

# Physicochemical and technological researches of marls from the area of the village Lovets related to the production of the new "Yellow paving stones"

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**Abstract:** Due to force majeure circumstances, new researches of marls from the Alexandra deposit to the village of Lovets (Shumen region) were carried out to replace the marls from the village Svetlen (Targovishte region), which are part of a plastic mass for the production of large, fine-ceramic parts (yellow paving stones) from peturgical phases. Marls are characterized in terms of mineral and chemical composition. Their properties, characterizing them as a ceramic raw material, have been determined. Three test masses with a chemical composition similar to the one with the participation of marls from the village of Svetlen were developed. The test specimens are characterized in terms of sintering and strength characteristics. It has been established that the marls can be used to replace the marl from the village Svetlen in the composition of the plastic fine-ceramic masses for the production of yellow pavers.

**Keywords:** MARBLE CLAYS, NEW YELLOW COATS, PHYSICOCHEMICAL STUDIES OF MARBLE

## 1. Introduction

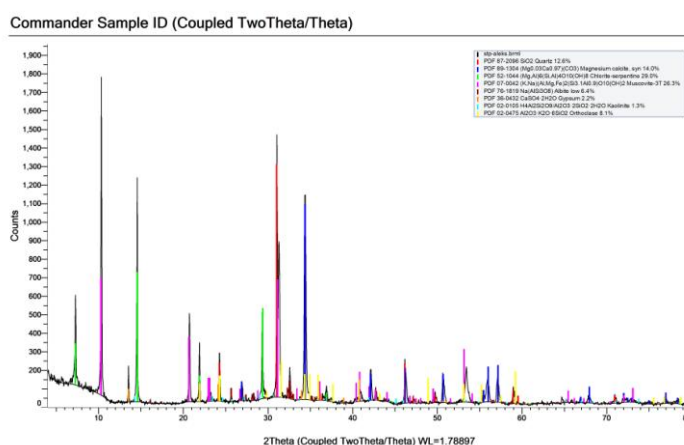
Due to the bankrupt of the company "Rodna Industria" Popovo, using the concession of the marl deposit in the village Svetlen in obligations to the state, insolvency and lack of prospects for future cooperation, it was necessary to urgently conduct current research to find new alternative raw materials.

## 2. Representation

Both the marl from the village Svetlen and the marl from the village Lovets are used for coarse ceramic products - bricks. As marls are suitable for the production of high quality majolica tiles, they can easily be used as a raw material for the production of fine ceramic products, because clay marls contain a larger amount of fine fractions than typical brick clays [1]. The carbonates in the marls are more evenly distributed. Table 1 shows the chemical composition of marl from the village Lovets, and Figure 1 shows a radiograph of the raw material and the content of mineral phases in it. Table 2 presents the grain size distribution in% by weight.

**Table 1:** Chemical composition of marl clay from the Alexandra deposit, Lovets village

Composition	Quantity %
Na <sub>2</sub> O	0,7
MgO	2,24
Al <sub>2</sub> O <sub>3</sub>	11,36
SiO <sub>2</sub>	35,19
P <sub>2</sub> O <sub>5</sub>	0,1
K <sub>2</sub> O	2
CaO	19,58
TiO <sub>2</sub>	0,47
MnO	0,11
Fe <sub>2</sub> O <sub>3</sub>	4,85
LOI	23,21
Σ	99,82
Cu	0,06
Zn	0,073
Sr	0,053



**Fig. 1.** Phase analysis of dried marl clay from the village of Lovets at  $t = 1140^{\circ}\text{C}$  and retention at a final temperature of 80 minutes.

**Table 2:** Grain size distribution of marl clay as a percentage of particle size.

Grain size distribution	Weight %
Faction under 0,005	45
Faction 0,005 - 0,05	42
Faction over 0,05	13

According to the standards, the studied clay belongs to the marls of group III - acidic below 15% Al<sub>2</sub>O<sub>3</sub> high-carbonate, over 17 - 18% alkaline earth oxides and high content of coloring Fe<sub>2</sub>O<sub>3</sub> - over 3%. According to the classification of Sitin, the clay marl used by us from the area of the village Lovets, the amount of alkaline earth oxides is 21.82% by weight. This implies a relatively narrow firing interval and difficulty in obtaining fine ceramic products. The DTA curve of marl showed a characteristic endoeffect at 800°C associated with the decomposition of CaCO<sub>3</sub> and MgCO<sub>3</sub>. The weight reduction is 22.57%, which coincides with the determined by chemical analysis A.L.(annealing losses). 23.71%. From the DTA curve shown in fig. 2, it has surprisingly been found that the melting interval begins with the appearance of small amounts of liquid phase as early as approximately 1000°C before the actual melting point at 1137-1140°C. This suggests that a practical temperature regime for marl firing could be established.

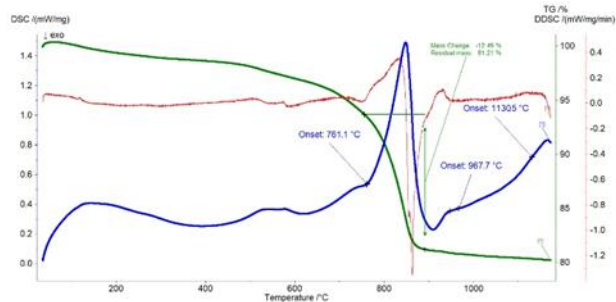


Fig. 2: DTA-DSC analysis of the test samples

X-ray phase analysis shows that marl contains, in addition to calcite ( $\text{CaCO}_3$ ), chloride, mica such as musk quartz, feldspar, plagioclase, gypsum and kaolin. The content of clay substance is in accordance with the fractional composition (fraction below 0.005 - 45%) fig. 1.

