

## VALORISATION OF CONTAMINATED MARINE SEDIMENTS TO PRODUCE CERAMIC CONSTRUCTION MATERIALS

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### Abstract

The effect of the heating temperature on the properties of sintered ceramic bodies from three different contaminated marine sediments was investigated. The optimum sintering temperature is 1125°C for Astilleros and Cuchia sediments and 1150°C for Raos sample. Water absorption values and mechanical properties of sintered bodies show that marine sediments are available to be used as secondary raw materials in ceramic tiles and bricks production. The results revealed that the firing process decrease the leaching of the species analyzed, except for As. Thus, the risk associated to fired sediments can be considered low.

**Keywords:** *Marine Sediments, Sintering, Traditional Ceramic, Leaching Behaviour*

### INTRODUCTION

Marine sediments are deposited material consisting of insoluble material (rock and soil particles), organic matter and remains of marine organisms that accumulate on the seafloor. Due to the exposure to industrial effluents, sediments may contain high levels of contaminants or pollution. Sediments from Santander and Suances Cantabrian estuaries (Northern Spain) contain significant concentrations of heavy metals and organic pollutants derived from intensive industrial, agricultural and urban activities, making necessary treatment and confined disposal to manage them properly [1].

The valorisation of wastes as secondary raw materials in the production of construction materials could allay the problems associated to both, the depletion of natural resources and the disposal of industrial wastes. Among construction

materials, traditional clay-based materials are heterogeneous products that can accommodate different inorganic wastes without modification of its production process or the final product properties [2-4]. Recent investigations focused in the development of clay/waste mixtures have shown same benefits as, i) saving of resource, raw material and energy; ii) positive effects on the brick-making process; iii) improving final product quality; iv) reducing the cost of final product.

The aim of this work is to evaluate the suitability of marine sediments with inorganic and organic contaminants as alternative raw materials in the manufacture of traditional clay based ceramic materials. For this, the sintering of three marine sediments following a conventional powder process has been studied.

### EXPERIMENTAL

Raw materials used in the present investigation were three Spanish marine sediments from the Santander Bay (Astilleros and Raos), and from the Suances Estuary (Cuchia). The as-received sediments were oven-dried at 105°C for 24 h and then crushed, grounded and finally powdered to <160µm prior to their characterization and further use. The powders were compacted at 40MPa to form disc-shaped specimens (2.0 cm in diameter and 0.5 cm in height), which were sintered in an electrically heated furnace at temperatures between 900° and 1200°C by using a ramp rate of 15°C/min. The samples were hold at the maximum temperature for 1 hour and then cooled inside the furnace at a rate of 50°C/min down to 500°C.

The sintering behaviour of the fired samples was evaluated on the basis of bulk density ( $\text{g/cm}^3$ ), open porosity (%) and water absorption (%), as required by ASTM C373, which involves boiling in water for 5 h and a further soaking of 24 h at room temperature. The development of porosity was also evaluated by scanning electron microscopy (SEM, Jeol JSM 540) on the broken surface of sintered samples. SEM specimens were polished using 6, 3 and 1  $\mu\text{m}$  diamond pastes after grinding with silicon carbide paper and water. The polished surfaces were Au-Pd coated.

The major crystalline phases of fired specimens were identified by X-ray diffractometry (XRD). Samples were crushed to fine powder in an agate mortar, passed through a 300 mesh sieve and then were scanned with  $\text{CuK}\alpha$  radiation from  $15^\circ \leq 2\theta \leq 75^\circ$  at a scanning speed of  $0.5^\circ/\text{min}$ , using a Philips X'PERT MPD diffractometer operating at 30 mA and 50 kV.

Bending and compressive strength was measured in an electronic universal testing machine (Servosis) on 10 test pieces for each sintered temperature. Bending strength determination was carried out by a three-point loading test with a span of 36 mm and crosshead speed of 3 mm/min. For compressive strength, the load had been applied uniformly with a speed of 15 N/s through two stiff and flat hardened steel plates.

Finally, the environmental risk of sintered sediments samples was evaluated on the basis of Leaching Standards Tests UNE-EN 12457 1-2. Leaching tests used two liquid/solid ratio, L/S=2 and 10, which simulate closed and open landfill respectively. The leachant was demineralised water and the contact time between the leachant-solid material was 24 hours. The leachates were analyzed to determine the concentrations of metals and anions considered in EU Waste Landfill Directive 2003/33/CE, in order to compare them with regulatory limits.

## RESULTS AND DISCUSSION

Table 1 shows the chemical analysis and mineralogical composition determined by X-ray fluorescence and X-ray diffraction respectively. According to their composition, the three sediments are suitable to be used as secondary raw material in a traditional ceramic paste [5]. Indeed, most clay

used for brick and roof tile production contains appreciable amounts of iron oxide and calcium oxide.

