



Prof. Dr. Alessandro F. Gualtieri
Università degli Studi di Modena e Reggio Emilia
Dipartimento di Scienze della Terra
Largo S. Eufemia, 19; 41100 Modena, Italy
Tel.: +39-059-2055810; Fax: +39-059-2055887
Email: alessandro.gualtieri@unimore.it



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OGGETTO: Articolo scientifico che riporta dati sperimentali su argille fornite dalla Ditta S.E.I.

Con la presente, il sottoscritto Prof. A. Gualtieri dichiara che il manoscritto originale dal titolo "*Thermal conductivity of fired clays: effect of mineralogical and physical properties of the raw materials*" di Magdalena Lassinanti Gualtieri, Alessandro F. Gualtieri, Silvio Gagliardi, Petra Ruffini, Roberto Ferrari e Miriam Hanuskova, in corso di pubblicazione sulla rivista **Applied Clay Science** (in allegato), contiene dati sperimentali innovativi sulle proprietà termiche di manufatti in laterizio realizzati utilizzando campioni di argilla naturale di provenienza nazionale. I campioni di argilla denominati (8) e (9), dalle località Migliarino e Copparo (Ferrara, Italia), sono stati forniti dalla Ditta S.E.I. di Ferrara e sono risultati di grande interesse per migliorare le proprietà termiche di conduttività dei prodotti in laterizio.

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Prof. Dr. Alessandro F. Gualtieri

1 **Thermal conductivity of fired clays: effect of mineralogical and**
2 **physical properties of the raw materials**

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4 Magdalena Lassinantti Gualtieri^a, Alessandro F. Gualtieri^b, Silvio Gagliardi^c, Petra
5 Ruffini^c, Roberto Ferrari^c and Miriam Hanuskova^a

6
7 ^aDipartimento Ingegneria dei Materiali e dell’Ambiente, Università degli Studi di Modena e Reggio
8 Emilia, Via Vignolese 905/a, I-41100 Modena Italy

9 ^bDipartimento di Scienze della Terra, Università degli Studi di Modena e Reggio Emilia, S. Eufemia 19, I-
10 41100 Modena Italy

11 ^cLaboratorio Tecnologico Mantovano s.r.l., Via A. Pitentino 12, I-46010 Levata di Curtatone, Mantova,
12 Italy

13
14
15
16
17 Corresponding author: Alessandro F. Gualtieri, e-mail: alessandro.gualtieri@unimore.it; Full postal
18 address: Dipartimento di Scienze della Terra, Università degli Studi di Modena e Reggio Emilia, Via S.
19 Eufemia 19, I-41100 Modena Italy; Tel. +39 059 2055810, Fax. +39 059 2055887

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22

23 **Abstract**

24 In the present work, the physical, chemical and mineralogical properties of representative
25 commercial Italian clays were investigated by X-ray Powder Diffraction and Rietveld
26 refinements, laser granulometry, X-ray Fluorescence Spectroscopy and Calcimetry. The clays
27 were used to prepare bricks by both extrusion and uniaxial pressing. The effective thermal
28 conductivity of the fired bricks was determined and correlated with physical and mineralogical
29 properties of the raw materials. Unfortunately, the complex nature of the system with many
30 influencing parameters and interactions does not allow linear correlations with single parameters.
31 Hence, a multiple linear regression approach was attempted and a statistically valid model was
32 built for extruded samples. Although the model can not be regarded conclusive, due to the system
33 complexity and the limited number of observations, the results gave some indications regarding
34 the role played by the raw materials properties on the effective thermal conductivity of the bricks.
35 The pore forming effect of organic material decreases the thermal conductivity of the bricks. On
36 the contrary, the thermal conductivity increases with decreasing particle size, possibly due to an
37 increased sintering rate and/or improved particle packing.

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40 *Keywords:* Clay brick; Thermal conductivity; Natural raw materials

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44 **1. Introduction**

45 Energy consume is nowadays a critical issue, particularly from an environmental point of view.
46 As a consequence, the thermal insulation properties of building materials such as traditional clay
47 bricks is of paramount importance. The factors that affect the effective thermal conductivity of
48 bricks, and solid bodies in general, can be classified in the following way: i) Geometrical design
49 (i.e. macroscopic structure) such as the presence of cavities and their configuration (Bouchair,
50 2008); ii) mineralogical composition (Kingery, 1959) and iii) microstructure. The bulk density is
51 since a long time known to correlate with thermal conductivity. Nevertheless, the variation in
52 thermal conductivity for ceramic bodies with the same bulk density can be considerable (Erker,
53 2002a; Dondi et al., 2004). Factors responsible for these variations may be the mineralogical
54 composition (Erker, 2002b; Dondi et al., 2004) but also the nature of the pore system, e.g. the
55 size and size distribution of the pores (Wagh, 1993). The pore system is also important
56 considering the stability of thermal isolation of bricks in humid air. In fact, larger porosity and
57 mean pore radius decrease the difference between the thermal conductivity measured at 0 and
58 100 % relative air humidity (Šveda, 1998).

