



Research paper

Mineralogical composition and particle size distribution as a key to understand the technological properties of Ukrainian ball clays



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ABSTRACT

The ball clays from the Donetz basin, Ukraine are widely utilized in the production of ceramic tiles. Their commercial success stems from unrivaled technological properties, whose link to mineralogical composition and particle size is not well understood yet. This work is an in-depth investigation of the mineralogical, chemical, and physical properties with the aim to disclose the reasons of the peculiar technological behavior of these clays. Five clay samples were studied by XRF, XRD (bulk and fractions $<2\ \mu\text{m}$ and $<0.2\ \mu\text{m}$), SEM, TEM, rheological characterization, particle size distribution, BET, MBI, Pfefferkorn index, Atterberg plasticity limits, and laboratory simulation of the tilemaking process. The Ukrainian clays are very fine-grained and characterized by poorly ordered kaolinite (Kaol), interstratified illite/smectite (I–Sm) and a low quartz content. The Kaol-to-I–Sm ratio is lower than in conventional ball clays and two different I–Sm types are found to be predominant in the colloidal fraction. Morphologically, clay minerals appear to be mostly subhedral lamellae that curl and fold under pressure. These characteristics explain the outstanding technological properties of Ukrainian clays and particularly their high plasticity and suitable rheological behavior. These properties depend on the peculiar conjunction of mineralogical and grain size factors that are difficult to be reproduced by clay blending or mixing design.

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1. Introduction

Ball clays have been increasingly utilized in the ceramic production to the point that the tilemaking industry turned to be the major end user, in particular in porcelain stoneware tiles (Sánchez et al., 2010; Dondi et al., 2014). Ball clay is defined as “fine-grained, highly plastic, mainly kaolinitic clay, the higher grades of which fire to a near white color in oxidizing atmosphere” (Wilson, 1998; Bergaya and Lagaly, 2013). The picture of compositional and technological properties of this kind of clays was well established (Worrall, 1975; Powell, 1996; Harvey and Murray, 1997; Wilson, 1998) by the time when the Ukrainian clays were for the first time exported at the end of 1992 (Fiederling-Kapteinat et al., 2000). These clays come from the Donetz basin (Donbas) where fluvio-lacustrine Miocene sedimentary deposits are exploited (McCustion and Wilson, 2006; Murray, 2006a; Mariani, 2010). Ukrainian clays rapidly gained two thirds of the international market, attaining a yearly output of around 2 million tons and an overall export of over 30 million tons up to date (Fiederling-Kapteinat, 2004; Bal and Fiederling-Kapteinat, 2007; Mariani, 2010). The reasons of such a commercial success stem from the unrivaled technological

features that Ukrainian clays exhibit: suitable rheological properties, high plasticity, proper behavior during compaction and drying, and easy sinterability (Dondi et al., 2003; Galos, 2011a,b). Along with a worldwide acceptance as a premium product (Fiederling-Kapteinat, 2004, 2005; Zanelli et al., 2011), these characteristics render Ukrainian clays very useful in the ceramic tile production to turn easier some manufacturing steps (less defects and higher rate of prime quality products) and to produce large ceramic slabs, e.g. 360 cm × 120 cm × 0.3 cm (Raimondo et al., 2010; Sánchez et al., 2010). Furthermore, they enable the recourse to low-priced raw materials, whose non-optimal features may be balanced by the better performances of the Ukrainian clays (Galos, 2011a,b; Zanelli et al., 2011). The same targets are harder to be achieved utilizing conventional ball clays of lower performance (Lombardo, 1996).

The causes of the outstanding properties of the Ukrainian ball clays are not fully understood yet. Although there are evidences of the role played by particle size distribution and “crystallinity” of clay minerals (Dondi et al., 2003; Galos, 2011a,b; Petrick et al., 2011), a comprehensive evaluation is still lacking.

The purpose of this work is an in-depth investigation of the mineralogical, chemical, and physical properties of Ukrainian clays in order to disclose the variables that control their peculiar technological behavior, comparing their performance with those of conventional ball clays,

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including smectite-bearing samples. The results will provide a key to improve the technological response of common ball clays exploited all over the world.

2. Experimental

Five clay samples (named UA, UB, UD, UK, US) were obtained by suppliers of Ukrainian raw materials. The sample selection was carried out in order to cover the spectrum of mineralogical and technological features of commercial clays, as inherited by differences between the main quarries in the Donetz basin (Fiederling-Kapteinat, 2005; Mariani, 2010). The features of conventional ball clays were taken from the literature (Dondi et al., 2014 and references therein).

The mineralogical composition was investigated by X-ray powder diffraction performed on both randomly oriented specimens (bulk) and on oriented specimens of the $<2\ \mu\text{m}$ and $<0.2\ \mu\text{m}$ fractions (air dried and saturated with ethylene glycol). The fine fractions were extracted by sedimentation, according to Stokes' law, and centrifugation (Moore and Reynolds, 1997). A Rigaku-Denki Geigerflex Max III C diffractometer ($0.5^\circ 2\theta\ \text{min}^{-1}$, graphite-monochromated $\text{CuK}\alpha$ radiation) was used. Kaolinite structural order was estimated according to the Hinckley's and Stoch's methods (Aparicio and Galan, 1999) and the AGF index (Aparicio et al., 2006). The interpretation of XRD patterns was performed according to Moore and Reynolds (1997) and Šrodoň (2006). A quantitative composition of the bulk samples was calculated following Domínguez et al. (2008). Composition of the fine fractions was estimated by diffraction peak deconvolution, taking into account the area of the 001 reflection of kaolinite (Kaol) and interstratified illite/smectite (I–Sm).

The microstructure was observed by both scanning electron microscopy (SEM, JEOL 35 CF) and transmission electron microscopy (TEM, JEOL 100 CX). Small clay fragments, mounted on copper holders and coated with Au–Pd alloy, were used for SEM observations. Clay–water dispersions were sprayed on 200 mesh copper holders and bright field technique was used for TEM observations. In addition, the texture of the rods (in section) used to determine the Atterberg plastic limit was observed under SEM.

Whole rock chemical analysis of major elements was performed by wavelength-dispersive X-ray fluorescence spectrometry (XRF-WDS) on powder pellet pressed with micronized wax.

Particle size distribution was measured by X-ray monitoring of gravity sedimentation (Micromeritics Sedigraph 5100, ASTM C 958) and wet sieving of the $>100\ \mu\text{m}$ fraction (ASTM C 325). Specific surface area (SSA) was determined by nitrogen absorption using the BET method (Micromeritics FlowSorb II, ASTM C 1069).

