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CARBONATIC CLAYS FOR THE PRODUCTION OF POROUS CERAMIC TILES BY FAST SINGLE FIRING

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Abstract: Plio-Pleistocene clayey marls are widespread in Italy and they have been widely used in the traditional Italian ceramic production. So, the present study was undertaken to verify the possible application of the same raw materials in the production of the modern porous tiles obtained through fast single firing ("monoporosa"). For this purpose, thirteen clay samples were collected in a wide area near Faenza (northern Italy). The analyses demonstrated that they are quite uniform from the chemical, mineralogical, and granulometric point of view. Technological tests at both laboratory and industrial level pointed out that the clayey marls in hand are suitable to be utilized in an up-to-date porous tile production. The optimum content in the starting body is around 25 %.

Key words: carbonatic clays, raw materials, porous ceramic.

Introduction

Carbonate-bearing clays of Pliocene-Pleistocene age widely outcrop all along the Apenninic chain in Italy. They are fine-grained raw materials, which have been extensively used to obtain different ceramic products with red paste: bricks, tiles, and artistic majolica wares (Bertolani et al. 1986). In particular, the tiles represented the typical Italian production of porous materials; they were processed through a double firing cycle: first the support and then the glaze. Since the last decade, this classic processing system has been supplanted by both rapid double firing and fast single firing. Single fired tiles represent the so called "monoporosa" (Biffi 1988).

The change of the technological route to obtain porous ceramic tiles required an adaptation of the composition of both bodies and glazes, to avoid gaseous emissions from the body during the glaze maturation (Fabbri 1992). Practically this means that the use of the above-mentioned Apenninic clays is being given up. For this reason, a series of studies regarding the Pliocene-Pleistocene clays which outcrop in a wide area near

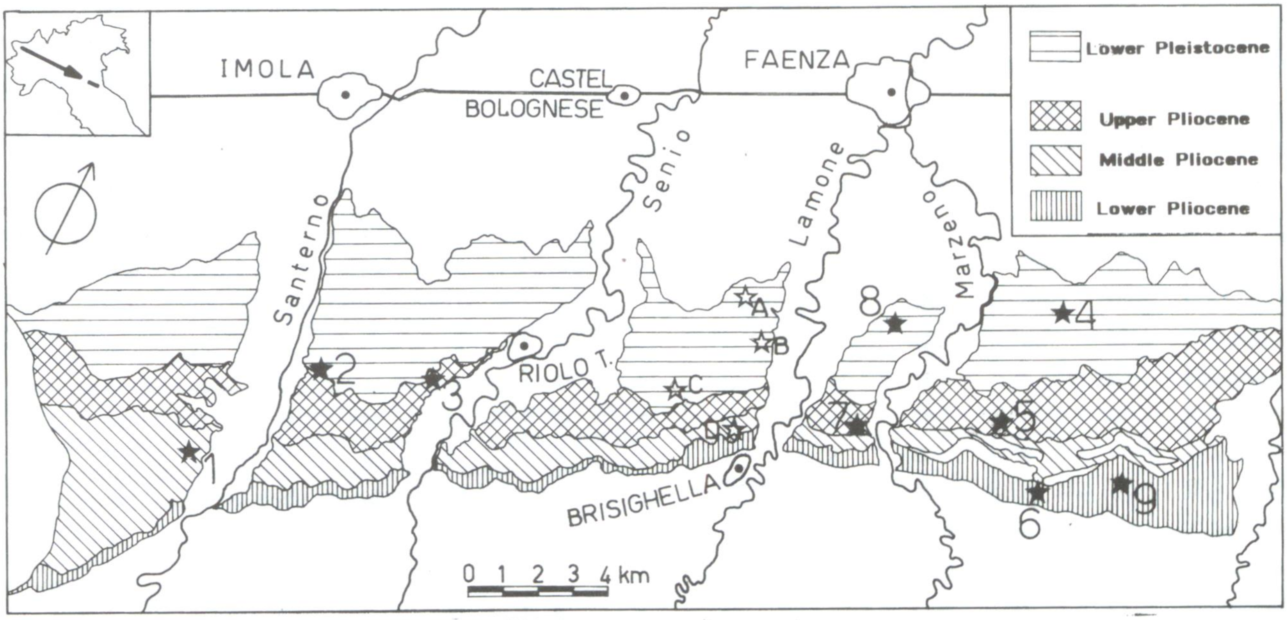

Fig. 1. Geological sketch of the area between Santerno and Montone rivers near Faenza (northern Italy). Stars indicate the sampling sites; numbers from 1 to 9: this work; letters from A to D: after Fabbri et al. (1988).

