with HCl were stabilized by the subsequent treatment with sodium salt (NaCl, NaNO₃ or Na₂SO₄) solution. The anions of these salts had negligible effect on the SV. Lower SV achieved after HCl + Na₂CO₃ treatments are supposed to be caused by the reaction of surface protons and CO₃²⁻. Only moderate differences in the SV were found between the sodium salt treated samples without previous HCl treatment. That confirms no negative effect of Na₂CO₃ alone on the SV. High SV achieved with the HCl treatment were not achievable without it.

INTRODUCTION

Smectites are aluminosilicates with an expanding layer structure. Being widely spread in clays and soils they are responsible for their various properties. The most unique and important properties of smectites are the high negative surface charge and the ability to separate the layers in contact with water to various spacings, i. e. to swell. Smectites are of great practical importance and utilization in the agriculture and industry.

Swelling of montmorillonite depends on the interlayer cation. Norrish [1] reported good swelling for Na-, Li- and fresh H-forms, and poor swelling for K-, NH₄- and Cs-forms. The decrease in the uptake of water with ageing of H-montmorillonites was ascribed to the release of aluminium from the structure. Low stability of H-montmorillonites and their autotransformation to (H, Al)- or (H, Al, Mg)-forms is known [2—5]. Polyvalent cations in exchangeable positions cause lower water uptake by the smectites, although hydration of the interlayers takes place [1, 6]. Both the interlayer cations and the layer surface affect the structure and the properties of the interlayer water [7—9]. Low [9] reported poor dissociation of Na⁺ cations in Na-montmorillonites and concluded the swelling of clays is primarily due to hydration of their surfaces. The reduction of octahedral Fe(III) to Fe(II) increased the negative charge of the layers and decreased swelling [10, 11].

In our earlier papers [12, 13] the preparation of high swelling materials was described. The SV values were found to be dependent on the clay and the acid used, on the temperature and duration of the reaction, and on the ageing of the activated materials. The aim of this study was to investigate the possibilities of stabilizing high SV using HCl + sodium salt treatments of three smectites.

MATERIALS AND METHODS

Materials

Under 2 μm fractions of the bentonites from Jelšovský Potok, Czechoslovakia (JP 2), Clay Spur, Wyoming, USA (CS) and Belle Fourche, South Dakota, USA (BF) were used. They were Ca²⁺ saturated, dialysed, air dried at 60 °C and ground to pass through a 0.2 mm sieve. Their composition is given in [13].

Methods

Acid treatment. Five grams of the sample were added to 500 ml preheated (96°C) 1.5 mol. dm^{-3} HCl. The mixture was kept at a constant temperature for 15 minutes being stirred every five minutes. The suspension was filtered and washed with $50 \text{ cm}^3 \text{ H}_2\text{O}$, 300 cm^3 of 1 mol. dm^{-3} sodium salt solution (NaCl , NaNO_3 , Na_2SO_4 or Na_2CO_3), $50 \text{ cm}^3 \text{ H}_2\text{O}$ and $150 \text{ cm}^{-3} \text{ C}_2\text{H}_5\text{OH}$. The filter cake was dried at 60°C and ground as to pass through a 0.2 mm sieve.

Swelling volume. Swelling volume (SV) was determined by pouring successively 400 mg of the sample into 25 cm^3 of H_2O in a graduated cylinder (25 cm^3). The next batch of the sample was added always after the previous amount sank to the bottom. The volume of the gel (SV) was measured two hours after the first part of the sample was poured in. The SV at time $t = 0$ was determined 3–4 hours after the acid treatment had been finished. The powder samples for investigation of ageing were stored at room temperature in sealed flasks. Two parallel measurements were made which did not differ more than $\pm 10\%$ from their average value.

RESULTS AND DISCUSSION

The changes in SV due to the ageing of HCl treated montmorillonites JP 2, CS and BF without and after nitrification are given in Fig. 1, 2 and 3, respectively. The SV values of HCl + H_2O treated samples on the 35th day after the preparation were 67% of the value at $t = 0$ for JP 2, 66% for CS and 80% for BF. The fresh HCl + H_2O treated BF sample produced lower SV values than JP or CS samples but the decrease of SV upon ageing was slower for BF than for the other two clays. This decrease was found to be the result of two simultaneous processes, namely spontaneous conversion of H-montmorillonite to (H, Al, Mg)-montmorillonite, and equalization of the originally inhomogenous surface charge distribution of adsorbed anions [13].

