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Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65th birthday

STABILIZATION OF AQUEOUS SUSPENSIONS OF PALYGORSKITE BY THERMAL VAPOUR PRESSURE SHOCK EXPLOSION (TSE) TREATMENT

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Abstract

A device was constructed in which a clay suspension is hermetically heated at 220°C for a few minutes. This thermal treatment is accompanied by a pressure increase in the cell. Once the valve is opened, there is a fast release of the pressure inside the cell and a sudden evolution of the interparticle water. This shock leads to a quasi explosion of the clay particle. This technique was named thermal vapour pressure shock explosion (TSE). The effect of TSE treatment on the properties of palygorskite suspensions was investigated. Palygorskite suspensions in water are rather unstable and particles smaller than 3 μm in size are not found before a TSE treatment. Stabilization of the suspension can be obtained by TSE treatments and/or by using a dispersing agent such as pyrophosphate, or both. As a result of TSE treatments smaller particles are obtained, the dispersiveness of the particles is improved and electrophoretic mobility is increased. Electron microscopy scans showed that the aggregates of needles which form the palygorskite fibres, disintegrate to separated thin needles as a result of the TSE treatment.

Keywords: clay minerals, palygorskite, thermal vapour pressure shock explosion

Introduction

The ability of clay minerals to be dispersed in aqueous solutions and in organic solvents is important in many natural and industrial processes. In the present communication we report on the application of a new device, designed to improve dispersiveness of clay minerals in different solvents. In reality clay particles obtained by grinding the clay rock are aggregates of flocs of smaller

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clusters of primary silicate particles (crystallites) [1]. The construction of the present device is based on the idea that a certain shock might lead to quasi explosions of the aggregates and their disruption to smaller clusters. Such a process can be realized when a clay suspension is heated in a hermetically closed chamber to a temperature higher than the boiling point of the liquid, followed by a sudden release of the pressure. We suggest the term 'thermal vapour pressure shock explosion' (TSE) for this technique.

As a first example, we describe herein the stabilization of an aqueous suspension of palygorskite, known also as attapulgite. Together with sepiolite, this mineral is unique among TOT clay minerals in having a channel structure [2, 3]. This structure is obtained from the repeated inversion of the silicate layers [4]. The mineral micro-crystal has the shape of a needle, with its long axis parallel to that of the channel [5]. An aggregate particle of the needles has a fibrous appearance. In addition to the structural water (octahedral OH groups) this mineral contains three types of water, (i) 'bound water', molecules located inside the channel, at the edges of the octahedral sheet, coordinating the edge Mg ions, (ii) 'zeolitic water', molecules filling the empty space in the channel and (iii) 'interparticle water', filling the empty space between the primary particles which form the fibre [6–13]. In atmospheric pressure zeolitic and interparticle water are evolved at 100–150°C. Bound water is evolved in two stages, at 220–370 and 370–625°C [14, 15]. The second stage is associated with the dehydroxylation of the clay and is not reversible [16]. It is therefore expected that during the TSE treatment the evolution of the interparticle water will lead to the disruption of the aggregate to smaller flocs and primary crystals.

Experimental

The TSE apparatus

The device is made of two stainless steel pressure cells connected by a valve (Fig. 1). The upper cell (10 ml) can be heated by a resistance wire whereas the lower cell (500 ml) has a small opening to the atmosphere and is kept at room temperature. The clay suspension is introduced into the upper cell, closed hermetically and is gradually heated until a temperature of 220 °C is reached (for about 5 minutes). This thermal treatment is accompanied by a pressure increase in this cell resulting from the vapour of the liquid phase. Due to the high pressure in this cell, water will not evolve from the clay at this temperature. Once the valve is abruptly opened, there is a fast release of the pressure inside the cell and a sudden evolution of the adsorbed water. This shock leads to a quasi explosion of the clay particles. This disruption of the aggregated particle should result in smaller flocs and primary particles. The lower cell may contains some

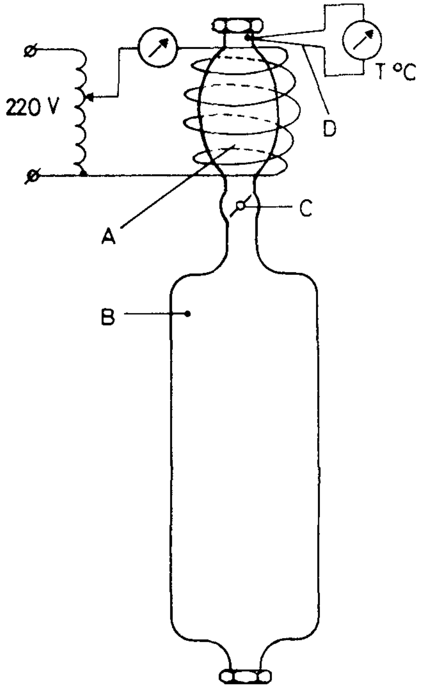

Fig. 1 Schematic presentation of the thermal vapour pressure shock explosion (TSE) device A - Heating cell (10 ml); B - Dilution cell (500 ml); C - Valve; D - Thermocouple

liquid, e.g. water or some aqueous solution, to dilute the heated suspension and is named the 'dilution cell'. We expect that after the TSE treatment dispersiveness of clay particles will be improved.