Faenza in the northern Italy has been undertaken (Fabbri et al. 1988; Dondi et al. 1991). The aim of the research, on the whole, is to verify the limits of the use, in up-to-date ceramic tile processing, of these red firing carbonatic clays. The present paper represents the last part of the work; it deals with technological tests at both laboratory and semi-industrial scale.

Experimental

Thirteen clay samples were collected in a wide area between Santerno and Montone rivers, nearby Faenza (Fig. 1) they are representative of the Lower Pliocene to Lower Pleistocene Santerno Formation (Dondi 1982). The samples were analyzed from the chemical, mineralogical, grain size, thermal and technological points of view.

The chemical determinations of the main composition were performed by means of an XRF spectrometer (Philips PW1480) on pressed tablets of the powdered samples; soluble salts were determined through treatment in distilled water and subsequent analysis of the solution by means of an AA spectrophotometer (Pye Unicam SP9). Mineralogical data were obtained by using a Philips diffractometer (CuK$_\alpha$ radiation) to recognize the minerals present, and a computerized program to elaborate the rational composition. Grain size distribution was determined through a sedimentation technique (Micromeritics SediGraph 5000ET). Thermal analyses (TG and DTA) were carried out by a Setaram apparatus, up to about 1000 *°C* with a thermal gradient of 10 *°C/minute*.

The technological behaviour of 5 samples (Nos. 1, 2, 3, 9 and A) was checked, at a laboratory scale, by preparing clay tablets (110 x 55 x 7 *mm*) through dry pressing (30 *MPa*, 6 - 7 % moisture). They were successively dried and then fired at several temperatures from 960 to 1100 *°C* with a cycle of 60 minutes from cold to cold; at the end, dimensional variations, water absorption and bending strength of the fired tablets were determined.

Table 1: Chemical, mineralogical and soluble salts composition of the clay samples.