Rheological properties were measured by a stress-controlled rotational rheometer (Bohlin CVOR 120, Malvern, UK) equipped with coaxial cylinders (C25: outer diameter 27.5 mm, gap 1.25 mm). The temperature was kept at $30\ ^\circ\text{C}$ with a thermal control unit based on water jacket. The same protocol of measure was applied to all the samples (Fig. 1). It was made of three main parts: the first one was an on–off procedure in order to study the effect of the rest time on the rebuilding of the dispersions; the second part was a sequence of steps with a decreasing shear rate in order to get steady flow curves; and the last one was a triangular procedure to obtain an indication on thixotropy (Gardini and Galassi, 2010).

For the rheological measurements, 50% of mass aqueous dispersions of Ukrainian ball clay in deionized water, in the presence of 0.3% mass of sodium polyphosphate (supplied by Riedel-deHaën) with respect to the dry powder, were prepared. The dispersions were gently ball milled for 16 h to disagglomerate the particles.

Plasticity was assessed by measuring Atterberg consistency limits (ASTM D 4318), Pfefferkorn plastic index and the methylene blue index (MBI, Chiappone et al., 2004, pH ~4, ASTM C 837).

A laboratory simulation of the tilemaking processing was carried out (Dondi, 2003) by wet ball milling (planetary mill); slip drying

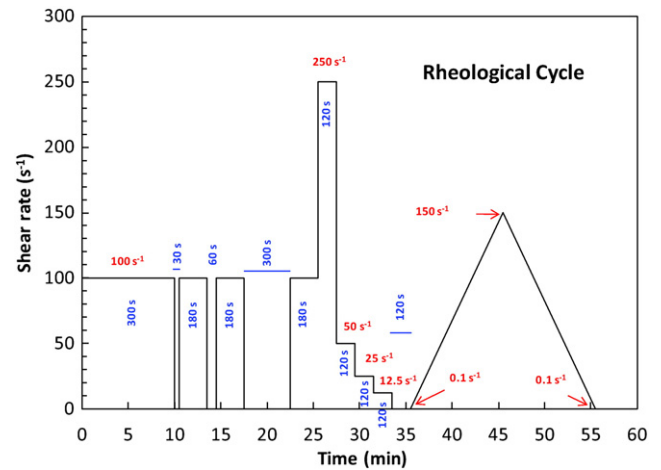


Fig. 1. Rheological protocol applied to the five samples of Ukrainian ball clays.

($105\ ^\circ\text{C}$ overnight in oven); powder agglomeration (8% mass moisture); uniaxial pressing (40 MPa) of $10\ \text{cm} \times 5\ \text{cm} \times 0.5\ \text{cm}$ tiles; drying in an oven ($105\ ^\circ\text{C}$ overnight); fast firing in roller kiln ($1200\ ^\circ\text{C}$, 60 min cold-to-cold). The following technological properties were determined: green bulk density (mass/volume); post-pressing expansion, powder compressibility and drying shrinkage (Dondi et al., 2008); green and dry modulus of rupture, firing shrinkage, water absorption and bulk density (Murray, 2006b).

3. Results and discussion

3.1. Technological properties

The behavior of Ukrainian clays during the tilemaking process can be compared with those of conventional ball clays by considering the key parameters governing the milling, pressing, drying and firing stages. The ball clays used in ceramic tile manufacturing show a wide range of technological properties (Dondi et al., 2014) as outlined by the rather large standard deviations (Table 1). The behavior during body preparation (ball milling to spray drying) will be considered at the next paragraph by discussing the rheological properties.

Ukrainian clays exhibit low values of expansion after pressing, stemming from poor elastic release once the load is removed. This plastic behavior eases pressing of large size and/or thin slabs by preventing breakage during decompression and tile removal from the mold. Thanks to the special properties of highly plastic clays difficult rectangular shapes and even tiles as big as $360\ \text{cm} \times 120\ \text{cm}$ and just 3 mm thick are currently manufactured (Raimondo et al., 2010).

Comparing the compaction behavior for analogous moisture content, Ukrainian clays present a lower compressibility than conventional ball clays, besides the latter exhibit a lower degree of plasticity. This circumstance is to a large extent a consequence of the particle size distribution, since fine-grained materials are harder to be compacted. In this case, the different compressibility is not detrimental, as the dry bulk density is practically the same or even better than conventional ball clays. This is technologically important: the denser are the unfired tiles, the lower is their firing shrinkage, for a given water absorption.

The mechanical strength of both green and dry Ukrainian clay bodies is distinctly better – by a factor of in between 1.5 and 1.8 – than the corresponding performance of bodies made up of conventional ball clays (Table 1). This fact ensures many advantages:

- low risk of damages to unfired tiles during their turning upside down and transportation along the manufacturing line;

Table 1
Technological properties of the Ukrainian ball clays and comparison with other ball clays used in the ceramic industry (Dondi et al., 2014).

Variable	Unit	Ukrainian ball clays											Conventional ball clays	
		UA		UB		UD		UK		US		average	Mean	S.D.
		Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.			
Expansion after pressing	cm·m ⁻¹	0.55	0.04	0.46	0.01	0.53	0.02	0.47	0.04	0.51	0.02	0.5	0.6	0.1
Powder compressibility	adim.	2.33	0.04	2.40	0.06	2.23	0.05	2.45	0.30	2.39	0.02	2.4	2.7	0.3
Green bending strength	MPa	1.83	0.12	1.77	0.15	1.53	0.07	1.74	0.13	1.78	0.09	1.7	1.0	0.3
Dry bending strength	MPa	4.48	0.50	4.25	0.39	3.53	0.26	4.31	0.59	4.35	0.42	4.2	2.7	0.7
Drying shrinkage	cm·m ⁻¹	0.19	0.02	0.14	0.04	0.17	0.03	0.14	0.40	0.14	0.03	0.2	0.0	0.2
Dry bulk density	g·cm ⁻³	1.927	0.010	1.951	0.008	1.862	0.005	1.987	0.012	1.929	0.006	1.93	1.92	0.09
Firing shrinkage (1200 °C)	cm·m ⁻¹	8.5	0.0	7.5	0.1	9.6	0.1	6.4	0.1	8.2	0.1	8.0	4.5	2.3
Water absorption (1200 °C)	% mass	0.3	0.1	0.7	0.2	0.7	0.3	1.8	0.2	0.2	0.1	0.7	7.3	4.3
Bulk density (1200 °C)	g·cm ⁻³	2.473	0.011	2.448	0.002	2.486	0.017	2.366	0.008	2.478	0.005	2.45	<2	–

- chance to use a lower amount of clay (that is the most expensive component of tile bodies, apart additives and pigments) to get the same modulus of rupture;
- proper mechanical performance during glazing, when the amount of water applied by wet techniques may depress the breakage load below the threshold for contact decoration (screen and roller printing).