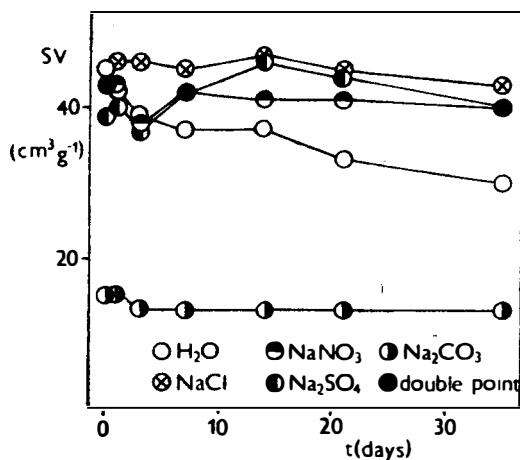


Fig. 1. Changes in swelling volume upon ageing for Ca-montmorillonite JP 2 treated with 1.5 mol. dm^{-3} HCl and H_2O or sodium salt solution.

The anions in the system saturate mainly the broken bonds on the edges of the crystallites, the cations compensate for the negative charge of the layers. Compensation by cations prevails on the faces, and that by anions on the edges of the crystallites. The volume of the sediment is affected by both cations and anions present in the system. No considerable differences in the cation population are supposed between the clays after a HCl + sodium salt (NaCl, NaNO₃, Na₂SO₄ or Na₂CO₃) treatment. The exchangeable Ca²⁺ cations of the original clays were exchanged for H₃O⁺ cations in the course of a short (15 min.) reaction with 1.5 mol . dm⁻³ HCl. Some octahedral cations from the edges of the clay particles were leached out and unsaturated oxygens were protonated, but no substantial

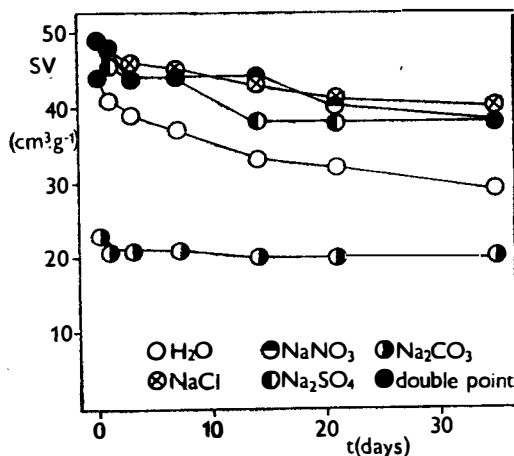


Fig. 2. Changes in swelling volume upon ageing for Ca-montmorillonite CS treated with 1.5 mol . dm⁻³ HCl and H₂O or sodium salt solution.

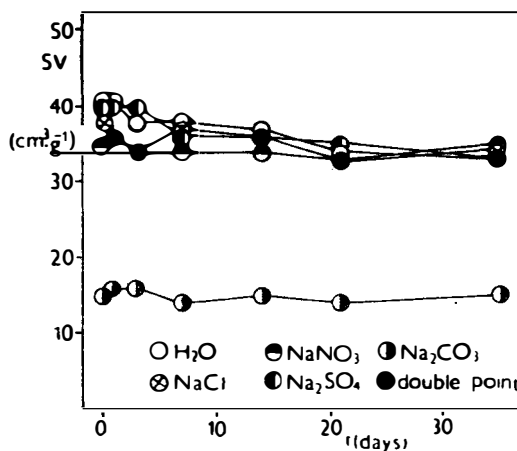


Fig. 3. Changes in swelling volume upon ageing for Ca-montmorillonite BF treated with 1.5 mol . dm⁻³ HCl and H₂O or sodium salt solution.

decomposition of clay layers could occur under these conditions. Protonation of unsaturated oxygens on the edges of the particles affects the surface charge of clay particles and the texture of the sediment in water. The subsequent treatment with a sodium salt solution forced the next exchange of interlayer H_3O^+ cations for Na^+ .

The sodium forms of smectites are known as stable materials, which do not undergo any autotransformation. The higher stability in the SV of HCl + sodium salt treated samples compared to that of HCl + H_2O treated ones is shown in Fig. 1 for JP 2 and in Fig. 2 for CS. According to the slow decrease of SV of HCl + H_2O treated BF upon ageing, little effect of NaCl, NaNO_3 or Na_2SO_4 treatment was observed for this sample (Fig. 3). The SV of JP 2, CS and BF after a HCl + sodium salt (NaCl , NaNO_3 or Na_2SO_4) treatment were within the first 35 days 42 ± 5 , 43 ± 6 and $36 \pm 4 \text{ cm}^3 \cdot \text{g}^{-1}$, respectively (Fig. 1—3). Consequently, the anions of these sodium salts had a negligible effect on swelling of these montmorillonites.

