RESEARCHES BASED ON THE RECYCLING OF SLUDGE IN SFÂNTU-GHEORGHE (COUNTY COVASNA)

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Recycling seems to be one of the most important element/ possibilities in finding a solution to the removal of residues from the environment. There is a great benefit in using these wastes, such as the sewage sludge used as a cheap and accessible raw material in the ceramics industry. In order to obtain raw ceramic masses, there were made mixtures from clay and sludge. This paper outlines the results of these analyses.

Keywords: sewage sludge, recycling sludge, Bodoc clay, raw ceramics

1. Introduction

Legislation concerning waste management foresees the reduction of biodegradable waste disposal through storage. As such, the disposal of unstable sludge on hazardous waste landfills will not be allowed anymore.

Sludge resulting from wastewater treatment could be used in agriculture (taking into account their predominant organic nature) unless they put the quality of the soil and that of the crops in danger. In order to be used as fertilizer in agriculture, the sludge acquired through certain probiotic solutions of wastewater treatment plants has to fulfill the conditions defined under the common agreement nr. 344/708/2004 made by the Ministry of Environment and Forests and the Ministry of Agriculture and Rural Development, and to obtain a license permitting its use in agriculture. [1]

In case the quality of the sludge at the treatment plant is not suitable for agricultural use, the plant has to find other ways to eliminate it. All types of energy recovery such as: co-incineration at cement plants, burning of fuel or fluidized bed incineration, need a calorific value that can be provided by sludge [2].

Sludge resulting from wastewater treatment has a water percentage of 97%. This percentage can be lowered to 70-80 % by the filtration of water or by centrifugal dewatering. Sludge draining is a prerequisite for easier transport and for either a possible storage or disposal.

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These days the sludge resulting from the wastewater treatment plants in the region is eliminated/transported to already existing landfills, therefore we cannot talk about their treatment or recycling, not even as fertilizer in agriculture.

The only exception is the sludge coming from the Sfantu-Gheorghe wastewater treatment plant which undergoes a sludge draining process, through a wet sludge concentrator and biogas producer, and it is used as a thermal energy source [3].

The subject of use of sludge resulting from wastewater treatment plants has been dealt with in recent articles [4, 5].

The partial use/employment of wastewater sludge in raw ceramics represents another possibility for its use [6-8].

An analysis of sludge management strategies indicates the best possible options in the short, medium and long sludge management for development regions and counties within the proposed county sludge management strategies presented in table 1.

Table 1

Sludge use	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R8**
Agriculture	x	x	x	x	x	x	x	x
Co-incineration	x	x	x	x	x	x	x	x
From landfills	x		x		x		x	
Prevent pollution of surface	x	x	x	x	x	x	x	x

R1 - R7- development regions of the country, R8 - Bucharest

2. Experimental

There were made mixtures of clay and sludge corresponding to some building ceramics masses. The sludge addition was of 7 and 20 gravimetric percent. Five samples were made for each determination, then made a average measurements.

The chemical, oxide composition of the clay is determined according to SR EN 771-1:2003/A1:2005.

The chemical, oxide analysis of wastewater sludge was determined according to STAS 9163-1:73. The chemical composition of the clay and sewage sludge was obtained by using the classical wet chemistry method, the main oxides being quantified.

The oxide compositions of the Bodoc clay and of the purification sludge made according to the previous standards are presented in table 2.

From the table it is found that the two materials containing seven common oxides.

In clay first three oxides decrease from silica (about 68%) in alumina (15%) and iron trioxide (about 5%) and loss on ignition at 1000ºC is under 4%. Instead, sewage sludge has a very high loss on ignition (over 62%), and most important oxides are silica (14%) and calcite (13%) followed by alumina (4%).

Table 2

%	Reference sample	
	Clay	**Sewage sludge**
SiO_2	67.97	14.06
Al_2O_3	15.41	3.97
Fe_2O_3	4.88	1.43
CaO	1.66	13.32
MgO	1.59	0.73
K_2O	2.43	-
Na_2O	1.54	0.87
L.O.I.	3.58	62.24

The mineralogical composition of the fired clays and sewage sludge was also investigated by XRD.