Drying shrinkage of Ukrainian clays is slightly higher than in conventional ball clays, but the absolute values are so small (on average 0.2%) that no practical drawback happens. This is because in tilemaking the water evaporation occurs during the drying stage without shrinkage (Dondi et al., 2008).

Ukrainian clays are characterized by a faster sintering kinetics once compared with most conventional ball clays, as outlined by the much lower water absorption and the high linear shrinkage and bulk density after a classical firing schedule for porcelain stoneware tiles (Dondi et al., 2003, 2008; Galos, 2011a,b). Body coloration is important in marketing (Dondi et al., 2014) and color after firing of Ukrainian clays is generally lighter than conventional ball clays. However, some variation in the concentration of “chromophores” (Fe and Ti oxides) has been occurring in the long run in every clay mining basin, including the Donetsk clay district. In the same time, the amount of chromophores tolerated in porcelain stoneware bodies has been increasing. Account must be taken that even an apparently small increase of iron oxide in the body, e.g. 0.3%, although it does not significantly affect its technological behavior, is able to provoke a loss of brightness of about 10 units L* (CIE, 1976) in a fully vitrified porcelain stoneware (Salem et al., 2009).

3.2. Rheological properties

During the stages preceding spray drying, the rheological properties of dispersions play an important role. In particular, it is of interest to investigate how the dispersions recover their structure when left at rest for some period of time (storage) and how they flow under continuous shear (ball milling, pumping, spraying). The protocol sketched in Fig. 1 allows the collection of information about these two aspects, as well as on the steady flow curves that better characterize the dispersions, being less dependent on testing parameters.

3.2.1. Rebuilding after rest time (on–off procedure)

The dispersions were pre-sheared at a high rate (100 s⁻¹) for 10 min in order to zero the previous mechanical history and then left at rest for increasing times (30, 60, 300 s). After each rest period they have been suddenly underwent to a high shear rate (100 s⁻¹), according to the protocol of Fig. 1. Typically, for a thixotropic system, the shear stress recorded just after the startup of flow has a high value at the beginning (peak) and then decreases with time towards an equilibrium value. This peak gives an indication of the structuring level (or thixotropy) occurred during the rest time: the higher is the peak, the greater is the structuring level. As expected, the Ukrainian ball clays show peaks that tend to increase with the rest time. However, such increment is moderate, meaning that the samples are little thixotropic. A comparison of the rate of structuring can be made for each sample by normalizing the peak intensity with respect to the steady value of shear stress at 100 s⁻¹ (Fig. 2).

It is evident from these results that the sample UK structures itself more quickly than the others, while the sample UA does not structure

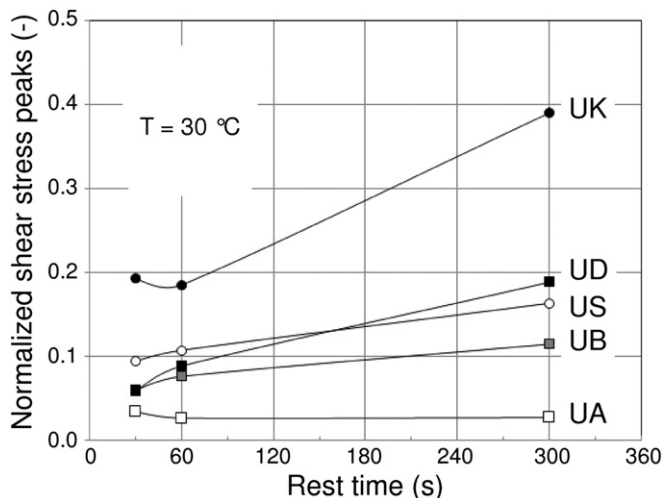


Fig. 2. Normalized shear stress peaks after rest times (30, 60, 300 s).

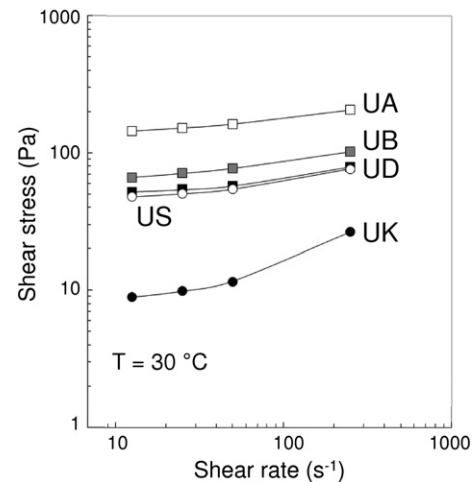


Fig. 3. Steady flow curves for Ukrainian ball clay dispersions. Solid lines represent the fitting with the Herschel–Bulkley model.

Table 2

Particle size distribution, specific surface area, plasticity and rheological properties of Ukrainian ball clays and comparison with other ball clays used in the ceramic industry (Dondi et al., 2014).

Parameter	Unit	Ukrainian ball clays						Conventional ball clays	
		UA	UB	UD	UK	US	Average	Average	S.D.
Specific surface area	m ² g ⁻¹	28.1	28.2	34.0	23.9	29.0	28.6	23.3	11.1
Methylene blue index	meq/100 g	14.5	13.5	14.5	12.5	13.0	13.6	10	6
Pfefferkorn index	% mass	38	37	43	36	38	38	41	8
Atterberg plastic limit	% mass	25	25	30	22	26	26	26	4
Atterberg liquid limit	% mass	75	69	76	60	69	70	50	13
Atterberg plastic index	% mass	50	44	46	38	43	44	24	10
Sand (>63 μm)	% mass	4	6	3	8	4	5	8	8
Silt (4–63 μm)	% mass	10	10	5	15	9	10	29	10
Clay (<4 μm)	% mass	86	84	92	77	87	85	62	15
>20 μm	% mass	6	7	3	11	4	6	11	6
2–20 μm	% mass	18	17	11	22	19	17	31	10
<2 μm	% mass	76	76	86	67	77	76	62	13
<0.2 μm	% mass	45	49	58	43	47	48	NA	–
Yield stress ^a	Pa	126.3	54.0	49.3	8.0	43.6	–	NA	–
Power law exponent ^a	adim.	0.48	0.45	0.81	1.00	0.69	–	NA	–

NA: not available.

^a Herschel–Bulkley model.

itself at all. The rate of structuring decreases in the order: UK > UD ~ US > UB > UA.

Such an on–off procedure puts also in evidence that, for all the samples, the microstructure changes are reversible, as the equilibrium value of shear stress (or viscosity) at 100 s⁻¹ achieved after each rest time remains practically the same.