59 Common clay bricks are normally produced by extrusion, drying and firing. The clays
60 generally contain illite, quartz and carbonates as major phases whereas chlorite, kaolinite,
61 smectite, montmorillonite and feldspars may be present in more or less important amounts
62 (Strazzer et al. 1997; Erker, 2002b). Clay raw materials for brick production can be divided into
63 lime-rich clays (containing calcite, dolomite or gypsum), red-firing clays (rich in mica), quartz-
64 rich clays and carbonaceous clays (high organic content) (Erker, 2002b). Decarbonation of calcite
65 and dolomite during firing results in a decreased density (e.g. Cultrone et al. 2004; Bauluz et al.
66 2003). Generally, a decreased density results in a decrease in thermal conductivity and strength.

67 Erker (2002b) found that this general rule is not strictly applicable to bricks of lime-rich clays
68 due to simultaneous formation of calcium aluminosilicates (such as wollastonite and anorthite).
69 These newly formed minerals have relatively high thermal conductivity and are highly bonded to
70 each other which results in an increase in both thermal conductivity and compressive strength
71 (Erker, 2002b). In fact, increasing the firing temperature results in a decreased bulk density due
72 to decarbonation with a simultaneous increase in thermal conductivity due to changed
73 microstructure of the solid skeleton, (see Tab. 5 in: Erker, 2002b). This observation is called “the
74 bulk density-thermal conductivity paradox”. The negative effect of calcium carbonate on thermal
75 insulation was also demonstrated by Šveda (2000a). He found that an addition of 10 wt% of
76 CaCO₃ resulted in a thermal conductivity increase of about 60 %. Hauck and Ruppik (1997) also
77 found that clay bodies with low contents of carbonate-containing minerals and high content of
78 micaceous minerals produce bricks with low thermal conductivity. In fact, bricks based on red-
79 firing clays are generally characterized by low thermal conductivity and low strength. If
80 comparing red-clay bricks with lime-rich clay bricks with similar bulk density, the thermal
81 conductivity of the former is considerably lower (see Fig. 5 in Erker, 2002b). This difference was
82 explained by the different thermal conductivities of the minerals composing the bricks and/or
83 bond strength between particles composing the solid skeleton.

84 Dondi et al. (2004) determined the mineralogical composition of 29 different fired bricks
85 manufactured using raw materials representative of the wide range used by the Italian brick
86 industry. Generally, the major phases in the fired bricks were quartz, amorphous material,
87 plagioclase and melinite, with more or less important amounts of illite, feldspar, pyroxene,
88 wollastonite, hematite, periclase and calcite. Hence, most of the phases in the clays, except for
89 quartz and feldspars which are inert up to the firing temperature, decompose (via dehydroxylation
90 for clay minerals and decarbonation for carbonates) and recrystallize during the firing cycle. The

91 aim of the work by Dondi et al. (2004) was to reveal any correlation between effective thermal
92 conductivity of the bricks with the mineralogical composition of the fired bodies and the brick
93 microstructure (in terms of open, closed and total porosity as well as pore size distribution and
94 bulk density). Multiple regression analyses evidenced open porosity, quartz and Ca-rich silicates
95 (wollastonite and melilite) as important factors governing the thermal conductivity, although the
96 regression coefficient was rather scarce ($R^2=0.608$). Open porosity was found to have a positive
97 effect on thermal insulation, whereas the opposite was found for quartz and Ca-rich silicates.

98 Erker (2002a) found a high correlation between abrasive volume (i.e. volume of material
99 recovered during grinding under fixed conditions) and thermal conductivity. This was explained
100 by the fact that the abrasive volume is dependent on both the bulk density and on the bonding and
101 strength of the ceramic body. Such tests were suggested to be suitable for routine control of the
102 thermal properties of bricks (Erker, 2002a). Another factor highly correlating with thermal
103 conductivity is the energy consumption during firing (Erker, 2002a;). Generally, higher energy
104 consumption is accompanied by higher thermal conductivity (Erker, 2002a; Galal et al., 1985).
105 However, the opposite can be observed in the case of high-quartz raw materials due to melting of
106 the highly conductive quartz grains which improves thermal insulation.

107 In previous work, empirical models have been developed in which easily measured physical
108 properties are related to the thermal conductivity by regression analyses (e.g. Dondi et al., 2004;
109 Rhee, 1975; Erker, 2002a; Šveda, 2000b). In addition, numerous works present numerical
110 calculations based on the mechanism of heat transfer through the material (e.g. Bhattacharjee and
111 Krishnamoorthy, 2004; Wagh, 1993). It is however surprising that these analyses mostly concern
112 properties of the fired brick (e.g. porosity, thermal conductivity, degree of sintering etc), even
113 though it is probable that these properties are directly related to the raw materials used. In fact,
114 design of mixture experiments were successfully used to model various technological properties

115 of clay bricks such as the fired bending strength and linear firing shrinkage (Correia et al., 2006a;
116 Correia et al. 2006b) as well as open porosity and water absorption (Correia et al., 2006b). Hence,
117 it was possible to define the combination of raw materials which resulted in a brick with specific
118 properties.

