Ceramic porcelain stoneware production with Spanish clays purified by means of the removal of iron compounds and organic matter using physical methods

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ABSTRACT

As the production of ceramic porcelain stoneware in Spain is totally conditioned by the importation of ball clays, because of the lack of adequate Spanish ball clays, this work has focused on the formulation of ceramic porcelain body from Spanish clays purified by means of physical removal processes. This method was applied to three Spanish clays containing common clay impurities of iron (hematite and siderite) and organic matter. Iron removal was carried out using the wet sieve method, the hydrocycloning method and the electromagnetic filtering method, obtaining a reduction in iron content of up to 80 wt%, while the clay containing organic matter was treated thermally at 400ºC for 30 minutes so as to leave it almost completely purified. These treated clays, after being characterized (chemical and mineralogical composition, plasticity, organic carbon, thermal behaviour and colour), were used in the porcelain stoneware body composition instead of imported clays, the result being a composition capable of substituting the standard porcelain stoneware formulation in terms of sintering, morphology, colour, flexural strength and dilatometry.

KEYWORDS

Clay, impurity, iron, organic matter, ceramic porcelain stoneware tiles

1. INTRODUCTION

In Spain, the white clays rich in kaolinite, so-called ball-clays, usually employed in white porcelain stoneware bodies because they confer strength and plasticity are mostly imported from other countries such as Ukraine, France, Germany or United Kingdom, due to the lack of appropriate quality of Spanish ball clays. In this regard, some Spanish kaolinitic clays, from the regions of Teruel and Ciudad Real, both of which are very near the province of Castellón, where the Spanish ceramic cluster is situated, are included in porcelain compositions, but in limited amounts. Typical clay impurities that are frequently found include pyrite, siderite, organic matter, iron and titanium oxides and their quantity, form and type can influence the usefulness, processing route and ceramic application of each clay (Barba et al., 2002; Bauluz et al., 2008; Carda and Sánchez, 2003; Jordán et al., 2015; Kogel et al., 2006; Sánchez, 2004; Sanfeliu and Jordán, 2009)

 The argillaceous minerals, such as these clays, contain substantial amounts of carbon and organic materials, sulphur and its compounds, and some oxides of transition metals (particularly iron) which can generate defects in the sintered ceramic products in their lower valence state (Romero and Pérez, 2015). The excess of organic matter in clays, due to the usual fast firing cycle in porcelain stoneware production, can cause the presence of a typical fault in ceramic tiles called "black core", which is formed by carbon residues from the thermal decomposition of the organic material contained in the clays (Abdrakhimov and Abdrakhimova, 1999; Maritan et al., 2006). The incomplete oxidation during the firing phase results in certain products being burnt in the ceramic product, and causes certain textural changes (and imperfections), which lowers the quality of the ceramic products and the mechanical resistance characteristics of the final product (Da Silva et al., 2000). As a slow firing cycle is not practical in industry, clays containing organic matter are not commonly employed in the formulation of porcelain bodies. The

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methods proposed to reduce the amount of organic matter consist in increasing the oxidising atmosphere and pre-treating the clay with a thermal route in order to decompose the organic matter, before it is used in the ceramic formulations (Baraldi and Zannini, 2014; Barba et al., 2002; Carda and Sánchez, 2003; Lores et al., 1997)

Although standard UNE-EN 14411:2013 does not establish the Fe_2O_3 content in porcelain body, in the ceramic sector it is known that the %Fe_2O_3 measured by X-ray fluorescence (XRF) must be less than 1 wt% (Fraga et al., 2016; Sánchez et al., 2010). Consequently, the clays used in porcelain stoneware tile formulation commonly should contain less than 1 wt% Fe_2O_3 (Dondi et al., 2014; Galos, 2011). Some of the Spanish sedimentary clays located in deposits in Teruel and Ciudad Real, however, present high percentages of iron compounds as impurities, thus restricting their use in the formulation of the white body of porcelain stoneware tiles (Barba et al., 2002). This paper presents a method for improving three Spanish clays containing impurities of iron compounds and organic matter in their original state, by means of physical methods. After removal of the impurities, the treated clays were used to replace some imported ball clays in the porcelain body composition, the result being a new formulation exhibiting the same properties as the standard reference.