3.2.2. Steady flow curves (steps procedure)

From the equilibrium values at the different shear rates imposed, steady flow curves can be obtained (Fig. 3). They show that in the range of shear rates investigated (12.5–250 s⁻¹) the flow behavior can be well described with a plastic model, like the Herschel–Bulkley's (Huang and García, 1998):

$$\sigma = \sigma_0 + k \cdot \dot{\gamma}^n, \quad 0 \leq n \leq 1 \quad (1)$$

with the exponent n ranging from about 0.45 (UB) to 1 (UK) and yield stresses ranging from about 8 (UK) to 126 (UA) (Table 2). The behaviors of UK and US are almost overlapped.

3.2.3. Thixotropy (triangular procedure)

The flow curves recorded by applying a continuous variation of shear rate from 0.1 to 150 s⁻¹ and back to 0.1 s⁻¹ (10 min for each ramp) are in good agreement with the steady values obtained for all samples. They are quite overlapped each other (i.e., the area enclosed is quite small) so confirming that the thixotropic behavior is not so pronounced (Fig. 4).

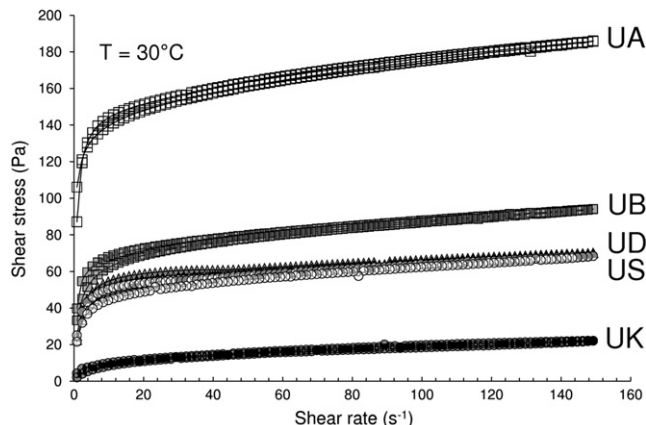


Fig. 4. Flow curves obtained with a triangular procedure for Ukrainian ball clay dispersions.

Putting such flow curves in a log–log graph in terms of viscosity as function of shear stress, the quick decrease of viscosity in a narrow range of shear stress, corresponding to the plastic behavior, can be appreciated (Fig. 5). Such a graph shows also how, at the lowest shear stresses, the viscosity increases with a lower slope, confirming the apparent nature of yield stress.

3.3. Plasticity

The excellent technological behavior of Ukrainian clays during pressing is related to their plasticity that is distinctly higher than that of conventional ball clays in terms of methylene blue (MBI) and Atterberg indices (Table 2). In particular, MBI is in between 12.5 and 14.5 meq/100 g in Ukrainian clays, a range higher than the average for conventional ball clays (10 meq/100 g) but much lower than the MBI of plasticity-boosting raw materials, like smectite-bearing clays and bentonites used in tilemaking (BC3 and WB classes according to Dondi et al., 2014) that can easily span from 20 to 35 meq/100 g. The clays under investigation are classified as BC2, according to their MBI values.

Interestingly, the capacity of Ukrainian clays to retain water prior to developing a plastic behavior, as conventionally expressed by both Atterberg plastic limit and Pfefferkorn index, is approximately the same with conventional ball clays (Dondi et al., 2003, 2008). Therefore, the Ukrainian clays do not need more water than conventional ball clays to behave plastically (Table 2). In contrast, the plastic field is much more extended in the Ukrainian clays, as their mean Atterberg plastic index

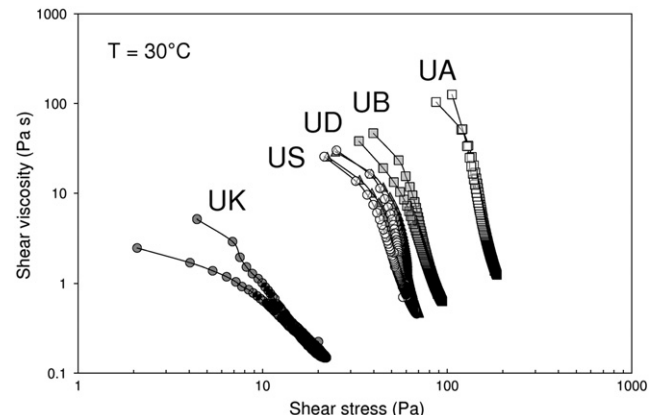


Fig. 5. Shear viscosity versus shear stress for Ukrainian ball clay dispersions.

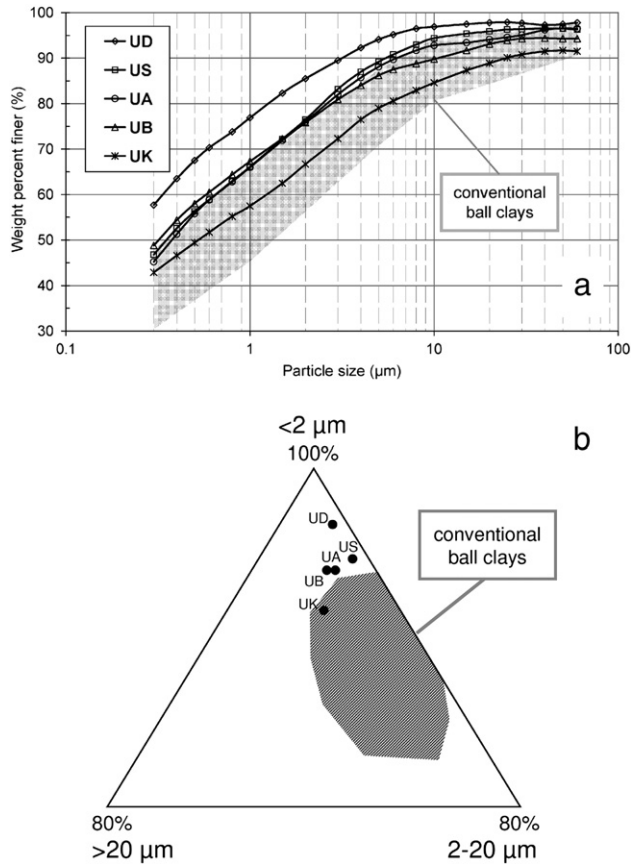


Fig. 6. Particle size distribution of Ukrainian and conventional ball clays used in tilemaking.

(44%) is outstandingly higher than the average of conventional ball clays (24%) and close to the smectite-bearing clays (40–60%).

