

# PROPERTIES AND POSSIBLE CERAMIC USES OF CLAYS FROM LIGNITE MINE SPOILS OF NW SPAIN

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## Abstract

Clay spoils from lignite mines are studied to know their industrial possibilities. The clays come from a coal mining area in NW Spain. In relation to their mineralogical composition, clays can be classified into three main groups. Group 1 was characterized by the presence of kaolinite with an average value of 39%, illite with an average value of 28% and quartz with an average value of 30%. Group 2 was characterized to have the lowest content of kaolinite (30%), 12% of illite content, the highest quartz content (47%), an absence of dolomite and calcite. Group 3 shows the highest kaolinite content (72%), illite (10%) and lower quartz content (15%). The chemical and mineralogical composition allows the evaluation of the applicability of the clays studied. The heated samples were composed of bulky particles, predominantly of quartz and hematite, which are agglomerated in a vitreous matrix. An intermediate phase between spinel and

hercynite was formed at 950 °C in the Groups 1 and 3, and remains in this series up to a temperature of 1150 °C. At higher temperatures other phases such as mullite was formed in Group 3 series together an abundant amorphous phase. Imported clays (ball-clays) from UK and France by Spanish ceramic industry have similar characteristics, behavior and uses that the clays from lignite deposits studied, (i.e. Group 1 and 3).

**Key words:** clay spoils, ceramic clays, firing transformations, industrial uses, Spain

## **1. Introduction**

In this paper the clay materials associated to the mined coal in the Utrillas-Escucha-Estercuel and Ariño-Andorra regions (western Spain) are studied (Figure 1). Such materials belong to the upper part of the Lower Cretaceous formations and they are mine spoils from the lignite mines. In particular, this note mainly refers to the clays associated to the Lignitos de Escucha (Escucha Lignites) and Arenas de Utrillas (Utrillas kaolonitic sands) formations. The main objective is to know the possibilities of such clayed mine spoils to be used as a raw material for ceramics, because in this Spanish area (provinces of Castellón, Valencia and Teruel) are concentrated most important ceramic industries for pavement and coating. The paper specifically discusses the mineralogical characteristics and firing transformations of those clays from lignite deposits around Teruel. Another secondary objective is to compare the quality of these study clays with other imported from UK and France, currently used by Spanish companies in the manufacture of floor and wall white ceramic bodies, which account for more than 25% of the ball-clays used in Spain (Lunar et al. 2006).

From this study it is possible to establish a classification on the clayed mine spoils for industrial uses on the basis on their mineralogy and firing behaviour, according to Dondi et al. (2014).

## **2. Materials and methods**

### *2.1 Raw materials.*

The geological background of the studied clays was described, among others, by Meseguer et al. (2009a). Fifty samples of clays were mineralogical and chemically analysed, 46 come from the mining areas of Teruel (Oliete-Estercuel (OE) and Ariño-Andorra (AA) and 4 were commercial industrial clay (ball-clays) from United Kingdom (UK1, UK2 and UK3) and France (F1). The last are clays usually imported from UK and France, and a comparison with the clays studied can be of paramount importance.

Four fractions were separate from the raw materials because ceramic industries, usually, separate ball-clays into three fractions for analyses, and in addition, the magnetic fraction of the coarser fraction was also separate for its study to know the presence of pyrite and other iron and titanium traces.

Mineralogical analysis was carried out using X- Ray diffraction (XRD) with a SIEMENS D-5000 (Cu- $K\alpha$ ) diffractometer. The separate fractions analysed were: F1 (particle size  $< 2\mu\text{m}$ ), F2 (particle size between 2 and 50  $\mu\text{m}$ ), F3 (particle size  $> 50\mu\text{m}$ ) and F3M (magnetic fraction of F3). Oriented aggregates of F1 and F2 were prepared to the clay minerals characterization and treated with ethylene glycol and calcined at 550°C during 2 hours. A mineralogical quantitative approach was carried out using the programmes EVA and EDQ. The fractions  $>50\mu\text{m}$  were studied by back-scattering scanning electron microscopy (SEM) with energy dispersion microanalysis (EDS). The electronic

microscope used was PHILIPS XL-30 with EDAX DX-4 microanalysis (0.3 mbar and 20 kV).