2. GEOLOGICAL SETTING

The study area is located in two Spanish provinces: Teruel (NE Spain) and Ciudad Real (Southern central Spain). The clayey rocks, shallow type, from Teruel was formed due to the continuous floods to which the peat-bogs were submitted, according to the sedimentary model of "Escucha" Formation. The main impurities of these clays are organic matter and siderite ($FeCO_3$). The clays from Ciudad Real, however, have their origins in sedimentary kaolins of the paleozoic levels and they are also considered altered slate rocks, exhibiting a very low degree of metamorphism and containing

78 mainly kaolinite, muscovite and pyrophyllite (Galán and Martín, 1974; García and

79 Martínez, 1992; Juan et al., 1993; Lores et al., 1997; Parra, 1996).

80

81 **3. MATERIALS AND METHODS**

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83 One clay from Ciudad Real (CR-01) and two clays from Teruel (TE-01 and TE-02) were

84 analysed: the clay from Ciudad Real (CR-01 clay) had hematite (Fe_2O_3) as its main

85 impurity, while TE-01 clay was rich in organic matter and TE-02 clay contained siderite.

86 The physical treatment to reduce the organic matter content consisted in the firing the

87 clay method (FCM), after previously being dried and crushed, at different temperatures

88 (range: 250ºC-600ºC with 30 minutes of residence time) in order to decompose the

89 organic matter to be removed.

90 The methods proposed in the current paper to remove the iron compounds in these

91 Spanish clays are physical methods, in contrast to the numerous chemical methods and

92 patents studied in other papers (Ambikadevi and Lalithambika, 2000; Asmatulu, 2002;

93 Cameselle et al., 1995; Council et al., 2000; González and Del, 2006; Murray, 2007;

94 Ramaswamy, 2007; Toro et al., 1993; Zegeye et al., 2013). The reason underlying this

95 decision was that, because they do not include the addition of chemicals, they are more

96 manageable processes for the ceramic industry. The reduction of the amount of iron

97 compounds was also carried out by means of three physical methods: (1) the wet sieving

98 method (WSM) was used to remove the coarse fraction: the clay was mixed with water

99 in a mechanical stirrer until it became a suspension with a slurry density of 1.50 g/cm^3

100 (Fig.). The suspension fluidity was improved by adding 0.5 wt% of deflocculant (sodium

101 silicate). (2) The hydrocyclone method (HCM) was implemented on a clayey slurry with

102 an inlet working pressure of 1.5 bar and a density of 1.25 g/cm^3: when the slurry enters

103 through the feed tangential inlet (a), cycloning starts to take place in the feed chamber

104   (b). Then, the heavier particles move to the outer walls and towards the apex (c), while

105   the lighter particles stay near the centre of the cone and are carried away by the vortex

106   finder (d), Fig. (911Metallurgy Corporation, 2016). (3) The electromagnetic filter method

107   (EFM) uses a non-permanent magnet capable of producing a 2500-Gauss magnetic field.

108   The removed hematite, together with a small quantity of finer clay particles, are stuck to

109   the electromagnetic filter, which must be cleaned before beginning each new operation

110   (Fig. 1). The conditions of the slurry to be filtered were: flow of 1.5 l/min and a density of

111   1.38 g/cm^3. These devices are usually utilised in the removal of impurities in minerals

112   such as clays, kaolin, feldspar, glass, etc. (Al-Momani and Khoury, 2010; Bradley, 2013;

113   Khramov and Sokolov, 1956; Rao and Vibhuti, 2004; Scott and Bristow, 2002).

114
115   The main purpose of these treated Spanish clays is to substitute the clays imported from

116   Ukraine used in the porcelain stoneware body compositions shown in Table 1. The raw

117   materials are as follows: TE-01, clay from Teruel rich in kaolinite and with organic matter

118   as an impurity; TE-02, clay from Teruel rich in siderite; CR-01, clay from Ciudad Real

119   rich in kaolinite and with the presence of hematite; CY-01 and CY-02, clays from Ukraine

120   rich in kaolinite and free of impurities; FD-01 sodium feldspar from Turkey; FD-02,

121   sodium-magnesium feldspar from Sardinia; and FS, feldspathic sand. The first

122   composition is the standard one (STD), for a typical porcelain stoneware body,

123   formulated exclusively with Ukrainian clays used as the reference composition;

124   composition A is a reformulation of STD using Spanish clays without treatment;

125   composition B is a modification of A, but using the treated Spanish clays.