Preparation of the palygorskite suspensions

Palygorskite (attapulgite) from Quincy, Florida, was supplied by Ward's Natural Science Establishment. The clay was ground manually and passed through an 80 mesh sieve. Five different types of aqueous suspensions were investigated, each subjected to several TSE treatments. In the first-type suspensions palygorskite was dispersed in triple distilled water (ATW). In the second- and third-type suspensions it was dispersed in sodium pyrophosphate, $Na_4P_2O_7{\cdot}10H_2O$ aqueous solutions, with final concentrations of 0.004 and 0.00114 *M* (ATP-X and ATP-Y, respectively). In the fourth- and fifth-type suspensions it was dispersed in aqueous solutions of NaCl with final concentrations of 0.1 and 0.029 *M* (ATN-X and ATN-Y, respectively).

The following colloidal properties of the suspensions were investigated before and after one, two and, in a few cases also three explosions: (i) dispersiveness of the clay, (ii) particle size distribution and (iii) electrophoretic mobility. According to the explosion number, suspensions were numerated by 0, 1, 2, and 3, respectively. For most studies the final clay concentration was 1.15 per cent.

All suspensions were obtained by starting with 8 ml of the suspension under study and diluting during the TSE treatments to 28 ml, so that the final suspensions had identical concentrations. For example, one explosion suspension was obtained by exploding 8 ml of a clay suspension (ATW, ATP or ATN) into 20 ml of distilled water or aqueous solutions of pyrophosphate or NaCl. Double explosion suspension was obtained in two steps. In the first step 8 ml of the clay suspension was exploded into 8 ml of the appropriate aqueous solution and the 16 ml thus obtained was divided into two portions of 8 ml each. In the second step both 8 ml portions were exploded into one portion of 12 ml of distilled water or of the appropriate aqueous solution.

Dispersiveness and sedimentation rates of palygorskite particles

Setting characteristics of the particles was studied in test tubes and in glass cylinders. The suspensions in the test tubes were thoroughly shaken 24 hours after the TSE treatment and photographs were taken after different time intervals. Suspensions in glass cylinders with a diameter of 1.2 cm were well shaken twenty four hours after the TSE treatment and were left for five days at room temperature. The settling of the particles was determined from time to time by measuring the height, h, of the clear liquid above the turbidity borderline, i.e., the distance from the top of the clear liquid to the boundary layer between this liquid and the turbid suspension. The turbidance of the upper layer of each cylinder was measured 15 min after the mixing of the suspensions. For this purpose a 3 ml layer was collected from the top of the glass cylinder and the UV-Visible spectrum was recorded by a Perkin-Elmer Lambda 5 spectrophotometer.

Determination of particle size distribution in the size range 3–3000 nm

This was carried out with a Malvern Autosizer II/C Particle Size Analyser. The operation technique is based on 5 mW He–Ne laser that illuminates a scattering sample held in a transparent cuvette placed inside a temperature regulated enclosure. Light scattered from the sample chamber at an angle 90° to the incident beam is received by a photomultiplier detector through an adjustable aperture with a diameter calibrated in μm.

This instrument counts particles in the range of 3–3000 nm in size. In most of the suspensions studied here these fine particles make only a small fraction of the total mass of the solids. When passing through the laser beam, larger particles which settle down faster, interfere with the counting of the small particles. Therefore, suspensions for this determination were prepared by taking few drops from the upper layer of the mother suspensions, three minutes after they had been well shaken, and diluting with distilled water in the measuring cuvette. In the absence of pyrophosphate, reproducibility of countings of suspensions with no TSE treatment of after one and two treatments was very poor and consequently, each figure showing the distribution of particle size is composed of sixty consecutive countings carried out for each suspension.

The calculated particle size distribution can be expressed either on the basis of particle mass or particle number. The latter method was adopted for presentation since it is more sensitive to small changes in the number of small particles.

Determination of particle size distribution in the size range 6–100 μm

The HIAC/ROYCO PC-320 Particle Size Analyser was used for this purpose. This instrument counts particles in the range of 6–300 μm in size. However, the relative number of particles with sizes in the range 100–300 μm in our system was small and counting of these particles gave irreproducible results.

For these measurements each suspension was diluted 100 times. The operation is based on optical blockage principle. Particles in fluid suspension flow through a channel past a window whose area is known accurately. A collimated light beam shines through the fluid at right angles to the direction of the flow, and passes through the window to fall on a photodiode.

Determination of electrophoretic mobility of the particles

Rank Brothers Particle Micro-Electrophoresis apparature Mark II was used for this purpose. Thirty measurements of individual particles were made in each of the treated clay suspensions under study.

Properties of the solid phase

The different suspensions were dried at room temperature and the solid phases were examined by X-ray diffraction (Philips), IR absorption spectroscopy in KBr discs (Perkin Elmer 597) and Electron Microscopy (Jeol). For this purpose suspensions were dried on carbon covered grids and shadow casted by Pt+Pd.

