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NOVEL AND RAPID DRYING CHARACTERIZATION TEST SUITABLE FOR THE BRICK AND TILE INDUSTRY

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Abstract: The industrial raw material compositions in brick or tile production are normally adapting from time to time with novel clays. The proper raw material change must be based on the reliable raw material characterization tests. Regardless to the fact that commonly used (Bigot, Muller-Biehl, Ratzenberger, Piltz, Hermansons, etc.) drying sensitivity criterions allow the comparison of different raw materials they are not related with the mineral composition and mechanical nature of clays. Besides these are time-demanding tests. The X-ray characterization of raw material is reliable only when orientated samples are prepared. In other cases, it is necessary to have additional characterization test such as thermo-differential (DTA) and thermo-gravimetric (TG) analysis in order to confirm the presence or absence of individual clay minerals. The quantity of the interlayer water content present in clays is in direct correlation with the mineralogical composition and the clay type. This effect can be easily qualified on the DTA/TG curves. This was a trigger for establishing the novel rapid drying sensitivity criteria. The analysis of different raw materials has confirmed that the moisture loss registered on TG curves at 200^0C can be used as novel drying sensitivity criterion. This value is respectively for insensitive raw materials less than 2.0 while for highly sensitive one is larger than 2.80. The proposed method is very simple, rapid and reliable for the application in brick and tile industry. The second objective of this paper was to compare the results of the proposed method with the widely used Bigoth, Ratzenberg and Piltz tests. A good correlation was found.

Key words**:** clay minerals, brick, tile, DTA, TG.

1. INTRODUCTION

In order to achieve the constancy of clay masonry products performance at the declared level of its essential characteristics it is necessary to have a permanent internal production control conducted by a manufacturer. Proper selection and characterization of the clay raw material is integral and delicate part of each factory control protocol. The upgrade of the existing and development of novel methods for characterization of the clay raw materials from which energy and material savings are expected is in line with the objectives outlined in the EU Construction 2020 strategy [1].

The need to qualitatively evaluate the "easiness" of clay raw material drying and accordingly predict the drying behaviour is still actual research objective. There are many drying characterization methods. Bigot's curve represents the moisture content as a function of linear shrinkage. This curve has a characteristic shape and can provide a lot of useful information about the drying. For example, the critical moment from which the clay product can tolerate sever drying with less risk of cracking. The value of moisture loss in critical point (ML_c) was proposed for classification. Four clay drying sensitivity groups were formed: insensitive ($ML_c \leq 5\%$), poorly sensitive ($5<ML_c<7\%$), sensitive ($7<ML_c<10$ %) and highly sensitive (ML_c >10%) [2-4]. Czysky has further improved the Bigot's classification by introducing the drying sensitivity index as DS-C=(Mi-Mc)/Mc where Mi and Mc represents the initial and the critical moisture content of the test samples. Three drying sensitivity classes were proposed: Light (0<DS-C<1.0), medium (1.0<DS-C<1.8) and important (DS-C≥1.8). This classification is used in situations where different clays which have similar Mc are necessary to compare [5].

Muller-Biehl method is based on measuring the moisture gradient in cylindrically extruded samples which are covered with plastic wrap at 65^0C. In this case evaporation is only allowed from both ends of the cylinder. At pre-set time (2.5, 5, 7.5, 10, 15 and 20h) the moisture gradient is determined by cutting the cylinder and by weighting the corresponding slices. The diagram which represents the difference between internal and external moisture content us drying time was used for determination of maximal moisture gradient D_{max}. Test samples were then additionally dried at 105^0C and afterwards the corresponding linear shrinkage L and flexural strength F were measured. The drying sensitivity criterion which correlates the maximum moisture gradient and the corresponding mechanical strength of the dried sample was defined as DS-M=(D_{max}·L)/F. Five drying sensitivity degrees were proposed: very limited (DS-M < 3), limited (3 < DS-

