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CHARACTERISATION OF RAW MATERIALS FOR PRODUCTION OF CERAMICS

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The aim of this paper is to characterize some raw materials used for ceramics material production. Five samples of clay have been analyzed. It has been carried out a patterned sampling in a quarry in Rosarno (South Italy).

Chemical-physical properties on clay samples are determined. Test pieces have been prepared and physical properties after firing are determined by DSC thermal analysis, XRD analysis and X-ray fluorescence. It is important to note the high amount of Fe_2O_3. The mixture principally contains quartz, illite and oligoclase. It has been observed the colour and the shape after firing: predominant colour is red. In this case the clay has been used in mixtures covered with glazes. The colour of internal clay is hidden by opaque of glazes. The analysed raw materials can be used in a slip for single fired red tiles. The A2sp clay produces best ceramics at 1000°C.

Keywords: *ceramics, chemical-physical properties, raw materials*

Introduction

Human activities are always connected with the use of ceramic materials in everyday life. The Mesopotamian and Egyptian cultures know leakage technique. The Grecian culture used the clay purification technique to obtain slip. Arabian culture introduced in Mediterranean area and Europe the employment of tile [1]. Today it is difficult to define ceramics, because in this category are considered some kind of products obtained by manufacturing and firing of inorganic substances different from clay. But the best definition is: ceramic is considered any product having shape, formed by inorganic and not metallic raw materials, that from an incoherent powder is transformed by firing in a solid object with a partial crystalline and vitreous structure. It is important to define two kinds of ceramics: traditional ceramics and technical ceramics. In first category are included product obtained from natural oxides as, for example, tiles, bathroom products, dishes, bricks and some kinds of refractories. In the second category are not included the oxides and special oxides as bioceramics, technical and electric porcelains, electronic ceramics catalyses and special refractories. Albuquerque *et al*. evaluated a low cost tile clay mixed kaolin for use kaolin characterizing the mineral and thermal changes during sintering by differential thermal analysis, thermogravimetry, thermomechanical analysis and X-ray diffraction [2]. In 2004 Xavier *et al*. synthesised by the polymeric precursor method of ZrO_2-based inorganic pigments, doped with cation like Fe, Ni and others [3]. This study defines the chemical-physical properties of raw materials for traditional ceramics drown out from south Italian quarry. The materials subject to investigation were taken by a quarry located in Rosarno's territory. In particular the quarrying area collocated in a sub-level territorial sector to the North-East of Rosarno's historical centre, characterized by not elevated to low gradient, interested by Mésima river's overflow in the past.

The Rosarno's territory is in fact located in Mesina river's basin, important tectonic structure of centre-eastern Calabria, delimits between the Serre Massif to the East and the Mount Poro to the West by important faults probable due to tectonic structures of big size.

From geological point of view in Rosarno's territory diffusely crop out sedimentary deposits, collocated in discordant way on crystalline-metamorphic basement, related to a large continental plain (Fig. 1) [4].

In detail in the quarrying area crop up Quaternary's alluvial sediments in contact with Pliocenic's sediments, superimposed to crystalline basement that normally is possible to find to considerable depth [5].

The aim of this study is to define chemical-physical properties of a potential Italian raw material to produce traditional ceramics, using usual characterisation methods [6, 7].

Experimental

A systematic sampling has been performed, so that to represent the whole lithology present outcropping on the actual breakthrough. Five samples of clay were

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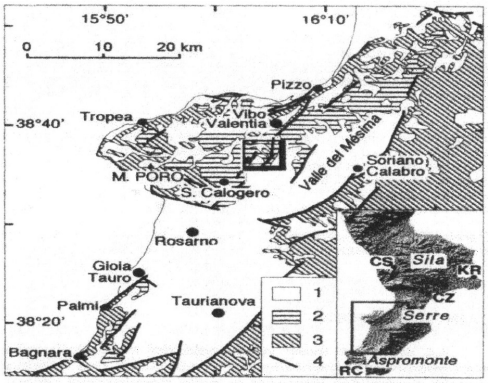

Fig. 1 Mésima basin's: simplified geological map. 1 – recent and pleistocenic deposits, 2 – miocenic and plio-pleistocenic deposits, 3 – crystalline basement, 4 – recent faults

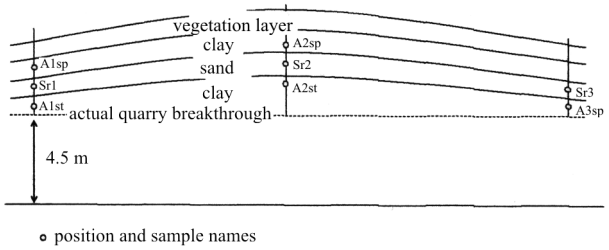

Fig. 2 Simplified scheme of position of samples in quarry

collected (A1sp, A1st, A2sp, A2st, A3sp) on which the characterisation has been carried out (Fig. 2).