Results and discussion

Colloidal properties of the suspensions

Dispersiveness of palygorskite

Figure 2 shows photographs of test tubes containing palygorskite suspensions in distilled water obtained after one, two and three TSE treatments. For comparison, a suspension obtained with no TSE treatment is also shown. Photographs were taken immediately and 2.5 h after thoroughly shaking the test tubes (a and b respectively). From the photograph it is obvious that after each TSE treatment the volume of the turbid suspension in the test tubes (which con-

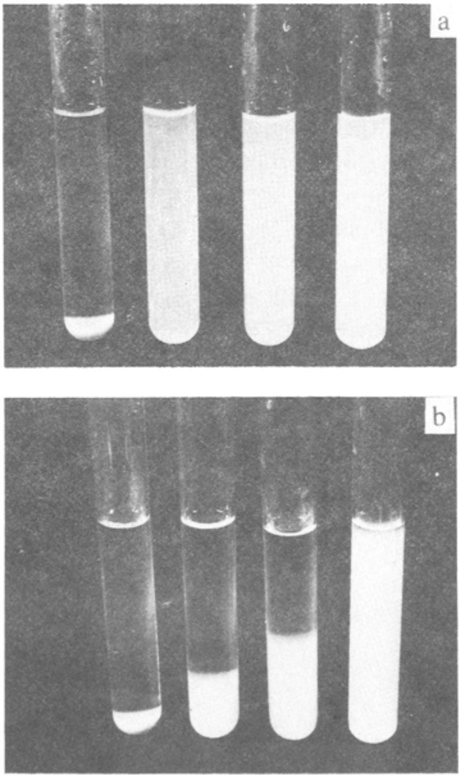

Fig. 2 Photographs of test tubes containing palygorskite suspensions in distilled water (1.15%), with no TSE treatment and after one, two and three TSE treatments. Photos were taken immediately and 2.5 h after thoroughly shaking the test tubes (a and b respectively)

tains sediment and water) increases. This implies changes in spatial arrangement of the needle-like particles, and/or an increase in the number of these particles by breakage into smaller particles, and/or an increase in repulsive forces between the particles. Figure 3 shows the same test tubes 30 days after shaking. By comparing the two figures it is obvious that the TSE treatment stabilizes the suspension of palygorskite and that stability increases with the number of treatments.

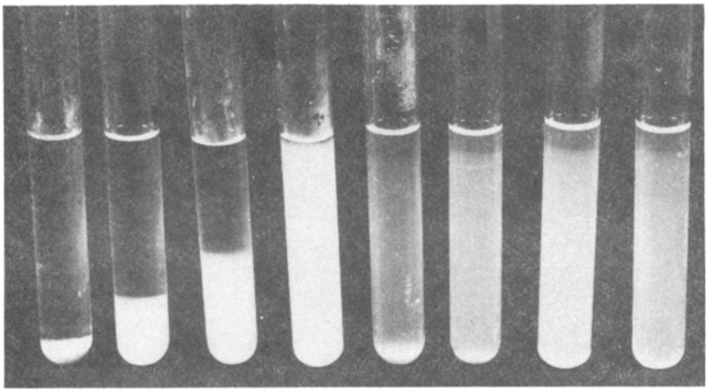

Fig. 3 Photographs of test tubes which are shown in Fig. 2, 30 days after shaking (left) and of suspensions of palygorskite obtained in the presence of pyrophosphate, with no TSE treatment and after one, two and three TSE treatments. Photos were taken 30 days after shaking (right)

The implication regarding the repulsive forces between palygorskite particles was further studied by introducing pyrophosphate into the suspension (Fig. 3). The pyrophosphate anion is specifically adsorbed onto positive charged sites, such as those of exposed Al and Mg, thus imparting the clay surface with additional negative charge. As a result, stronger repulsive forces between particles inside aggregates become effective, particles disaggregate to some extent and suspensions become more stable. The combination of pyrophosphate and TSE treatments resulted in the most stable suspensions, which implies mechanical disruption of the fibre, in addition to the electrochemical dispersing effect of the pyrophosphate.

For comparison, similar clay suspensions were heated to 220°C in the pressure cell but were left to cool to room temperature before the opening of the valve. These suspensions showed colloidal properties similar to those of the untreated suspensions, indicating that heating alone has no effect on the dispersiveness of palygorskite and that the TSE treatment is essential for this purpose.

Table 1 summarizes measurements taken at different times of the height, *h*, of the clear liquid above the turbidity borderline of the settling suspension, in the absence or presence of NaCl, before and after the TSE treatments, carried out in the glass cylinders. In reality, the movement of the turbidity borderline represents the sedimentation of the smallest particles in the suspension. The slower sedimentation in the presence of NaCl (compare ATW-0 to ATN-Y0) is attributed to the Na^+ ion which stabilizes clay suspensions in dilute salt solutions. The table also shows that sedimentation becomes slower with the number of TSE treatments. Since the clay concentration in these suspensions is identical, these results suggest that particles are disrupted by the TSE treatments and that they become smaller and smaller during each treatment.