119 In this work, the physical and chemical properties of selected Italian clays were investigated
120 using X-ray powder diffraction (both qualitative and quantitative phase analyses), X-ray
121 fluorescence spectroscopy, laser granulometry and calcimetry. In addition, thermal conductivity
122 measurements were performed on fired bodies of each clay fraction. The measured
123 physical/chemical properties of the different clay raw materials were correlated to the effective
124 thermal conductivity of the fired bricks. The results presented here, will contribute to the
125 discussion about the factors playing in the determination of the effective thermal conductivity of
126 clay bricks.

127

128 **2. Materials and Methods**

129 *Raw materials characterization*

130 The samples are representative batches of commercial clays from different quarries in
131 Northern Italy from the mining districts of Gorizia (1); Treviso (2); Modena (3); Verona (4);
132 Sassuolo, Modena (5); Bologna (6); Vicenza (7); Migliarino, Ferrara (8) Copparo, Ferrara (9).

133 X-ray powder diffraction (XRPD) data were collected using a θ/θ diffractometer
134 (PANalytical, $\text{CuK}\alpha$ radiation), equipped a real time multiple strip (RTMS) detector. A 0.125°
135 divergence slit and a 0.25° anti-scattering slit as well as a soller slit (0.02 rad) were mounted in
136 the incident beam pathway. The diffracted beam pathway included a Ni filter, a soller slit (0.02
137 rad) and an antiscatter blade (5 mm). A virtual step scan of the RTMS detector of $0.0167^\circ 2\theta$ was
138 used. Data were invariably collected with high counting statistics (100 s/step). Initial qualitative

139 analyses of the clay fraction of each sample were performed on as-prepared, calcined (550 °C)
140 and glycerol-treated oriented samples (Azaroff and Burger, 1958), using X'Pert Highscore Plus
141 (PANalytical, version 2.1) with a PDF2 reference data base implemented in the software. XRPD
142 data for quantitative phase analyses were collected from carefully ground powders, side-loaded in
143 aluminum sample holders. The analyses were performed using Rietveld refinements which were
144 carried out using GSAS (Larson and von Dreele, 1994) in conjunction with its graphical interface
145 EXPGUI (Toby, 2001). For fired samples, the quantitative phase analysis method using the
146 Rietveld technique was combined with the internal standard method in order to quantitatively
147 determine the glass content (Gualtieri, 2000). Corundum (NIST 676) was added to the samples
148 (10 wt%) as internal standard and included in the refinements. The refined weight fraction of
149 each crystalline phase (X_{ic}) was rescaled with respect to the known weight fraction of added
150 standard (X_s) in order to obtain the real crystalline phase weight fraction (X_i) according to the
151 following equation;

$$152 \quad X_i = \frac{\mathbf{1}}{\mathbf{1} - X_s} \left[\left(\frac{X_s}{X_{sc}} \right) X_{ic} \right]$$

153 where X_{sc} is the refined weight fraction of the internal standard.

154 After calculating the real weight fraction of the crystalline phases, the glass content (X_a) is
155 calculated by the following equation:

$$156 \quad X_a = \mathbf{1} - \sum_i X_i$$

157 Calcimetry (Dietrich-Fruhling apparatus) was used to determine the carbonate
158 content in the raw clay samples.

159 A laser granulometer (Mastersizer 2000, Malvern Instruments), equipped with a system for
160 measurement in humid (Hydro 2000S), was used to determine the grain size distribution of each
161 raw clay fraction. The particle size distribution (cumulative volume fraction) curves were
162 successfully fitted with the following bounded exponential model;

162 $V_f = 1 - e^{-\alpha \cdot D}$ (1)

163 where V_f is the volume fraction, D is the particle diameter in μm , and α is the fitting parameter
164 which was used as independent variable in the multiple linear regression analyses. An increased
165 value of α is equivalent to a decreased overall particle size and a narrower grain size range.

166 Chemical analyses by X-ray fluorescence were conducted with a Philips PW1480 spectrometer.
167 Lost of ignition (LOI) was determined by thermal analyses not reported here.

168 The real density (ρ_r) of the fired samples was determined using a gas displacement pycnometer
169 instrument (AccuPyc 1330, Micromeritics Inc., USA). The measurements were performed on fine
170 powders, which had been kept at 110 °C for at least 24 h and subsequently stored in a dessicator.
171 The bulk density (ρ_b) was determined by accurate determination of the sample dry weight and
172 dimensions.

173 The total porosity (TP) was calculated according to:

174 $TP = \left(1 - \frac{\rho_b}{\rho_r} \right) \cdot 100$

175 The determination of the organic content was performed according to ASTM standards (ASTM
176 D2974-95. The ignition temperature was 440 °C.

177

178 *Preparation and characterization of bricks*

179 Green bodies with the dimensions 20×10×1 cm were prepared by extrusion using a standard
180 industrial procedure. For comparison, pressed (50 Bar) sample biscuits with a diameter of ca 40
181 mm were also prepared. The number of samples prepared by extrusion and pressing were 5 and
182 10, respectively. The as-prepared green bodies were dried at 105 °C and consequently fired in an
183 electric furnace (heating from 25 to 850 °C in 8 h followed by a 30 min long isotherm at 850 °C
184 and consequent cooling to 25 °C in 1,5 h).