	Pliocene							Pleistocene					
	Lower		Middle		Upper			Lower					
cg/g	6	9	1	D	3	5	7	2	4	8	A	B	C
SiO_2	46.46	47.75	48.90	48.64	42.70	45.92	48.10	45.79	45.43	46.80	44.81	46.82	46.89
Al_2O_3	11.41	11.47	12.80	13.03	12.04	12.51	13.08	12.45	13.01	12.37	12.28	12.26	12.43
TiO_2	0.55	0.64	0.61	0.64	0.56	0.60	0.63	0.59	0.61	0.60	0.56	0.62	0.55
Fe_2O_3	4.33	4.56	4.76	4.99	4.61	4.98	4.95	4.74	4.94	4.81	5.27	4.70	4.93
MnO	0.06	0.09	0.11	n.d.	0.11	0.10	0.09	0.11	0.10	0.11	n.d.	n.d.	n.d.
MgO	2.98	2.68	3.09	3.14	3.61	3.47	3.15	3.68	3.56	3.42	3.68	3.45	3.56
CaO	14.39	14.93	11.57	10.68	15.58	13.28	11.53	13.56	12.95	12.93	12.96	11.76	11.76
Na_2O	1.49	0.79	1.35	1.11	1.67	1.24	1.51	1.17	1.30	1.01	1.11	1.38	1.02
K_2O	2.28	2.34	2.38	2.51	2.39	2.55	2.57	2.55	2.58	2.50	2.51	2.47	2.53
P_2O_5	0.15	0.15	0.17	n.d.	0.15	0.16	0.15	0.15	0.15	0.16	n.d.	n.d.	n.d.
S	0.81	0.09	0.16	0.06	0.13	0.15	0.20	0.21	0.11	0.02	0.01	0.12	tr.
F	0.08	n.d.	0.09	n.d.	0.09	0.08	0.09	0.10	0.09	0.09	n.d.	n.d.	n.d.
L.O.I.	15.54	16.77	14.20	14.29	17.41	15.97	14.20	15.56	15.57	16.07	16.58	15.43	15.38
S^{--}	0.13	0.05	0.16	tr.	n.d.	n.d.	n.d.	0.45	n.d.	n.d.	tr.	0.03	tr.
Cl^-	0.01	0.01	0.02	0.05	n.d.	n.d.	n.d.	0.05	n.d.	n.d.	0.03	0.18	0.02
Na^+	0.10	0.02	0.19	0.25	n.d.	n.d.	n.d.	0.39	n.d.	n.d.	0.15	0.35	0.10
K^+	0.07	0.04	0.05	0.08	n.d.	n.d.	n.d.	0.07	n.d.	n.d.	0.07	0.08	0.08
Ca^{++}	0.03	0.03	0.02	tr.	n.d.	n.d.	n.d.	0.13	n.d.	n.d.	0.01	0.06	0.02
Quartz	26	25	27	28	21	24	25	25	23	26	22	26	27
Feldspars	12	8	11	11	13	10	12	9	11	8	11	11	9
Calcite	22	22	17	16	23	19	16	19	18	18	22	17	17
Dolomite	7	8	8	8	9	8	8	9	9	8	9	9	9
Illite	21	26	26	26	22	25	26	25	26	26	24	24	26
Chlorite	6	6	6	5	7	7	6	7	7	7	6	6	6
Fe-oxides	3	3	4	4	3	4	4	3	4	4	4	4	4
Accessory	3	2	3	2	2	3	3	3	3	3	2	3	2

n.d. = not determined; tr. = traces

As the final phase phase of the experimental work, a semi-industrial test was carried out using an experiment a body prepared by employing the same raw materials, in the same proportions, used for a current industrial body, except for the use of the carbonatic clay under examinationa in place of a marly clay (sample A). The industrial body was suitable for the production of porous tiles through fast single firing ("monoporosa"). The composition of the two bodies is summarized in Tab. 3.

Dry grinding, pressing and drying of both the experimental and the industrial bodies were carried out in a pilot plant, while glazing and firing was realized in a production plant. The firing was carried out at 1080 °C with a 40 minutes long cycle; then an evaluation of the results was made by comparing the data for water absorption, dimensional variations and mechanical strength of the two products obtained.

Results and discussion

Raw material characterisation

All the clays taken into consideration show a quite uniform composition (Tab. 1).

From the chemical viewpoint, the samples are characterized by not elevated values of silica (42 - 49 %) and alumina (11 - 13 %); with the Al_2O_3/SiO_2 ratio is always within in the range 0.24 - 0.28. On the other hand, there are high concentrations of CaO (10.7 - 15.6 %) and considerable contents of iron (4.3 - 5 % total as Fe_2O_3), magnesium (2.7 - 3.7 MgO), and alkalies (2.3 - 2.6 K_2O; 0.8 - 1.7 Na_2O). Low but not negligible are the percentages of sulphur (0.06 - 0.21 % S) and fluorine (0.08 - 0.10 % F). In contrast to the main composition, the data relative to the soluble salts reveal themselves a little more inhomogeneous, in particular with reference to sulphur, chlorine and sodium. This could be at least partially due to the poor accuracy of sulphur and chlorine determination, but sodium analysis, which is much more precise and reliable, confirms the differences.

As regards the mineral composition, both X-ray diffractograms and thermal analyses show that the samples are constituted by clay minerals, quartz, calcite, feldspars (Na-plagioclase), dolomite, and poorly crystalline iron oxides or hydroxides, in approximate order of abundance. As far as the clay minerals are concerned, illite (and randomly interstratified I/S terms) is largely prevalent on chlorite, while kaolinite and smectite seem to be present only in traces. Rational mineralogical data confirm the qualitative indications deduced from the diffractograms: quartz 21 - 28 %, illite 21 - 26 %, calcite 17 - 23 %, dolomite 7 - 9 %. This composition is consistent with that of clayey marls.