126
127   Table 1. Detailed formulation of porcelain compositions based on Spanish treated clays (wt%).

RAW MATERIALS	STD	A	B
TE-01 (organic matter)	-	10	-
TE-02 (siderite)	-	5	-
CR-01 (hematite)	-	10	-
TE-01 after treatment	-	-	10

TE-02 after treatment	-	-	5
CR-01 after treatment	-	-	10
CY-01	20	10	10
CY-02	25	15	15
FD-01	35	25	25
FD-02	10	15	20
FS	10	10	5

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130 Each composition was micronised in a planetary mill with water and 0.7 wt% of

131 deflocculant (sodium silicate) at a suspension density of 1.70 g/cm^3 and sieved at under

132 100 micrometres. To simulate industrial pressing conditions, the compositions were

133 homogenised and moistened with water to 6.5 wt% to be pressed in a uniaxial laboratory

134 press (Nannetti), resulting in rectangular pieces. After having been dried at 110ºC for 24

135 h, the pieces were fired at different temperatures in a fast kiln (Nannetti), following the

136 firing cycle shown in Fig. .

137

138 The characterisation of the treated clays and the porcelain stoneware body compositions

139 consisted in being micronised at less than 100 micrometres, so as to be homogeneous

140 enough and to have an accurate grain size that allowed it to be measured correctly by

141 various instrumental techniques, which are detailed in the following. The chemical

142 analysis was performed by an X-ray fluorescence spectrometer (XRF) with a sequential

143 X-ray wavelength dispersion S4 Pioneer, Bruker (Rh anode, 4 kW); the mineralogical

144 study was conducted with an X-ray diffractometer (XRD) Bruker-AXS D4 Endeavor in

145 the range of 10°-80° (2θ) with a step of 0.05°/2s; the thermodifferential analysis was

146 carried out by DTA STA 503 Bahr; plasticity was measured by means of a Pfefferkorn

147 apparatus, based on the principle of impact deformation; elemental analysis of organic

148 and inorganic carbon and total sulphur was performed using a SC144 Leco model; the

149 colorimetric parameters were analysed using a Konica Minolta UV-Visible

150 spectrophotometer (CM-3600) and the colour space CIELab; the flexural strength was

6

151 determined by a HOYTOM plasticinometer with a load cell of 5000 N and a force

152 threshold of 16N; in the sintering diagram, the linear shrinkage was evaluated by a

153 Mitutoyo digital calliper, considering the initial length (L_i) as the length of the dried piece

154 and the final length (L_f) as the length of the fired piece: $\%LS=(L_i-L_f)/L_i \cdot 100$, and water

155 absorption (%WA) was determined according to the Quality of Ceramic Tiles Standard

156 (UNE-EN-ISO 10545-3); the microstructural morphology was studied with a scanning

157 electron microscopy (SEM) model JEOL 7001F fitted with an energy dispersive X-ray

158 analyser (EDX), operating at 15-20kV; and the dilatometric analysis was performed using

159 a 801L Bähr dilatometer.

160

161 **4. RESULTS AND DISCUSSION**

162

163 **4.1 Characterisation of Spanish clays after being treated**

164

165 In order to present the original quality of these Spanish clays, Fig. shows the comparison

166 of Fe_2O_3 (wt%), lightness (L* measured in fired pieces at 1185ºC) and organic carbon

167 (wt%) between Ukrainian clays (CY-01 and CY-02) and Spanish clays (TE-01, TE-02

168 and CR-01) in their natural state, without being treated. As can be observed, Ukrainian

169 clays displayed about 10 points more in lightness thanks to their low content in iron

170 oxides, while Spanish clays presented at least almost three times more iron oxides than

171 those from Ukraine. However, the only clay that was completely free of organic matter

172 was CR-01, while this impurity reached the highest value in the case of TE-01.