185 The thermal conductivity measurements were performed according to ISO 8301, using the
186 guarded heat flow method.

187

188 **3. Results and discussions**

189 XRPD data collected from oriented samples of as-prepared, calcined (550 °C) and glycerol-
190 treated clay fraction was used for initial qualitative analyses. That is, these data was used to
191 confirm/rule out the presence of smectite, clorite and kaolinite (Azaroff and Burger, 1958).

192 The mineralogical composition, as determined by XRPD data and Rietveld refinements, of each
193 clay fraction under investigation are reported in Table 1. The agreement factors of the
194 refinements are also displayed. The raw clays contain a small fraction of organic matter
195 (determined separately and reported in Table 1) and the refined fractions of the minerals were
196 renormalized accordingly. The investigated raw materials are mainly composed of quartz,
197 micas/interlaminate, kaolinite, calcite and feldspars with minor amounts of smectite and
198 dolomite. Small quantities of hematite and gypsum were also found in some of the samples.

199 Table 2 reports the calcite content in each clay fraction estimated by calciometry
200 measurements. For comparison, the refined weight fraction of calcite (XRPD and Rietveld
201 refinements) is also included. The agreement of the results from the two independent methods is
202 satisfactory and indicates a good accuracy of the quantitative phase analyses.

203 Table 3. reports the chemical composition of each investigated clay fraction, as determined by
204 XRF.

205 Table 4 reports the results from the laser granulometry measurements of the raw materials
206 under investigation. In addition to the standard output values from such measurements (i.e.
207 $d(0.1)$, $d(0.5)$ and $d(0.9)$), the parameter α (fitting parameter in eq. 1) is also reported together

208 with the regression coefficient for the fit. As an example, Fig. 1 shows the experimental and
209 calculated cumulative volume fraction curves for sample 2.

210 Table 5 reports the effective thermal conductivity (λ_{eff}), the bulk density (ρ_b) and the total
211 porosity (TP) of the fired bricks prepared using the different clay raw materials and procedures
212 (extrusion and pressing). The reported values are means and the standard errors (95 % confidence
213 interval) are also displayed. As can be observed from the table, the values obtained for the
214 samples prepared using the different procedures (extrusion and pressing) are significantly
215 different, which is not surprising as the conditions are very different. However, a factor could be
216 the different measurement direction of the thermal conductivity which was along and across the
217 direction of the pressure in the pressed and extruded samples, respectively. This could have some
218 effect as the clay minerals tend to orient with the c-axis parallel to the pressure direction,
219 resulting in a anisotropic ceramic body with a higher thermal conductivity in the direction
220 parallel to the direction of pressure (e.g. Erker, 2002b).

221 Table 6 reports the results of the Rietveld quantitative phase analyses of the fired extruded
222 samples. Comparing these results with the ones obtained by Dondi et al. (2004) for 29 clay bricks
223 prepared using different clays, some differences are observed. Dondi et al. observed wollastonite
224 and pyroxene whereas these phases were absent in the samples studied here. Here, mica was
225 observed whereas the samples studied by Dondi et al. (2004) did not contain this mineral. These
226 differences are most likely due to a lower firing temperature used in this work. Considering the
227 minor amount of calcite present in the fired samples, the firing temperature was surely high
228 enough for a near complete decomposition of the carbonates. In fact, the observed calcite could
229 eventually be of secondary nature. The only high temperature crystalline phase observed in our
230 samples is melilite or actually an intermediate in the akermanite and gehlenite series.

231 Fig. 2 shows the thermal conductivity versus the bulk density of the fired clay bricks prepared
232 using the different clay raw materials and preparation procedures. For comparison, data from the
233 literature are also shown (Dondi et al., 2004; Šveda, 2000a,b,c). The bulk density is documented
234 as the major factor that governs the thermal conductivity of solids in general. In fact, considering
235 all data reported in Fig. 2, there seems to be a correlation between the two factors ($R^2=0.54$).
236 However, other variables also play a role in the determination of the thermal conductivity, as
237 stated by others (see introduction). Such variables are e.g. mineralogical composition and
238 microstructure of the fired bricks (e.g. Dondi et al. 2004) which should be, in case of fixed
239 process parameters, correlated to the physical and chemical properties of the raw materials used.
240 Such correlations are however expected to be rather complex due to interactions between
241 variables. During firing, a sequence of both intramineral and intermineral reactions take place
242 such as dehydroxylation of clay minerals and the consequent formation of pseudo-amorphous
243 products (such as meta-kaolinite from kaolinite); decomposition of carbonates with a consequent
244 crystallization of calcium silicates (e.g. gehlenite-akermanite), the formation of an amorphous
245 phase, solid state sintering, etc. Considering the complexity of the system, it is quite obvious that
246 the mineralogical composition and microstructure of the fired samples are not necessarily linearly
247 correlated to the raw materials properties. Another consideration is that it might be difficult even
248 to identify the main effects as all independent parameters differ from sample to sample.
249 Nevertheless, important raw materials properties such as mineralogical composition, organic
250 content and grain size distribution were correlated with the effective thermal conductivity with
251 the hope to observe some trends. Figure 3 shows the effective thermal conductivity as a function
252 of wt% organic content (a), fitting parameter α (b), carbonate content (c), wt% clay (d), wt%
253 quartz (e) and wt% feldspars (f). In most cases, no significant relationship can be observed as
254 expected ($R^2<0.2$). Exceptions could be the organic content (Fig. 3a, $R^2=0.41$) and the grain size

