PHYSICO-CHEMICAL PROPERTIES OF ILLITE SUSPENSIONS AFTER CYCLES OF FREEZING AND THAWING

V. Schwinka[1] and H. Mörtel[2]

[1] Technical University Riga, Institute for Silicate Materials, Azenes Str. 14, LV-1048, Riga, Latvia

[2] University Erlangen Nuerenberg, Institute of Material Science, Glass and Ceramics Department, Martensstraße 5, D-91058, Erlangen, Germany

Abstract—The effect of freezing and thawing on the rheological behavior of illite suspensions was studied by examining viscosity and plasticity. Stability of suspensions was characterized by a hysteresis loop of thixotropy. Thermal gravimetric and differential scanning calorimetry analysis were also used. After initial freezing and thawing, the flow curves of the suspensions show an increased viscosity, an "irregular up line", and a greater hysteresis loop of thixotropy. The ratios of mean viscosity of previously frozen (F) and control (O) samples (η_F/η_O) for non-expandable 2:1 phyllosilicates ranges from 1.3 to 2.1. Addition of monovalent (0.1% Na_2SiO_3) and divalent cations (0.3% $CaCl_2$ or $BaCl_2$) increase and decrease the shear-stress difference between F and O samples, respectively. Prior freezing of clay samples results in an increase of plasticity by ~20–30%. The thermal analysis data of F samples show an increase in weight loss, and a decrease in enthalpy of dehydration. The changes of physico-chemical properties from cycles of freezing and thawing are long lasting. The freezing memory effect of illite-type clays is expected to play an important role in ceramic processing, *i.e.,* casting processes, plastic formation, and sintering.

Key Words—Illite-Type Clays, Plasticity, Pretreatment With Cold, Thermal Analysis, Thixotropy, Viscosity.

INTRODUCTION

Freezing is a technological method to change the plasticity of clay materials (Salmang and Scholze, 1982; Schwinka and Mörtel, 1995a). The thermal behavior of illite is of special interest because the presence of illite can have a profound effect on the properties of clay products. Some studies highlight macrostructural changes, such as orientation and stratification of particles in natural clays subject to freezing and thawing (*e.g.,* Schababerle *et al.,* 1988). Other studies consider the plasticity of clays as they undergo freezing and thawing (Mörtel *et al.,* 1995; Schwinka and Mörtel, 1995b). Cyclic freezing-thawing of clay suspensions may result in dispersion and orientation changes of clay particles, oxidation of admixtures, changes in cation adsorption of the clay surface, and changes in the electrolyte composition of the bulk solution. The latter two processes result in the change of contact between particles (Schababerle *et al.,* 1988; Kumor, 1989). There is considerable research on changes occurring in adsorbed and/or bound water of clay suspensions with increasing temperature (Sposito and Prost, 1982; Xu and Yoon, 1989; Murad and Wagner, 1996; Guo *et al.,* 1997). Although much is known of rheological behavior of clays during heating, little is known about the effect of freezing-thawing cycles on the physico-chemical properties of clays.

The goal of this investigation is to study the effect of cyclic freezing on the physico-chemical properties of different illite clay suspensions. Characteristics of interest in this study include viscosity, plasticity, stability as characterized by a hysteresis loop of thixot-ropy, and the intensity of exothermic and endothermic reactions as measured by thermal analysis.

MATERIALS AND EXPERIMENTAL METHODS

Clay materials

Illite clays from Latvian deposits (Table 1) were studied. The mineralogy of these clays is shown in Table 1. Chemical analyses of the ≤1-μm fractions are given in Table 2. These fractions were used for thermal analysis. The fractions generally contain ~90% illite and 5–10% of kaolinite. Other samples used include kaolins (Zetlitz, Sedlec, Czech Republic and Prosja-novsk, Ukraine), and a bentonite (Askangel, Georgia).

About 1 kg clay was ground to ≤200-μm particle size. The sample was divided into five parts, 200 g each. The 1-μm size fraction was then separated by sedimentation. For viscosity measurements, the clay concentration in suspension was 45–60 wt. % and 70–80 wt. % for the plasticity measurements. The cation-exchange capacity (CEC) for each investigated sample is presented in Table 3. The CEC was estimated using the methylene blue index (Kahr and Madsen, 1994; Funk, 1996) and NH_4Cl method.

Experimental procedure

For the viscosity measurements, two samples (200 g each) were dispersed overnight with deionized water using a propeller mixer (490 min^{-1}) to obtain two 250 mL of clay suspension. One part (F) was frozen, the other used as a control (O) was kept at room temperature (20°C). Each suspension was maintained so that the water content was uniform during the experiment.

Table 1. Mineralogical compositions (wt. %) of clay samples.