173

174

175 As regards the reduction in organic matter, Fig. shows the DTA of original TE-01 and

176 some TE-01 samples treated by the FCM, where two main peaks can be observed: one

177 exothermic peak at around 400ºC, corresponding to the combustion of organic matter,

178 and another endothermic peak representing the dehydroxylation of kaolinite. In this sense,

179 the DTA curve indicates that the combustion peak is reduced while the treatment

180 temperature increases with a residence time of 30 minutes. At the same time, the

181 dehydroxylation peak is reduced in the same direction but with a lower tendency. Two

182 other common peaks of clays also appear in the DTA: at 573ºC there is an endothermic

183 peak representing the allotropic transformation alpha-quartz to beta-quartz, and at 960ºC

184 there is the exothermic reaction of mullite formation.

185

186 Fig. shows the variation of organic matter and kaolinitic dehydroxylation vs temperature,

187 calculated from area measurements of DTA peaks. At 350ºC, the organic matter is still

188 excessive and the water of constitution of the kaolinite is almost the same as in the original

189 clay. However, at 400ºC there is around 30 wt% of organic matter although the

190 dehydroxylation is similar to the case of 350ºC. At 500ºC and 600ºC, the removal of

191 organic matter increases but dehydroxylation is higher.

192

193 The importance of avoiding kaolinitic dehydroxylation is related to the fact that, thanks

194 to its plasticity, the presence of kaolinite allows the clay to be shaped when it is wet – an

195 essential characteristic of clays. Hence, plasticity, measured using the Pfefferkorn index

196 (And(Andrade et al., 2011), is inversely proportional to the temperature, as determined in

197 Table 2, because the water of constitution of the kaolinite has disappeared with

198 temperature. With the treatment at 400ºC-30 min, the plasticity presents similar values to

199 the original TE-01 and Ukrainian clays: 24 vs 28 Pfefferkorn index. Regarding organic

200 matter, in this case, at 400ºC there is a significant reduction from 0.52 to 0.10 wt%,

201 according to the results of the elemental analysis obtained from a LECO device. This

202 reduction is similar to those corresponding to 500ºC and 600ºC, but these tests present

203 lower plasticity values. Consequently, it is considered that the optimal result is the

204 treatment of TE-01 at 400ºC for 30 minutes.

205

206 **Table 2. Comparison of Pfefferkorn index of plasticity and organic carbon (wt%) presence between Ukrainian**
207 **clays and TE-01 (original and treated at 400ºC - 30 min).**

CLAYS	CY-01	CY-02	Original TE-01	TE-01 350ºC-30 min	TE-01 400ºC-30 min	TE-01 500ºC-30 min	TE-01 600ºC-30 min
Pfefferkorn index	29	27	28	26	24	20	19
Organic carbon (wt%)	0.08	0.05	0.52	0.48	0.10	0.06	0.02

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210 The comparative chemical analysis of the original and the treated TE-02 clay is indicated

211 in Table 3. After being treated by the three methods, TE-02, contaminated with iron

212 carbonate or siderite as given in Fig. , has reduced the Fe_2O_3 content 60% wt in all cases.

213 This suggests that the siderite is mainly located in the coarse fraction over 100

214 micrometres and the siderite particles below this mesh are difficult to separate by means

215 of HCM or the EFM. Experience with these types of minerals suggests that this could

216 most probably be caused because siderite particles are confined in quartz granules.

217 Consequently, these granules would be too heavy to be separated by HCM and their

218 magnetic susceptibility is too low to be caught by the EFM.

219

220 **Table 3. Chemical analysis (wt%) of TE-02 measured by the X-ray fluorescence method (XRF) after being**
221 **treated.**

TE-02 (siderite)	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	LOI*
ORIGINAL	0.29	0.89	21.09	59.42	3.34	0.32	0.91	5.39	8.51
100 μm WSM	0.52	0.69	23.21	61.25	3.46	0.24	0.87	2.21	7.32
HCM	0.54	0.72	23.74	61.34	3.48	0.13	0.62	2.17	7.25