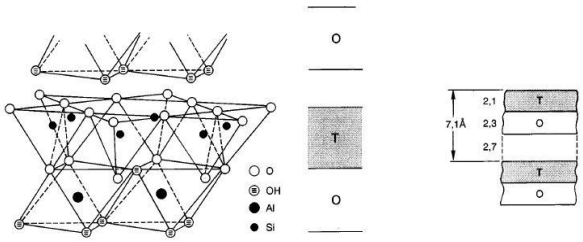
M < 6), intermediate (6 < DS-M < 9), strong (6 < DS-M < 12) and very strong (DS-M > 12) [5]. In German laboratories the Ratzenberg modification of the Muller-Biehl model is commonly used. The moisture gradient determined at 7.5h is used instead of D_{max}. The DS-R sensitivity criterion is not any more correlated with the flexural strength of the dried material. It is calculated as $D_{7,5} \cdot L$. Based on DS-R value clays were classified as: insensitive (DS-R ≤ 30), sensitive (30 < DS-R < 70) and highly sensitive (DS-R > 70) [6]. Prapun has studied the drying sensitivity of 11 clay mixtures form Thailand by determining the DS-C and DS-R sensitivity. A good correlation between DS-C and DS-R was reported with linear correlation coefficient of 0.92 [7].

Procedure for determination of industrial green products drying sensitivity which requires determination of shrinkage-curves for mild and intense drying conditions was proposed by Hermanson. The drying sensitivity index DS-H was defined as time to reach half of the final mid plane shrinkage divided with time to reach half of the final surface shrinkage. This classification recognizes insensitive (DS-H <1.1), sensitive (1.1 < DS-H < 1.3) and highly sensitive (DS-H > 1.3) clay categories [8]. Piltz has firstly put the hand formed clay cylinder sample on a glass plate which was then transferred in a laboratory recirculation dryer. The air flow rate, temperature and humidity were set at 0.5 m/s, 80^0C and 10%. The first crack turning up time was recorded and used as a drying sensitivity criterion. Clays were divided in 7 categories. For example, highly sensitive clays had the first crack turning up time between 4 and 6 minutes [9].

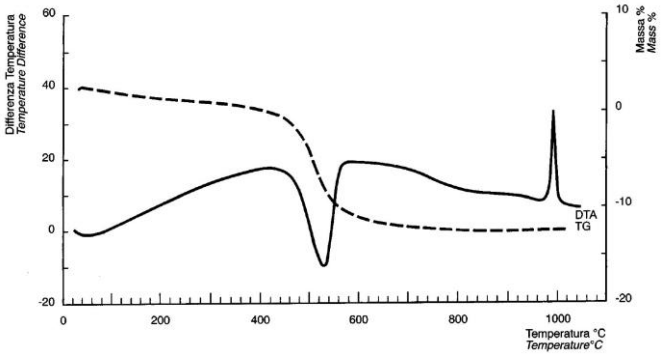
The established drying sensitivity qualities criterions are different and in most cases are not used for adjusting the real dryer. The reason is that those criterions inevitably do not cover the same drying parameters, while at the same time some parameters are intrinsic to the dryer type, product shape and the dryer loading degree.

2. NOVEL DRYING SENSITIVITY MODEL

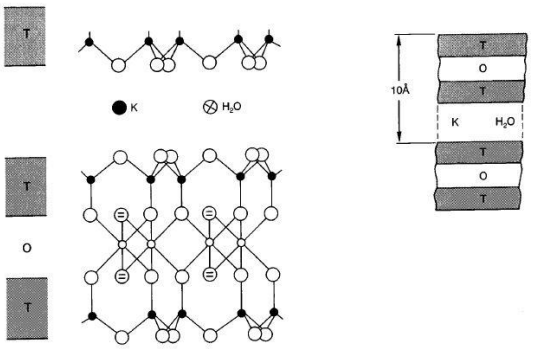
The raw material commonly used in brick and tile industry is a mixture of different clays, feldspar, sand, carbonate, hematite, organic material etc. That's why the interpretation of the registered X-ray diagrams for these materials is not a simple task. It is only totally reliable when orientated clay samples are prepared and used. In other cases, the presence or absence of clay minerals (suspicious, superimposed or overlapped X-ray peaks) must be figured out by using additional characterization methods for example thermo-gravimetric (TG) and thermo-differential (DTA) analysis. A large data base which includes characterization results of Serbian and regional clay raw materials used in various ceramic factories in the last 20 years was established in our laboratory. Standard tests which we used for identification of clay minerals were X-ray and DTA/TG analysis. Pfefferkorn test was chosen for classification of the raw material plasticity. Clays are then divided into 5 plasticity groups (low, moderate, well, highly and the most plastic) [10]. Bigot and Piltz methods are commonly used for determination of the drying sensitivity in our lab, while Ratzenberg method was occasionally applied. Mentioned drying sensitivity criterions are not directly related with the mineralogical composition of clays present in raw materials and their physico-chemical properties. Besides, several days are necessary for the sample preparation and determination of the drying sensitivity. This was a trigger for establishing the novel rapid drying sensitivity method. Mineralogical structure and DTA/TG results of the most relevant clay mineral groups which are commonly present in brick and tile raw materials is reported on figure 1.