Deposit	Size fraction	Illite	Kaolinite	Chlorite	Quartz	Dolomite	Calcite	Montmorillonite
Liepa (Devonian)	≤200 μm	50–55	8–10	—	25–30	≤2	—	—
Liepa (Devonian)	≤1 μm	90	10	—	—	—	—	—
Kuprava (Devonian)	≤200 μm	75–80	5	—	15–20	≤3	5–10	—
Kuprava (Devonian)	≤1 μm	95	5	—	—	—	—	—
Liberti (Quaternary)	≤200 μm	40–45	8–10	3	15–20	4–8	3–5	—
Liberti (Quaternary)	≤1 μm	80	15	5	—	—	—	—
Usma (Quaternary)	≤200 μm	40–50	5–10	5	10–15	5–10	10–15	—
Tumuzi (Quaternary)	≤200 μm	50–60	10	3	5–10	10	15	—
Kaolin (Zetlitz, Czech Republic)	≤200 μm	—	95	—	5	—	—	—
Kaolin (Prosjanovsk, Ukraine)	≤200 μm	10–15	75–80	—	5	—	—	—
Bentonite (Askangel, Georgia)	≤200 μm	10–15	—	—	5–10	—	—	60–75

The procedure was: (1) F samples were frozen for 24 h at −20°C and O samples were maintained for 24 h at 20°C; (2) both samples were maintained an additional 24 h at 20°C; (3) samples were mixed for 2 h; (4) viscosity was measured with a Rheomat 200; (5) viscosity was measured daily for 12 d after each sample was mixed for 2 h prior to the measurement. The procedure was repeated 6–8 times. Freeze-thawing cycles are defined by (1) + (2). In some experiments two to five freezing-thawing cycles were performed.

Salt treatments were made also. At stage (1) or (3), sodium silicate (Formsil D; 22.14 wt. % SiO_2, 22.61 wt. % Na_2O, 55.25 wt. % H_2O determined by loss on ignition at 1000°C) was added in concentrations of 0.1–0.4 wt. % (number of samples, n = 36). $CaCl_2$ or $BaCl_2$ were used in concentrations of 0.05–0.4 wt. %.

Viscosity was determined by measuring shear stress τ. Each time a certain value of shear rate D (s^{-1}) was

Table 2. Chemical analyses of illite (<1-μm size) from Kuprava and Liepa Latvia (wt. %).

Chemical composition	Kuprava clay	Liepa clay
SiO_2	50.75	44.70
Al_2O_3	20.04	25.60
Fe_2O_3	9.13	10.47
FeO	0.37	0.42
TiO_2	0.50	0.95
CaO	1.67	1.16
MgO	3.45	2.95
Na_2O	0.00	0.11
K_2O	6.01	5.10
Loss on Ignition	6.74	8.20
Tetrahedral position		
Si^{4+}	3.45	3.03
Al^{3+}	0.55	0.97
Octahedral position		
Al^{3+}	1.13	1.08
Fe^{3+}	0.47	0.55
Fe^{2+}	0.02	0.02
Mg^{2+}	0.35	0.30
Interlayer position		
K^+	0.52	0.45
Ca^{2+}	0.12	0.08
H_3O^+	0.36	0.47

applied, the corresponding shear stress τ (MPa) was determined and flow curves were recorded. Measurements were performed under the following conditions: D was increased linearly, from 5 to 350 s^{-1}, over a period of 300 s. D was then reversed in direction to 5 s^{-1} in 50 s. Each curve per direction ("up" refers to increase, "down" refers to decrease) consisted of ten measuring points sampled against D.

Under a given D, the absolute value of viscosity η was calculated as η = τ/D. For some samples, the ratio η_F/η_O was calculated, where η_F is the mean viscosity 2 d after freezing and η_O is the control viscosity without freezing. Thixotropy was characterized by a τ-D curve, *i.e.,* an irregular up line and a large hysteresis loop of thixotropy.

For plasticity measurements, 600 g of dry clay were used to create a paste with a clay concentration ~70–80 wt. %. The experimental procedure for the plasticity measurements differed only in stages (3) and (4). In this case, (3) involved 10 min kneading of the clay and (4) involved the determination of plasticity using the shear-strength testing method of Schober (1991). Each sample of 100 g was used only once. The samples (1-cm thick layers) were placed between two riffled metal plates (60 × 60 mm), and the shear strength (N/mm^2) as based on shear displacement (mm) was measured. The maximum value of shear strength is characteristic of the plasticity of the clay sample.

Thermal gravimetric (TG) and differential scanning calorimetry (DSC) experiments were performed. Twenty mg samples (≤1-μm fraction) prepared in the same way as for viscosity measurements were dried at 60°C and analyzed. The samples were equilibrated at a common relative humidity prior to the thermal analysis. Each sample was kept at 60°C for 12 h.

Student's paired t-test was used for the determination of statistical significance. Probability <0.05 was considered statistically significant.

RESULTS

Viscosity measurements

After freezing, the flow curves of the suspensions exhibit increased viscosity, an irregular "up" curve,

Table 3. Cationic-exchange capacity (mg eq/100 g) of clay samples.

Deposit	Na^+	K^+	Ca^{2+}	Mg^{2+}	$\Sigma\ (Na^+ + K^+ + Ca^{2+} + Mg^{2+})$
Liepa Devonian (grain size ≤ 200 μm)	—	2.0	9.9	3.4	15.3
Kuprava Devonian (grain size ≤ 200 μm)	1.0	1.0	11.9	9.7	23.7
Tumuzi (grain size ≤ 200 μm)	0.4	1.0	6.5	4.6	12.5

and a larger hysteresis loop of thixotropy relative to O samples (Figure 1, hysteresis loop shown by shading). After aging 6 d, the shear strain difference between F and O samples remains (Figure 1b). The viscosity difference of freezing-thawing cycles between F and O samples corresponds to: expandable 2:1 phyllosilicates > non-expandable 2:1 phyllosilicates > 1:1 phyllosilicates.

