Ceramics - Materials and Ceramic Pastes

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Abstract: *In this article are presented the study of the chemical composition of pastes and ceramic dyes. This study includes types of clays, properties of calcareous and siliceous clays and the preparation of ceramic masses. The study was carried out using clay from the Dobrogea area, more precisely from the Medgidia quarry. The research used specific equipment and various mixing processes (wet and dry) with the aim of obtaining a homogeneous dispersed system, with a controlled granulation, necessary in the shaping process and in accessing the texture and final composition of the material. The study of the chemical composition of ceramic paste and dyes, the use of thermoluminescence for chronological dating, the restoration of the technological process through experimental archeology, all served the researchers in discovering new analysis criteria regarding the structure of ceramic paste, modeling, finishing, decorating and firing techniques.*

Key-words: *ceramic; materials; pastes; clay; degreaser; oxides; mill*

1. Introduction

The research of ceramic pastes, without taking into account the chronological periods in which they were made, tends to materialize in a distinct study discipline, called ceramology. The study of the chemical composition of ceramic paste and dyes, the use of thermoluminescence for chronological dating, the restoration of the technological process through experimental archeology, all served the researchers in discovering new analysis criteria regarding the structure of ceramic paste, modelling, finishing, decorating and firing techniques.

2. Objectives

The purpose of this research work is to find a method for preparing clays from Dobrogea quarries, which would allow obtaining a ceramic paste used in pottery activities, and more.

Using clay from the Dobrogea area, more precisely from the Medgidia quarry, the study of the chemical composition of ceramic paste and dyes, the use of thermoluminescence for chronological dating, the restoration of the technological process through experimental archeology, all served the researchers in discovering new analysis criteria regarding the structure of ceramic paste, modelling, finishing, decorating and firing techniques.

3. Material and Methods

Ceramic products can consist of:

- chemical elements (carbon - C, silicon - Si)
- chemical compounds - oxide or non-oxides (carbides, borons, nitrides, silicides)

Oxides from group I of the periodic table of elements – Li_2O, Na_2O, K_2O - are fluxes (they have a melting temperature below 1000^0 C and are used to lower the firing temperature

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in ceramic masses). Those in groups II, III and IV melt at much higher temperatures and are therefore used either alone or in combination, to obtain ceramic and refractory masses:

• group II: CaO, MgO, BaO, SrO
• group III: Al_2O_3, Cr_2O_3
• group IV: SiO_2, ZrO_2, TiO_2, CeO_2, ThO_2, UO_2

SiO_2 (silicon) is a very important oxide because it is the starting point for the class of natural and artificial silicates (anhydrous, hydrated).[2]

Regarding the defining characteristics of the paste, there was a wide variation of its shade and texture due to the multitude of offices (many of them operating as branches of the parent workshops in Arretium) spread over a fairly large geographical area. Following these researches of the defining characteristics of the ceramic paste, in terms of its hue and texture, several series with different attributes of them have been established in the literature.

d. Types of clays

Clays commonly used in the manufacture of ceramics can be classified into three groups:

• calcareous clays - these are clays with a percentage of lime between 6 and 25%; there are clays with a higher limestone content, but they are generally unsuitable for the manufacture of ceramics;

• siliceous or non-calcareous clays - these are clays whose percentage of lime is between 0 and 6%;

• kaolin clays - a variety of siliceous clay, which offers the peculiarity of presenting in very small quantities of fluxes (potassium, iron, manganese), which makes it a very good refractory soil; the absence or very small amount of iron oxide gives it, when burned, a characteristic white colour.

Kaolin clays have certain advantages over others. They are especially suitable for the manufacture of culinary ceramics because they combine resistance to thermal as well as mechanical shocks.[3]

e. Properties of calcareous and siliceous clays

The main disadvantage of calcareous clays is the formation of limestone stains. At a certain temperature (approximately 700° C), the calcareous grains are transformed into lime, as a result of the chemical reaction $Ca0_3$> CaO + CO_2. However, after cooling, the lime present in the soil is transformed into calcium, absorbing moisture from the air.[4] This transformation is accompanied by an increase in volume which causes the dough to break into the ceramic mass. This disadvantage can be remedied in two ways: “by burning the pottery at a temperature lower than the formation of limestone stains or higher than 900^0 C. Indeed, at over 900^0 C, this lime is combined with other elements to silicate form that remain stable.”[5]

f. Preparation of ceramic masses

Before the modelling operation, the clay must be prepared very carefully in order to be processed. Thus, the elaboration of the ceramic paste involves several operations. The most common cycle is as follows:

- clay extraction in the quarry;
- drying (removal of moisture from the soil);

[2] V. Burghelea and A. Melinescu. 2002. *Tehnologia Produselor Ceramice si Refractare*, Bucureşti: Arvin, p. 47.
[3] Guggenheim & Martin. 1995. *op. cit.*, pp. 255 - 256.
[4] V. Mutihac, M. Stratulat and R. Fechet. 2004. *Geologia României*. Bucureşti: Editura Tehnică, p. 242.
[5] M. Picon. 1992. *Ethnoarchéologie et recherches en laboratoire, le cas des techniques céramiques.*In *Ethnoarchéologie, justification, problèmes, limites, XIIe Rencontres Internationales d'Archéologie et d'Histoire d'Antibes*, Juan-les-Pins: Audouze, pp. 115 - 126.

- crushing and grinding - this operation is intended to separate the pulses and facilitate the following operations;
- sieving (optional) - to remove excess impurities or degreaser;
- soaking or mixing - the clay powder is diluted in pits or basins filled with water;
- extraction - the clay is extracted from the basin and allowed to dry to remove excess water;
- leavening - the soil is left to rest in a cool place for a period of time, which can vary from a few weeks to a few months, even a few years;
- kneading - the clay extracted from the basin is trampled, progressing in a spiral;
- manual cutting - designed to homogenize the clay paste and remove air bubbles.

To remove excess degreaser, in case of too weak or too coarse clay, the material is washed. One method is to mix the dried clay in water to form a highly liquid paste that passes through two or more containers, communicating with each other. Gravity through the sieve collects the finest particles from the lower basket, while the excessive degreaser is in the first container. The same process is also used to prepare angobe.

g. Adding degreaser

The addition of degreaser is common for vessels used for combustion. It is most often taken near workshops, but there are also cases when it is transported over medium or long distances (this is the case of the micaceous degreaser of Marseille amphorae, produced between the 6th and 2nd centuries BC). "The addition of the degreaser changes the petrographic characteristics and the chemical composition of the clay. This is important information that must be taken into account when researching the initial determination."[6]

Returning to the topic of this topic, for the preparation of the ceramic paste I used clay from the Dobrogea area, more precisely from the Medgidia quarry. Through specific operations for clay processing, we made a mass called composition, having the appropriate granulation and homogenization for the chosen shaping process, as well as the texture that the ceramic mass must acquire after heat treatment.

Fig. 1. *Medgidia Career*

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[6] M. Picon. 1986. *Les transports d'argile ou de dégraissant et la détermination en laboratoire de l'origine des céramiques.* Archéologie du Midi Méditerranéen. Valbonne: Centre D`Archeologie Medievale du Ganguedoc, pp. 37-44.

The prepared ceramic mass is considered homogeneous when, being composed of a dispersed system, the phases of the mass become equally dispersed (mix homogeneously) or have a homogeneous granulation.

The processing operations of the raw materials (sorting, crushing, grading, etc.) of homogenization of the components and of the formation of fluid masses (slips), plastics (pastes) or granules, take place in the first stage of preparation of the ceramic mass.[7]

All these operations aim at obtaining a homogeneous dispersed system, with a controlled granulation, necessary in the shaping process and in the access to the texture and the final composition of the material. The degree of dispersion required for the raw materials is obtained by crushing operations.

To obtain objects that have a fine texture, they must be made of clay that contains granules of the order of 0-0,2 mm or smaller. The crushing of the ceramic mass can be done dry or wet. The equipment used to grind the material is chosen depending on the size and hardness of the granules to be obtained.

After the crushing operation, the material is sorted and sorted. Classification is the separation of polydisperse solids into particle size fractions (classes). The sorting process consists in eliminating the unwanted phases. Usually, the grinding process results in granules that differ in shape and size. In order to determine the particle characteristics of a dispersed system, their weight and equivalent diameter are considered to be representative quantities. When the shape of the granules is very far from the spherical one, the equivalent diameter is no longer representative. The particle size distribution, the proportion of particles with certain dimensions (particle size fractions), is an important characteristic of the polydisperse solid. The polydisperse solid has a certain volume of voids that depends on the proportion of monodisperse particles, the particle size distribution, as well as the ratio between the largest and smallest particles. The smaller component decreases the number of voids corresponding to the ratio of small and large particle size. Dispersed raw materials can be mixed and homogenized as fluid, plastic or granular systems. There are two ways in which raw materials can be subjected to the combination process: dry and wet.