a – Mineralogical structure of kaolinite

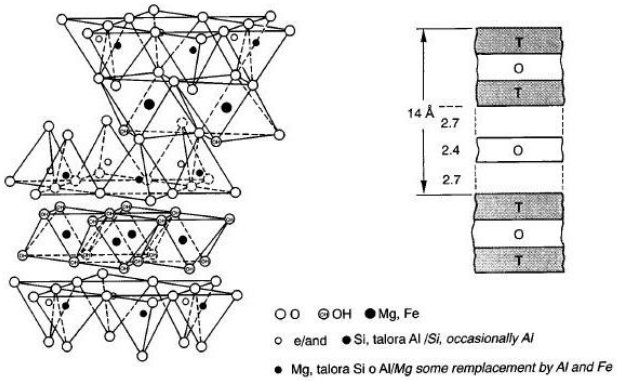


b – DTA of kaolinite

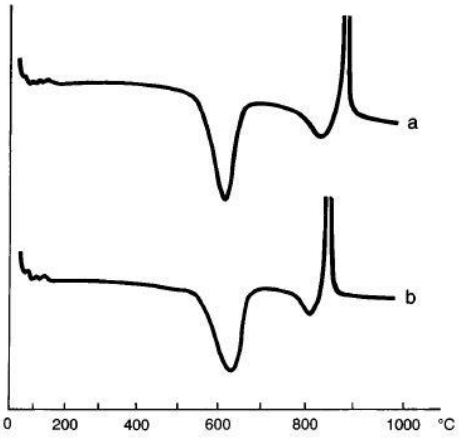


c – Mineralogical structure of Illite

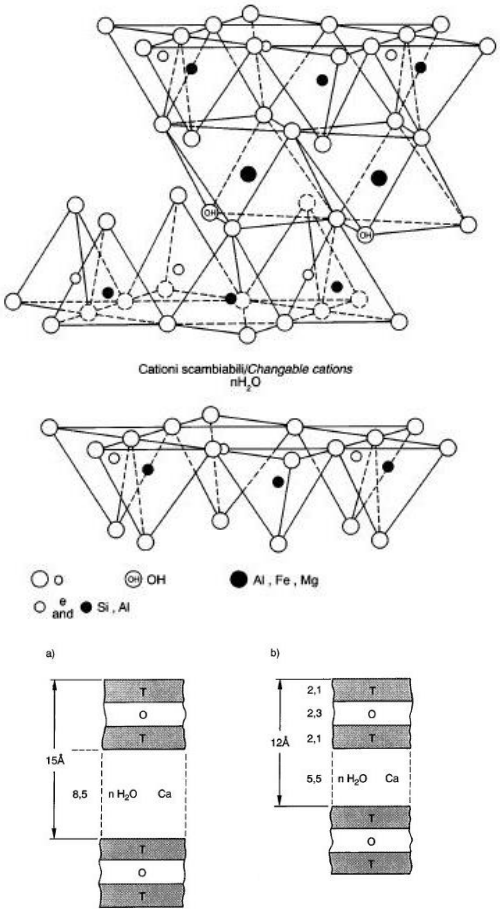
d – DTA of Illite



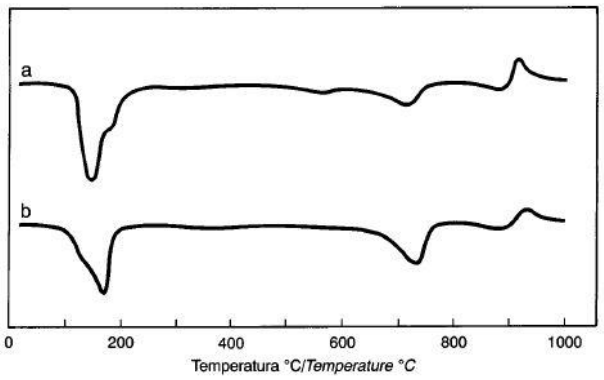
e – Mineralogical structure of chlorite

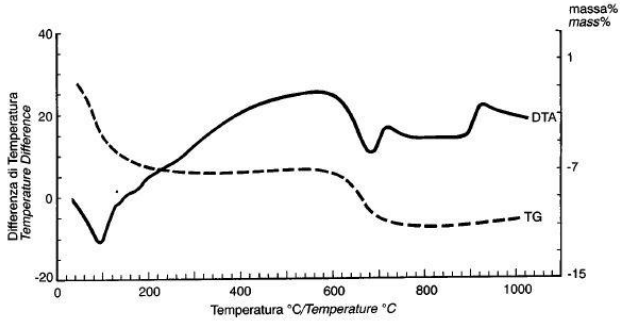


f –DTA of chlorite



a) Ca- montmorillonite; b) Na – montmorillonite
g – Mineralogical structure of montmorillonite