The chemical analysis of major elements was made by X-ray fluorescence (XRF) using conventional techniques (Sanfeliu and Jordán, 2009) with a PW2400 X-ray spectrometer with rhodium target X-ray tube, controlled by SuperQ/Quantitative version 1.1 software.

## *2.2 Statistical analysis.*

Statistical correlations and cluster analysis have been established, by using the Windows SPSS programme following the methodology described in Meseguer et al (2009a).

## *2.3 Fired samples.*

The clays were moistened by hand mixed sufficiently and sieved (1 mm) until homogeneous agglomerates with 6% of water were obtained. They were left to rest for 24 h and then pressed ( $300 \text{ kg/cm}^2$ , 80x 40 x 5 mm) by using a laboratory press. The pieces were heated to 900, 950, 1000, 1050, 1100, 1150 and 1200 °C. A mineralogical analysis of fired samples was also carried out by XRD following the methodology described in Jordan et al. (1999) and Jordán et al. (2008).

## **3. Results and discussion**

The mineralogical composition of the bulk materials was: kaolinite, illite, chlorite and smectites (in traces), with quartz and feldspar, and minor siderite, hematite, calcite, dolomite and pyrite. The quantitative analysis is shown in table 1. The crystalline phases identified in the clay fraction (F1) were: kaolinite and illite, sometimes

accompanied by chlorite and smectite. The relative percentage of the main components, illite and kaolinite, is recorded in Table 2.

Fraction F2 has a similar composition to F1, but the illite content increases substantially and the kaolinite content decreases. In F3 quartz is the major and always present component, and muscovite, dolomite, calcite, feldspars, siderite, hematite and occasional pyrite can be present. F3M is mainly composed of hematite, pyrite and/or siderite.

The characterization of the sand fraction (F3) has been completed with SEM/EDX observations. The mineral composition was quartz and muscovite in all the samples, and other minerals such as siderite, calcite, dolomite, pyrite, hematite and feldspar are also present. Siderite showed cationic substitutions of  $\text{Fe}^{2+}$  by  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , according to the EDS analysis.

Table 3 shows the chemical analysis of the major components (mean and range) grouped according the sampling areas. From the statistical analysis of the data it was deduced that there was a high correlation of the LOI with  $\text{Al}_2\text{O}_3$ . This high correlation was due to the fact that the most important source of  $\text{Al}_2\text{O}_3$  is the clay minerals (Echajia et al., 2005).

From the statistical cluster analysis, three mineralogical groups have been differentiated (Table 4). Group 1 was characterized by the presence of kaolinite with an average value of 39%, illite with an average value of 28%, quartz with an average value of 30%, and feldspars, calcite, dolomite, hematite and siderite (< 1%). Group 2 was characterized to have the lowest content of kaolinite (30%), 12% of illite, the highest quartz content (47%), feldspars (> 2%), and siderite (1.8 %), and no or little dolomite and calcite. Group 3 showed the highest kaolinite content (72%), illite (10%), and the lowest quartz content (15%), but with some concentration of hematite (~1%).

As clays for refractories must contain *ca.* 80% of kaolinite, more than 30%  $\text{Al}_2\text{O}_3$ , less than 2.5%  $\text{Fe}_2\text{O}_3$ , and less than 1% of  $\text{CaO}+\text{MgO}$  and  $\text{K}_2\text{O}+\text{Na}_2\text{O}$  (Berton and Le Berre, 1983; Meseguer et al., 2009b), most clays of Group 3 do not meet all the requirements to be marketed for the refractory industry. In general those clays from Group 3 with around 72% of kaolinite may be classified as fine clays, and particularly those with a kaolinite content between 50-80%, less than 2%  $\text{Fe}_2\text{O}_3$ , no soluble salts and less than 5% of smectites could be used as white paste of pavement and coating, If the percentage of  $\text{Fe}_2\text{O}_3$  is higher than 5%, red colorations during the heating cycles appear. Depending on the paste type (white or red), the carbonate content will have to be controlled. The groups 1 and 2, with kaolinite content below 50% would be excluded for use as fine clays.