Table 1 The height, *h*, of the clear liquid above the turbidity borderline of the suspension (in mm) in vertical cylinders containing palygorskite aqueous suspensions (1.15%), with no TSE treatment and after one and two TSE treatments (0, 1 and 2, respectively), in the absence and presence of 0.1 *M* NaCl (ATW and ATN-Y, respectively)

Time after mixing / min	Height of clear liquid above turbidity borderline / mm Suspension					
	ATW-0	ATW-1	ATW-2	ATN-Y0	ATN-Y1	ATN-Y2
40	155	100	≈ 0	130	45	≈ 0
300	155	125	55	130	95	5
1335	155	133	92	130	105	37
4215	155	130	92	130	110	58
5655	155	130	90	130	105	58

In the presence of sodium pyrophosphate the whole cylinder remained turbid until the end of experiment. In spite of the high turbidity of the suspension, after several hours particles were observed at the bottom of the glass cylinder, but their amount decreased with the number of TSE treatments (Fig. 3).

Table 2 Turbidance at 400 nm in the electronic spectra of the upper layers of vertical cylinders containing palygorskite aqueous suspensions, with no TSE treatment and after one and two TSE treatments, in the absence and presence of 0.1 *M* NaCl and 0.004 *M* pyrophosphate (ATW, ATN-Y and ATP-Y, respectively), separated 15 min after the samples were shaken thoroughly

No. of explosion	Turbidance at 400 nm Suspension		
	ATW	ATN-Y	ATP-Y
0	0.36	0.41	1.60
1	1.80	1.60	1.78
2	2.80	3.10	3.10

Table 2 summarizes the turbidance at 400 nm of the upper 3 cm of the different suspensions, separated 15 min after shaking. Turbidance is related to the concentration of the fine clay fraction, which has not been sedimented from this layer. Before the TSE treatment, in the presence of NaCl this concentration was slightly higher than in its absence, but in the presence of pyrophosphate it was much higher. In agreement with the previous results, Table 2 shows that the concentration of the fine fraction of the suspensions increased as a result of the TSE treatment.

Size distribution of particles smaller than 3 μm

Palygorskite suspensions in water are rather unstable and particles smaller than 3 μm in size were not found before the TSE treatment. The fast sedimentation of the aggregates makes it impossible to measure their particle size distribution without first disrupting the particles. As shown below, this can be performed by either TSE treatments, or by using a dispersing agent such as pyrophosphate, or both. As a result of TSE treatments, smaller and smaller particles appear, which corroborate with the improved stability of the suspensions shown above. The effect of TSE treatment on the decrease of particle size is more pronounced in suspensions with no pyrophosphate.

One TSE treatment of aqueous palygorskite dispersion (Fig. 4) brought about the formation of a rather stable suspension, in agreement with the above observations (Figs 2 and 3). Though the particle sizes range from ≈450 to ≈2700 nm, there seems to be two populations, with particle size below and above 2000 nm. A second TSE treatment further decreased the particle size of the small range, where the larger size range remained about the same. The third treatment resulted in a population of much smaller particles in the range of 185 to 1700 nm. Apparently, the TSE treatments brought drastic changes in the particle size distribution.

Treatment with pyrophosphate bring about both, dispersion of aggregates and considerable stabilization of the primary particles in suspension. The particle size distribution of palygorskite dispersed in pyrophosphate is shown in Fig. 5.

Applying one treatment shifted the particle size distribution curve to the left. A second treatment did not have a strong effect, but seems to have increased this tendency. However, a third treatment resulted in a rather large spread of particle size, where the upper range is considerably larger than in the non-treated sample. This dramatic effect may be explained by assuming that large particles, which were not counted by the instrument, are more liable to disruption by the TSE treatment, and thus contribute their own 'offsprings' to the population of the small particles.