EFM	0.61	0.71	23.28	61.27	3.48	0.11	0.95	2.18	7.31

* Loss on ignition

In the case of CR-01 clay, the WSM reduces the amount of Fe_2O_3 contained in it by around 64 wt%, corresponding to hematite (see Fig.), while the HCM allows a reduction of 72 wt% (Table 4). However, the hematite content is still too high to be used as white clay (Fig.). With the EFM, the hematite content in CR-01 is reduced by around 80 wt%, with respect to the original Fe_2O_3 content (in wt%). Thus, its iron oxide content is similar to that of Ukrainian clays (CY-01, see Fig.). In this case, both methods, HCM and EFM, are useful to reduce the hematite content (wt%) in CR-01 clay by around 70%, at least. This could be produced thanks to the fact that the hematite particles in CR-01 clay are not confined in granules with other materials, and have a weight that is low enough to be caught by HCM and exhibit an adequate magnetic susceptibility to be extracted by means of EFM.

Table 4. Chemical analysis (wt%) measured by the X-ray fluorescence method (XRF) of CR-01 after being treated.

CR-01 (hematite)	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	K$_2$O	CaO	TiO$_2$	Fe$_2$O$_3$	LOI*
ORIGINAL	0.82	0.07	23.45	59.77	2.72	0.01	1.14	**6.05**	5.76
100 μm WSM	0.80	0.17	26.71	59.50	3.39	0.05	1.15	**2.17**	5.85
HCM	0.96	0.22	27.5	58.2	3.19	0.13	1.18	**1.64**	6.31
EFM	0.93	0.24	26.91	59.84	2.81	0.09	1.06	**1.18**	6.52

* Loss on ignition

4.2 Characterisation of compositions

243 The compositions studied here present the expected tendency of chemical analysis, hence

244 composition A, formulated from untreated Spanish clays, contains 1.39 wt% Fe_2O_3, while

245 composition B, reformulated with the treated clays and after removal of around 60 wt%

246 of siderite and around 80 wt% of hematite impurities, exhibits only 0.86 wt% Fe_2O_3,

247 which is comparable with the STD composition (Table 5).

248

249 **Table 5. XRF results corresponding to compositions A, B and STD.**

Composition	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	K$_2$O	CaO	TiO$_2$	Fe$_2$O$_3$	LOI*
STD	4.31	0.7	19.7	67.5	1.24	0.79	0.59	0.73	3.86
A	3.94	0.6	19.5	67.7	1.22	0.81	0.77	1.39	4.06
B	3.89	0.8	19.6	67.8	1.64	0.66	0.63	0.86	3.48

250 * Loss on ignition

251

252 The importance of iron removal is directly related to the visual aspect of the stoneware

253 bodies when they are fired at maximum densification temperatures, which in this case are

254 around 1165ºC and 1185ºC. The colorimetric parameters expressed using the CIELab

255 system of each temperature are shown in Table 6. The parameter a* (a*>0 red; a*<0

256 green) increases when the Spanish clays are used without being previously treated in

257 composition A, but if the iron impurities are removed (composition B), this parameter is

258 reduced significantly with a value similar to the composition STD. At the same time, b*

259 (b*>0 yellow; b*<0 blue) increases with raw Spanish clays, but goes down when the

260 treatment is applied. Finally, the parameter L* (L* = 0 black; L* = 100 white) decreases

261 with temperature, and is improved if treated clays are used in the formulation of the

262 porcelain stoneware body (Table 6).

263 **Table 6. Colorimetric parameters of compositions A, B and STD for 1165ºC and 1185ºC measured by the**
264 **CIELab system.**

COMPOSITION	T (ºC)	L*	a*	b*
STD		74.76	2.01	11.08
A	1165	66.73	3.39	12.84
B		71.58	2.80	11.56
STD		70.67	2.26	12.23
A	1185	64.88	2.71	11.79
B		69.19	2.42	12.79

265 As regards the removal of organic matter, Table 7 summarises the values for compositions

266 related to the presence of this impurity in TE-01 clay. The thermal treatment of this clay

267 allows the amount of organic matter in composition B to be reduced to levels similar to

268 those of composition STD, but the decrease in plasticity due to the dehydroxylation of

269 the clay (a parameter that is essential to allow the stage involving the pressing of ceramic

270 bodies) is not notable. Moreover, the flexural strength of the still-unfired dried pieces is

271 very similar in the three compositions. Consequently, the use of this treated clay in the

272 porcelain compositions is possible.