According to Dondi et al. (2014), clays from groups 1 and 2 can be classified as raw kaolin (RK). However, the kaolinite content of some samples from group 1 is  $< 25\%$ . Therefore these samples can be classified as light-firing clays poor in kaolinite (LFK). Such clays find application in bodies where they play simultaneously the role of filler and plastic component. However, their use must be balanced with high plasticity clays (Sánchez et al., 1997). Raw kaolin may play as a sort of mix, thanks to comparable amounts of kaolinite, quartz and flux minerals (feldspars or rock fragments) whose technological behaviour has to be balanced by the other clays and fluxes making up the body (Dondi et al, 2014). Clays from Group 3 can be classified as low-grade kaolin (LK). The behavior of low-grade kaolin in the ceramic cycle is influenced by components associated to kaolinite in the plastic and non-plastic fractions. The technological performance of the clays rich in kaolinite and poor in feldspar do not substantially differ from that of high-grade kaolin, although their use is restricted to

vitrified and porous bodies being generally not utilized in slips and glazes (Dondi et al, 2014).

Tables 5, 6 and 7 show clear differences in firing behavior of clays studied. The presence of illite was observed up to at least 900 °C in the three groups of clays. From the destruction of illite an intermediate phase between spinel ( $\text{MgO}\cdot\text{Al}_2\text{O}_3$ ) and hercynite ( $\text{FeO}\cdot\text{Al}_2\text{O}_3$ ) originates. In the samples richer in illite, hercynite formed directly. This phase was formed at 950 °C in the Groups 1 and 3, and remains in this series up to a temperature of 1150 °C. At higher temperatures other phases such as mullite was formed in Group 3 series together abundant amorphous phases. Firstly, at 900-1100 °C, a great change took place in the structure leading the formation of spinel phase and thereafter the subsequent formation of poorly crystalline mullite at 1150-1200°C. According to the XRD study, the crystallinity of spinel and glassy phases evolved in a wide temperature range between 900 and 1200 °C. The kaolinite decomposition was determined at 600°C (Bastida et al. 2006), the intermediate spinel type aluminosilicate formation was also identified at 980°C. The incongruent fusion of the feldspars was observed together with the final mullitization and the glassy phase formation.

In addition, between 1050 and 1100 °C a considerable decrease in the porosity occurs, coinciding with the beginning of vitrification. At 1150 °C the ceramic bodies become earthenware and the pores close, and the porosity decreases significantly.

#### **4. Conclusions**

Clays from lignite mine spoils studied from a coal mining area in NW Spain can be classified into three groups according their mineralogical and chemical composition. Group 1 was characterized by the presence of kaolinite with an average value of 39%, illite with an average value of 28% and quartz with an average value of 30%. Group 2 was characterized to have the lowest content of kaolinite (30%), and the highest quartz content (47%) and Group 3 showed the highest kaolinite content (72%), illite (10%) and lower quartz content (15%). After firing an intermediate phase between spinel and hercynite was formed at 950 °C in the Groups 1 and 3, and they remains in this series up to a temperature of 1150 °C. At higher temperatures other phases such as mullite was formed in Group 3 series together an abundant amorphous phase. Materials from Group 1 are light-firing clays poor in kaolinite (LFK), those from Group 2 are can be classified as raw kaolin (RK), and Group 3 clays can be classified as low-grade kaolin (LK). Imported clays from UK and France by Spanish ceramic industry have similar characteristics, behavior and uses to that studied clays from lignite deposits. Specifically, samples UK1 and FR1 belong to Group 3 and the samples UK2 and UK2 belong to Group 1.

