Sintering behaviour of ceramic bodies from contaminated marine sediments

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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 sintering behaviour was evaluated by means of the variation of shrinkage degree, bulk density, water absorption, open and closed porosity, while the phases transformation were investigated by differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results have shown that the sintering process follows a viscous liquid phase mechanism due to the formation of a glassy phase. The optimum sintering temperature is 1125°C for Astilleros and Cuchia sediments and 1150°C for Raos sample. Above this temperature, a significant overfiring with an increase of closed porosity was observed. Water absorption values and mechanical properties as bending and compressive strengths of sintered bodies show that the investigated marine sediments are suitable to be used as secondary raw materials in ceramic tiles and bricks production.

Keywords: A. Sintering; B. Electron microscopy; D. Traditional ceramics; Marine sediments

1. Introduction

Marine sediments are deposited material consisting of insoluble material, primarily rock and soil particles transported from land areas to the ocean, organic matter in various stages of decomposition and remains of marine organisms that accumulate on the seafloor. Marine sediments vary widely in composition and physical characteristics as a function of water depth, distance from land, variations in sediment source, and the physical, chemical, and biological characteristics of their environments.

Due to the exposure to industrial effluents, sediments constitute a pollutant trap and may contain high levels of pollutant. Indeed, marine sediments are normally utilized as indicators to identify environmental impacts [1-3]. Once the potential risks of contaminated sediments have been assessed by tiered ecological risk assessment frameworks, it would be necessary remediation actions including dredging [4]. On the

other hand, dredging actions are necessary to allow all the uses of a water system. In both cases, a sustainable process of dredged material management will be applied. Since dredged material may be contaminated, it will be necessary to carry out a characterization to decide the most suitable destination for the material [5]. In this context, the Action Levels (ALs) have been established as numerical criteria of dredged material management that define different classes of dredged material, and each class is associated with a destination or management. The options in dredged material management, depending on the legal framework [6, 7], are re-collocation in the water system, beneficial use, treatment and confined disposal.

Sediments from Santander and Suances Cantabrian estuaries (Northern Spain) have been previously characterised by different chemical and ecotoxicological parameters in order to study the pollution of these coastal areas. Sediments from both estuaries 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 [8-11].

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 or sub-products without modification of its production process or the final product properties [12-14]. Consequently, the incorporation of industrial wastes or sub-products in bricks and tiles is becoming a frequent practice in the ceramic factories. In this sense, it has been conducted several studies in last years concerning the production of bricks with the incorporation of both organic [15-17] and inorganic wastes, such as, sewage sludge ash [18-20], waterworks sludge [21], natural stone wastes [22-26], fly and bottom ashes [27-34], metallurgical wastes [35-38] and boron waste [39, 40].

These investigations, focused in the development of clay/waste mixtures in order to obtain marketable ceramics materials, 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 due to using waste additive in the process.

Marine sediments can be use as clay replacement in ceramic processes to obtain a building material. During the sintering process, organic contaminants are oxidized and metal contaminants are either converted to stable immobile compounds or volatilized. Harbour sediments are suitable for light weight aggregates production, obtaining a construction material that is not hazardous during its whole life cycle [41]. Dredged material has been used as a suitable raw material in the production of ceramics materials that fulfil the physical requirements of constructional standards [42-44].

Anyway, the main factors that determine the applicability of ceramic technology are the properties of the sediments and the possibilities for using the end-products as building materials. In this sense it is essential to understand sediment characteristics and evaluate

the feasibility of treating the dredged material under a site-specific framework. 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 in order to determine the effect of the varying heating temperature on bulk density, water absorption, porosity and mechanical properties of the sintered samples.

2. Experimental procedure

Samples of 20 kg of 50 cm polluted depth sediment were obtained from the estuary of Suances (Cuchia) and the bay of Santander (Astilleros and Raos) using a grab sampler [8]. All samples were homogenised and transferred in clean glass jars, capped with aluminium foil and kept in the dark at 4°C until analysis. Table I shows the chemical analysis determined by X-ray fluorescence. According to the XRF analyses, the three samples consists of SiO₂ and Al₂O₃ as major components along with Fe₂O₃ as main constituent, in Astilleros sample, and CaO, in Cuchia and Raos samples. All sediments present a significant loss of ignition (LOI) determined according to the DIN 38414-3 Standard [45], which is likely associated to carbonate and sulphate decomposition and also to burn-off of organic matter that is usually adsorbed in this kind of materials.