255 distribution (Fig. 3b, described by the parameter α , $R^2=0.59$). The organic content seems to have
256 a negative influence on thermal conductivity of the fired brick, probably because pores are
257 formed upon combustion. In fact, the use of combustible organic pore formers such as sawdust to
258 improve thermal insulation is common practice in fired clay brick production (Ruppik, 2006).
259 The influence of grain size distribution of the raw clays on effective thermal conductivity is not
260 surprising. An increased value of α is equivalent to a smaller overall particle size which in turn
261 should increase the sintering rate during firing of the bricks. A higher level of sintering should
262 increase the thermal conductivity. The grain size distribution could also have an effect on the
263 bulk density of the green body which should be dependent on the way in which the particles are
264 packed. Particle packing is dependent on the particle size distribution (Hall and Hoff, 2002). A
265 better particle packing is obtained when finer particles fill the void space between the larger
266 particles (Hall and Hoff, 2002; Dinger and Funk, 1992). It can not be excluded that α , and
267 therefore the particle size distribution, influences the particle packing during extrusion of the
268 bricks and hence the bulk density and thermal conductivity. The influence of carbonates on the
269 effective thermal conductivity of clay bricks has been frequently addressed in the literature, as
270 discussed in the introduction. Carbonates act as pore formers, but at the same time form relatively
271 heat conductive calcium aluminosilicates in the solid skeleton (Erker, 2002b). These two
272 phenomenon have opposite effects on the thermal conductivity. The results obtained in this work
273 does not show any clear correlation between wt% carbonates in the clay raw material and
274 effective thermal conductivity (see Fig. 3c). In addition, no clear correlation is found between
275 wt% carbonates and bulk density. A doubt arose if these results could be explained by an
276 incomplete decomposition of the carbonates. However, X-ray diffraction analyses of the fired
277 bricks confirmed a near to complete decomposition of the carbonates (see Table 6). Hence, the

278 apparent lack of correlations between wt% carbonates and effective thermal conductivity is most
279 likely linked to the complexity of the system as discussed previously.

280 In order to have some indications regarding parameters which possibly could have a significant
281 influence on the thermal conductivity of the samples prepared in this work, a multiple linear
282 regression technique (least squares) was used to fit a first order linear model (intercept-free
283 model) to the data collected from the samples prepared by extrusion. These analyses were
284 performed using Essential Regression 2.219, a free statistical software for Microsoft Excel. The
285 insignificant terms were removed by stepwise regression and analysis of variance (ANOVA, 95
286 % confidence level). The following equation represents the optimized linear model for the
287 effective thermal conductivity of the fired bricks;

$$288 \lambda_{\text{eff}} = 3.896X_1 - 0.08518X_2 + 0.0094X_3 + 0.00411X_4 \quad (2)$$

290
291 where X_1 is the fitting parameter α and X_2 , X_3 and X_4 are the weight% of organic material,
292 feldspars and clays, respectively. The statistics of the optimized linear model were $R^2=0.915$ and
293 R^2 prediction=0.895. The significance (95 % confidence level) of the model and the individual
294 regression coefficients are shown in Table 7 and 8, respectively. The statistical approach
295 identifies the organic content and the fitting parameter α as important parameters determining the
296 thermal conductivity, as expected. In addition, the weight fractions of clays and feldspars are also
297 identified as having some influence of the thermal conductivity of extruded samples.

298 As a final remark, the development of a conclusive model for the effective thermal conductivity
299 of clay bricks is a difficult task due to the complexity of the system, determined not only by
300 interactions between different minerals during firing but also by the high influence of the process
301 parameters on the properties of the fired product. For these reasons, the results presented here can

302 only be regarded as preliminary. More data points are needed for the development of a model
303 which will give reliable indications for the a priori evaluation of thermal insulation properties of
304 clay bricks using basic knowledge of the clay raw material.

305

306 **4. Conclusion**

307 In this work, selected Italian clays were thoroughly characterized using various analysis
308 techniques such as X-ray Powder Diffraction and Rietveld refinements, laser granulometry, X-ray
309 Fluorescence Spectroscopy and calcimetry. The effective thermal conductivity of bricks
310 manufactured using these clays was determined and correlated with various properties of the raw
311 materials such as mineralogical composition, organic content and grain size distribution. In
312 addition, multiple linear regression was used to fit a first-order linear model to the data. The
313 results indicate that the organic content and the grain size distribution significantly influence the
314 effective thermal conductivity. The pore forming action of organic material had a positive
315 influence on the thermal insulation. Instead, the thermal insulation decreased with decreasing
316 particle size, possibly due to an increased sintering rate during brick firing. On the contrary what
317 was expected, the carbonate content did not seem to significantly affect the effective thermal
318 conductivity. The results presented here further contribute to the discussion regarding factors
319 effecting the thermal conductivity of clay bricks, but does not allow a conclusive model to be
320 built due to the complexity of the system and the limited number of observations.