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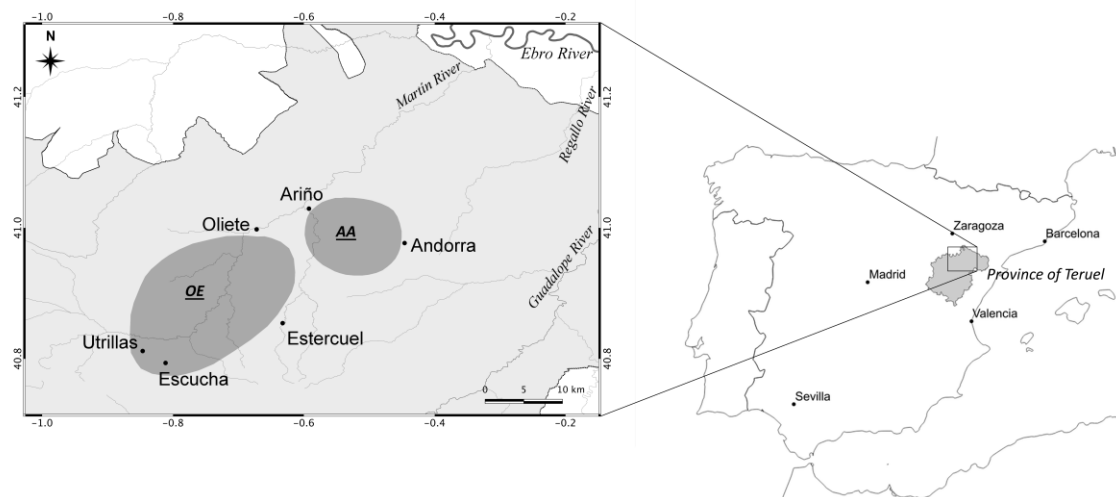
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## FIGURES CAPTIONS

**Figure 1.** Location of the studied areas. Legend: OE: Oliete-Estercuel; AA: Ariño-Andorra.



## TABLE CAPTIONS

**Table 1.** Mineralogical composition of the studied samples (bulk rock). Legend: 0: non-present; +: Minor component). Q: quartz; K: kaolinite; I: illite; Ch: chlorite.; S: Smectite; F: feldspars; Cc: calcite; D: dolomite; Hm; hematite; Si: siderite; Py: pyrite.

**Table 2.** Mineralogical composition of clay fraction (% kaolinite, % illite/muscovite).

**Table 3.** Major elements (weight percentage).

**Table 4.** Classification of samples in three groups (cluster analysis).

**Table 5.** Formation of new mineral phases (in c.p.s.) according to the firing temperature of the green body for Group 1 clays.

**Table 6.** Formation of new mineral phases (in c.p.s.) according to the firing temperature of the green body for Group 2 clays.

**Table 7.** Formation of new mineral phases (in c.p.s.) according to the firing temperature of the green body for Group 3 clays.

# TABLES

Table 1

Series (%)	Q		K		I		F		Cc		D		Ch	S	Hm	Si		Py
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range				Mean	Range	
<b>OE</b>	18.7 (48-4)		54.8 (90-23)		19.5 (40-5)		1.0 (3-0)		1.5 (6-0)		0.46 (2-0)		+	+	+	+		+
<b>AA</b>	42.3 (59-17)		35.1 (49-17)		19.1 (50-8)		0.85 (6-0)		0		0		+	+	+	0.80 (4-0)		+
<b>UK</b>	24.0 (35-13)		46.0 (59-36)		28.4 (32-25)		0.7 (1-0)		0.6 (1-0)		0.3 (1-0)		0	+	0	0		0
<b>FR1</b>	15		74		11		0		0		0		0	+	0	0		0

**Table 2**

<b>Series (%)</b>	<b>Kaolinite</b>		<b>Illite</b>	
	<b>Mean</b>	<b>Range</b>	<b>Mean</b>	<b>Range</b>
<b>OE</b>	81.5	(98-42)	18.5	(58-2)
<b>AA</b>	64.1	(79-38)	35.9	(62-21)
<b>UK</b>	69.4	(74-67)	30.7	(33-26)
<b>FR1</b>	97		3	