The ratio η_F/η_O is a measure of sensitivity of different clays to freezing. Thus, the ratio η_F/η_O is observed as 1.0 for kaolin (Zetlitz, Czech Republic), 1.1 for kaolin (Prosjanovsk, Ukraine), and 1.8–2.8 for bentonite (Askangel, Georgia). The illite clays from Latvian deposits show the ratio η_F/η_O from 1.3 to 2.1. The ranges given represent the values of 6–8 measurements for each specimen.

Plasticity measurements

The effect of freezing is observed in suspensions containing 45–60 wt % clay and in pastes with 70–80 wt. % clay. The dependence of shear strength on shear displacement shows differences between the F and O samples (Figure 2). Freezing produces an increase of shear strength by ~20–30%. Repeated freezing further enhances the shear-strength difference between F and O (Figure 2, F_2).

Thermal-analysis data

TG analysis shows a greater weight loss by F samples as compared to the controls (Figure 3). There is significant ($p < 0.005$) weight loss in the interval of 60–180°C, which is related to loss of physically adsorbed water (Post *et al.*, 1992). This weight loss is 3.21 ± 0.45 (mean, standard error, n = 7) and 2.69 ± 0.40 (n = 6) for F samples and O samples, respectively. From 450 to 580°C, the effect is less pronounced. The weight loss is observed also in unfractionated samples ≤ 200 μm (not shown).

The DSC analysis (Figure 4) is consistent with the influence of freezing as determined by TG analysis on illite. Differences exist between O and F clays in the endothermic DSC-peak at 50–180°C (adsorbed water) and at ~550°C which shows the loss of chemically bonded water. In Figure 4a the enthalpy of dehydration in the 50–150°C interval in F decreases to 20.64 J/g as compared to O (30.14 J/g). The decrease of adsorption enthalpy after freezing is observed by thermal analysis in illite from all deposits.

The d(001)-value does not appear to change after the freezing-thawing cycles. X-ray diffraction experiments (not shown) demonstrated that there are no shifts in the diffraction peaks of illite after freezing.

Influence of aging on the effect of freezing memory

Figure 5 illustrates both freezing and aging effects. The difference of mean viscosity between F and O samples is observed even after 14 d (*e.g.,* Figure 5, Tumuzi). For the sample from Liberti, the viscosity difference increases with aging. However, note that in kaolin the freezing does not lead to noticeable changes of viscosity (Figure 5).
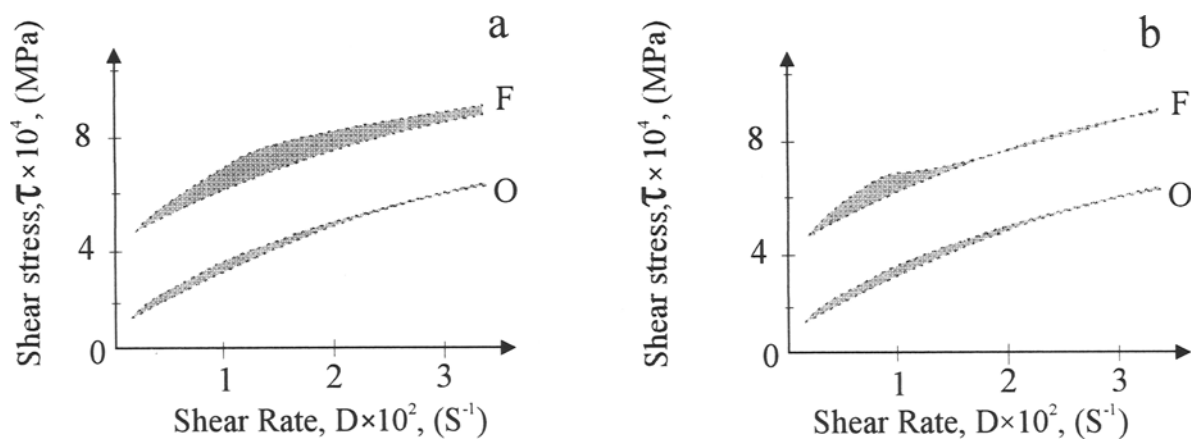