h – DTA of montmorillonite

Fig. 1. Mineralogical structure and DTA/TG results of the most relevant clay mineral groups.

Clay minerals are layer silicates mostly characterized by a structural motive formed by two kinds of units. The first one is formed by SiO_4 tetrahedrons while the second structural units is consisted of an aluminium, iron and magnesium atom layers to which atoms of oxygen and hydroxyl have octahedrons coordination. The combination of one or more structural units of the first kind with the one or more of the second one gives origin to basic structure of clay minerals and of layer silicate in general, which for approximation can be then classified based on the combination of two kinds of units as: Type 1:1 (T-O), Type 2:1 (T-O-T) and type 2:1:1 (T-O-T+O). Each clay unit type has different interlayer spacing. This is clearly seen of figure1a, figure 1c, figure 1e and figure 1g.

The typical curve of a kaolinite (figure 1b) shows a decisive endothermic peak between 550-600^{0}C corresponding to the dehydration reaction and formation of meta-kaolinite, followed by an exothermic peak between 900 and 1000^{0}C, due to the mullite and or γ-Al_2O_3 crystallization. The TG curve shows a strong loss in weight around 590-600^{0}C as a result of the lattice (crystallization) water removal.

The DTA of the illite group is characterized by weak endothermic effects (figure 1d). A first endothermic peak is reached between 100-150^{0}C (interlayer water elimination), followed by another one at 550-600^{0}C

(dehydroxylation). The third endothermic peak is scarcely seen at 900^0C. It is possible related with the formation of spinel structure. The TG curve shows moderate loss in weight corresponding to interlayer and lattice removal.

The DTA curve for chlorite is characterized by an endothermic peak at 550-650^0C corresponding to hydroxyl displacements followed by a series of peaks which are related with further combined and simultaneous dehydroxylation and or recrystallisation changes. If iron content is increased (figure 1f), there is a gradual decreasing of temperature at which recrystallization reaction occurs. The TG curve shows two weight losses which are correlated with the endothermic DTA peaks. The first is large while the second is moderate.

Two endothermic and one exothermic peak are visible on the montmorillonite DTA curve. The first one, between 100 and 150^0C, is due to interlayer water elimination. Its shape is very sensible and is related with the presence of Ca^{2+} and Na^+ ions (see figure 1h). This peak is asymmetrically orientated towards higher temperatures if Ca^{2+} is the mostly preset interlayer ion and towards lower ones if Na^+ ion is dominantly present. The second endothermic peak, between 500 and 700^0C, is a consequence of hydroxyl (lattice water) elimination. The exothermic peak is registered at 900-950^0C. The TG shows two weight losses which are correlated with the corresponding DTA endothermic peaks. The first one is large and is registered before 200^0C, while the second one is moderate and can be seen at 450-650^0C.

It is well known that kaolinite and montmorillonite clay minerals are on the opposite side in regard to the drying sensitivity while illite and chlorite are someware between. The quantity of the interlayer water content present in clays is in direct correlation with the mineralogical composition and the clay type. In order to be sure that this effect is completed the temperature of 200^0C was set as a reference point for comparison of the characteristic peak intensities registered on the DTA/TG diagrams corresponding to the various clay types. It was found that the lowest weight loss (WL) is related with the kaolinite while the largest one is linked with the montmorillonite. The illite and chlorite weight loss were someware between. This can be clearly seen on figure 1b and figure 1h. The value of water loss at 200^0C was established as a drying sensitivity criterion after all the TG curves from the last 20 years found in our laboratory data base were compared. This classification recognized insensitive (WL < 2.0), sensitive (2.0 < WL< 2.8) and highly sensitive (WL > 2.8) raw materials. Well drying (insensitive) clays are commonly classified as semi-acid, moderately plastic materials with linear shrinkage of 4-6 %. This is closely related with the presence of kaolinite mineral. Medium drying (sensitive) clays are representatives of semi-acid towards acid clay group which plasticity is moderate or well and linear shrinkage is in range of 6-8 %. These properties are mostly correlated with the presence of illite (muscovite) and kaolinite-hlorite compositions. Finally, poorly (highly sensitive) drying clays belongs to acid clay group, which plasticity is moderate or well and linear shrinkage is usually larger than 8%. This feature is attributed to the montmorillonitized illite-muscovite and montmorillonite clay minerals.