The mineralogical analysis of the clay was performed by a diffractometer DRON-3 with the radiation Cu-Kα, and a wave length λ=1.54056Å. A Ni filter was used in order to filter the Kβ component of the radiation. The angle of the scanned sample was 2θ = 11-70°, the angular pitch 0.02° and count time 3sec/pitch.

Bodoc type clay is illite, strongly contaminated with degreasers (quartz, plagioclase feldspar, hematite, muscovite). Calcium carbonate cannot be identified as below the detection limit of X-ray diffraction method.

Mineralogical analysis of sewage sludge by X-ray diffraction, like the clay of Bodoc.

The sludge contains alike oxides as the Bodoc clay, as it can be seen from the mineralogical analyses in Fig. 2, namely α-quartz, plagioclase feldspar and muscovite (small white).

Beta radiation activity was examined by using a UMO LB123. It can be used as monitor of contamination (contamino meter) to detect and measure alpha and beta contamination. Device with which to work is one type of detector counting tube alpha-beta counter LB 1232 with counter filled with butane.

The value of sludge radioactivity is 662.884 Bq/kg [9]. The legal limit for building materials in Romania is determined by the Order of the Ministry of Health nr. 51/1983 [10] and allows a maximum of 832.50 Bq/kg. As a result the wastewater sludge used as raw material in manufacturing building ceramics does not represent any danger of radioactive contamination.