Figure 1. Flow characteristics of clays after freezing. F = sample after freezing, O = control; (a) samples at the first day after freezing, (b) aging in 6 d; clay samples from Tumuzi deposit.
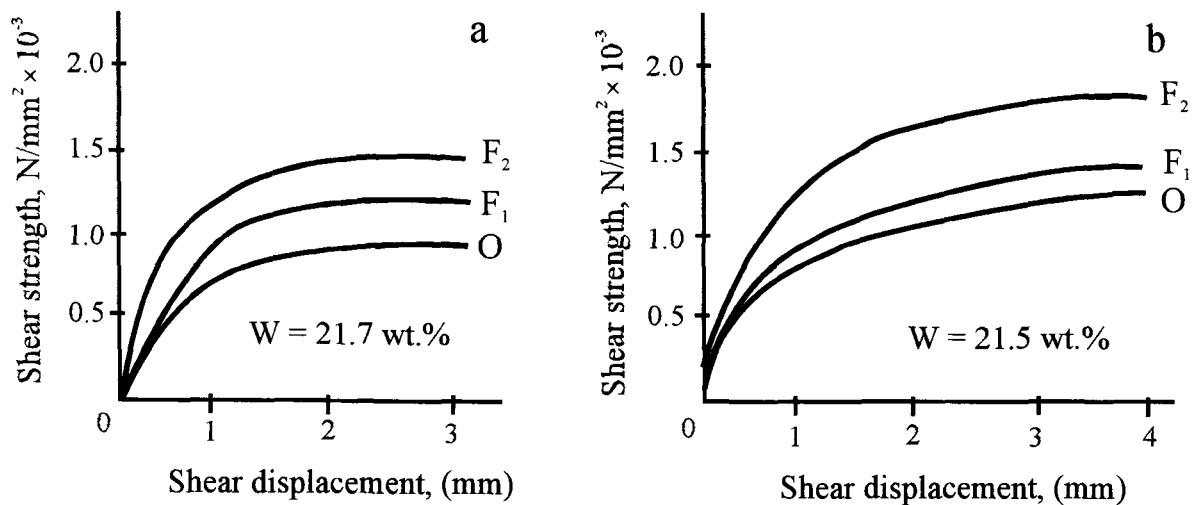
Figure 2. Effect of repeated freezing on plasticity of clay from (a) Liepa and (b) Liberti deposits. F_1 = once frozen, F_2 = twice frozen, O = control, W = content of water in wt. %.
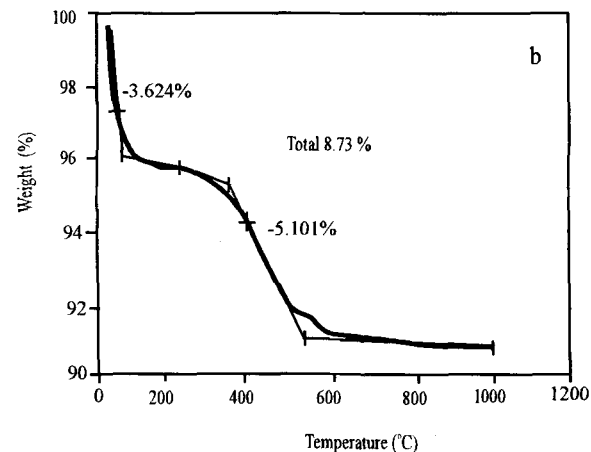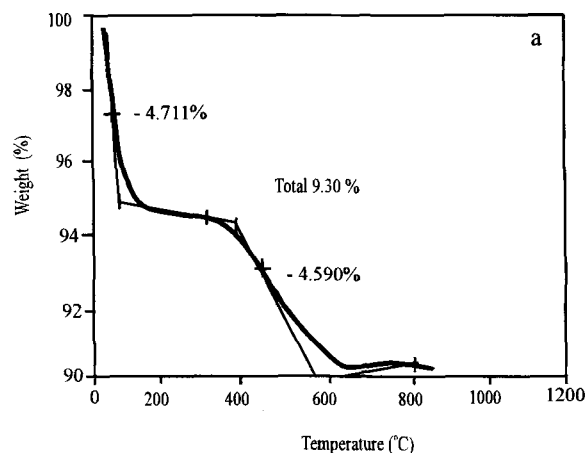