Investigating the effect of various acids on SV, high values were reported for HCl and HNO_3 , and lower ones for H_2SO_4 treated JP 1 [13]. That means Cl^- and NO_3^- have not affected the SV substantially neither in the form of acid, nor in that of a sodium salt. The treatment with H_2SO_4 lowered the SV compared to those after HCl + H_2O or HCl + Na_2SO_4 treatments. This could be explained by the presence of Ca^{2+} ions in the clay used for H_2SO_4 treatment. Low soluble calcium sulphate hydrate produced in the interlayers could affect the texture of the swollen sediment and the SV. No substantial decrease in SV was observed with any montmorillonite used after a HCl + Na_2SO_4 treatment, when the Ca^{2+} ions were first exchanged for H_3O^+ (Fig. 1—3). Thus the presence of SO_4^{2-} ions is insufficient to decrease the SV of HCl treated montmorillonites.

All three clays produced low SV after the HCl + Na_2CO_3 treatments (Fig. 1—3). The authors suppose the main reason is the reaction of surface protons with CO_3^{2-} and the consequent lower concentration of protons on the clay particles. This change of surface charge affects negatively the SV values. Further investigation is necessary to prove this assumption.

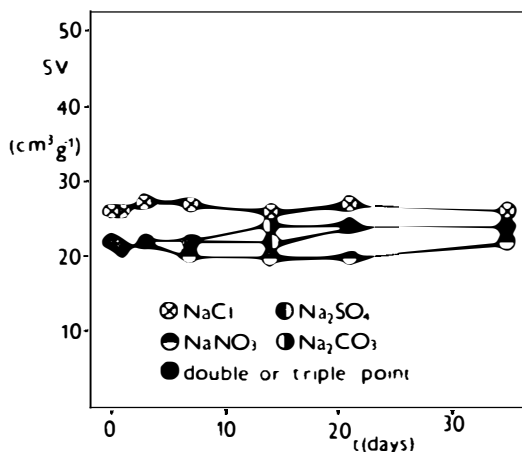


Fig. 4. Changes in swelling volume upon ageing for Ca-montmorillonite JP 2 treated with a sodium salt solution.

Only moderate differences in the SV were observed between the JP 2 montmorillonite treated with various sodium salt solutions without previous HCl treatment (Fig. 4). The exchange of Ca^{2+} for Na^{+} increased swelling in all the cases and the differences caused by various anions were low. That confirms Na_2CO_3 alone has no negative effect on the SV.

Comparing the SV with (Fig. 1) and without (Fig. 4) previous HCl treatment higher values were observed for NaCl, NaNO_3 and Na_2SO_4 treated materials with HCl and for Na_2CO_3 treated ones without it. The SV of HCl + NaCl, NaNO_3 or Na_2SO_4 treated JP 2 were within the first 35 days after the treatment $42 \pm 5 \text{ cm}^3 \cdot \text{g}^{-1}$, while those of Na_2CO_3 treated JP 2 were $23 \pm 2 \text{ cm}^3 \cdot \text{g}^{-1}$. This suggests the high SV achieved with the HCl treatment are not achievable without it.

CONCLUSIONS

The ability to produce voluminous sediments of HCl treated montmorillonites could be stabilized by a subsequent treatment with NaCl, NaNO_3 or Na_2SO_4 solution. Lower SV values after HCl + Na_2CO_3 treatments are supposed to be the consequence of a reaction of surface protons with CO_3^{2-} . High SV values achieved with the HCl treatment are not achievable without it.

References

- [1] Norrish K.: Disc. Faraday Soc. 18, 120 (1954).
- [2] Harward M. E., Coleman N. T.: Soil Sci. 78, 181 (1954).
- [3] Aldrich D. G., Buchanan J. R.: Soil Sci. Soc. Proc. 22, 281 (1958).
- [4] Coleman N. T., Craig D.: Soil Sci. 91, 14 (1961).
- [5] Barshad I., Foscolos A. E.: Soil Sci. 110, 52 (1970).
- [6] Tobias M. M., Poyato J., Trillo J. M.: J. Mater. Sci. 24, 3254 (1989).
- [7] Sposito G., Prost R.: Chem. Rev. 82, 553 (1982).
- [8] Low P. F.: Soil Sci. Soc. Am. J. 44, 667 (1980).
- [9] Low P. F.: Langmuir 3, 18 (1987).
- [10] Stucki J. W., Low P. F., Roth C. B., Golden D. C.: Clays Clay Miner. 32, 357 (1984).
- [11] Wu J., Low P. F., Roth C. B.: Clays Clay Miner. 37, 211 (1989).
- [12] Komadel P., Čičel B.: Silikáty 31, 247 (1987).
- [13] Komadel P., Čičel B.: Proc. 10th Conf. Clay Miner. Petrol. Ostrava (1986), 267 (1988).