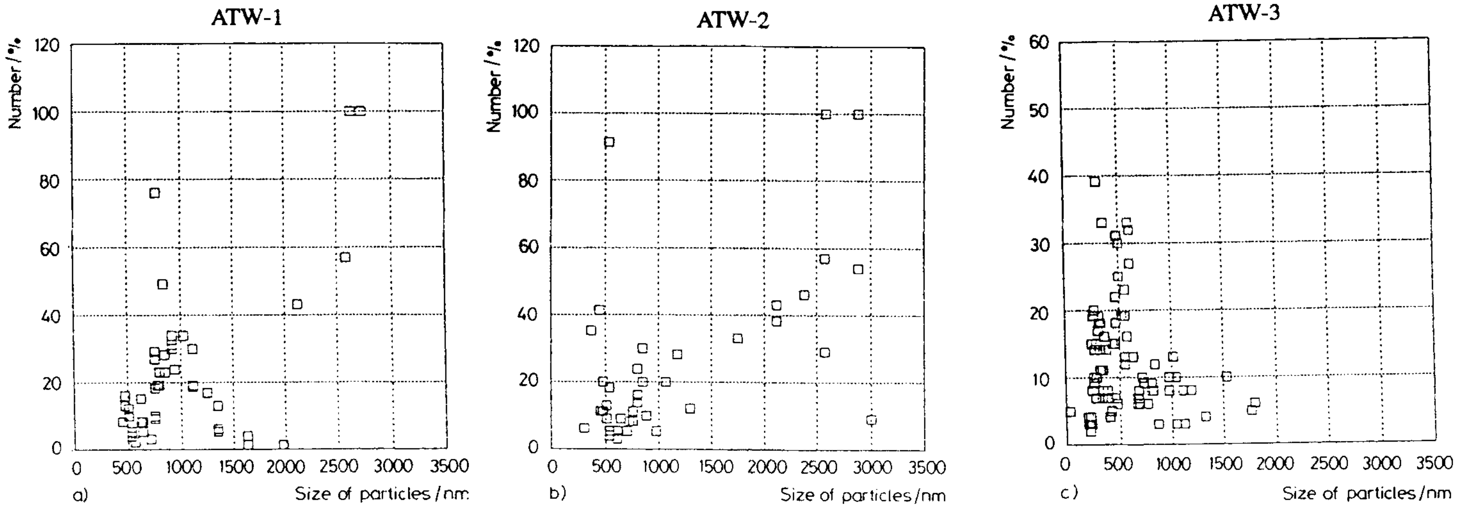

Fig. 4 Particle size distribution of aqueous palygorskite suspension in the range of 3-3000 nm in size (composed of sixty consecutive countings), (a), (b) and (c) after one (ATW-1), two (ATW-2) and three (ATW-3) TSE treatments, respectively

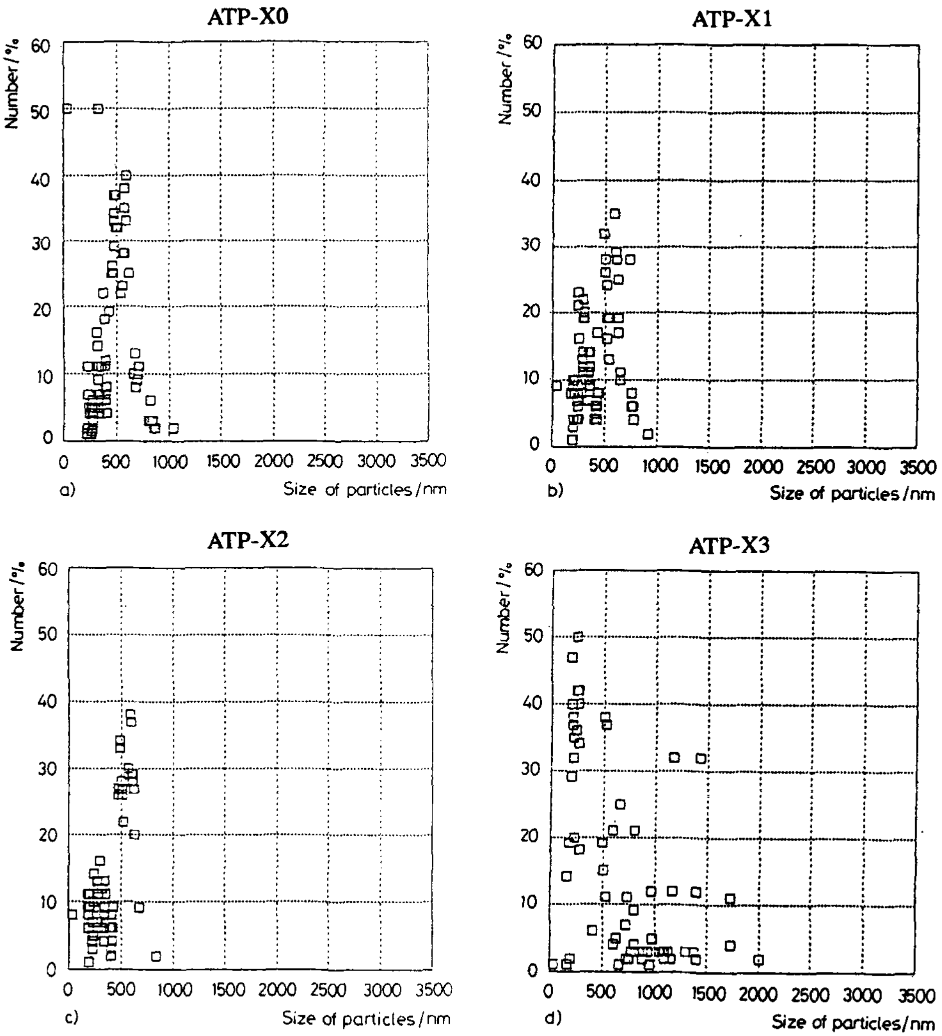

Fig. 5 Particle size distribution of aqueous palygorskite suspension in the range of 3–3000 nm in size (composed of sixty consecutive countings) in the presence of pyrophosphate, (a), (b), (c) and (d), with no TSE treatment (ATP-X0) and after one (ATP-X1), two (ATP-X2) and three TSE treatments (ATP-X3), respectively