321

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327

328 **References**

329 ASTM, Standard Test Method for Moisture, Ash, and Organic Matter of Peat and Other Organic
330 Soils: D2974.

331

332 Azaroff, L.V., Burger, M.J., 1958. The powder method in X-ray Crystallography, McGraw Hill,
333 New York.

334

335 Bauluz, B., Mayayo, M.J., Fernández-Nieto, C., Cultrone, G., González López, J.M., 2003.

336 Assessment of technological properties of calcareous and non-calcareous clays used for the brick-
337 making industry of Zaragoza (Spain). *Appl. Clay Sci.* 24, 121-126.

338

339 Bhattacharjee, B., Krishnamoorthy, S., 2004. Permeable porosity and thermal conductivity of
340 construction materials. *J. Mater. Civ. Eng.* 16, 322-330.

341

342 Bouchair, A., 2008. Steady state theoretical model of red clay hollow bricks for enhanced
343 external wall thermal insulation. *Build. Environ.* 43, 1603-1618.

344

345 Correia, S.L., Grun, E., Denardi, C.D., Hotza, D., Folgueras, M.V., 2006a. Using experiments
346 design to model the effect of raw materials on the sintering and technological properties of brick
347 compositions. *Mater. Sci. Forum.* 514-516, 1424-1428.

348 Correia, S.L., Grun, E., Denardi, C.D., Hotza, D., Folgueras, M.V., 2006b. Effects of raw
349 materials on the technological properties of brick compositions using a statistical design
350 approach. Mater. Sci. Forum. 530-531, 486-491.
351

352 Cultrone, G., Sebastián, E., Elert, K., de la Torre, M. J., Cavalla, O., Rodriguez-Navarro, C.,
353 2004. Influence of mineralogy and firing temperature on the porosity of bricks. J. Eur. Ceram.
354 Soc. 24, 547-564.
355

356 Dinger, D.R., Funk, J.E., 1992. Particle packing II-review of packing of polydisperse particle
357 system. Interceram, 41, 95-97.
358

359 Dondi, M., Mazzanti, F., Principi, P., Raimondo, M., Zanarini, G., 2004. Thermal Conductivity
360 of Clay Bricks. J. Mater. Civ. Eng. 16, 8-14.
361

362 Erker, A., 2002a. The thermal conductivity of the brick ceramic body (part 1). Ziegelindustrie
363 International 55(10), 34-42.
364

365 Erker, A., 2002b. The thermal conductivity of the brick ceramic body (part 2). Ziegelindustrie
366 International 55 (11), 32-37.
367

368 Galal, A.F., Abd El-Wahed, M.G., El-Didamony, H., 1985. Effect of the mineralogical
369 composition of Shale/Clay on the physical properties of building bricks, Sprechaal, 118, 621-
370 624.
371

372 Gualtieri, A.F., 2000. Accuracy of XRPD QPA using the combined Rietveld-RIR method, J.
373 Appl. Cryst. 33, 267-278.
374

375 Hall, C., Hoff, W.D., 2002. Water Transport in Brick, Stone and Concrete, Taylor & Francis.
376

377 Hauck, D., Ruppik, M., 1997. Influence of raw materials on the thermal conductivity of brick
378 ceramic bodies. Ziegelindustrie international 50, 921-922.
379

380 Kingery, W D., 1959. Thermal conductivity:XIV, Conductivity of Multicomponent systems. J.
381 Am. Ceram. Soc. 42, 617-627.
382

383 Larson, A.C., von Dreele, R.B., (1994). GSAS Generalized structure analysis system. Laur 86-
384 748, Los Alamos National Laboratory, Los Alamos, New Mexico.
385

386 Rhee S.K., 1975. Porosity-thermal conductivity correlations for ceramic materials. Mater. Sci.
387 Eng. 20, 89-93.
388

389 Ruppik, M., 2006. Use of organic and inorganic pore-forming agents in the brick and tile
390 industry. Ziegelindustrie International 59 (8), 22-29.
391

392 Strazzera, B., Dondi, M., Marsigli, M., 1997. Composition and ceramic properties of Tertiary
393 clays from southern Sardinia (Italy). Appl. Clay Sci. 12, 247-266.
394

395 Šveda, M., 1998. Influence of equilibrium humidity on the thermal conductivity of brick
396 products. *Ziegelindustrie International* 51 (12), 810-817.
397
398 Šveda, M., 2000a. Influence of calcium carbonate on the physical properties of a clay body. Part
399 1. *Ziegelindustrie International* 53 (1-2), 40-46.
400
401 Šveda M., 2000b. New look at mathematical relationships among physical properties of brick
402 products. *Br. Ceram.Trans.* 99, 181-186.
403
404 Šveda M., 2000c. The influence of sawdust on the physical properties of a clay body.
405 *Ziegelindustrie International* 53 (11), 29-35.
406
407 Toby, B.H., 2001. EXPGUI, a graphical user interface for GSAS. *J. Appl. Cryst.* 34, 210-213.
408
409 Wagh, A.S., 1993. Porosity dependence of thermal conductivity of ceramics and sedimentary
410 rocks. *J. Mater. Sci.* 28, 3715-3721

FIGURE CAPTIONS

Fig. 1. The measured and calculated (eq. 1) particle size distribution (cumulative volume fraction) for sample 1.