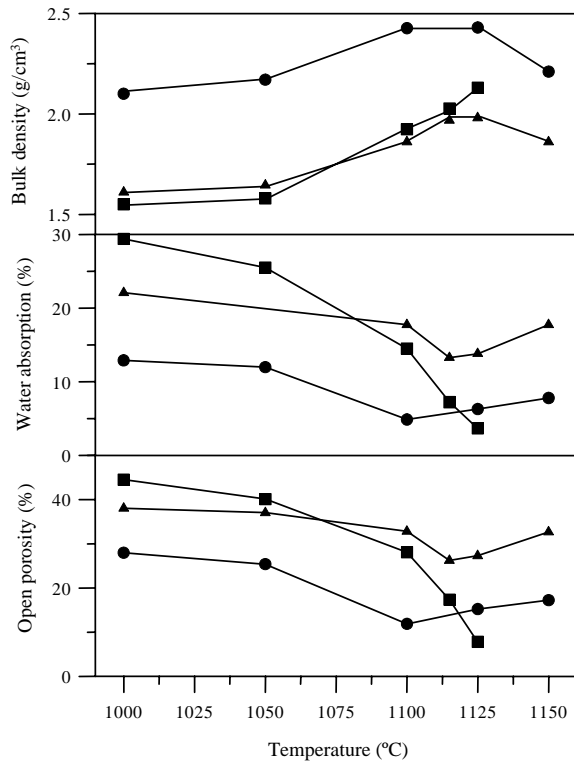
Moreover, quartz is one of the main components in ceramic pastes. The only problem could be caused by the presence of anhydrite, which is a soluble salt that can cause efflorescence. Nevertheless, its effect can be palliated by adding an adequate efflorescence-restraining additive [6]. On the other hand, since alkaline and alkaline-earth oxides are fluxing agents and promote vitrification, the addition of these sediments to a ceramic paste will likely decrease the firing temperature, with the corresponding energy saving.

**Table 1.** Chemical (wt. %) and mineralogical composition of the sediments

	Astilleros	Cuchia	Raos
$\text{SiO}_2$	47.13	53.54	57.26
$\text{Al}_2\text{O}_3$	11.73	8.43	7.69
$\text{Fe}_2\text{O}_3$	21.55	4.50	4.13
MnO	0.31	0.03	0.05
MgO	1.46	2.36	3.60
CaO	1.41	7.48	6.81
$\text{Na}_2\text{O}$	1.08	1.51	1.23
$\text{K}_2\text{O}$	1.62	1.85	1.83
$\text{TiO}_2$	0.63	0.55	0.57
$\text{P}_2\text{O}_5$	0.23	0.17	0.17
LOI	12.01	19.35	16.69
quartz	x	x	x
goethite	x		
calcite		x	x
anhydrite		x	x
dolomite		x	x
$\text{Mg}_2\text{SiO}_4$			x

Figure 1 plots the open porosity, water absorption and bulk density as function of firing temperature in the  $1000^\circ\text{--}1150^\circ\text{C}$  temperature range. Upon firing, all the measured properties show the typical trend of conventional clay based ceramic products. Bulk densities increase with increasing temperature, reached a maximum value in Astilleros and Raos samples, and at higher temperatures decreases rapidly likely due to the increasing of closed porosity because of the so-called body bloating due to the pressure of the gas inside the closed pores, which tends to expand the pores. Open porosity decreases with increasing firing temperature indicating that the sintering process follows a viscous liquid phase mechanism due to the formation of a glassy phase [7]. Increasing temperatures causes both an increase in liquid phase amount and a decrease in liquid phase viscosity. Under the surface energy forces created by the fine pores contained in

the ceramic body, the liquid phase tends to approach the particles and, therefore, open porosity decreases. Finally, since water absorption is directly related to open porosity, both properties show the same trend in the overall temperature range.

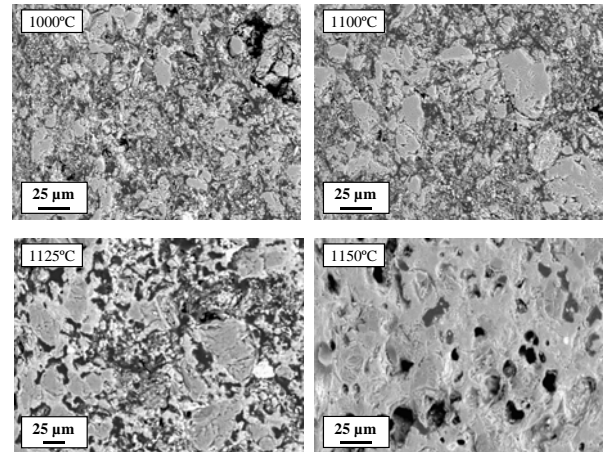


**Figure 1.** Bulk density, water absorption and open porosity, as function of firing temperature (● Astilleros; ■ Cuchia; ▲ Raos).