SEDIMENTAČNÉ OBJEMY H-MONTMORILLONITOV III. NATRIFIKÁCIA

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Z jemných frakcií bentonitov Jelšový Potok (JP 2), Clay Spur (CS) a Belle Fourche (BF) sa pripravili reakciou s $1,5 \text{ mol} \cdot \text{dm}^{-3}$ HCl materiály s vysokým sedimentačným objemom (SV). Tieto sa stabilizovali následným premytím roztokom sodnej soli (NaCl , NaNO_3 alebo Na_2SO_4). Anióny týchto solí mali zanedbateľný efekt na hodnoty SV (obr. 1—3). Predpokladá sa, že nižšie hodnoty SV pozorované po aktivácii montmorillonitov s HCl a Na_2CO_3 sú dôsledkom reakcie povrchových protonov a CO_3^{2-} . Iba malé rozdiely sa našli medzi SV materiálov pripravených zo vzorky Jelšový Potok premytím roztokmi sodných solí bez predchádzajúcej reakcie s HCl (obr. 4). Tým sa potvrdilo, že samotný Na_2CO_3 nemá negatívny vplyv na SV. Vysoké hodnoty SV dosiahnuté po aktivácii s HCl a NaCl, NaNO_3 alebo Na_2SO_4 nemožno dosiahnuť bez použitia kyseliny.

Комарел, Чичел:

- Obr. 1. Zmeny sedimentačného objemu pri starnutí pre Ca-montmorillonit JP 2 po aktivácii v 1.5 mol. dm^{-3} HCl a premytí vodou alebo roztokom sodnej soli.
- Obr. 2. Zmeny sedimentačného objemu pri starnutí pre Ca-montmorillonit CS po aktivácii v 1.5 mol. dm^{-3} HCl a premytí vodou alebo roztokom sodnej soli.
- Obr. 3. Zmeny sedimentačného objemu pri starnutí pre Ca-montmorillonit BF po aktivácii v 1.5 mol. dm^{-3} HCl a premytí vodou alebo roztokom sodnej soli.
- Obr. 4. Zmeny sedimentačného objemu pri starnutí pre Ca-montmorillonit JP 2 po premytí roztokom sodnej soli.

СЕДИМЕНТАЦИОННЫЕ ОБЪЕМЫ Н-МОНТМОРИЛЛОНИТОВ III. НАТРИФИКАЦИЯ

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Из тонких фракций бентонитов Елшовой Поток (JP 2), Clay Spur (CS) и Belle Fourche (BF) приготовили путем реакции с 1.5 mol. dm^{-3} HCl материалы с высоким седиментационным объемом (SV), которые стабилизировали последующей промывкой раствором натриевой соли (NaCl, NaNO₃ или Na₂SO₄). Анионы приводимых солей оказывали пренебрегаемое влияние на величины SV (рис. 1—3). Предполагается, что более низкие величины SV, установленные после активации монмориллонитов HCl и Na₂CO₃, являются результатом реакции поверхностных протонов и CO₃²⁻. Только незначительные различия установили между SV материалов, приготовленных из пробы Елшовой Поток промывной растворами натриевых солей без предшествующей реакции с HCl (рис. 4). Таким образом было доказано, что отдельный Na₂CO₃ не оказывает отрицательное влияние на SV. Высокие величины SV, полученные после активации HCl и NaCl, NaNO₃ или Na₂SO₄ нельзя получить без использования кислоты.

- Рис. 1. Изменения седиментационного объема при старении в случае Ca-монтмориллонита JP 2 после активации в 1.5 mol. dm^{-3} HCl и промывки водой или раствором натриевой соли.
- Рис. 2. Изменения седиментационного объема при старении в случае Ca-монтмориллонита CS после активации в 1.5 mol. dm^{-3} HCl и промывки водой или раствором натриевой соли.
- Рис. 3. Изменения седиментационного объема при старении в случае Ca-монтмориллонита BF после активации в 1.5 mol. dm^{-3} HCl и промывки водой или раствором натриевой соли.
- Рис. 4. Изменения седиментационного объема при старении в случае Ca-монтмориллонита JP 2 после промывки раствором натриевой соли.