273

274 **Table 7. Results of organic carbon measurement (wt%) , plasticity measurement (Pfefferkorn index) and**
275 **flexural strength for dried pieces (N/mm^2) of compositions A, B and STD.**

COMPOSITION	Organic carbon (wt%)	Pfefferkorn index (wt%)	Flexural strength for dried unfired pieces (N/mm^2)
STD	0.00	21.23	3.67
A	0.20	20.86	3.61
B	0.05	20.35	3.65

276

277 Fig. 7 shows the sintering diagram of each composition, namely the linear shrinkage

278 (L.S.) and the water absorption (W.A.) vs temperature according to the industrial firing

279 cycle plotted in Fig. 2. The shrinkages of compositions A and B are very similar to that of

280 STD, while both A and B present lower W.A. values than STD, thereby allowing higher

281 densification at a lower temperature.

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283

284 The scanning electron micrographs of each composition, measured in pieces fired

285 at 1185ºC, can be seen in Fig. 8. It is worth noting the reduction in the size and number of

286 bright areas, corresponding to the heavier elements, these being iron and titanium

287 compounds in the case of composition B, the result being a micrograph similar to that

288 obtained for composition STD. Furthermore, there is no significant difference in the open

289 porosity, which matches the water absorption obtained from the sintering diagram (Fig.

290 7).

291

292 Finally, the dilatometric results of the compositions under study, expressed as alpha

293 parameters, are comparable enough to be used as porcelain stoneware body or

294 composition STD (Table 8).

295
296 **Table 8. Dilatometric results of compositions STD, A and B.**

COMPOSITION	ALPHA·10^7 1/K		
	30ºC-300ºC	300ºC-500ºC	500ºC-650ºC
STD	69.16	83.82	101.51
A	68.50	85.12	105.82
B	69.72	85.90	103.69

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299 **5. CONCLUSION**
300

301 Three Spanish clays from the provinces of Teruel and Ciudad Real, containing impurities

302 of iron compounds and organic matter, were treated physically and characterised for use

303 in the formulation of porcelain stoneware body, substituting the clays imported mainly

304 from Ukraine, Germany and United Kingdom. The methods used to remove the iron in

305 two clays were the mechanical stirrer, the hydrocyclone and the electromagnetic filter,

306 obtaining an iron removal rate of 60 wt% (siderite), 72 wt% (hematite) and 80 wt%

307 (hematite), respectively. The thermal treatment allowed the amount of organic matter to

308 be reduced to acceptable levels for use as a white clay, while keeping enough plasticity

309 to allow it to be pressed. All these treated clays have permitted the formulation of a

310 composition of porcelain stoneware body that is very similar to the standard composition,

311 thus improving the properties of these contaminated Spanish clays and saving the need to

312 rely on clays imported from other countries.

Acknowledgements

321**References**

322

323 911Metallurgy Corporation, 2016.
324   https://www.911metallurgist.com/blog/category/grinding/classification/hydrocyclones (accessed, 15.05.16)

325 Abdrakhimov, V.Z., Abdrakhimova, E.C., 1999. Formation of the black core in high-speed firing of floor tiles. Glas.
326   Ceram. (English Transl. Steklo i Keramika) 56, 263–265. doi:10.1007/BF02681509

327 Al-Momani, T.M., Khoury, H.N., 2010. Processing and treatment of Hiswa clay deposits, South Jordan using
328   hydrocyclone separation and high iIntensity wet magnetic separation. Dirasat, Pure Sci. 37, 36–47.

329 Ambikadevi, V.., Lalithambika, M., 2000. Effect of organic acids on ferric iron removal from iron-stained kaolinite.
330   Appl. Clay Sci. 16, 133–145. doi:10.1016/S0169-1317(99)00038-1

331 Andrade, F.A., Al-Qureshi, H.A., Hotza, D., 2011. Measuring the plasticity of clays: A review. Appl. Clay Sci. 51, 1–
332   7. doi:10.1016/j.clay.2010.10.028

333 Asmatulu, R., 2002. Removal of the discoloring contaminants of an East Georgia kaolin clay and its dewatering.
334   Turkish J. Eng. Environ. Sci. 26, 447–453.