Table I. Chemical composition of the sediments, as determined by XRF (wt.%)

	Astilleros	Cuchia	Raos
SiO₂	47.13	53.54	57.26
Al₂O₃	11.73	8.43	7.69
Fe₂O₃	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
Na₂O	1.08	1.51	1.23
K₂O	1.62	1.85	1.83
TiO₂	0.63	0.55	0.57
P₂O₅	0.23	0.17	0.17
LOI	12.01	19.35	16.69

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 thermal behaviour was determined by Differential Thermal Analysis coupled with thermogravimetric analysis (Setaram Labsys equipment). DTA/TG test were recorded at a heating rate of 10°C/min, in platinum crucibles and air atmosphere. Calcined alumina was used as reference material. The mineralogical composition was determined by X-ray diffraction analyses (Siemens D5000 diffractometer), using CuK α radiation and operating at 30 mA and 50 kV.

The powders were compacted at 40 MPa to form disc-shaped specimens (2.0 cm in diameter and 0.5 cm in height). Moreover, rectangular bodies of 50x10x8mm and squared bodies of 20x20 mm were pressed for bending strength and compressive strength measurements respectively. The compacted specimens 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 h and then cooled inside the furnace at a rate of 50°C/min down to 500°C.

The shrinkage degree during the sintering process was determined by hot-stage microscopy (Misura 3.0 microscope) on small pressed specimens. The HSM measurements were carried out in air with a heating rate of 10°C/min. Images of the sample profile were taken at 10°C periods from room temperature to 1400°C.

The sintering behaviour of the fired samples was evaluated on the basis of bulk density (g/cm³), 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 μ m diamond pastes after grinding with silicon carbide paper and water. The polished surfaces were Au-Pd coated.

Finally, bending and compressive strength was measured in an electronic universal testing machine (Servosis) on 10 test specimens 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 platens.

3. Results and discussion

Characterization of marine sediments

Figure 1 shows the X-ray diffraction patterns of the three marine sediments. It can be seen that all the samples contain quartz as major crystalline phase. Ca-containing phases as calcite (CaCO₃), anhydrite (CaSO₄) and dolomite (CaMg(CO₃)₂) are detected in Cuchia and Raos samples, whereas Mg₂SiO₄ is also presents in Raos sediment with a great content in magnesium. As for Astilleros sample, its chemical composition shows a

significant percentage of iron, which appears in the diffractogram as goethite (FeO(OH)). The crystalline phases identified by XRD are in agreement with the results obtained by XRF (Table I). According to their chemical and mineralogical composition, the three sediments are suitable to be used as secondary raw material in a traditional ceramic paste [46]. Indeed, most clays used for brick and roof tile production contain appreciable amounts of iron oxide and calcium oxide, which is usually present as CaCO_3 and $\text{CaMg}(\text{CO}_3)_2$. 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, such as BaCO_3 or BaCl [47]. On the other hand, since alkaline and alkaline-earth oxides are fluxing agents and promote vitrification, the addition of these sediments as secondary raw material to a ceramic paste will likely decrease the firing temperature, with the corresponding energy saving.

Figure 1. X-ray diffraction patterns from Astilleros, Cuchia and Raos sediments (Q = quartz; G = FeO(OH); $\square$ = $\text{CaMg}(\text{CO}_3)_2$; Δ = CaCO_3 , CaSO_4 ; $\circ$ = Mg_2SiO_4).

In order to investigate the reactions taking place during the sintering process, the samples were studied in non-isothermal conditions by HSM and ATD/TG. Figure 2 plots the variation of shrinkage degree with temperature. There is no evidence of any volume change related to low temperature phase transformations. The densification in all the samples starts at 1100°-1150° and is followed by a volume increase, which is more evident in Astilleros sample, probably due to bubbles formation as result of volatile components losses. After that, the shrinkage strongly increases due to the formation of a liquid phase.

Figure 2. Variation of shrinkage degree with temperature for Astilleros, Cuchia and Raos sediments (determined by HSM).

Figure 3 depicts the DTA/TG curves. All samples show several exothermic effects in the 250°-550°C interval, which are likely due to the oxidation of the organic matter adsorbed in the sediments [48]. The characteristic endothermic peak due to $\alpha \rightarrow \beta$ quartz inversion at $\approx 570^\circ\text{C}$ is only detected in Raos sample with the biggest SiO_2 content. Small endothermic peaks perceived in both Cuchia and Raos samples at 700°-900°C are due to carbonate decomposition [49]. Finally, an endothermic effect over 1000°C indicates a liquid phase formation in agreement with HSM results. As for thermogravimetric analysis, TG curves exhibit weight losses slightly higher than those showed by LOI analyses, which is likely due to the higher temperature reached in TG experiments (1200°C).

Characterization of sintered samples

The compacted samples were heat treated at different temperatures in the range 900°-1200°C for 1 h. The effect of heat treatment on sintering as observed by the naked eye is summarized in Table II.