Grain size distribution of the samples (Fig. 2) is rather constant and characteristic for silty clays; in fact, the clay fraction (> 4 μm) prevails on the silt portion (4 - 64 μm), while sand component (< 64 μm) is always negligible. It has to be stressed the thinness of these clays, which show an average particle diameter around 3 μm and a fraction less than 2 μm as high as 40 - 50 %; this will yield a plastic behaviour in presence of water. On the other hand, the absence of a significant amount of smectitic minerals will insure the body against possible difficulties during drying.

Technological behaviour

The technological properties of the 5 samples taken into account are at first sight similar and consistent with the usual behaviour of carbonate-bearing ceramic raw materials (Tab. 2). But, because the properties are the consequence of the combination of all the mineralogical, chemical and physical characteristics of the raw materials, in detail some interesting differences can be evidenced from one sample to another. The fired clays experimented are characterized by limited dimensional variations, always comprised in the range 0.7 % (Fig. 3), but it is possible to individuate two groups of samples with a different behaviour when the temperature increases. Samples 1, 2 and 3 show an expansion from 960 to 1040 °C then the dimensions remain practically constant. Samples 9 and A present an analogous trend up to 1000 °C, while the dimensions clearly decrease from 1000 °C to 1040 °C. It cannot be excluded that the different behaviour of the two groups of samples depends on the diverse humidity of the pressed powders, other than the physico-chemical characteristics of the clays; in fact it was about 7 % in the samples 9 and A, and about 6 % in the samples 1, 2 and 3.

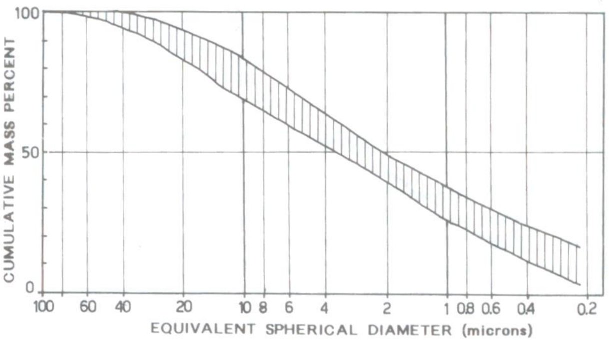

Fig. 2. Range of variation of the grain size distribution of the clay samples.

Table 2: Technological properties of the fired clay samples.

Samples No.		Temperature [°C]					
		960	1000	1040	1060	1080	1100
Dimensional variations (%)	1	+0.0	+0.3	+0.6	+0.5	+0.7	+0.5
	2	-0.2	+0.1	+0.4	+0.2	+0.3	+0.2
	3	-0.2	+0.2	+0.4	+0.2	+0.3	+0.2
	9	-0.3	+0.1	-0.2	-0.1	-0.5	n.da.
	A	-0.5	-0.1	-0.2	-0.3	-0.5	-0.5
Water absorption (%)	1	17.4	17.9	17.7	18.7	17.9	17.1
	2	20.0	19.8	21.1	21.2	22.2	21.7
	3	23.0	23.3	24.1	24.1	24.2	24.2
	9	17.5	18.9	20.8	20.9	19.6	16.1
	A	n.d.	20.3	21.9	21.6	21.8	21.0
Bending strenght (*MPa*)	1	17.7	18.3	18.2	18.4	22.8	24.8
	2	21.0	20.9	20.2	22.9	29.2	28.3
	3	19.8	23.2	24.2	22.7	25.5	30.6
	9	24.6	24.1	27.6	28.3	29.1	n.da.
	A	n.d.	29.4	27.3	27.4	30.8	32.8

n.d. = not determined; n.da. = not determinable.