335 Baraldi, C., Zannini, P., 2014. Study of Black Core, ceramic tile's defect, by a multitechnique approach, in: XXIV
336   International Conference on Raman Spectroscopy. Jena.

337 Barba, A., Beltrán, V., Feliu, C., García, J., Ginés, F., Sánchez, E., Sanz, V., 2002. Raw materials used for ceramic
338   tiles bodies manufacturing, first ed. Ceramic Technology Institute, ITC-AICE, Castellón (Spain).

339 Bauluz, B., Mayayo, M.J., Yuste, A., Lopez, J.M.G., 2008. Genesis of kaolinite from Albian sedimentary deposits of
340   the Iberian Range (NE Spain): analysis by XRD, SEM and TEM. Clay Miner. 43, 459–475.
341   doi:10.1180/claymin.2008.043.3.10

342 Bradley, D., 2013. The Hydrocyclone: International Series of Monographs in Chemical Engineering, first ed.
343   Pergamon Press, London.

344 Cameselle, C., José Núñez, M., Lema, J.M., Pais, J., 1995. Leaching of iron from kaolins by a spent fermentation
345   liquor: Influence of temperature, pH, agitation and citric acid concentration. J. Ind. Microbiol. 14, 288–292.
346   doi:10.1007/BF01569941

347 Carda, J.B., Sánchez, L., 2003. Ceramic raw materials and additives. Ceramic Encyclopaedia Vol.II., first ed. Faenza
348   Editrice Ibérica, Castellón (Spain).

349 Council, S.T., Herpfer, M.A., Shaked, D., 2000. Method of making bleaching clay. US6365536 B1.

350 Da Silva, S., Herter, C., Sobrinho, T., Paskocimas, C.A., Tasca, A., 2000. Method for reducing defects in ceramic tile
351   production. EP 1083397 B1.

352 Dondi, M., Raimondo, M., Zanelli, C., 2014. Clays and bodies for ceramic tiles: Reappraisal and technological
353   classification. Appl. Clay Sci. 96, 91–109. doi:10.1016/j.clay.2014.01.013

354 Fraga, D., Stoyanova Lyubenova, T., Martí, R., Calvet, I., Barrachina, E., Carda, J.B., 2016. Ecologic ceramic
355   substrates for CIGS solar cells. Ceram. Int. 42, 7148–7154. doi:10.1016/j.ceramint.2016.01.104

356 Galán, E., Martín, J.L., 1974. Spanish kaolins; geology, mineralogy and genesis Part VI.. Bol. Soc. Esp. Ceram. Vidr.
357   13 (6), 523-546.

358 Galos, K., 2011. Composition and ceramic properties of ball clays for porcelain stoneware tiles manufacture in
359   Poland. Appl. Clay Sci. 51, 74–85. doi:10.1016/j.clay.2010.11.004

360 García, J., Martínez, J., 1992. Mineral resources of Spain, first ed. CSIC, Madrid (Spain).

361 González, J.A., Del, M., 2006. Bleaching of kaolins and clays by chlorination of iron and titanium. Appl. Clay Sci.
362   33, 219–229. doi:10.1016/j.clay.2006.05.001

363 Jordán, M.M., Meseguer, S., Pardo, F., Montero, M.A., 2015. Properties and possible ceramic uses of clays from
364   lignite mine spoils of NW Spain. Appl. Clay Sci. 118, 158–161. doi:10.1016/j.clay.2015.09.015

365 Juan, R., Ruiz, C., Querol, X., Fernández, J.L., A. López, 1993. Characterization and classification of the cretaceous
366   coals of Teruel (Spain). Relationship between their characteristics and the geological environment, 1st ed,
367   Notebooks of Iberian geology. Universidad Complutense de Madrid, Madrid (Spain).

368 Khramov, P.G., Sokolov, I.G., 1956. Beneficiation of glass-making sands in a hydrocyclone. Glas. Ceram. 13, 56–60.
369   doi:10.1007/BF00672359

370 Kogel, J.E., Trivedi, N.C., Barker, J.M., 2006. Industrial minerals & rocks: commodities, markets, and uses, seventh
371   ed. Society for Mining, Metallurgy and Exploration, Inc., Colorado, USA.