3. RESULTS AND DISCUSSION

Three clay raw materials which had different mineralogical compositions were taken from our lab data base as an example. Characterization results are summarized in table 1. Kaolinite, hydrochlorite along with some illite minerals were detected on X-ray curves in the case of the raw material A. Raw material B was consisted of kaolinite and small amounts of illite while montmorillonite - illite combination with some hydro-chlorite and small amounts of kaolinite were registered in the raw material C. These results were pointing out that the raw material A and C could be problematic for drying due to the presence of the swelling minerals. Linear drying shrinkage, plasticity as well the shape of DTA/TG curves were in accordance with the reported mineralogical composition.

Table 1. Different drying sensitivity classification opportunities.

Raw material		A	B	C
Moisture cont. after forming (wt. %)		24.22	23.08	25.26
Pfefferkorn plasticity	PI	29.8	27.30	35.1
	Plasticity	Good	Good	highest
	h_0/h	1.53	1.60	1.29
	ctg α	0.59	0.31	0.50

Bigoth	A	B	C
Linear shrinkage at 105^0C (wt. %)	6.27	3.97	9.40
Shrinkage at critical point (wt. %)	5.69	3.51	6.78
Moisture loss at critical point (wt.%)	9.81	6.41	12.00
Moisture content in critical point %	12.03	15.19	10.05
DS - C Drying sensitivity at critical point	0.82 (Light) Sensitive	0.49 (light) Poorly	1.18 (important) Highly
Ratzenberg	A	B	C
$MD_{7.5}$ DS – R Drying sensitivity	7.36 47 sensitive	4.40 18 poorly	8.42 80 highly
Piltz	A	B	C
Time to form the first crack (min) Industrial sensitivity degree Drying sensitivity	7 4 Highly	14 7 Slightly	3.5 3 Extraordinary
Novel method	A	B	C
TG loss at 200^0C Drying Sensitivity	2.62 Sensitive (moderate drying)	1.50 Insensitive (well drying)	6.10 Highly sensitive (poor drying)

The drying sensitivity determined using Bigoth, Ratzenberg, and novel method is similar. Piltz test results have given us some more information about the drying behaviour at the beginning. For example, the raw material C was classified as highly sensitive to drying in accordance with Bigot, Ratzenberg and novel method test. When Piltz test was applied, the same raw material was seen as extraordinary sensitive with a possibility of deep crack formation especially at the beginning of drying. Calculated DS-C values for clay A and C are equal to 0.82 and 1.18. So if this parameter is used alone for classification of the drying sensitivity the corresponding drying behaviour of those clays could be estimated as lightly safe and important respectively. That assessment does not correspond with the actually determined drying behaviour in which ML_c is used for classification of the clay A. This is only a proof that DS-C has to be only used in situations where different clays which have similar Mc are necessary to compare. Two main conclusions are: The novel method for determination of drying sensitivity is the fastest and most objective one since sensitivity criterion is directly correlated with the mineralogical composition and the clay type. The best characterization results are obtained if novel method is combined with the Piltz method.

4. CONCLUSION

The most relevant clay mineral groups, which are commonly present in brick and tile raw materials, have different combination of the tetrahedron and octahedron structural units. Besides the value of interlayer spacing is unique for each clay type and accordingly the quantity of interlayer moisture present in the corresponding green clay products is also constant and in direct correlation with the mineralogical composition of the clay. The ability to visually track the interlayer water removal during heating on DTA/TG curve was used for establishing the novel drying sensitivity criteria as the value of WL at 200^0C. Three drying sensitivity groups were formed: insensitive ($WL < 2.0$), sensitive ($2.0 < WL < 2.8$) and highly sensitive ($WL > 2.8$). As example the drying sensitivity was determined on three clays using the novel and common models. It was confirmed that all models can classify different clay raw materials in the same designating order. It is expected that the brick and tile industry will very fast accept the novel model since it is rapid, simple and most objective one.

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