Size distribution of particles in the size range 6–100 μm

Tables 3–5 summarize the distribution of clay particles in the different suspensions, according to their size, in the range 6–100 μm. In order to understand the changes in the particle size distribution which result from the TSE treatment, it is assumed that the total number of clay particles in the size range

6–100 μm and their distribution according to particle size, after the TSE treatments depend on the number and distribution of particles initially present in the suspension and also on the disruption or disaggregation of these particles, i.e.:

(1) disruption of particles larger than 100 μm in size, is shown by an increase in the number of detected particles, mainly in the range 20–100 μm;

(2) disruption of particles smaller than 100 μm in size to smaller particles but larger than 6 μm, is shown by an increase in the number of particles in the range 6–20 μm and a decrease in the number of particles in the range 20–100 μm and

(3) disruption of particles with sizes in the range 6–100 μm to particles smaller than 6 μm in size, is implied from a decrease in the total number of detected particles.

In suspensions with no additives (ATW-0, ATW-1 and ATW-2, Table 3) the total number of particles in this range increased as a result of the TSE treatments. Since the clay concentration in these three suspensions was identical, these results indicate that particles were disrupted during the TSE treatment. After the first treatment, the number of particles below 20 μm increased whereas their number in the range 20–100 μm decreased. This indicates that particles smaller than 100 μm were disrupted from this treatment. After the second TSE treatment, the number of particles in the range 20–100 μm also increased, suggesting that particles larger than 100 μm, initially not counted in this system, were also disrupted during this treatment. The disruption of parti-

Table 3 Distribution of clay particles according to their size (number of particles), in the range 6–100 μm in palygorskite aqueous suspensions (0.015%), with no TSE treatment (ATW-0) and after one and two TSE treatments (ATW-1 and ATW-2, respectively) in the absence of additives

Size range / μm	Number of particles Suspension ATW-0	ATW-1	ATW-2
6 - 10	23 625	46 209	51 587
10 - 15	26 670	43 429	46 552
15 - 20	12 336	13 782	14 411
20 - 30	12 006	8 909	9 350
30 - 40	4 283	2 175	2 416
40 - 60	2 867	1 172	1 504
60 - 80	915	295	464
80 -100	336	118	207
6 -100	83 038	116 089	126 491

cles smaller than 100 µm and of those larger than 100 µm occur simultaneously. Apparently the contribution of particles larger than 100 µm is greater in the second treatment than in the first one.

In a suspension containing 0.00114 *M* pyrophosphate, which was not subjected to TSE treatment, the number of clay particles with a size smaller than 15 µm increased, whereas their number in the range 15–100 µm decreased, compared to their number in the absence of this dispersing agent. However, the total number of particles in the range 6–100 µm did not increase (compare the distribution of particles in ATW-0 to that in ATP-X0). Since the clay concentration in these suspensions is identical, these results indicate that particles smaller than 6 µm which are not counted in this system, are obtained from the disaggregation of the larger particles. The disaggregation process increases with increasing concentrations of the dispersing agent and the number of all particles, including the range 15–100 µm, increases (ATP-X0 and ATP-Y0, Table 4). This is an indication that particles larger than 100 µm, which are not counted in this system, are also disaggregated. To conclude, in the presence of pyrophosphate, most palygorskite particles are smaller than 15 µm, even before the TSE treatment.

The total number of particles in the size range 10–100 µm showed a considerable decrease with the TSE treatments whereas the number of particles in the range 6–10 µm increased only very slightly (Table 4). Since the clay concentration in these suspensions was identical, the decrease in number of observed par-

Table 4 Distribution of clay particles according to their size (number of particles), in the range 6–100 µm in palygorskite aqueous suspensions (0.0115%), containing sodium pyrophosphate (0.00114 or 0.004 *M*, X and Y, respectively) with no TSE treatment (ATP-0) and after one and two TSE treatments (ATP-1 and ATP-2, respectively)

Size range /	Number of particles					
	Suspension					
µm	ATP–X0	ATP–X1	ATP–X2	ATP–Y0	ATP–Y1	ATP–Y2
6 - 10	39 561	42 318	43 441	58 201	58 266	60 314
10 - 15	28 397	27 893	25 294	49 848	46 050	43 549
15 - 20	7 376	6 539	4 865	14 183	11 226	8 612
20 - 30	4 712	3 867	2 424	8 597	6 076	3 047
30 - 40	1 282	948	502	2 040	1 219	322
40 - 60	688	510	241	1 091	631	108
60 - 80	174	141	52	300	160	19
80 -100	72	49	15	126	54	8
6 -100	82 762	82 265	76 824	134 512	123 682	115 979

ticles must be associated with the enrichment of the suspensions with particles having a size smaller than 6 μm, not detected in the present instrument. These particles were formed by the disruption of 6–100 μm particles during the TSE treatment.