Fig. 2. Effective thermal conductivity (λ_{eff}) as a function of bulk density.

Fig. 3. Effective thermal conductivity versus wt% organic content (a), fitting parameter α (b), carbonate content (c), wt% clay (d), wt% quartz (e) and wt% feldspars (f).

TABLES

Table 1. Mineralogical composition of the investigated clays as determined by XRPD data and Rietveld refinements.

Sample	^b Mineralogical composition (wt%)												Agreement factors		
	quartz	micas/ interlaminar	kaolinite	calcite	smectite	albite	hematite	gypsum	micro- cline	dolomite	clorite	^a organics	Rwp (%)	RF ²	CHI ²
1	29.0 (1)	22.5 (5)	11.4 (6)	16.2 (2)	3.2 (1)	9.0 (4)	-	-	-	0.6 (2)	6.0 (7)	1.8	6.93	0.1590	1.720
2	32.4 (2)	18.3 (4)	15.1 (6)	8.2 (4)	3.8 (1)	8.0 (5)	-	-	-	4.1 (3)	7.6 (6)	2.6	7.96	0.3018	2.336
3	24.6 (1)	14.2 (3)	16.9 (4)	20.5 (2)	2.0 (1)	8.9 (4)	0.71 (8)	-	-	2.9 (2)	6.7 (5)	1.8	6.33	0.1255	1.616
4	33.8 (2)	12.6 (3)	6.0 (5)	10.4 (2)	1.0 (1)	10.0 (3)	-	-	18.0 (1)	3.4 (2)	3.0 (2)	2.4	7.20	0.1618	2.844
5	27.8 (2)	41.5 (6)	9.5 (5)	7.2 (2)	0.6 (1)	8.1 (4)	-	1.5 (2)	-	1.0 (2)	1.7 (3)	1.4	7.5	0.1512	2.197
6	33.4 (2)	9.8 (3)	6.1 (5)	16.9 (2)	0.2 (1)	13.0 (5)	-	-	6.2 (5)	0.8 (1)	12.7 (9)	1.5	8.95	0.1996	2.693
7	36.7 (2)	30.0 (4)	5.0 (5)	0.9 (3)	2.2 (1)	9.0 (6)	-	-	6.3 (7)	0.9 (2)	6.9 (4)	2.2	8.06	0.3471	2.620
^c 8	28.4 (2)	16.8 (5)	5.6 (3)	12.2 (2)	1.8 (1)	18.6 (5)	-	-	5.9 (5)	2.9 (2)	5.7 (5)	2.2	8.51	0.1566	2.347
9	23.5 (2)	18.3 (5)	10.6 (6)	12.1 (2)	2.2 (1)	15.0 (6)	-	-	1.7 (4)	4.1 (2)	9.5 (6)	2.9	8.85	0.1677	2.602

^aDetermined separately

^bMineralogical composition corrected for the presence of organic material.

^cTrace amounts of amphibole and an additional unknown phase

Table 2. Comparison between calcite content in each clay fraction as determined by Rietveld refinements and calcimetry.

Sample	Wt% Calcite								
	1	2	3	4	5	6	7	8	9
Rietveld refinements	16.2 (2)	8.2 (4)	20.5 (2)	10.4 (2)	7.2 (2)	16.9 (2)	0.9 (3)	12.5 (2)	12.1 (2)
calcimetry	16.7	9.2	21.9	13.8	8.5	15.3	3.5	13.8	12.6

Table 3. Chemical composition of each investigated clay fraction.

Sample	Chemical composition (%)										
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	L.O.I.
1	0.84	3.30	14.50	51.40	0.09	2.36	7.63	0.69	0.17	6.24	12.78
2	0.71	5.49	15.01	47.71	0.09	2.29	7.47	0.62	0.08	5.53	15.00
3	0.89	4.41	12.79	47.42	0.07	2.04	10.77	0.59	0.14	5.45	15.42
4	1.09	4.75	12.94	53.36	0.10	2.10	6.46	0.52	0.12	5.41	13.16
5	1.18	4.21	16.03	53.05	0.10	2.89	3.60	0.67	0.19	6.15	11.94
6	1.14	3.85	13.53	52.38	0.09	2.28	8.73	0.57	0.13	5.26	12.05
7	0.58	3.71	20.65	51.85	0.22	4.06	1.26	0.82	0.15	7.33	9.37
8	0.7	4.1	13.8	51.6	0.1	2.7	9.7	0.5	0.1	5.3	11.3
9	0.9	4.6	19.4	56.4	0.1	3.0	4.5	0.8	0.1	7.0	3.1

Table 4. Results from laser granulometry measurements of the raw clays as well as fitting parameter α (see eq. 1).