The evolution of porosity with temperature has been also observed by SEM. The three sediments show a similar trend of porosity versus firing temperature. Figure 2 shows SEM observations on polished surfaces of Cuchia sediment compacts fired at different temperatures in the 1000°-1125°C range. At lower temperature, the porosity is mainly due to open porosity, which is formed by fine, interconnected and irregular shape pores. As firing temperature increases, the capillary pressure due to the surface tension of the liquid phase tends to approach the particles, which in turn changes the porosity from open to closed porosity, which is formed by greater, isolated and spherical pores. At higher temperatures, the pressure of the gas inside the closed pores tends to expand the pores and closed porosity increases.

The optimum sintering range is achieved when open porosity reaches a minimum value and simultaneously linear shrinkage is maxima. It can be

established that the optimum sintering temperature is 1125°C for Astilleros and Cuchia sediments and 1150°C for Raos sample.



**Figure 2.** SEM observations on polished surfaces of Cuchia sediment compacts fired at different temperatures.

The mineralogical evolution examined by X-ray diffraction (XRD) revealed that quartz, which is a main crystalline phase in the original marine sediments, remains as a main phase in the sintered bodies. In addition, new crystalline phases, such as hematite ( $\text{Fe}_2\text{O}_3$ ), augite ( $\text{Ca}(\text{Mg},\text{Fe})\text{Si}_2\text{O}_6$ ), magnesioferrite ( $\text{MgO}\cdot\text{Fe}_2\text{O}_3$ ), ferrosilite ( $(\text{Mg},\text{Fe})\text{Si}_2\text{O}_6$ ) and magnesium iron aluminium silicate ( $(\text{Mg},\text{Fe},\text{Al})(\text{Si},\text{Al})\text{O}_3$ ) appear as result of different chemical reactions during firing. Besides, a glassy phase is formed as result of the dissolution of quartz grains and augite decomposition.

At the optimum firing temperatures, sintered bodies show water absorption values of 6% for Astilleros, 4% for Cuchia and 14% for Raos sediment. Astilleros and Cuchia specimens fulfil the requirements prescribed by AENOR (Spanish Association for Normalization and Standardization), which establishes water absorption values, as determined by the European Standard EN-771-1 Annex C [8], of  $\leq 14\%$  and  $\leq 6\%$  for high density traditional bricks and high density clinker bricks respectively. Those sintered sediments satisfy also the values specified by ASCER (Spanish Association of Ceramic Pavement and Covering Tiles), which establishes water absorption values, as determined by the European Standard EN ISO 10545-3 [9], of 11-15% and  $\leq 6\%$  for covering and pavement ceramic tiles respectively. As for Raos sample, its addition to a ceramic paste for clinker brick or pavement tile production, requires a previous study

to determine its effect in water absorption of the final product and its addition limit.

At optimum firing temperatures, the sintered bodies show bending strength values of 22 MPa for Astilleros, 19 MPa for Cuchia and 16 MPa for Raos sintered sediment. The values showed by Astilleros and Cuchia samples comply with the requirements of the European Standard EN 14411 [10], which propose bending strength values, as determined by the European Standard EN ISO10545-4 [11], of > 15 MPa and >20 MPa for covering and pavement ceramic tiles respectively. As regards compressive strength at optimum firing temperatures, the sintered bodies show values of 11 N/mm<sup>2</sup> for Cuchia and 34 N/mm<sup>2</sup> for Astilleros and Raos sediments. In this case, the three sintered samples comply with the value fixed by AENOR, which establishes a compressive strength value, as determined by the European Standard EN-772-1 [12], of >10 N/mm<sup>2</sup> for high density traditional bricks.

Figure 3 shows the results of the analysis of the leachates obtained in an equilibrium leaching test developed in sintered specimens from both Astilleros sediment and a clay sample. Arsenic is the only specie that exceeds the limits established by 2003/33/CE in both sediments and clay.

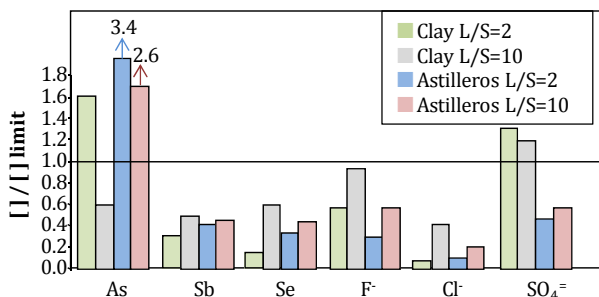


Figure 3. Comparison of cation and anion concentrations in leachates according to regulatory limits collected in 2003/33/CE.

## CONCLUSIONS

Based on these preliminary analyses, it can be concluded that studied marine sediments can be used as secondary raw materials for the production of ceramic bricks and ceramic floor and wall tiles by powder technology. Water absorption and mechanical properties show that Astilleros and Cuchia samples fired at their respective optimum sintering temperature met the requirement values established by different European Standards for high-density traditional bricks, covering ceramic tiles

as well as for the more demanding criteria to high-density clinker bricks and pavement ceramic tiles. As for Raos sediments, its addition to a ceramic paste for clinker brick or pavement tile production requires a previous study to determine its effect in water absorption and bending strength of the end-products. In general, the hazardous potential of the sediments is not much higher than the hazardous potential associated to the clay sample.

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