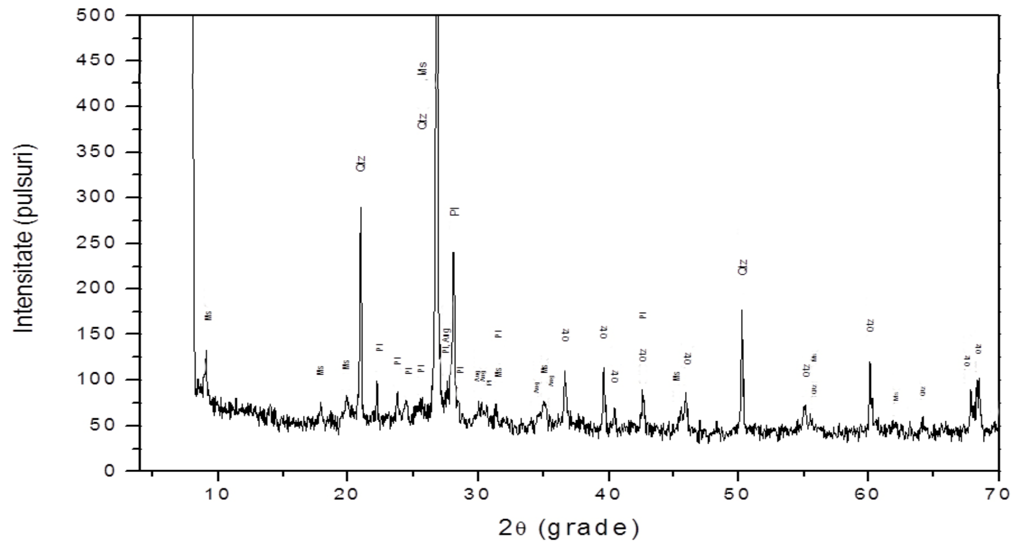

Fig. 1. –XRD spectrum of clay

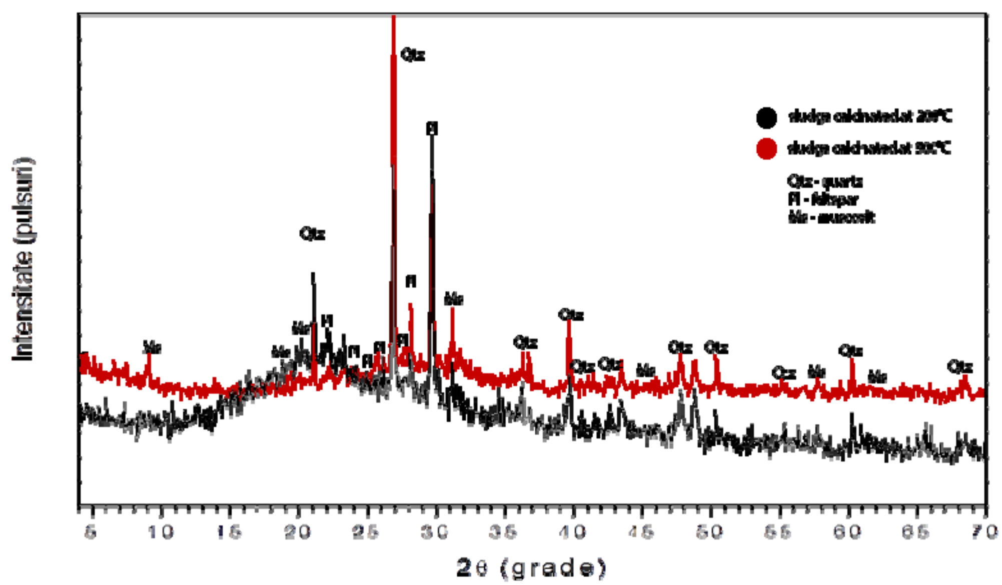

Fig.2 –X-ray diffraction pattern of calcinated sludge at 200 ºC and 500ºC

A Nikon Eclipse E-200 Microscope with polarized light was used in optical microscope analysis. The test specimens (thin sections < 25 μm thick) were analysed by transmitted light optical microscopy on a Nikon Eclipse E200 polarising microscope.

If such raw materials and polycrystalline ceramics with randomly oriented minerals to nicoli cross (N+) examination, the polished samples without appeal, to obtain the image microstructure.

The optical microscopy's in polarized light of the clay confirms the data of the roentgen analyses, Fig. 3.

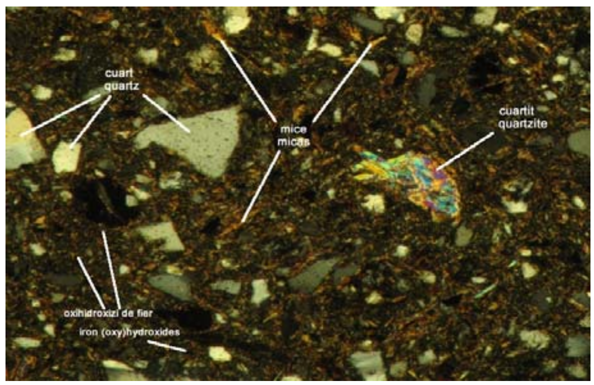

Fig. 3. Microscopic aspect of unburned clay
(photo scale 8 mm = 0,1 mm real, N+, 80 x)

In this way quartz and feldspar crystals can be revealed as dominant minerals and argillaceous ones.
The chemical components of the researched samples are presented in table 3.

Table 3.

Chemical composition of materials

%	Sludge mixtures	
	7%	20%
SiO_2	64.07	60.42
Al_2O_3	14.09	13.76
Fe_2O_3	4.49	4.01
CaO	2.67	1.84
MgO	1.92	2.28
K_2O	1.49	1.07
Na_2O	1.67	1.23
L.O.I..	6.69	13.73

The compatibility of the two types of raw materials – the clay from Bodoc and the wastewater sludge—is reflected in these chemical compounds of the obtained ceramic mixtures.

3. Results and discussion

The mixtures were thermal treated for an hour at maximum temperatures 960, 1050 and 1100°C. The fired samples were characterized from the point of the physical and mechanical properties (mechanical resistance, density, porosity).

The apparent density, water absorption and apparent porosity (compactness properties) of the mixtures were determined according to STAS 125-87.

The compression strength, when analyzing brick properties according to SR EN 771/1-2003, has been determined on a batch of five bricks. The average of properties has a value of 8.37 N/mm^2. The sample bricks have the following description: type 63, brand 75 and class C3, quality A, according to STAS 457/86. The values describing the physical characteristics (apparent density, water absorption, apparent porosity) and mechanical properties (compressive strength, bending strength) of samples fired at 960, 1050 and 1100°C are shown in table 4.

Tabel 4.