Sample	d (0.1) (μm)	d (0.5) (μm)	d (0.9) (μm)	Fitting parameter α	Regression coefficient R^2
1	1.582	7.055	29.646	0.08739	0.996
2	1.774	6.943	26.171	0.0903	0.997
3	1.638	7.066	35.417	0.0845	0.994
4	1.92	8.357	58.677	0.0694	0.988
5	1.494	6.146	31.010	0.0968	0.994
6	2.116	11.267	49.358	0.0566	0.996
7	2.616	12.482	42.458	0.0539	0.999
8	2.180	13.110	58.972	0.049	0.995
9	2.107	10.182	39.220	0.0640	0.998

Table 5. The effective thermal conductivity (λ_{eff}), the bulk density (ρ_b) and the total porosity (TP) of the fired bricks prepared using the different clay raw materials and preparation procedures.

The standard error of the mean (95 % confidence interval) is also reported.

Clay raw material	Extruded			Pressed		
	λ_{eff} (W m ⁻¹ K ⁻¹)	ρ_b (kg m ⁻³)	TP (%)	λ_{eff} (W m ⁻¹ K ⁻¹)	ρ_b (kg m ⁻³)	TP (%)
1	0.450 ± 0.021	1813 ± 12	34.7 ± 0.5	0.401 ± 0.008	1755 ± 8	36.9 ± 0.3
2	0.421 ± 0.054	1845 ± 12	31.3 ± 0.5	0.382 ± 0.006	1665 ± 6	40.4 ± 0.3
3	0.401 ± 0.009	1761 ± 13	37.6 ± 0.6	0.434 ± 0.002	1695 ± 11	39.6 ± 0.6
4	0.411 ± 0.025	1809 ± 10	35.0 ± 0.4	0.335 ± 0.009	1685 ± 16	39.8 ± 0.8
5	0.563 ± 0.020	1853 ± 7	32.4 ± 0.5	0.478 ± 0.008	1840 ± 14	32.5 ± 0.7
6	0.410 ± 0.011	1788 ± 27	35.9 ± 0.8	0.375 ± 0.009	1791 ± 14	35.5 ± 0.7
7	0.325 ± 0.008	1827 ± 10	35.0 ± 0.4	0.375 ± 0.008	1820 ± 30	34.5 ± 1.5
8	0.361 ± 0.012	1765 ± 6	36.8 ± 0.3	0.428 ± 0.006	1678 ± 8	41.2 ± 0.4
9	0.334 ± 0.008	1668 ± 12	40.7 ± 0.6	0.362 ± 0.004	1643 ± 15	42.3 ± 0.7

Table 6. Results of the full quantitative phase analyses of the fired extruded samples.

Sample	Mineralogical composition (wt%)								Agreement factors		
	quartz	calcite	K-feldspar	mica	plagioclase	melilite	amphibole	glass	Rwp (%)	RF ²	CHI ²
1	32.2 (5)	5.6 (2)	5.8 (2)	28.1 (5)	3.8 (2)	2.1 (2)	1.9 (3)	20.3 (9)	6.16	4.23	3.704
2	28.4 (4)	1.7 (1)	13.4 (5)	16.7 (2)	10.0(4)	2.5 (2)	1.0 (2)	26.0 (9)	6.73	4.67	4.737
3	28.5 (4)	5.2 (1)	10.8 (3)	11.2 (7)	3.6 (2)	5.9 (2)	1.3 (2)	33.3 (9)	5.56	4.01	2.839
4	42.3 (7)	2.2 (2)	17.9 (5)	10.7 (2)	3.3 (4)	3.5 (2)	2.0 (3)	17.8 (1.1)	8.46	5.59	7.499
5	27.9 (4)	4.0 (2)	8.6 (4)	23.4 (3)	5.2 (2)	1.6 (1)	0.9 (2)	28.3 (8)	6.14	4.2	3.942
6	35.8 (5)	1.7 (1)	12.1 (4)	15.6 (1.0)	9.4 (3)	3.3 (2)	1.4 (2)	20.7 (1.3)	7.02	4.9	4.701
7	30.2 (6)	0.4 (1)	10.4 (4)	42.1 (1.1)	1.9 (2)	0	1.8 (3)	13.2 (1.4)	6.93	4.88	5.622
8	39.2 (7)	2.5 (2)	12.5 (5)	19.0 (1.5)	9.9 (3)	4.3 (2)	2.1 (3)	10.4 (1.9)	7.81	5.3	5.854
9	28.3 (5)	1.7 (1)	11.7 (3)	25.2 (8)	6.0 (2)	4.3 (2)	1.9 (2)	20.7 (1.1)	5.84	4.2	3.475

Table 7. ANOVA table

Source of variation	Sum of squares	Mean squares	F	F significant
Regression	0.139	0.0347	96.9	1.99e-22
Residual	0.013	0.000359		
Lack-of-fit error	0.0094	0.00188	16.5	5.98e-8
Pure error	0.0035	0.000114		

Table 8. Parameter table.

Name	Coefficient	Standard error	P-value
X ₁	3.896	0.204	1.9e-20
X ₂	-0.0852	0.0075	1.7e-13
X ₃	0.0094	0.00052	1.7e-19
X ₄	0.0041	0.00044	3.0e-11