Initially clay samples have been powdered and dried. They have been analyzed by X-ray diffraction (XRD), thermal analyses and X-ray fluorescence. The samples were identified by powder XRD on a Philips PW 1830 diffractometer using CuK_α radiation. The scanning speed was 0.02° s^{-1} in the 5–45° 2θ range. The thermal stability and the mass loss were determined by thermogravimetry, DTG, DSC using an STA 429 Netzsch instrument. The speed of temperature increase was 10°C min^{-1} in static air. The temperature range was 20–750°C. Subsequently the raw materials have been wetted (using different mass% of water – 5, 10 and 15 mass%) and sieved at 500 μm. Chemical analysis was carried out by an atomic absorption Shimadzu AA-660 spectrometer. The Si/Ti ratios were determined by EDS ZAF-4/FLS analysis.

To prepare the clay's test pieces has been used a laboratory press with a pressure of 250 and 300 bar. The size of test pieces obtained by dry pressing were 1 cm±0.1 of height and 2.6 cm± 0.1 of diameter. They have been fired at 900 and 1000°C for 2 h.

Results and discussion

Clays are composed of several phases, as we can see in Fig. 3. The diffractograms present the phases in clay. The mixture principally contains quartz (Qz),

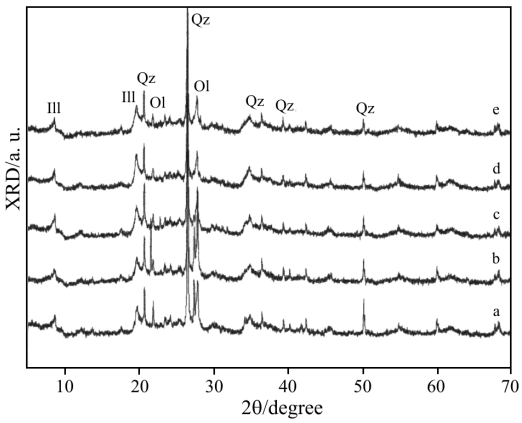

Fig. 3 XRD spectra of different clays collected and used to produce the tests pieces. a – A1sp, b – A1st, c – A2sp, d – A2st and e – A3sp

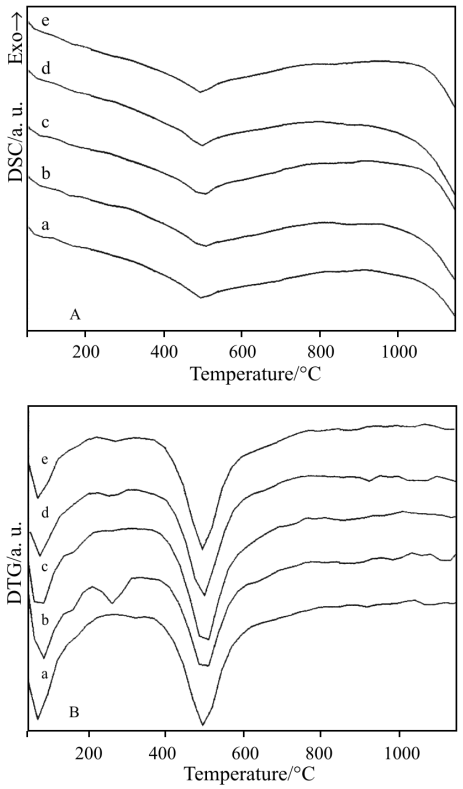

Fig. 4 A – DSC and B – DTG curves of clays used: a – A1sp, b – A1st, c – A2sp, d – A2st and e – A3sp

illite (Ill), and oligoclase (Ol). The diffractometric analyses highlight the illite phase have a basal refraction at about 10 Å (corresponding to 8.7455° 2θ). The XRD patterns does not show impurities in clays, but it is necessary to use additives.

Figure 4 shows the DSC and DTG curves of samples of clay collected. The endothermic peaks at 100 and 500°C are well evident (Fig. 4A). They are respectively correlated with DTG peaks ranging between 66.6 and 77.4°C, due to the loss of interlay water (first peak of DTG curve at 100°C) and the second ranging

Table 1 Chemical composition of several clay samples taken by a quarry located in Rosarno's territory

Clay samples	SiO_2	Na_2O	K_2O	SO	CaO	Fe_2O_3	MgO	TiO_2	Al_2O_3	L.O.I.*
A1sp	50.84	1.17	4.76	2.57	0.98	7.68	3.75	1.29	21.40	5.57
A2sp	59.10	0.00	4.27	0.00	0.50	5.69	1.90	0.58	22.09	5.88
A3sp	53.26	2.05	3.16	0.95	1.14	9.97	2.49	1.12	20.70	5.17
A1st	51.06	1.91	3.14	3.52	1.31	9.64	2.19	1.33	19.99	5.93
A2st	52.00	3.05	2.97	2.95	1.24	10.33	1.55	1.09	19.47	5.35