Physical characteristics of clay and sludge samples (7 and 20%) at different firing temperatures

Firing temperature [°C]	Sample nr.	Sludge [%]	Apparent density [g/cm³]	Water absorbtion [%]	Apparent porosity [% vol.]	Mechanical strength [MPa]	
						Rc	Rî
960	1	0	1.96	13.84	27.11	31.60	6.63
	2	7	1.90	15.22	28.99	28.85	6.11
	3	20	1.78	18.29	32.48	22.60	5.74
1050	1	0	2.47	8.11	20.03	38.50	8.75
	2	7	2.17	12.05	26.15	35.30	8.56
	3	20	1.72	16.53	28.43	27.10	5.78
1100	1	0	2.58	6.15	15.86	39.70	8.52
	2	7	2.18	11.77	25.65	37.20	-
	3	20	1.87	14.33	26.79	30.10	5.97

As it was expected (table 3) the increasing of the burning temperature favored the densification of the samples and their mechanic resistance properties.

The increasing of the proportion of the mud from 7 to 20% has a little influence on the decreasing of the mechanical resistance, together with the increasing of the burning temperature.

Compactness characteristics (water absorption, apparent porosity) increase while apparent density decreases as the percentage of added sludge is increased. There is a close connection between these properties. As such, a lower density of the samples brings about a higher porosity ratio as a result of greater water absorption.

The same phenomenon can be observed when the firing temperature of the mixtures is increased. Mechanical strength decreases as soon as the percentage of the added sludge is increased.

The increase of firing temperature leads to an increase of the sample's density at the same percentage of added sludge. At the same time crystalline compounds are formed in increasing proportion: either the same compounds or different types of compounds (also called as significant crystallisation).

This implies that in case of similar structures overlapping diffraction patterns appear, the same applies for two or more clay minerals.

Roentgenographic analysis highlights the existence of the following minerals in high quantities:

- Quartz SiO_2
- Feldspar plagioclase

  -albite $(Na,Ca)Al(Si,Al)_3O_8$,

  - anorthite sodian $(Ca,Na)(Si,Al)_4O_8$
- Hematite Fe_2O_3
- Augite $Ca(Mg,Fe)Si_2O_6$ (clinopiroxenes group)
- Muscovite-3T $(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$

A comparison in the mineralogical structure of the samples fired at 960 °C/1 hour does not show a significant change even if the temperature was increased to 1000 °C-Fig. 4.

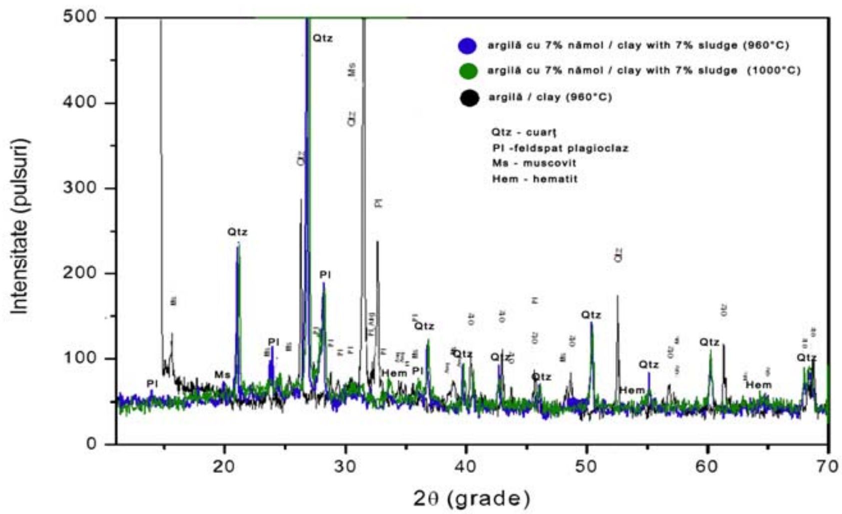

Fig. 4. The XRD spectra for clay and clay with 7 % sludge fired

The microscope images in Fig .5-8 show the followings:

- the transformation of minerals gained by rising the temperature,
- quartz with crown reaction, diffusion of iron in melt,
- decreases the micelles birefringence with temperature increase, thus demonstrating the beginning of transformation and melting.