Figure 3. TGA curves of samples after freezing (a) and without freezing (b). Illite samples from Kuprava deposit (<1-μm fraction).
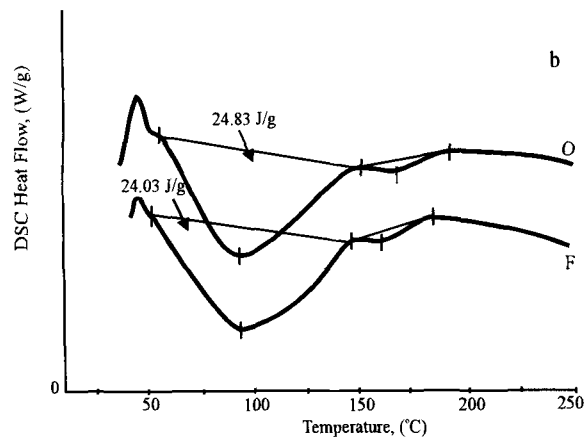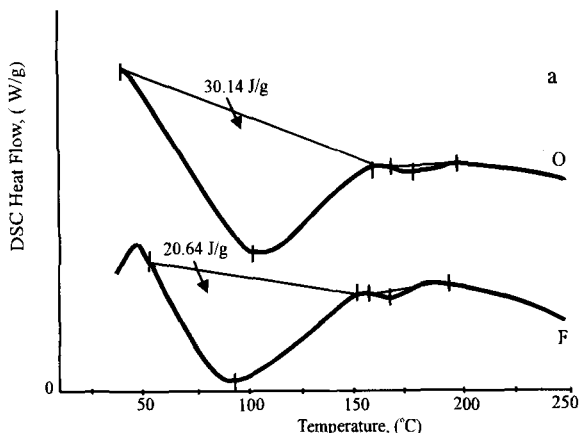
Figure 4. DSC curves of frozen (F) and control (O) clay samples from Liepa (a) without and (b) with 0.4 wt. % $CaCl_2$. $CaCl_2$ added at stage (1) of the experimental procedure.
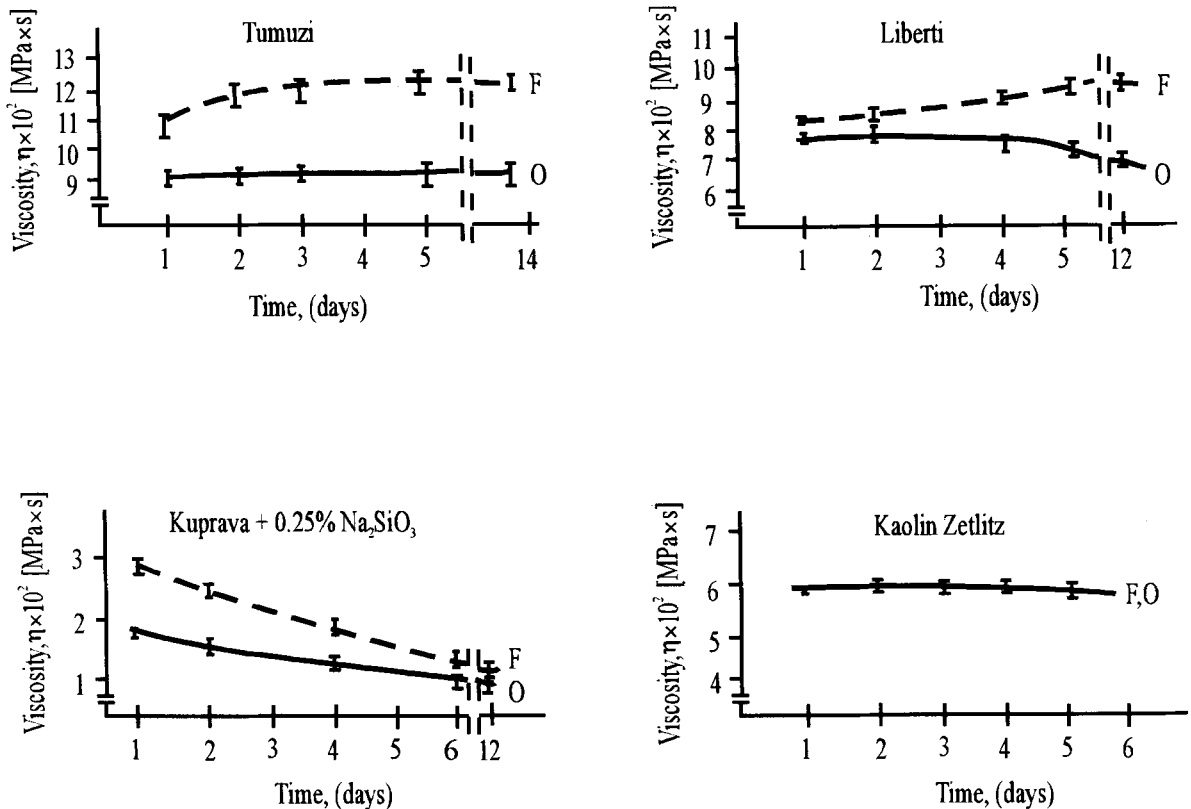
Figure 5.   Effect of freezing on the mean viscosity of clay suspensions. Each point represents the mean value of 5–6 measurements ±SD (standard deviation). Sample from Kuprava deposit with 0.25% sodium silicate added at stage (3). The mean viscosity corresponds to the mean shear rate calculated from the changing values of shear rate over 300 s.

Salt treatment and effects on freezing memory

Note that the addition of electrolytes remarkably affects the freezing effects. Thus, sodium silicate at concentrations of 0.1 wt. % increases the hysteresis loop of thixotropy of both F and O samples (*cf.,* Figure 6a *vs.* 6c) as well as the shear stress difference between F and O samples during the aging process (*cf.,* Figure 6d *vs.* 6b and 6c). Higher concentrations of sodium silicate (0.25 wt. %) result in an opposite effect—the decrease of the freezing-induced mean viscosity difference during aging (Figure 5, Kuprava). Similar effects were observed by addition of sodium silicate both during freezing at stage (1) and after freezing at stage (3). This is illustrated in Table 4 where the difference of the mean viscosity η between F and O samples is shown at the fourth day when freezing was in the presence of sodium silicate (0.25 wt. %) applied at stage (1). The difference of η is significant (*p* < 0.001) and nearly identical for 0.25 wt. % sodium silicate at stage (3) (Figure 5, Kuprava, aging 4 d).