Figure 4 plots the open porosity, water absorption and bulk density as function of firing temperature in the 1000°-1150°C temperature range. Upon firing, all the measured properties show the typical trend of conventional clay based ceramic products. Figure clearly display differential changes in bulk density through the firing temperature. The

bulk densities increase, 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 [50]. 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 trends 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 3. DTA/TG curves recorded from Astilleros, Cuchia and Raos sediments.

Table II. Effect of heat treatment temperature on sintering of sediments compacts

	Temperature (°C)	Appearance
Astilleros	900	Low sintering
	1000	High sintering. Without defects
	1050	High sintering. Without defects
	1100	High sintering. Without defects
	1125	High sintering. Without defects
	1150	High sintering. Small surface bubbles
Cuchia	1000	Low sintering
	1100	High sintering. Without defects
	1115	High sintering. Without defects
	1125	High sintering. Without defects
	1150	Softening
Raos	1000	Low sintering
	1050	Low sintering
	1100	Low sintering
	1115	High sintering. Without defects
	1125	High sintering. Without defects
	1150	High sintering. Without defects
	1200	Softening

The evolution of porosity with temperature has been also observed by SEM. Figures 5-7 show SEM observations on polished surfaces of sediments compacts fired at different temperatures in the 1000°-1200°C range.

The three sediments show a similar trend of porosity versus firing temperature. At lower temperatures the porosity is mainly due to open porosity, which is formed by fine, interconnected and irregular shape pores. The occurrence of open porosity in the fired samples could be favoured by different causes, such as entrapped air in the ceramic slurry; formation of voids during the different drying steps; gases released in the thermal decomposition of carbonates and sulphates or even by the liberation of gases dissolved in quartz particles. As firing temperature increase, 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.

Figure 4. Bulk density, water absorption and open porosity, as function of firing temperature in the 1000°-1150°C temperature range (● Astilleros; ■ Cuchia; ▲ Raos).

Figure 5. SEM observations on polished surfaces of Astilleros sediment compacts fired at different temperatures in the 1000°-1150°C range.

Figure 6. SEM observations on polished surfaces of Cuchia sediment compacts fired at different temperatures in the 1000°-1125°C range.

Figure 7. SEM observations on polished surfaces of Raos sediment compacts fired at different temperatures in the 1100°-1200°C range.

The optimum sintering range is achieved when open porosity reaches a minimum value and simultaneously linear shrinkage is maxima. Firing at upper temperatures results in a drastic fall of the physical properties due to forced expulsion of the entrapped gases, resulting in blisters and bloating. From Table II and Figures 2 and 4-7 it can be established that the optimum sintering temperature is 1125°C for Astilleros and Cuchia sediments and 1150°C for Raos sample. At these 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 [51], 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 [52], 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, which must lead to water absorption value $\leq 6\%$.

Figure 8 shows that porosity plays an important role in the bending strength. Open porosity due to irregular shaped elongated pores decreases the bending strength, in contrast, spherical pores formed at higher temperatures lead to relatively high strength. 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 [53], which propose bending strength values, as determined by the European Standard EN ISO10545-4 [54], of > 15 MPa and > 20 MPa for covering and pavement ceramic tiles respectively. As for Raos sediment, the sintered specimen is conformed to the value proposed for covering tile but yet again, prior to its use as secondary raw material in a ceramic paste for pavement tile production it is necessary to determine its effect in bending strength of the end products.

Figure 8. Bending strength as function of firing temperature in the 1000°-1200°C temperature interval (● Astilleros; ■ Cuchia; ▲ Raos).

Finally, Figure 9 shows the evolution of compressive strength with temperature for the three sediments investigated. At optimum firing temperatures, the sintered bodies show compressive strength values of 11 N/mm² for Cuchia and 34 N/mm² 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 [55], of > 10 N/mm² for high density traditional bricks.

Figure 9. Compressive strength as function of firing temperature in the 1000°-1200°C temperature interval ●Astilleros; ■Cuchia; ▲ Raos).

4. Conclusions

The present study has shown that it is possible to obtain dense sintered compacts from highly contaminated marine sediments dredged from the Santander Bay and Suances estuary (Spain). The sintering behaviour of three marine sediments was studied in the 900°-1200°C temperature interval for 1 h. During the sintering process, the development of a liquid phase progressively causes a decrease in open porosity and water absorption, until minimum value is reached, while open porosity increases. With increase temperature, the gas pressure inside the closed pores causes a meaningful growth of their size. Water absorption and mechanical properties determined for Astilleros and Cuchia samples show that the specimens 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.

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.

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55. EN-772-1 Methods of test for masonry unit. Part. 1. Determination of compressive strength.