3.4. Particle size and specific surface area

Ukrainian clays are very fine-grained, being on average much finer than conventional ball clays; just the granulometric curve of the UK sample falls entirely in the region typical for conventional ball clays (Fig. 6a). As these raw materials are particularly rich in the $<2 \mu\text{m}$ fraction, they fall close to this vertex in the particle size triangle, thus

Table 3
Bulk chemical and mineralogical composition of Ukrainian ball clays and comparison with other ball clays used in the ceramic industry (Dondi et al., 2014).

Component (% mass)	Ukrainian ball clays						Conventional ball clays	
	UA	UB	UD	UK	US	Average	Average	S.D.
SiO ₂	58.2	60.0	54.5	65.0	60.9	59.7	60.6	4.9
TiO ₂	1.3	1.6	1.1	1.1	1.2	1.2	1.2	0.5
Al ₂ O ₃	26.9	26.0	29.8	22.0	25.3	26.0	24.9	3.5
Fe ₂ O ₃ total	0.8	1.0	1.0	1.2	1.0	1.0	1.5	0.6
MgO	1.3	0.6	0.5	0.5	0.6	0.7	0.5	0.2
CaO	0.3	0.4	0.4	0.3	0.4	0.4	0.2	0.1
Na ₂ O	0.2	0.5	0.5	0.5	0.4	0.4	0.1	0.1
K ₂ O	2.0	2.6	1.7	2.1	2.3	2.1	1.6	0.8
L.o.I.	8.9	7.2	10.1	6.7	7.9	8.2	9.0	1.7
Total	99.9	99.9	99.5	99.3	99.8	99.7	99.6	
Kaolinite	47	40	57	38	39	44	48	11
Illite + I-Sm	32	36	25	26	35	31	20	8
Smectite	–	–	–	–	–	–	3	3
Quartz	19	20	13	31	23	21	25	10
Feldspars	traces	3	2	3	1	2	2	2
Fe-oxyhydroxides	1	1	1	1	1	1	1	1
Accessories	1	1	1	1	1	1	1	1
Total	100	100	100	100	100	100	100	

plotting onto an area where no conventional ball clays are usually found (Fig. 6b).

A large colloidal fraction is particularly distinctive (on average 48% $<0.2 \mu\text{m}$) being higher of both smectite-bearing types (ranging from 22 to 47%) and conventional ball clays (Table 2).

On the other hand, the specific surface area of Ukrainian clays is not so high – being on average $29 \text{ m}^2 \text{ g}^{-1}$ – compared with the $23 \text{ m}^2 \text{ g}^{-1}$ that is the mean value for conventional ball clays. It is clearly lower than the $36\text{--}54 \text{ m}^2 \text{ g}^{-1}$ range characterizing the plasticity-boosting clay materials (Dondi et al., 2003; Domínguez et al., 2008; Zanelli et al., 2011).

3.5. Chemical composition

No apparent difference arises from the comparison of Ukrainian clays and conventional ball clays in terms of bulk chemical composition (Table 3). Ukrainian clays seem to exhibit slightly higher contents in aluminum, alkaline-earths and alkali oxides, especially K₂O, as well as lower amounts of iron oxide and loss on ignition. Anyway, these differences fall within the standard deviation of average data.

The most relevant features of Ukrainian clays are the rather low Fe₂O₃/Al₂O₃ ratio and a very low content of organic carbon (Fiederling-Kapteinat, 2005) versus the mean 0.4% of conventional ball clays (Dondi et al., 2014). Anyway, all these differences are so limited that cannot convincingly explain the better technological behavior of Ukrainian clays with respect to the general picture of ball clays used in tilemaking.

3.6. Bulk mineralogical composition

The XRD patterns of bulk samples of Ukrainian clays exhibit the intense reflections of Kaol and quartz, associated to a broad hump attributable to “micaceous terms” (Fig. 7). No other components are detected, apart from weak reflections attributable to plagioclase and K-feldspar. The occurrence of traces of iron oxyhydroxides and titanium oxides can be hypothesized on the basis of the chemical composition.

This bulk mineralogical composition is in good agreement with the overall composition of conventional raw materials, although these latter may contain smectitic terms, especially in the case of the very high plasticity ball clays (BC3 type, Dondi et al., 2014). The Ukrainian clays are somehow less rich in Kaol and quartz, and their content of “micaceous terms” is more abundant than the average conventional ball clays (Table 3). At all events, these differences – falling within the global variability range of ball clays – do not justify the technological peculiarities of Ukrainian clays for which more important are the characteristics of clay minerals.

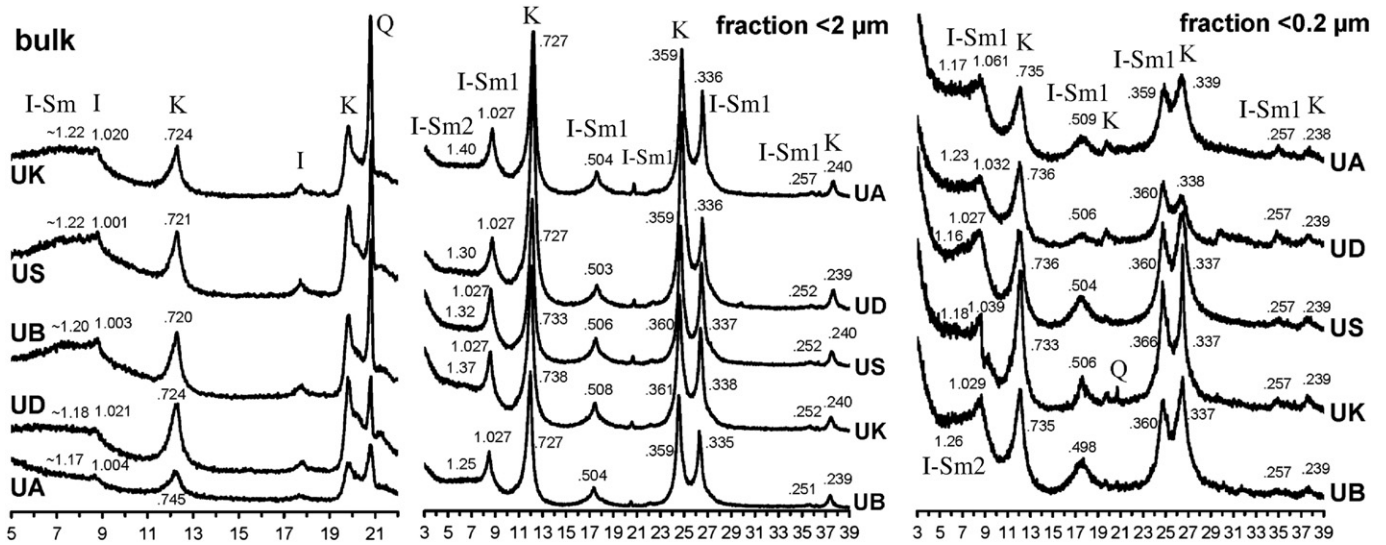


Fig. 7. XRD patterns of Ukrainian clays: bulk and fractions below 2 μm and 0.2 μm. K = kaolinite, I = illite, I-Sm (I-Sm1 and I-Sm2) = interstratified illite/smectite.

