Abstract. Because of the rapid evolution in the last decade of science and engineering materials, development of new advanced materials, particularly in construction, we must find solutions, namely, new performed materials, with functional and aesthetic qualities. In recent years, there have been made alternative attempts to reuse various types of wastes, including the incorporation of products in ceramic clay. This theme concerning the achievement of some durable, economic and ecological materials represents a high-level preoccupation in this domain, the problems related to the ecosystem being permanent issues of the century.

1. Introduction

The present work refers to gross porcelain (semi-fabricated ceramic) which contains clay from Bodoc (Covasna county) and sewage sludge treatment plants from Saint George (Covasna county) best for the manufacturing of bricks used in construction.

This paper aims to get gross porcelain with embedding sewage sludge. The quarry from Bodoc exploits the clay used in manufacturing of the bricks, approximate 15.000 t/year.

The sewage sludge from wastewater treatment plants in Saint George is obtained through thickening, fermentation and drying, after that it is transported to the landfills. The humidity of the dehydrated sludge is of 70-75%. The use of the sewage sludge from the waste dump near the treatment plants in Saint George contributes to the environmental improvement [1].

The addition of sludge also reduces the energy consumption during the combustion because it contains over 60% organic part which decays by exothermic reaction – revealed through L.O.I. = 62.24

The sewage sludge having the humidity of 74.72% was dried, bonded and mixed with clay from Bodoc [2].

The sludge’s radioactivity shows the value of 662.884 Bq/kg. The allowable limit for construction materials is set by the Health Ministry Order nr. 51/198 and considers max. 832.50 Bq/kg so this sludge can be used as added material in the manufacture of bricks without being harmful to the environment [3].
During the recent years, alternative attempts of reusing various types of waste have been made, including the incorporation of products in ceramic clay [4, 5, 6].

The sewage sludge was introduced in ceramic mixtures at a rate of 5-20% gravimetric percent [7, 8].

2. Materials, theoretical and/or experimental procedures

At the sewage works station Saint George the sludge is resulted from the primary decantation and from the biological purification in the form of unwanted biological sludge. Both types of sludge are stabilized through anaerobic digestion where the primary sludge is placed as such and the unwanted sludge is placed following prior gravity thickening.

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.

There were made mixtures of clay and sludge corresponding to some building ceramics masses. The sludge addition was of 7 and 20 gravimetric percent.

The mineralogical analysis of the clay was performed by a diffract meter DRON3 with the radiation Cu $K\alpha$, and a wave length $\lambda=1.54056\text{Å}$. A Ni filter was used in order to filter the $K\beta$ component of the radiation. The angle of the scanned sample was $20=11-70^\circ$, the angular pitch 0.02° and count time 3sec/pitch.

The basic property of the clay from Bodoc is that it has a polymineral composition and it contains clay minerals with a wide array of crystallographic structures ranging from quartz to muscovites.

Beta radiation activity for sludge was examined using UMo LB123 proportional counter.

3. Results and discussions

The radiography analysis of the clay from Bodoc shows that significant amounts of minerals are present:

- Quartz $\text{SiO}_2$
- Plagioclase feldspar, bleached calcian $(\text{Na,Ca})\text{Al(Si,Al)}_3\text{O}_8$
- Anorthite sodian $(\text{Ca,Na})(\text{Si,Al})_4\text{O}_8$
- Hematite $\text{Fe}_2\text{O}_3$
- Augite $\text{Ca(Mg,Fe)}\text{Si}_2\text{O}_6$ (group of clinopyroxenes)
- Muscovite $3\text{T}(\text{K,Na})(\text{Al,Mg,Fe})_2(\text{Si}_{1,1}\text{Al}_{0,9})\text{O}_{10}(\text{OH})_2$

The majority of minerals in the clay from Bodoc consist in quartz and feldspar.

The characteristics of the clay from Bodoc in normal condition, after drying and burning are shown in table 1.

| Characteristics       | Values | Units of measurement |
|-----------------------|--------|----------------------|
| Plasticity index      | 25.91  | -                    |
| Strength              | 2.03   | MPa                  |
| Filling water         | 3.1    | %                    |
Drying shrinkage & 7.22 & % \\
Bulk density & 1.96 & g/cm$^3$ \\
Water absorption & 13.84 & % \\
Bulk porosity & 27.11 & % vol. \\
Rezistance to bending (960°C) & 6.63 & N/mm$^2$ \\
Burning Contraction (960°C) & 1.07 & % \\

The elements of construction are obtained by pressing, drying and heat treatment in the interval of 960-1100 °C depending on the rate of sewage sludge addition.

Ceramic mixtures are characterized by a typical chemical-oxide composition. These compositions are presented in table 2.

Table 2. Chemical- oxide composition of the raw materials and of the mixtures

| %   | Reference sample | Sludge mixtures | Sludge mixtures | Sludge mixtures | Sludge mixtures |
|-----|-----------------|----------------|----------------|----------------|----------------|
|     | Clay            | Sludge         | 5%             | 7%             | 10%            | 15%            | 20%            |
| SiO$_2$ | 67.97         | 14.06         | 66.1           | 64.07          | 62.44          | 61.28          | 60.42          |
| Al$_2$O$_3$ | 15.41        | 3.97          | 15.3           | 14.09          | 13.84          | 13.79          | 13.76          |
| Fe$_2$O$_3$ | 4.88          | 1.43          | 4.85           | 4.49           | 4.19           | 4.02           | 4.01           |
| CaO   | 1.66           | 13.32         | 2.89           | 2.67           | 2.33           | 2.41           | 1.84           |
| MgO   | 1.59           | 0.73          | 1.40           | 1.92           | 1.93           | 2.04           | 2.28           |
| K$_2$O  | 2.43           | -             | 1.99           | 1.49           | 1.21           | 1.12           | 1.07           |
| Na$_2$O | 1.54           | 0.87          | 1.69           | 1.67           | 1.57           | 1.31           | 1.23           |
| L.O.I. | 3.58           | 62.24         | 6.95           | 6.69           | 9.78           | 12.35          | 13.73          |

The mixture obtained this way was shaped using a classic technology of pressing at a hydraulic press at a pressure of 15 MPa.