**Table 3**

<b>Serie</b>	<b>SiO<sub>2</sub></b>		<b>Al<sub>2</sub>O<sub>3</sub></b>		<b>CaO</b>		<b>MgO</b>		<b>Na<sub>2</sub>O</b>		<b>K<sub>2</sub>O</b>		<b>Fe<sub>2</sub>O<sub>3</sub></b>		<b>P<sub>2</sub>O<sub>5</sub></b>		<b>LOI</b>	
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range
<b>OE</b>	55.3 (63-41)		24.7 (31-19)		0.62 (2.9-0.2)		0.70 (1.7-0.4)		0.16 (0.24-0.02)		1.88 (3.4-0.6)		4.34 (9.2-1.3)		0.08 (0.09-0.05)		13.8 (17.2-6.19)	
<b>AA</b>	65.6 (71-58)		19.71 (22-14)		0.31 (0.5-0.2)		0.39 (0.7-0.2)		0.10 (0.2-0.04)		2.01 (3.6-0.1)		2.99 (4.5-1.3)		0.09 (0.2-0.04)		7.79 (9-4.8)	
<b>UK</b>	59.6 (65-54)		24.57 (28-21)		0.12 (0.2-0.06)		0.53 (0.54-0.52)		0.26 (0.32-0.17)		2.08 (2.3-2)		1.08 (1-1.3)		0.08 (0.1-0.07)		9.4 (11.8-7.4)	
<b>FR1</b>	59.8		24.9		0.34		0.45		0.05		0.79		1.25		0.08		10.9	

Table 4

Group	Samples	Q		K		I		F		Cc		D		Hm	Si	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range		Mean	Range
1	OE1. OE10. AA1. AA2. AA3. AA7.AA9.AA10. AA15.AA18.AA19.AA20	30 (61-17)		39 (49-17)		28 (50-13)		0.9 (2-1)		1.1 (2-0)		0.35 (1-0)		+	0.4 (2-0)	
2	OE2.OE3.OE4.OE5.OE6.OE7.OE8.OE9. OE11. OE13. OE22. OE24. <b>UK2. UK3</b> OE25. AA4. AA5. AA6. AA8. AA11. AA12. AA14. AA16. AA17. AA22	47 (59-26)		30 (54-23)		12 (56-3)		2.2 (3-1)		0.2 (1-0)		0		+	1.8 (4-0)	
3	OE12. OE14. OE15. OE16. OE17. OE18. OE19. OE20. OE21. OE23. <b>UK1.</b> <b>FR1.</b> OE26	15 (21-3)		72 (90-65)		10 (40-0)		0.5 (1-0)		1.2 (2-0)		0.40 (1-0)		1.09	0.2 (1-0)	



**Table 5**

<b>T (°C)</b>	<b>Q</b>	<b>Hm</b>	<b>Sp</b>	<b>I</b>	<b>F</b>
Units	C.p.s.	C.p.s.	C.p.s.	C.p.s.	C.p.s.
900	3500	495		612	425
950	1860	390	466		390
1000	1720	335	435		
1050	1520	299	334		
1100	1346	206	129		
1150	1520	198			
1200	1622	182			
<b>d (Å)</b>	3.34	2.69	2.46	9.98	3.24

**Legend:** C.p.s = Counts per second; Q = Quartz; Hm = Hematite; Sp=Spinel; I = Illite; F = Feldspar

**Table 6**

<b>T (°C)</b>	<b>Q</b>	<b>Hm</b>	<b>Sp</b>	<b>I</b>	<b>F</b>
Units	C.p.s.	C.p.s.	C.p.s.	C.p.s.	C.p.s.
900	2800	578		708	529
950	1370	480	572		456
1000	1220	335			
1050	1170	296			
1100	1100	287			
1150	890	198			
1200	754	89			
<b>d (Å)</b>	3.34	2.69	2.46	9.98	3.24

**Legend:** C.p.s = Counts per second; Q = Quartz; Hm = Hematite; Sp=Spinel; I = Illite;  
F = Feldspar

**Table 7**

<b>T (°C)</b>	<b>Q</b>	<b>Hm</b>	<b>Sp</b>	<b>I</b>	<b>F</b>	<b>Mu</b>
Units	C.p.s.	C.p.s.	C.p.s.	C.p.s.	C.p.s.	C.p.s.
900	3027	478		392	428	
950	2270	380	773		356	
1000	1320	235	805			
1050	1270	196	1003			
1100	1200	187				
1150	1090	98				102
1200	987	78				206
<b>d (Å)</b>	3.34	2.69	2.46	9.98	3.24	3.42

**Legend:** C.p.s = Counts per second; Q = Quartz; Hm = Hematite; Sp=Spinel; I = Illite; F = Feldspar, Mu = Mullite