Depending on the proportion of solid phase, dispersed systems may be classified as follows:

- systems with fluid conduct (slips)
- systems with plastic conduct (paste);
- granular masses.

If in the mixing process, the degree of dispersion is high, the gravitational force or the one coming from the process itself is annihilated by the cohesive forces and the mass agglomerates itself. The preparation of the ceramic mass can be done by the wet or dry process. The wet process involves the following operations: wet crushing of non-plastic components and thinning (wet crushing) of plastic components, dosing, wet homogenization, separation of the liquid phase by filtration or atomization, maceration, deaeration. Through the procedure wet ensures the exact control of the dosage of the components, a better fineness and a better homogenization of the raw materials.

[7] R. Cahn and E. Lifshin.1993. *Concise Encyclopedia of Materials Characterization*, Oxford: Pergamon Press, p. 641.

Fig. 2. *Ball mill*

Fig. 3. *Mixer*

The preparation of the material by the dry process involves the operations of crushing the degreasing and plastic components using a ball mill, then their dosing, wetting, homogenization in mixers and their maceration. Comparing the wet process with the dry one, the latter requires fewer operations, less complex equipment and less space. The control of the dosage of the materials is instead more deficient because their natural humidity (3-13%) is a more difficult parameter to control.

In order to obtain a fine crushing of the materials, rotary drum mills and grinding bodies are used. The material is crushed with the help of rollers, then the dilution is performed (disintegration in water), in vessels provided with stirrers. The mixture is then passed through a sieve with a mesh size of 0.06 mm and deferred, to be dosed for homogenization. The dosing of the mixture can be done volumetrically or gravimetrically depending on the literal weight.

Homogenization is performed in mixing vessels provided with paddle or helical stirrers. After the homogenization process, the mixture is passed through a sieve, and the magnetic referencing follows, the impurities are screened so as not to be found in the ceramic paste.

Dehydration is the process of removing some of the water that is in the mixture. Water removal can be done either mechanically - by filtration, or thermally - by evaporation, or electrically - by electrophoresis.[8]

Fermentation is the process by which the paste resulting from the processes described above is kept for a time in a humid environment. During this maceration period, the material undergoes metamorphoses of substance, necessary to increase the plasticity of the mass. After dehydration and maceration, the raw mass obtained is aerated and contains a certain percentage of moisture. For these reasons, the operation of homogenization and deaeration performed with the help of mixers or vacuum presses is necessary.

[8] R. J. Brook. *1999. Processing of Ceramics* - part 1, New-York: V.C.H, p. 56.

Fig.4. *Filter press*

Fig. 5. *Extruder*

Fig. 6. *Clay slabs*

4. Results and Discussions

The experimental results obtained can be used to establish general principles regarding the production of ceramics in Dobrogea.

The experiment showed that the ceramic produced from local clay (Dobrogea) does not require a combustion temperature greater than 950-1000 ° C, with a burning time of 14-15 hours. As some researchers have already shown, a higher temperature and a prolonged burning time can have negative effects on clay.

Regarding the surface of the objects created experimentally, it can be stated that the

firing temperature had no influence on the decoration used or on the colour of the objects.

5. Conclusions

Following the study carried out on the clays from Dobrogea, it can be concluded that using a mixture of several types of clay (sandy clays and clays with a high degree of plasticity) a ceramic paste can be obtained that can be used in pottery and in artistic creation, which has as vitrification point 1100^0 C.

As expected, for an oxidizing combustion around 1000˚C, even if the raw material comes from different sources, there are no visible colour differences from one sample to another. The different shades of red were the result of the raw materials used, because it is known that the clay used in the production of ceramics has different qualities, depending on the composition and the mineralogical characteristics.

It should be noted that the surfaces of the objects exposed to the oxidation burn did not obtain a uniform red-brick hue. This aspect was related to the positioning of the vessels in the combustion chamber and their direct contact with the flame.

All the technological information, together with the results of the chemical analyzes of the ceramic pastes, helped to outline the identification of the operative stages specific to the field of ceramics.

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