The specimen obtained this way were dried until a constant weight, at a temperature of 100-120°C after they were burnt in a laboratory electric oven tip Kammeröfen 1600°C at a temperature of 960°C, 1050°C and 1100°C.

Following the physical characteristics stipulated at the burnt samples at 960°C ( the bulk density, water absorption and bulk porosity) of these gross porcelains it was noticed that the addition of 7 respectively 20 % of sewage sludge gave the best results.

Therefore further gross porcelains containing those percentages of sewage sludge were examined.

A ceramic mixture is carried out through combining the clay from Bodoc 93% and sewage sludge 7%. The mixture obtained this way is pressed at a hydraulic press at a pressure of 15 MPa, is dried at 100-120 °C and is burnt at 960 °C, 1050 °C and 1100°C. The main features of this mixture are the following table 3.
Table 3. Characteristics of the ceramic compositions (7% sludge)

| Temperature [°C] | Bulk density [g/cm³] | Water absorption [%] | Bulk porosity [%vol.] | Resistance to bending [N/mm²] |
|-----------------|----------------------|----------------------|-----------------------|-------------------------------|
| 960             | 1.90                 | 15.22                | 28.99                 | 6.31                          |
| 1050            | 2.17                 | 12.05                | 26.15                 | 7.18                          |
| 1100            | 2.18                 | 11.77                | 25.65                 | 8.56                          |
| **Values in literature**[9] | **1.8-2.2** | **11.3-26** | **13-30** | **1.6-7.5** |

A ceramic mixture is carried out through combining the clay from Bodoc 80% and sewage sludge 20%. The mixture obtained this way is pressed at a hydraulic press at a pressure of 15 MPa, is dried at 100-120 °C and is burnt at 960 °C, 1050 °C and 1100°C. The main features of this mixture are the following table 4.

Table 4. Characteristics of the ceramic compositions (20% sludge)

| Temperature [°C] | Bulk density [g/cm³] | Water absorption [%] | Bulk porosity [%vol.] | Resistance to bending [N/mm²] |
|-----------------|----------------------|----------------------|-----------------------|-------------------------------|
| 960             | 1.78                 | 11.29                | 32.48                 | 8.75                          |
| 1050            | 1.72                 | 14.33                | 28.43                 | 8.52                          |
| 1100            | 1.87                 | 16.53                | 26.79                 | 5.97                          |
| **Values in literature**[9] | **1.8-2.2** | **11.3-26** | **13-30** | **1.6-7.5** |

The mixture has the following advantages:

The products – bricks – that are obtained this way have got similar properties as the burnt clay bricks.

Because waste is used as raw material – sewage sludge – that are currently stored in dumps near the waste treatment plants; the waste has not been developed in any way until the present.

The development of sewage sludge has got positive ecological consequences by releasing the land for waste storage (dumps) and it also minimizes the contamination of the environment.

Taking into consideration the economic efficiency the sewage sludge does not involve any liabilities and its transport from the waste treatment plants to the processing quarry does not require significant additional expenditures.

The obtained gross porcelain shows a plasticity that allows shaping by pressing.

The physical characteristics stipulated on the burnt samples of the clay/sewage mixtures in different proportions (bulk density, water absorption and bulk porosity) can be compared with the
characteristics of the common bricks used in construction. The measurements were performed according to current standards.

The values of strength (bending) fall with the increase of the percentage of the added sludge 5-20%, but they correspond to the regulation STAS 457/86, at the same time it reduces the density which has more advantages in construction.

Increasing the temperature of the combustion increases the density of the samples at the same % of added sludge.

Increasing the percentage of the sludge on the same combustion temperature results the fall of the bulk density.

The porosity of the sample is increased due to the processing of the sludge. (processes of carbonate decomposition, combusting organic compounds, etc)

To obtain the bricks a flow sheet has been developed which falls into common technologies used in building ceramic industry (gross).

Next it is given an embodiment of the process that is carried out according to the invention, in connection with the figure 1 which is the main of the technological process.

![Flow chart for brick manufacturing](image)

Figure 1. Flow chart for brick manufacturing
4. Conclusion
There are not very big changes in the gross porcelain’s content when sludge is used. The use of sludge as raw material in the ceramic industry does not cause any sanitary risks, if one takes into consideration the high temperature used for produce burning. Also, the sludge radioactivity (of 662,884 Bq/kg) does not present conditions of radioactive contamination at the ceramic construction products.

The mixture of different components in order to attain a new masonry unit, namely clay mixed with sewage sludge can be characterized the following way: the gross porcelain obtained from clay and sewage sludge mixture can be used between 7-20%. The mixtures obtained this way are pressed at a hydraulic press at a pressure of 15 MPa, are dried at 100-120 °C and are burnt at 960 °C, 1050 °C and 1100°C, in neutral atmosphere.

The physical characteristics stipulated on the burnt samples of the clay/sewage mixtures in different proportions (bulk density, water absorption and bulk porosity) can be compared with the characteristics of the common bricks used in construction. The measurements were performed according to current standards.

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