372

373 Lores, M.T., Font, S., De la Torre, J., Bastida, J., 1997. Study of the organic matter removal in clay by means of
374   thermal treatment. Analysis of the process to different scales. Bol. Soc. Esp. Ceram. Vidr. 36, 419–424.

375 Maritan, L., Nodari, L., Mazzoli, C., Milano, A., Russo, U., 2006. Influence of firing conditions on ceramic products:
376   Experimental study on clay rich in organic matter. Appl. Clay Sci. 31, 1–15. doi:10.1016/j.clay.2005.08.007

377 Murray, H.H., 2007. Applied Clay Mineralogy: Occurrences, Processing and Applications of Kaolins, Bentonites,
378   Palygorskite Sepiolite and Common Clays, first ed. Elsevier, Amsterdam (The Netherlands).

379 Parra, J., 1996. Mineralogy and ceramic properties of paleozoic slate rocks from Ciudad Real, Doctoral Thesis,
380   University of Castilla y La Mancha (Spain).

381 Ramaswamy, S., 2007. Study of ferruginous and titanoferrous impurity minerals in China clay, Doctoral Thesis,
382   Cochin University of Science and Technology (India).

383 Rao, G. V., Vibhuti, M.N., 2004. 5th International Seminar on Mineral Processing Technology, in: International
384   Seminar on Mineral Processing Technology (2004 : Bhubaneswar, India). pp. 19–21.

385 Romero, M., Pérez, J.M., 2015. Relation between the microstructure and technological properties of porcelain
386   stoneware . A review. Mater. construcción 65. doi:10.3989/mc.2015.05915

387 Sánchez, E., García-Ten, J., Regueiro, M., 2004. Raw materials for the Spanish ceramic industry: state of the current
388   trends. Bol. Soc. Esp. Ceram. Vidr. 45, 1–12.

389 Sánchez, E., García-Ten, J., Sanz, V., Moreno, A., 2010. Porcelain tile: Almost 30 years of steady scientific-
390   technological evolution. Ceram. Int. 36, 831-845. doi:10.1016/j.ceramint.2009.11.016

391 Sanfeliu, T., Jordán, M.M., 2009. Geological and environmental management of ceramic clay quarries: a review.
392   Environ. Geol. 57, 1613–1618. doi:10.1007/s00254-008-1436-4

393 Scott, P.W., Bristow, C.M. (eds)., 2002. Industrial minerals and extractive industry geology, first ed. The Geological
394   Society of London, London (U.K.).

395 Toro, L., Marabini, A.M., Paponetti, B., Passariello, B., 1993. Process for removing iron from kaolin, quartz and
396   other mineral concentrates of industrial interest. United States Patent, Pat. Number. 5.190.900.

397 Zegeye, A., Yahaya, S., Fialips, C.I., White, M.L., Gray, N.D., Manning, D. a C., 2013. Refinement of industrial
398   kaolin by microbial removal of iron-bearing impurities. Appl. Clay Sci. 86, 47–53.
399   doi:10.1016/j.clay.2013.08.041

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408Fig. 1. Diagrams of the physical methods used to remove iron compounds from clays: WSM, wet sieving method; 409HCM, hydrocycloning method; EFM, electromagnetic filter method.

410Fig. 2 .Graph representing the industrial firing cycle used to obtain ceramic porcelain tiles.

411Fig. 3. Comparison of ball clays with Spanish clays before treatment designed for use in porcelain stoneware 412formulation.

413Fig. 4. DTA curves corresponding to TE-01 (original and treated for 30 minutes at different temperatures).

414Fig. 5. Removed organic matter (wt%) and removed kaolinitic dehydroxylation (wt%) of TE-01 treated at different 415temperatures for 30 minutes.

416Fig. 6. X-ray diffractograms of sieve residue obtained at 100 micrometres (R100) corresponding to Spanish clays TE-41702 and CR-01. TE-02 R100 and CR-01 R100 are the residues of TE-02 and CR-01 clays sieved at 100 micrometres, 418respectively.

419Fig. 7. Sintering diagram: linear shrinkage and water absorption vs temperature of compositions A, B and STD.

420Fig. 8. Scanning electron micrographs of pieces fired at 1185ºC: a) composition STD, b) composition A, and c) 421composition B.

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