In suspensions containing NaCl which were not subjected to TSE treatment, the number of particles smaller than 100 μm increased (compare between ATW-0 and ATN-X0 or ATN-Y0, Tables 3 and 5), indicating that this additive leads to the disaggregation of aggregates larger than 100 μm. This is in agreement with the sedimentation experiments which showed that in the presence of NaCl the sedimentation rate was slightly slower than in its absence (Table 1). The disaggregation process increased with increasing concentrations of the salt.

Table 5 Distribution of clay particles according to their size (number of particles), in the range 6–100 μm in palygorskite aqueous suspensions (0.0115%), containing NaCl (0.029 or 0.1 *M*, X and Y, respectively), with no TSE treatment (ATN-0) and after one and two TSE treatments (ATN-1 and ATN-2, respectively)

Size range / μm	Number of particles Suspension					
	ATN–X0	ATN–X1	ATN–X2	ATN–Y0	ATN–Y1	ATN–Y2
6 – 10	41 268	40 406	60 262	42 413	47 259	61 391
10 – 15	44 630	31 538	61 130	46 544	37 120	65 829
15 – 20	20 305	9 372	21 143	21 921	11 766	24 317
20 – 30	18 893	6 212	14 441	21 651	8 245	17 151
30 – 40	6 462	1 637	3 807	7 712	2 094	4 388
40 – 60	4 276	894	2 269	5 402	1 296	2 708
60 – 80	1 386	261	727	1 803	360	855
80 –100	609	103	327	796	159	376
6 –100	137 829	90 423	164 112	148 642	108 304	177 012

In the presence of NaCl the first TSE treatment resulted in a decrease in the number of particles in the range of 6–100 μm (Table 5). This is characteristic for disruption of particles in this size range and the enrichment of the suspension with particles smaller than 6 μm. From the first to the second TSE treatment, the number of particles in the range 20–100 μm also increased suggesting that particles larger than 100 μm, were also disrupted during this treatment.

Electrophoretic mobility of palygorskite particles

The effect of the TSE treatment on the electrophoretic mobility of palygorskite particles suspended in 0.1 *mM* NaCl solution is shown in Table 6. The

TSE treatment increased the electrophoretic mobility of the palygorskite particles, and thus, the electrokinetic (zeta) potential of the suspended particles and their surface charge density.

Table 6 Electrophoretic mobility of palygorskite particles in aqueous suspensions (0.0115%), before and after TSE treatments and *pH* values of the suspensions (1.15%) and the supernatants

Suspension	Electrophoretic mobility / $\mu m \cdot s^{-1} \cdot V^{-1} \cdot cm^{-1}$	*pH* of suspension stirred	*pH* of supernatant
ATW–0	1.55±0.49	8.6	8.7
ATW–1	1.82±0.22	9.7	9.7
ATW–2	2.10±0.25	9.6	9.7
ATW–3	n.d.	9.7	9.6

n.d. – not determined

These results corroborate with the above interpretation regarding particles disruption. The following mechanisms are suggested for the increase in the electrophoretic mobility. On the negatively charged surface of the untreated natural clay particles, polyvalent cations and positively charged amorphous hydrous oxides are specifically adsorbed, thus lowering the net surface charge of the particle. Disruption of the aggregated clay particle to smaller particles leads to the exposure of inner surfaces which were hidden inside the cluster. These surfaces have not been in contact with natural water from the time that the aggregated particle was formed, and should be almost free of specific adsorbed polyvalent cations and positively charged amorphous hydrous oxides. Consequently, their net negative surface charge should be higher than that of the surfaces which were exposed before the TSE treatment.

Properties of the solid particles

IR spectra and X-ray diffractions

The IR spectrum of the sample before and after the TSE treatments was typical of palygorskite. No new absorptions appeared after the treatments and there were no indications of any kind of destruction of the clay, even after three treatments. However, the characteristic O–H and Si–O bands became sharp.

The X-ray diffraction of the sample before and after TSE treatments was typical of palygorskite. However, characteristic peaks became sharper. A peak at 1.4 nm, which characterizes smectite, was detected only after the first TSE treatment.

Electron microscopy

Figure 6 shows selected SEM scans of the palygorskite before and after TSE treatments. By comparing the scans of palygorskite before treatment to those obtained after TSE treatment, no significant changes in the needle shape of the mineral particle is observed. The only significant observation is that the aggregates of needles which form the fibres, disintegrate to separated thin needles as