High- to medium-defect kaolinites occur in the Ukrainian clays, inferred by indices as high as 1.6–1.9 (Stoch), 0.4–0.7 (Hinckley) and 0.7–1.1 (AGFI, Aparicio et al., 2006). In contrast, low- to medium defect

kaolinites are usually found in conventional ball clays (e.g., Hinckley index: 1.2 ± 0.4) thus close to the distribution observed in kaolins (Sare et al., 2003). This fact is coherent with the small particles size of

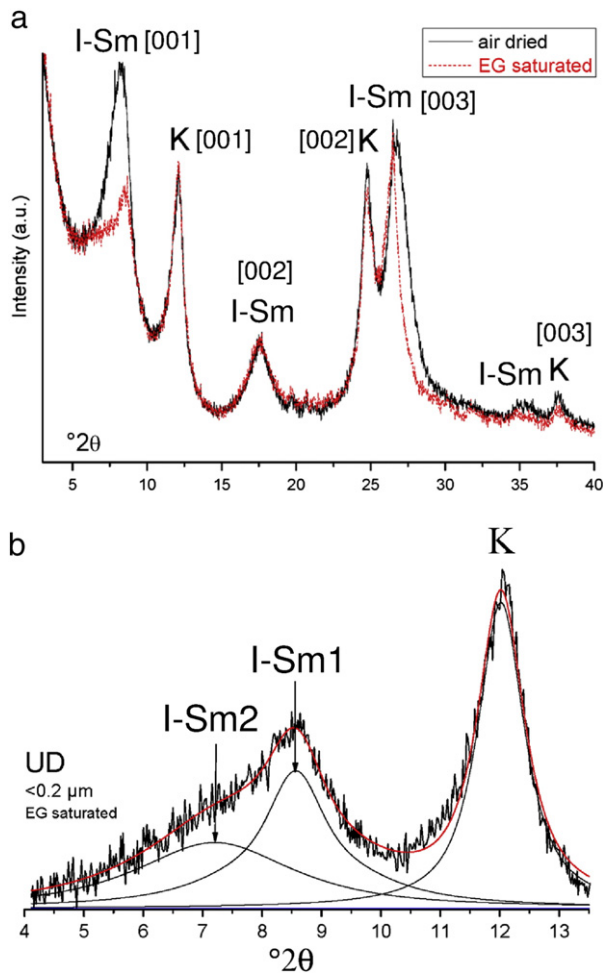


Fig. 8. XRD patterns of Ukrainian clay (sample UD as an example): a) oriented <2 μm fraction, air dried and saturated with ethylene glycol (K = kaolinite; I-Sm = interstratified illite-smectite); b) oriented <0.2 μm fraction saturated with ethylene glycol with deconvolution of reflections of kaolinite (K) and two interstratified illite/smectite (I-Sm1 and I-Sm2).

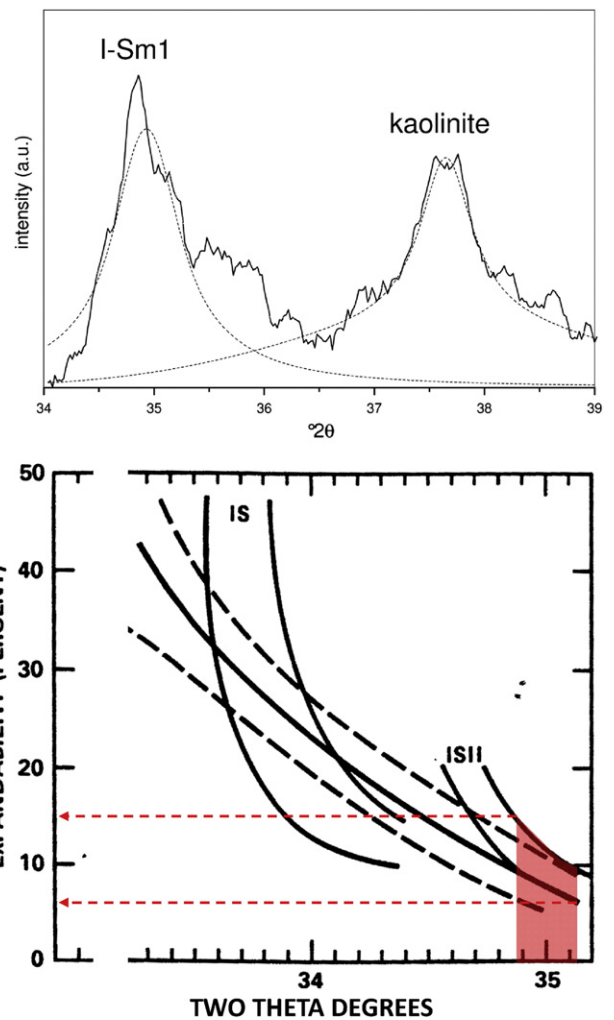


Fig. 9. Detail of XRD pattern of Ukrainian clays (US as an example) with the reflection position used to estimate the degree of expandability of illite/smectite interstratified according to Šrodoň and Eberl (1984).

Table 4
Clay minerals in the bulk, <2 μm and <0.2 μm fractions of the Ukrainian ball clays (% mass).

Fraction	Mineral	UA	UB	UD	UK	US
Bulk	Kaolinite	58	53	62	61	52
	Illite + I-Sm	42	47	38	39	48
<2 μm	Kaolinite	55	50	65	60	50
	R3, I-Sm1 (smectite content 5–15%)	25	25	25	25	25
	Randomly interstratified I-Sm2 (smectite content 15–30%)	20	25	10	15	25
<0.2 μm	Kaolinite	35	35	40	40	30
	R3, I-Sm1 (smectite content 5–15%)	40	50	30	50	50
	Randomly interstratified I-Sm2 (smectite content 15–30%)	25	15	25	10	20

Ukrainian clays and is likely to act through an increase in the concentration of structural defects in Kaol (Reynolds and Bish, 2002; Aparicio et al., 2006). The “micaceous terms” occurring in the bulk XRD patterns are predominantly I-Sm – a broad hump culminating around 12 Å – and minor illite (a weak reflection at ~10 Å). Their amount appears to be distinctive of Ukrainian clays.