In the presence of divalent cations, Ca^{2+} or Ba^{2+}, the difference between F and O samples decreases. Figure 7 shows that in the suspension containing 0.3 wt. % $CaCl_2$ the difference of shear strength between

F and O samples is reversed. Figure 8 demonstrates that O is much more sensitive to the addition of 0.25 wt. % $BaCl_2$ as compared to F sample.

The data involving electrolyte effects on the DSC curves support the results from viscosity measurements. The difference in enthalpy between F and O samples for the DSC peak at 50–150°C is lower when 0.4 wt. % $CaCl_2$ is added [Figure 4b, Δ = 0.80 (J/g)] compared to samples without added salt [Figure 4a, Δ = 9.50 (J/g)]. The decrease is due to both the increase of peak energy in F and a decrease of peak energy in O samples (Figure 4b).

Mineralogical influence on the memory effect of freezing

The Kuprava and Tumuzi clays exhibit greater rheological changes after freezing compared to samples from Liepa and Liberti. The more pronounced effects of the Kuprava clays correlate with increased CEC (Table 3). Moreover, Kuprava and Tumuzi clays have comparatively large illite contents. Thus, the freezing-memory effect depends also on the mineralogical composition of the clays. Kaolin, which demonstrates only horizontal ice structures upon freezing (Schababerle *et*
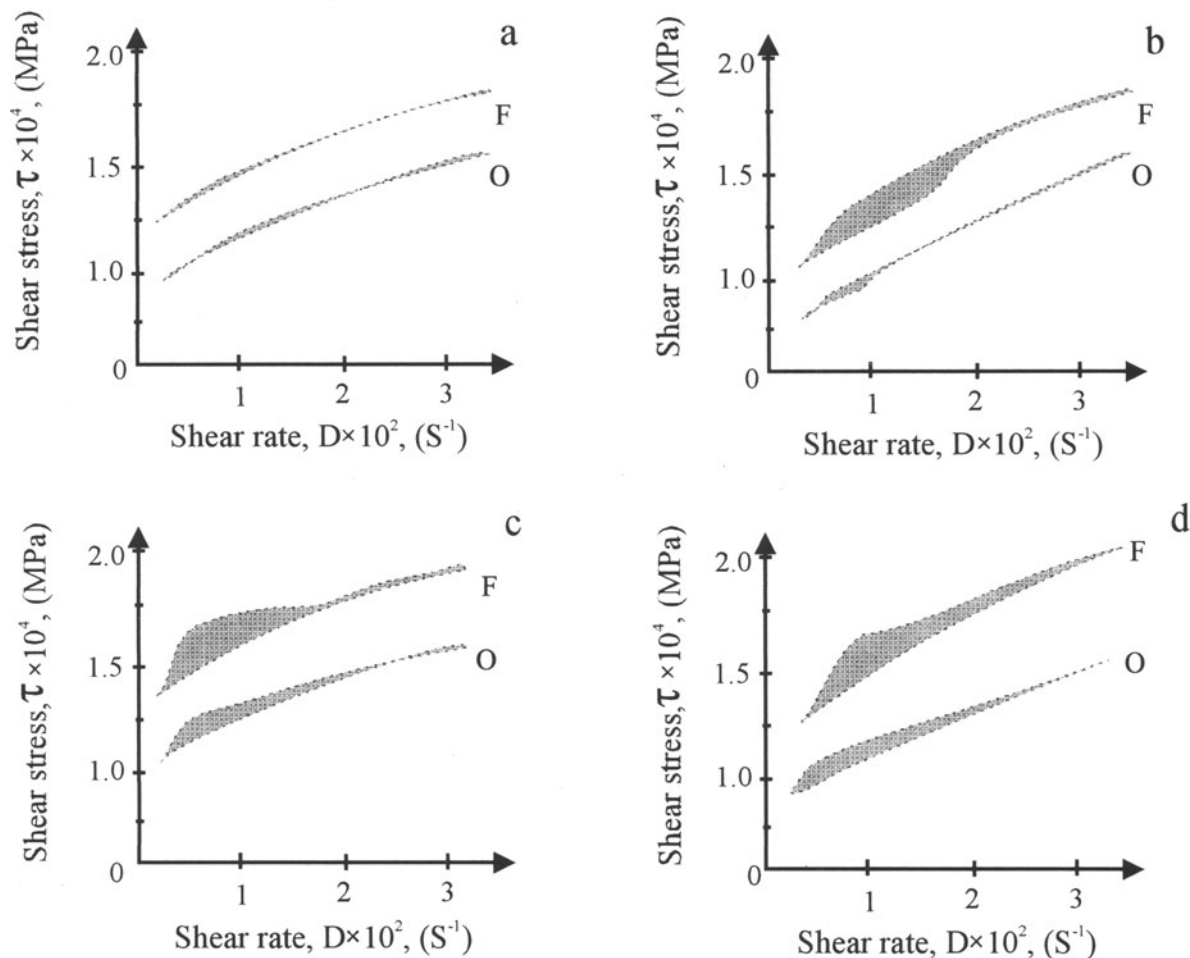
Figure 6.   Flow characteristics of clays after treatment with sodium silicate: (a) after freezing for 1 d; (b) after aging for 6 d; (c) after freezing for 1 d with 0.1 wt. % sodium silicate added at stage (3); and (d) after aging for 6 d with 0.1 wt. % sodium silicate added at stage (3). Clay samples from Kuprava deposit. F = sample after freezing; O = control.

al., 1988), does not show a noticeable freezing-memory effect.