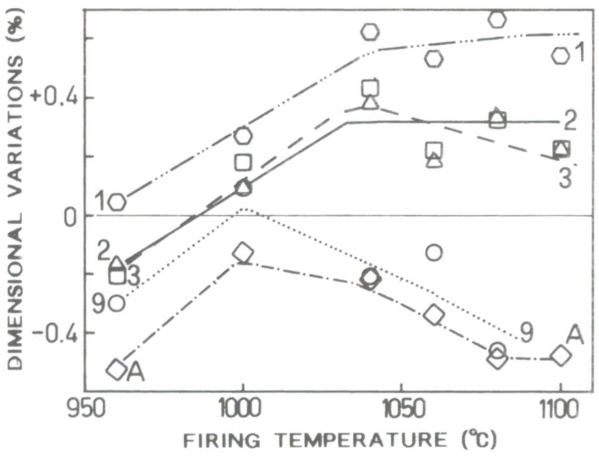

Fig. 3. Dimensional variations of the fired samples.

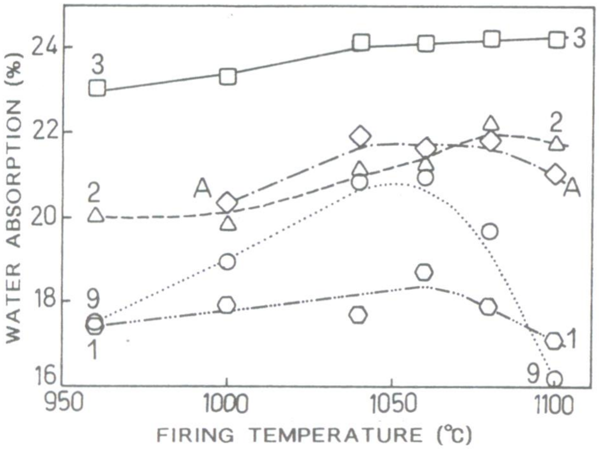

Fig. 4. Water absorption of the fired samples.

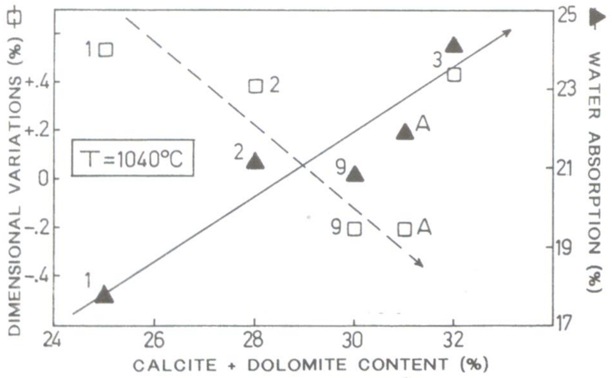

Fig. 5. Relationship between carbonate content of the clays and dimensional variations or water absorption of the fired samples.

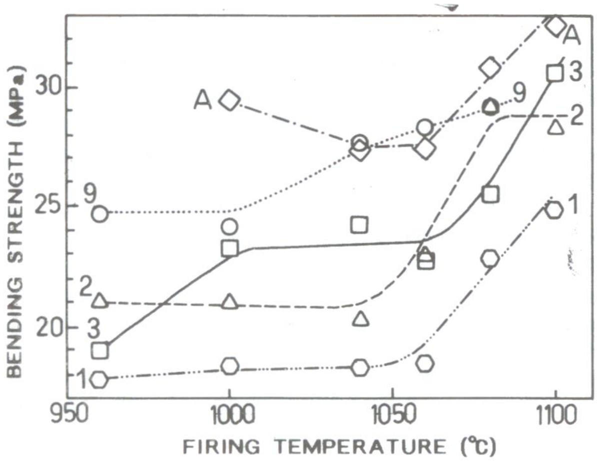

Fig. 6. Bending strength of the fired samples.