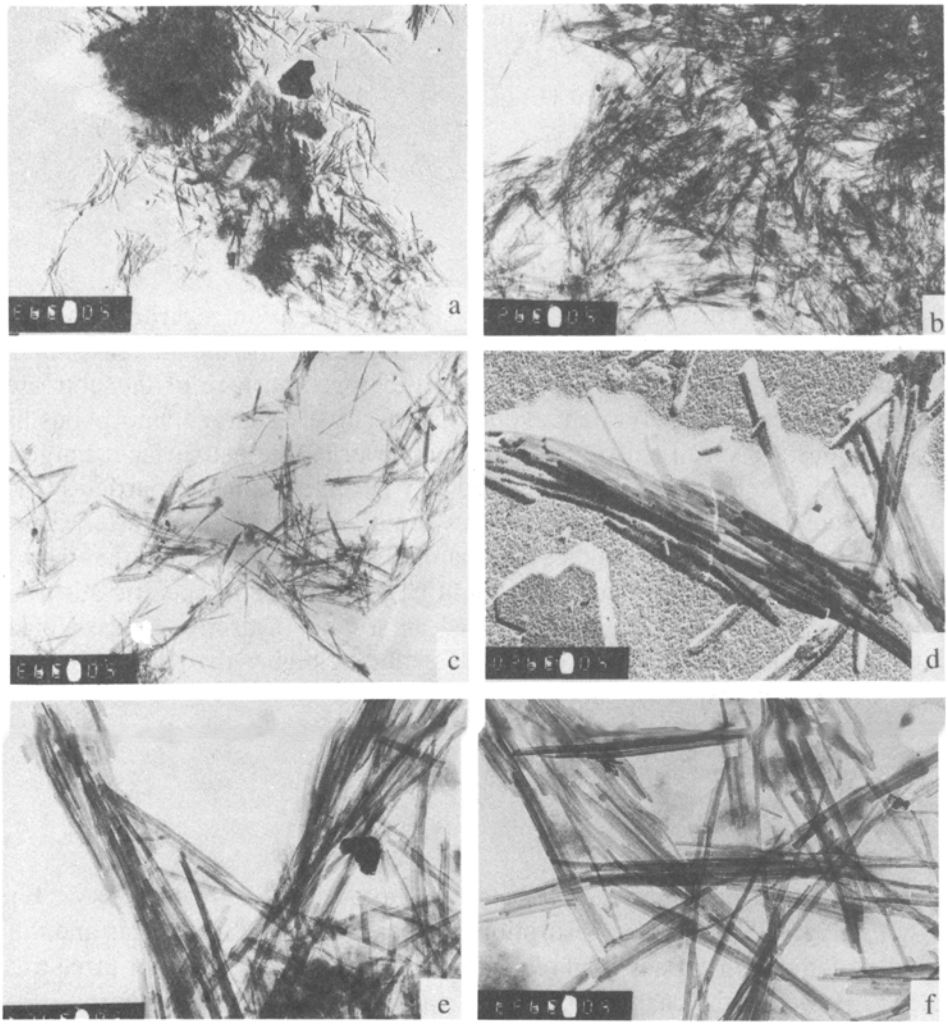

Fig. 6 Selected SEM scans of the palygorskite before (a and d) and after one (b and e) and two (c and f) TSE treatments. Magnification in a–c is 5000 and in d–f, 50 000

a result of the TSE treatment. Before the treatment the needle dispersion was inhomogeneous and distinct 'colonies' of fibres were observed. No clusters were observed after the second treatment and the dispersion of the needles was quite homogeneous.

Conclusions

The present investigation shows that the dispersiveness of palygorskite in aqueous suspensions can be improved by the TSE treatment. The greater the number of treatments a better dispersiveness is obtained. Palygorskite fibres obtained by grinding the mineral, are composed of Mg-silicate needles, held together by micro drops of water, known as 'interparticle water'. In the pressure cell of the TSE system, as a result of the rise in temperature, the internal pressure inside the palygorskite particle increases. However, because of the high external pressure in this cell, the interparticle water is not evolved. When the valve of this cell is opened, the external pressure operating on the particle, suddenly falls down and water molecules are desorbed from the heated particle. The sudden water eruption gives rise to the disruption of the fibres and disjointing of the needles. Improvement in dispersiveness is thus obtained by disruption and decreasing the particle size of the dispersed solid phase, as well as increasing the net negative charge.

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Zusammenfassung — Es wurde ein Gerät gebaut, in dem eine Tonerdesuspension hermetisch verschlossen und für einige Minuten bis 220°C erhitzt wird. Diese thermische Behandlung wird von einer Druckzunahme in der Zelle begleitet. Wird der Behälter geöffnet erfolgt ein rascher Druckabfall innerhalb der Zelle als auch eine plötzliche Freisetzung des interpartikulären Wassers. Dieser Schock führt zu einer Quasiexplosion der Tonerdepartikel. Diese Technik wird als Thermische Dampfdruck-Schockexplosion (TSE) bezeichnet. Es wurde der Effekt von TSE-Behandlungseigenschaften auf Palygorskit-Suspensionen untersucht. Palygorskit-Suspensionen sind in Wasser eher instabil und kleinere Partikel als 3 μm wurden vor der TSE-Behandlung gar nicht gefunden. Durch eine TSE-Behandlung und/oder durch die Verwendung eines Dispersionsmittel wie zum Beispiel Pyrophosphat kann die Stabilität der Suspension erreicht werden. Im Ergebnis der TSE-Behandlung erhält man kleinere Partikel, die Dispersivität der Partikel wird erhöht, ebenso wie die elektrophoretische Mobilität. Scans mit dem Elektronenmikroskop zeigten, daß die Aggregate von Nadeln, welche die Palygorskit-Fasern bilden, infolge der TSE-Behandlung in einzelne dünne Nadeln zerlegt werden.