*L.O.I.=loss of ignition

Table 2 Shrinkage values in drying and after firing (900 and 1000°C)

Sample name and moisture percentage	Shrinkage after firing		
	in drying	900°C	1000°C
A1st 5%	0.28	4.95	7.82
A1st 10%	1.39	3.45	7.94
A1st 15%	1.57	3.47	8.08
A2st 5%	1.22	3.54	9.48
A2st 10%	1.95	2.43	7.43
A2st 15%	1.88	2.51	8.36
A1sp 5%	0.58	2.33	5.06
A1sp 10%	1.70	0.78	3.75
A1sp 15%	1.96	0.90	7.00
A2sp 5%	0.98	3.97	8.74
A2sp 10%	1.92	2.38	7.70
A2sp 15%	1.89	3.44	9.00
A3sp 5%	0.94	3.33	8.36
A3sp 10%	1.30	2.13	7.46
A3sp 15%	1.76	1.89	7.09

Table 3 Water absorption of several samples fired at different temperatures

Sample name and moisture percentage	Water absorption after firing/%	
	900°C	1000°C
A1st 5%	9.77	0.79
A1st 10%	7.67	0.12
A1st 15%	11.00	0.62
A2st 5%	11.83	0.80
A2st 10%	10.02	0.47
A2st 15%	13.29	1.95
A1sp 5%	9.66	1.14
A1sp 10%	8.49	1.18
A1sp 15%	10.90	2.79
A2sp 5%	10.36	0.58
A2sp 10%	8.46	0.12
A2sp 15%	9.23	0.63
A3sp 5%	10.41	3.88
A3sp 10%	8.78	2.59
A3sp 15%	12.83	4.45

between 493.5 and 498.2°C that of dehydroxylation (second peak of DTG curve at 500°C) of clay 'matrix' of the samples. DTG curve b (Fig. 4B) presents an evident peak at 261.5°C due to probable impurity traces. These phases are below 5%, because it is not possible to note them in XRD patterns (Fig. 3). At ca. 1150°C, it can be noted an endothermic peak due to an initial melt. This phenomenon does not permit to use the materials as refractory material. The low melting temperature is due to presence of alkalines and alkaline-earths as silicates and not as carbonates. It can also see in DTG curves in which it is not present the thermal effects of carbonates.

Table 1 presents the chemical composition of different clays used to form the test pieces. It is important to note the high amount of Fe_2O_3. The Si content is between 50.84 (A1sp) and 59.10 (A2sp) and Al content is between 19.47 (A2st) and 22.09 (A2sp). Besides Mg and K are present at about 3 mass% in all clay types. While Na and Ca have low composition of about 1 mass%.

Table 2 presents the percentage shrinkage in drying and linear shrinkage after firing obtained at 250 bar and 900°C. The content of water of slip affects the shrinkage in drying. Indeed, this shrinkage increases as function of water amount in wet pieces. The shrinkage after firing is in the range 4.95–0.78. The results of shrinkage at 1000°C (and 250 bar) are very interesting. The shrinkage after firing values are greater than those made at 900°C. This behaviour is due to a vitrification effect at 1000°C [8].

Table 3 shows the water absorption of the pieces obtained at 250 bar, 900 and 1000°C. The fired test pieces, weighed, are in water and boiled for 2 h: they are left to cool for 4 h always submerged in the same water and then, once properly dried, are reweighed.

The behaviour of samples is very different as a function of firing temperature. The test pieces fired at 1000°C show a smaller water absorption than those obtained at 900°C. The higher values of samples fired at 1000°C are obtained with A3sp. The high shrinkage values after firing at 1000°C can lead to pyroplastic deformations, deterioration and technical characteristic of ceramic glazes during the production of tiles. This possibility must be considered to produce a good tile with the raw materials used in the study. The optimal firing temperature seems to be at 1000°C. Indeed, this temperature value causes a strong vitrification effect in the test pieces. The phenomenon is very important to produce good quality tiles.

Conclusions

The analysed raw materials can be used in a slip for single fired red tiles. The clays have similar chemical-physical characteristics. The optimal firing temperture is 1000°C. Their behaviour during the firing is the same. Although the A2sp clay produces best ceramics. The slip produced can be formed by these kinds of clay up to 40–45 mass%. It is necessary to find kaolinite to add in the slip up to 10–15%. The conditions to produce tiles exist with a water absorption lower than 3%. These results will be verified with industrial tests.

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