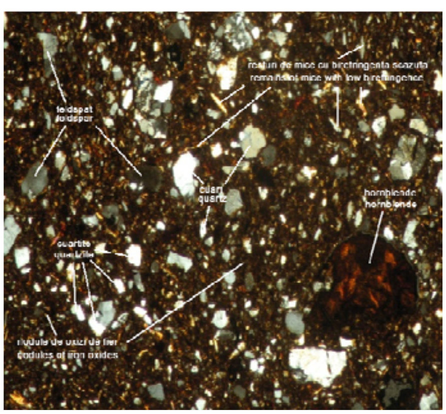

Fig. 5 Microscopic aspect of burned clay at 960°C

(photo scale 8 mm = 0,1 mm real) (N+, 80 x)

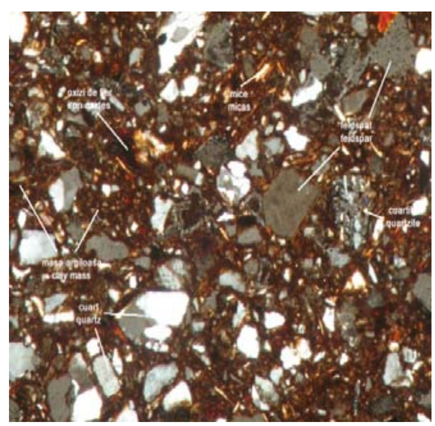

Fig. 7. Microscopic aspect of clay with 7% sludge burned at 1050°C

(photo scale 7 mm = 0,1 mm real) (N+, 70 x)

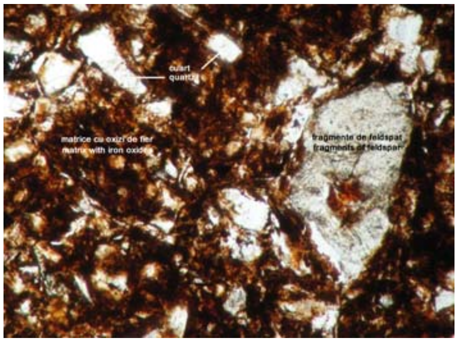

Fig. 6 Microscopic aspect of burned clay 1050°C

(photo scale 8 mm = 0,1 mm real) (N+, 80 x)

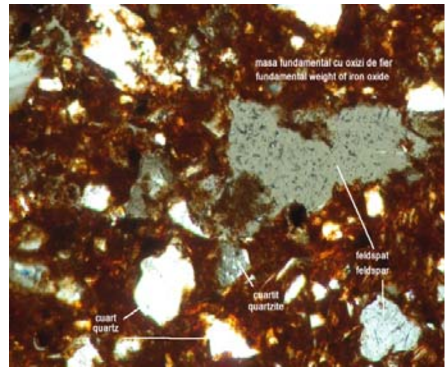

Fig. 8. Microscopic aspect of clay with 20 % sludge burned at 1050ºC (photo scale 7 mm = 0,1 mm real) (N+, 70 x)

It can be noticed that just 7% of sludge in the clay mass do not lead to structural leaks of homogeneity. In the same time at an increase of the proportion of sludge to 20% a non-homogenous structure can be noticed (agglomeration of feldspar and quartz minerals), this fact explains the lower values of the mechanical resistance properties.

4. Conclusion

The physical characteristics of the samples having sludge added to the clay in different proportions (apparent density, water absorption and apparent porosity) are comparable to the ones manufactured in the usual way. The values have been defined according to the applicable standards. The values of mechanical strength decrease with the added sludge percentage 7 and 20%, but they remain suitable according to the Romanian standards STAS 457/86.

However, a small percentage, only 7 % of gross porcelain does not cause big changes in strength compared with the sample product, while a percentage of 20 % of sludge can cause fall of strength, even on a burning temperature of 1100°C (simple reference 39.70MPa, while the sample with 7% sludge 37.20MPa and in case of 20% of the sewage sludge 30.1MPa).

The increase of burning temperature determines the increase of density of the sample at the same % to that of the added sludge. Crystalline compounds are also formed in an increasing proportion: either of the same compounds or different types of compounds (significant crystallization).

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