DISCUSSION

The experiments suggest that the clays with 2:1 layer structures are affected by freezing, presumably because of structural differences compared to other clays. Freezing results in changes of viscosity, plasticity, and thermal behavior. The shear-thinning behavior of τ-D curves after freezing indicates that the clay particles form a connected network. Viscosity decreases when the network is sheared because it is broken into smaller flow units. Although the details of the network structure are not determined, the network strength is probably related to interparticle potentials. It is likely that in special conditions after freezing-thawing cycles, the electrostatic part of the total potential is lowered and an additional short-range hydration potential is responsible for the rheological behavior of the clays. Chang *et al.* (1994)

suggested that such potential is effective relative to other potentials only for interparticle-separation distances ≤ 5 nm. The observed increase in the adsorbed water after freezing based on weight loss supports this interpretation. However, the lack of change in *d*-value after freezing-thawing in X-ray experiments indicates that freezing did not affect the amount of underlayer H_2O, but H_2O molecules may have become repositioned. Our data involving added salts are in qualitative agreement with this suggestion. The hydration potential becomes effective only when the amount of salt added is sufficient to produce a hydration layer and to decrease the electrostatic potential barrier. Apparently, this occurred by addition of low concentrations of Na_2SiO_3. In contrast, by adding $CaCl_2$ or $BaCl_2$, divalent cations can decrease the layer of structural water bound to the surface by counterions. It is well known that divalent cations form a much thinner hydration layer compared to monovalent cations (Krause *et al.*, 1982).

Table 4. Effect of freezing-thawing on the difference of the mean viscosity ($\eta \times 10^2$) for clay from Kuprava with 0.25% Na_2SiO_3 added at the stage (3) of the experiment.

	[1]F	[2]O
	199.77	116.52
	175.83	110.00
	179.66	106.99
	176.69	100.11
	168.29	107.72
	169.41	103.59
Statistical parameters		
[3]N	6	6
Mean	178.28	107.49
[4]SD	11.41	5.62
[5]SE	4.66	2.29
[6]$p < 0.001$		

[1] F—Sample after freezing.
[2] O—Control.
[3] N—Number of experiments.
[4] SD—Standard Deviation.
[5] SE—Standard Error.
[6] p—Probability.

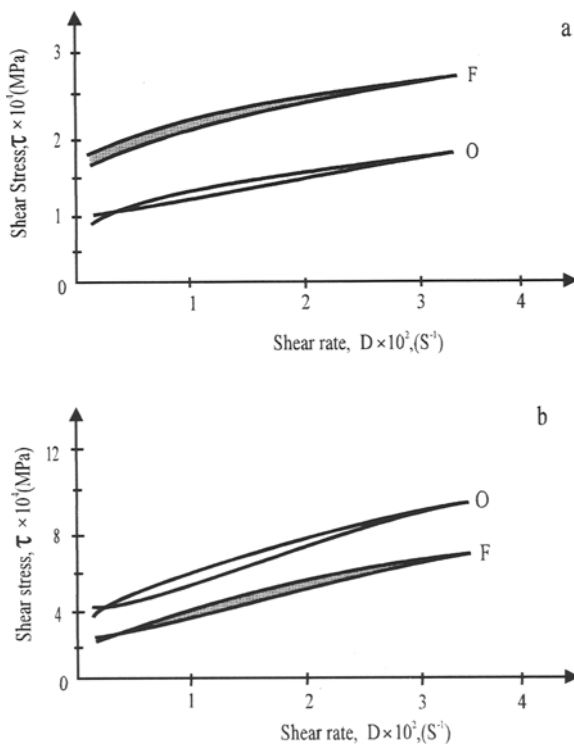

Figure 7. Effect of 0.25 wt. % $BaCl_2$ on the flow curves of F and O Liepa samples. The experiment is performed after the first day and after freezing. $BaCl_2$ added at stage (1) of the procedure.

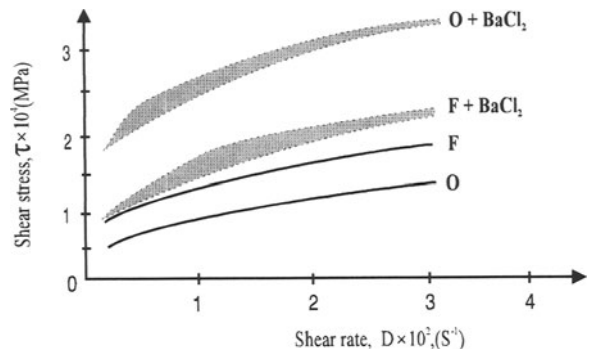Figure 8. Flow curves after prior freezing of clays (a) without electrolyte and (b) with 0.3 wt. % $CaCl_2$. F = sample after freezing, O = control. (a) and (b) involve samples from Liepa deposit after the first day and after freezing; (b) 0.3 wt. % $CaCl_2$ added at stage (1) of the experiment.