3.7. Mineralogical composition of fine fractions

The XRD patterns of the <2 μm and <0.2 μm fractions of the Ukrainian clays mainly display the basal reflections of Kaol and I-Sm with evident changes from the bulk to the colloidal fraction, especially about the low-angle interval (Fig. 7).

In particular, EG-saturation caused a peculiar modification in the basal reflections of I-Sm (Fig. 8a): the swelling of the smectite component induced an apparent splitting of the 001 reflection (I-Sm) in two components (one with a conspicuous shift to lower angle). The expected shift to lower angle of the 003 reflection (I-Sm) is more pronounced than in the case of the 002 reflection (I-Sm). Such a behavior is the complex result of the occurrence of two distinct I-Sm terms, that is supported by the structure of the 5–10°2 θ region (Ferrell et al., 2010; Plançon, 2010; Brigatti et al., 2013). Here, one interstratified mineral has the 001 reflection at 1.03–1.06 nm (10.3–10.6 Å) while the other has the

basal reflection at 1.15–1.3 nm (see example of Fig. 8b). According to both the distance $\Delta_{003-001}$ between 001 and 003 reflections (Moore and Reynolds, 1997) and the expert system by Środoń and Eberl (1984), the former is attributable to a R3-type interstratified, rich in illite (hereafter called I-Sm1) and the latter to a randomly interstratified I-Sm (henceforth abbreviated I-Sm2). The occurrence of different types of interstratified illite/smectite has been already found in the ball clays from Westerwald (Petrick et al., 2011).

About I-Sm1, the distance $\Delta_{003-001}$ ranges from 17.82 to 17.86°2 θ , thus slightly below the expected value for illite s.s. (17.9). This circumstance suggests a limited amount of smectite component, varying from 5% to 15%, in both the <2 μm and <0.2 μm fractions. This is confirmed by the expert system for I-Sm (Środoń and Eberl, 1984) on the basis of the weak reflection plotting at ~35°2 θ , which is compatible with 5–15% of the smectite amount (Fig. 9).

In contrast, I-Sm2 is distinguished by a basal reflection around 1.2 nm (12 Å) that is consistent with a randomly I-Sm with a higher content of smectitic component, that can be estimated around 15–30% according to Środoń and Eberl (1984).

The estimated relative abundances of clay minerals in the bulk and the <2 μm and <0.2 μm fractions are summarized in Table 4.

3.8. Morphological characterization

The electron microscopy micrographs show that the Ukrainian clays are composed mainly by thin subhedral platelets with a face to face texture predominant over some scarce border to face arrangements (Fig. 10).

Illite and interstratified clay minerals are distinguishable only when they have fibrous or tubular shapes (Fig. 11). Classical smectite morphologies were not identified, although some irregular platelets are not mineralogically discriminable by morphological criteria.

The microstructure changes under the conditions (moisture and stress) adopted to shape the rods for the Atterberg plastic index. Observing the rod in section, clay minerals appear to be tightly compacted in a face to face texture that was folded to form a typical “plastic deformation” (Fig. 12a). The same observations performed on a conventional

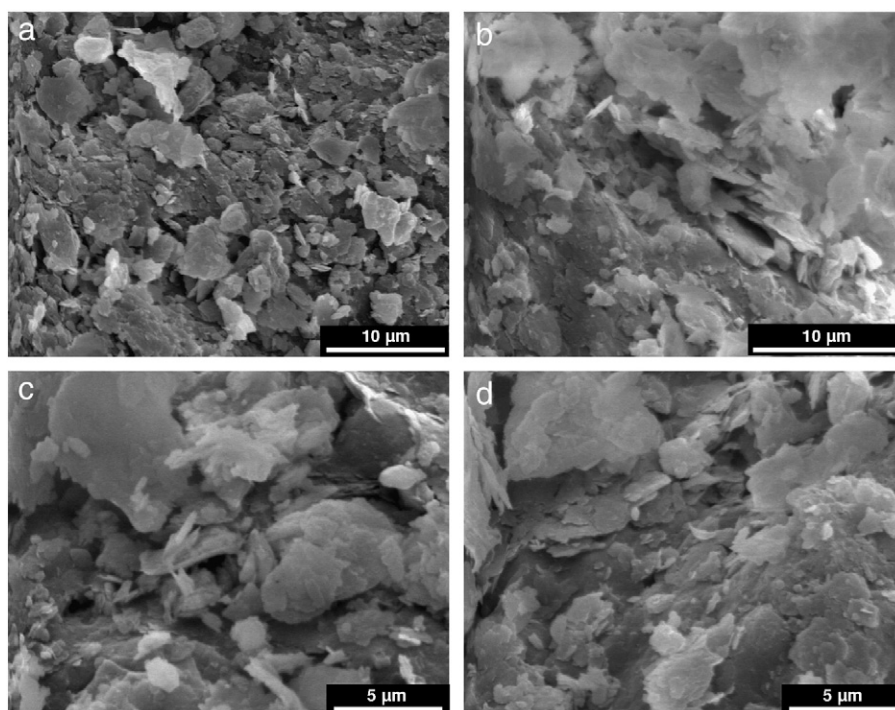


Fig. 10. SEM micrographs of the UK (a and c) and US clays (b and d). See text for details.

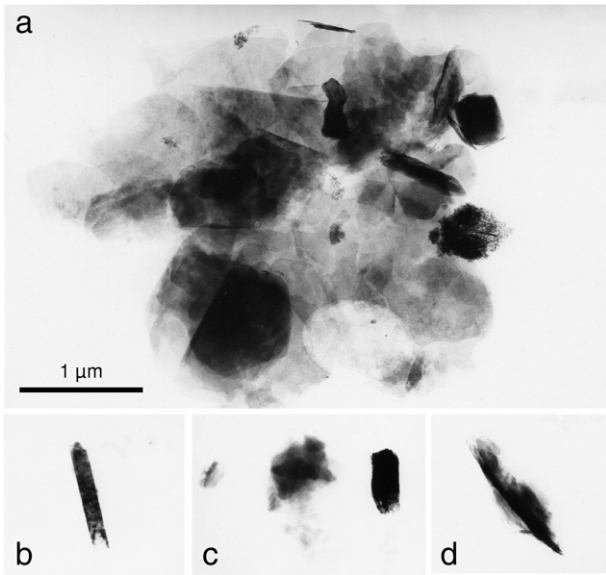


Fig. 11. TEM micrographs of the sample UK: irregular thin kaolinite platelets with some fibrous and tubular I-Sm (a); fibers and tubular shapes with fringed borders attributable to illite or I-Sm (b, c, d).

ball clay do not exhibit such a strongly curled texture, that is only incipiently formed at the borders due to the thicker Kaol platelets (Fig. 12b).