Table 3: Technological properties of the experimental and the industrial bodies.

	industrial body	experimental body
marly clay	25%	–
sample A	–	25%
badia clay	25%	25%
colombara sand	27%	27%
shaping moisture (%)	7.5	8.7
green bending strength (*MPa*)	1.9	1.3
water absorption (%)	17.7	18.9
shrinkage (%)	1.9	2.9
bending strength (*MPa*)	9.2	13.0

The water absorption seems to be little dependent on the temperature in the interval 960 - 1100 °*C*, so that it is quite constant for each sample (Fig. 4). In particular, it slightly increases up to about 1050 °*C*, then remains constant (samples 2 and 3) or decreases more or less slowly (sample 9 or samples 1 and A respectively). If we consider the restricted temperature range at which all the samples show quite constant water absorption and dimension, that is around 1040 °*C*, we can see a good direct correlation between the values of water absorption and the contents of calcite plus dolomite (Fig. 5). Furthermore, in the same fig., it can be seen that the dimension of the different samples decreases as the carbonate content increases.

Bending strength data, on the whole, are within in the range 18 - 33 *MPa*, with strong variations for both the different samples and the various firing temperatures. The lowest data are shown by sample 1 (from 17.7 to 24.8 *MPa*), while the highest ones were recorded by sample A (from 27.3 to 32.8 *MPa*), approximately depending on the carbonate content and the pressing moisture: the higher the carbonate content and the pressing moisture, the higher the mechanical strength. With reference to the firing conditions, the bending strength tends to be constant up to about 1050°*C* and rapidly increasing for the higher temperatures (Fig. 6).

Semi-industrial test

On the ground of the above-mentioned technological properties, sample A was selected for the industrial test, since it is characterized by the highest bending strenth values as well as intermediate values of water absorption and dimensional variations.

The results obtained after the semi-industrial test are a bit far from the current parameters of "monoporosa" tiles for both the industrial and the experimental bodies (Tab. 3). This is probably due to the different conditions of both body processing and tile shaping in pilot plant with respect to the industrial plant.

Notwithstanding this, the comparison of the technological properties of the two bodies points out just slight differences in the values of water absorption, shrinkage and bending strength. In particular, the experimental product seems to be worse with reference to shrinkage (2.9 versus 1.9 %) and porosity (18.9 % versus 17.7 % water absorption) if compared to the industrial tiles. On the other hand, the experimental product presents a much better bending strength (13.0 versus 9.2 *MPa*).

Conclusion

The clayey marls widely outcropping in the hillsides near Faenza (northern Italy) are characterized by quite uniform chemical and mineralogical composition as well as homogeneous grain size distribution. The contents of soluble salts and pollutant elements (S, F, Cl) are usual and tolerable for ceramic applications.

Technological tests carried out both in laboratory and in industrial plant highlight that these raw materials are perfectly suitable to be used in the production of porous tiles ("monoporosa") through the up-to-date fast single firing process. The amount of clayey marls that can be introduced into normal "monoporosa" bodies is estimated in 20 - 30 % wt. at maximum.

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References

Bertolani M., Fabbri B., Fiori C. & Loschi Ghittoni A. G., 1986: Influenza dell'evoluzione impiantistica sull'uso delle materie prime per la fabbricazione di piastrelle. *Ceramica Informazione*, 243, 333 - 336.

Biffi G., 1988: La tecnologia della monocottura porosa delle piastrelle ceramiche. *Ceramurgia*, 18 (3 - 4), 123 - 129.

Dondi L., Mostardini F. & Rizzini A., 1982: Lessico delle Formazioni del bacino padano orientale. In: Cremonini G. & Ricci Lucchi F. (Eds.): *Guida alla Geologia del margine appenninico-padano. Soc. Geol. Ital.*, 205 - 236.

Dondi M., Ercolani G., Fabbri B. & Vincenzi S., 1991: Possibilita di estrazione di argilla faentina per la produzione di maiolica ed impasti similari. *Ceramica Informazione*, 299, 97 - 102.

Fabbri B., 1992: Influence of the production cycle on the formulation and properties of bodies and glazes for "monoporosa" tiles. Proceedings of the conference "New technologies for the rational use of energy in the ceramic industry", Orléans, France, 20 - 22 May 1992, 255 - 263.

Fabbri B., Tateo F. & Vincenzi S., 1988: Rilevamento geo-litologico delle argille plio-pleistoceniche a monte di Faenza fra i fiumi Senio e Marzeno. *Ceramica Informazione*, 265, 220 - 227.