The effect of freezing memory seems to be very sensitive to the electrolyte content of the samples. This conclusion is supported by the data of Schbaberle *et al.* (1988) where the role of the cations adsorbed on the clay surface and the composition of the bulk solution on structural changes caused by freezing in montmorillonite (Schbaberle *et al.*, 1988) was shown. The influence of exchangeable cations on the amount of non-frozen water in the frozen paste of montmorillonite was demonstrated by Suzuki *et al.* (1988).

In summary, our study demonstrates: a) pretreatment by freezing of illite leads to an increase of viscosity and plasticity by 20–40% and 20–30%, respectively; b) nonlinear shear stress-shear rate curves indicate that a structural network exists in suspensions of previously frozen clays; c) the effect involving freezing memory is very susceptible to electrolyte content of the clay samples, electrolyte type, and the concentration in bulk solution; and d) the thermal analysis data of previously frozen clays shows an increase in weight loss and a decrease of enthalpy of dehydration at 50–180°C.

The mechanism of the changes induced by prior freezing remains unclear. A better understanding of the effect of freezing-thawing cycles on rheological properties of illite slurries may be important in ceramic processing. Previous freezing results in an increase of duration of the casting process, improvement of plastic formation, and energy economy in sintering. Freezing results in a decrease in texture formation and porosity and an increase in mechanical strength in ceramic materials.

ACKNOWLEDGMENTS

mal analysis experiments. This study was supported by a Volkswagen grant.

REFERENCES

Chang, J.C., Lange, F.E., and Pearson, D.S. (1994) Viscosity and yield stress of alumina slurries containing large concentrations of electrolyte. *Journal of the American Ceramic Society,* **77,** 19–26.

Funk, J.E. (1996) *The Methylene Blue Index for Whiteware Body Control.* Science of Whiteware, Alfred, New York, 6–15.

Guo, L., Zhang, Y., Uchida, N., and Uematsu K. (1997) Influence of temperature on stability of aqueous alumina slurry containing polyelectrolyte dispersant. *Journal of the European Ceramic Society,* **17,** 345–350.

Kahr, G. and Madsen, F.T. (1994) Bestimmung der Kationenaustauschvermögens und der Oberfläche von Bentoniten, Illit und Kaolinit durch Methylenblauadsorbtion, Kohler, E.E., Herausgeber, *Berichte der Deutschen Ton- und Tonmineralgruppe, Regensburg,* 154–159.

Krause, E., Berger I., Plaue, T., and Schulle, W. (1982) *Technologie der Keramik, Bd.2,* VEB Bauwesen, Berlin, 252 pp.

Kumor, M.K. (1989) Microstructural changes of monomineral clay under cyclic freezing-thawing processes. *Rozprawka Academia Techniczna Polska, Bydgoszovy,* **N 34,** 1–139. (in Polish).

Mörtel, H., Cimmers, A., and Schwinka, V. (1995) The influence of porosing additive on properties of Latvian bricks. In *Fourth Euro-Ceramics Conference, Volume 12, Bricks and Roofing Tiles,* I. Braga, S. Cavalini, and F.G. Di Cesare, eds., CNR - IRTEC, Italy, 107–116.

Murad, E. and Wagner, U. (1996) The thermal behavior of an Fe-rich illite. *Clay Minerals,* **6,** 45–52.

Post, E., Winkler, S., and Selb. (1992) Characterization of ceramic materials by thermal analysis. *Keramische Zeitschrift,* **44,** 762–766. (in German).

Salmang, H. and Scholze, H. (1982) *Keramik. Teil I. Allgemeine Grundlagen und wichtige Eigenschaften.* Springer-Verlag, Berlin, 308 pp.

Schababerle, R., Wagner, I.F., and Czurda, K.A. (1988) Influence of freeze-thaw-cycles on clay structures. In *Tone in der Umwelttechnik,* Karlsruhe, 247–273. (in German).

Schober, G. (1991) Characterization of plastic clay masses processing and the effect of microorganisms. Doctoral thesis, University Erlangen-Nuerenberg, 56 pp. (in German).

Schwinka, V. and Mörtel, H. (1995a) Der Einwirkung vorhergehender Kälteeinwirkung auf physikochemische Eigenschaften von Tonen, *Sprechsaal Keramik + Materials,* **128,** 1–5.

Schwinka, V. and Mörtel, H. (1995b). The influence of additives on the "Freezing-memory effect" of Baltic clays, In *Fourth Euro-Ceramics Conference, Volume 12, Bricks and Roofing Tiles,* I. Braga, S. Cavalini, and F.G. Di Cesare, eds., CNR - IRTEC, Italy, 97–105.

Sposito, G. and Prost, R. (1982) Structure of water adsorbed on Smectites. *Chemical Reviews,* **82,** 553–573.

Suzuki, K., Hiroyuki, M., and Toshiani, M. (1988) Non-frozen water in the frozen paste of montmorillonite. The influence of replaceable cations on the amount of non-frozen water. II. *Reports of the Industrial Research Institute of Nagoya,* **137,** 256–260.

Xu, Z. and Yoon, R.H. (1989) A study of hydrophobic coagulation. *Journal of Colloid Interface Science,* **134,** 427–434.