4. Implications for ceramic tile technology

The peculiar ceramic behavior of Ukrainian clays can be explained through their mineralogical composition and particle size distribution. In fact, the clay response during the tilemaking cycle is to a large extent dictated by the amount of clay minerals and colloidal fraction. Despite the rather strict correlation between methylene blue, Atterberg and Pfefferkorn indexes, fine particle fractions, specific surface area, and slip yield stress which characterizes the Ukrainian clays, some exceptions to the overall picture indicate that the ceramic behavior is a complex convolution of all these characteristics. As a consequence, the

technological behavior of a given ball clay cannot be straightforwardly predicted on the basis of a single set of data (e.g., Kaol content or specific surface area). Instead, more comprehensive parameters have to be considered, like the Kaol-to-I-Sm ratio, the relative abundance of the different interstratified I-Sm, and an “activity index” (calculated as the ratio of the Atterberg plastic index to the colloidal fraction ($<0.2 \mu\text{m}$)).

For instance, UD is the finest-grained clay, confirmed by the widest specific surface area. It is the most plastic sample according to MBI, Pfefferkorn index and Atterberg plastic limit (although UA has the highest plastic index). These features explain the fastest sintering kinetics, but fail to justify the lowest compressibility and bending strength values. However, the technological tests were carried out with the same moisture for all samples; the clay UD, due to its wider specific surface area and relative abundance in Kaol, would need a larger amount of moisture to be efficaciously compressed with respect to the other clays under examination. This leads to the low powder compressibility that implies higher porosity of green compacts which is the cause of the lower mechanical strength. Overall, the reason for the higher plasticity of the sample UD is to a large extent related with its finer particle size distribution and a larger amount of the I-Sm richer in expandable component (I-Sm2).

On the other hand, the sample UA exhibits the highest values of mechanical strength and drying shrinkage, besides its particle size distribution and specific surface area are comparable to samples UB and US. Its rheological behavior is extreme with respect to the other clays in terms of relative recovery after rest times, viscosity, yield stress, and the slope of the flow curves at high shear rates. These features can be explained by its large amount of clay minerals, the lower Kaol-to-I-Sm ratio, the larger fraction of I-Sm2 (or perhaps a higher percentage of expandable component in it) and the highest activity index.

At the other behavioral extreme is the sample UK, which has on the one side the lowest values of SSA and colloidal fraction, a high Kaol-to-I-Sm ratio and a low fraction of I-Sm2 on the other side. This justifies the empirical parameters describing plasticity (the lowest methylene blue, Pfefferkorn and Atterberg indexes) and its low slip viscosity. However, the occurrence of a larger coarser particle fraction with a relatively high quartz amount makes it possible the best powder compressibility. The low viscosity of the UK slip in reality masks a noteworthy thixotropy (slow recovery after rest times) that is a consequence of its enhanced

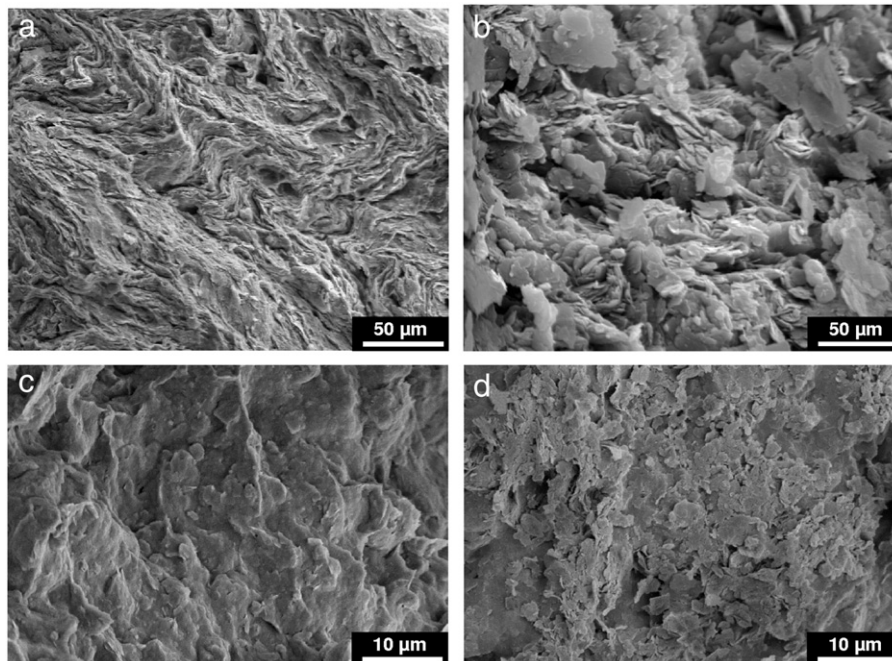


Fig. 12. SEM micrographs on the section of clay bars of Atterberg test: Ukrainian clay UK (a and c) and conventional ball clay (b and d).

slip structuration. In contrast, the highly plastic clays (like UA and UD) give rise to highly viscous slips with little changes after rest times. This is a desired behavior in order to get stable dispersions with a large solid load (that is close to 70% of mass in porcelain stoneware slips).

5. Conclusions

The peculiar technological properties of Ukrainian ball clays are due to a particular conjunction of mineralogical composition and grain size distribution, as their chemical composition is similar to conventional ball clays, but with lower iron amounts. Ukrainian clays are characterized by a particle size distribution much finer than common ball clays, with on average about 50% of colloidal fraction ($<0.2\ \mu\text{m}$). The Ukrainian raw materials consist of abundant clay minerals, mostly high-defect Kaol and randomly I–Sm with a low expandable component, and scarce quartz. The Kaol-to-IS ratio is low and two interstratified terms turn to be predominant in the colloidal fraction. The morphology of clay minerals appears mostly as subhedral thin flexible lamellae that curl and fold under pressure.

These characteristics explain the technological behavior of Ukrainian clays in the ceramic tile production, particularly their higher plasticity and slip viscosity, lower compressibility and faster sintering kinetics with respect to conventional ball clays. However, within the Ukrainian clay variability, the correspondence between the technological behavior and the physical properties are a complex convolution of mineralogical (especially Kaol-to-I–Sm ratio) and granulometric features (particularly the colloidal fraction).

On the whole, Ukrainian clays exhibit outstanding technological properties that are very difficult to be reproduced by clay blending and mixing design. This is because their main traits consist in the abundance of colloidal fraction, where low activity clay minerals (high-defect Kaol, I–Sm with low expandable component) predominate and high activity clay minerals (smectite and smectite-rich interstratified) are absent. The strategy of adding a small amount of high activity clays (e.g., bentonites) to common ball clays does not produce the same technological behavior of the Ukrainian clays.

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