Marl has the following properties, characterizing it as a ceramic raw material:

- Normal molding humidity - 20.5%;
- Plasticity according to Pfefferkorn - 29%;
- Critical humidity - 17.3%;
- Coefficient of sensitivity to drying - 0.18.

The clay marl used in plastic plastics has a favorable high critical humidity and is slightly sensitive to drying. This is in accordance with its mineral, chemical and fractional composition, which determines a simplified drying regime and the possibility of forming according to the classical technologies of ceramic technology. The recipe composition of the working tables used is presented in Table 3.

Tabl. 3. Prescription composition of working tables

Raw materials	Composition of test masses by weight %			
Marl from the village of Lovets	25	30	30	30
Fireclay from marl in the village of Lovets	55	55	60	70
Washed kaolin, dried at 120°C	20	15	10	-

The calculated chemical composition of the test masses is given in Table 4.

Tabl. 4. Prescription composition of work tables

Оксиди	M1	M2	M3	M4
$\text{Na}_2\text{O}$	0,60	0,66	0,67	0,70
$\text{MgO}$	2,16	2,14	2,14	2,24
$\text{Al}_2\text{O}_3$	12,60	13,00	13,10	11,36
$\text{SiO}_2$	41,30	39,98	40,10	37,19
$\text{P}_2\text{O}_5$	0,07	0,072	0,73	0,10
$\text{K}_2\text{O}$	1,80	1,85	1,90	2,00
$\text{CaO}$	16,70	17,32	19,30	20,58
$\text{TiO}_2$	0,33	0,34	0,34	0,47
$\text{MnO}$	0,10	0,11	0,11	0,11
$\text{Fe}_2\text{O}_3$	4,75	4,80	4,83	4,85
A.L.	19,425	20,90	21,00	20,21

Cu	0,05	0,06	0,06	0,06
Zn	0,066	0,069	0,068	0,073
Sr	0,049	0,051	0,052	0,053
	100,00	100,00	100,00	100,00

Slips with a humidity of 60% are prepared from the work tables. The plastic mass for the test samples was obtained by dehydrating the slip in gypsum forms to normal molding humidity, which for all four masses was 22%. The obtained samples from the plastic masses are tiles with dimensions 56.5 x 56.5 x 5.65, dried to a residual humidity of 2-3%.

The properties of the obtained water-dispersed colloidal systems (slips) are presented in Table 5.

Tabl. 5. Properties of the four slips obtained from clay

Properties	M1	M2	M3	M4
Liter weight g/l	1490	1485	1480	1492
Viscosity, Pas	2,30	2,25	2,23	2,22
Dry matter in the dispersed system, kg/l	0,80	0,79	0,78	0,77
Sieve residue in the sieve 0.063 mm g / l	0,09	0,10	0,11	0,25

The firing mode is determined by the DTA curve and is as follows: heating rate 3°C / minute; delay at 112°C and 148°C for 30 minutes; retention at 576°C, 687°C and 800°C - 20 minutes and retention at final temperature 1130°C - 60 minutes. The cooling rate is 3°C / minute and a hold at 576°C and 687°C for 30 minutes.

The results of the degree of sintering of the test samples up to 1160°C are presented in Table 6, and the mineral phases in the synthesized mass sample №4 are presented in Figure 3.

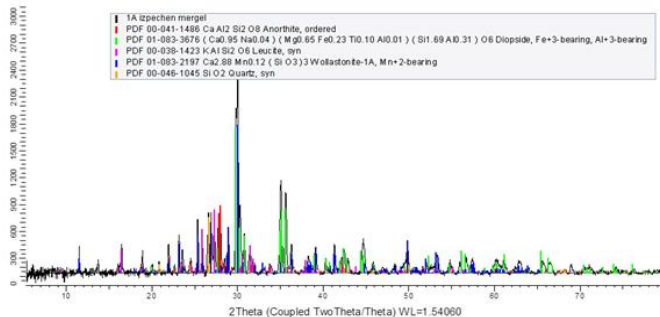
Tabl. 6. Characteristics and degree of sintering of the test specimens at three temperature processes

Maca	T°C calcination	contrastility	Water absorption	Appearant density
M1	1000	5,0	22,0	1,70
	1130	7,0	12,0	1,72
	1160	8,0	0,2	1,85
M2	1000	6,5	24,5	1,65
	1130	7,9	0,06	1,67
	1160	melt	0,0	-
M3	1000	6,0	20,2	1,63
	1130	8,0	0,04	1,65
	1160	melt	0,0	-
M4	1000	7,1	14,8	1,80
	1130	8,4	0,02	1,85
	1160	melt	0,0	-

Samples of mass M4 at annealing temperature of 1130°C and mass M1 at annealing temperature of 1160°C are best sintered, in

which the water absorption is 0 and 0%, respectively, and the apparent density of both samples is 1.85 g / cm<sup>3</sup>

The higher content of CaCO<sub>3</sub> reduces the viscosity of the mass during sintering, respectively the interval of sintering. The M4 mass burns the fastest and at the lowest temperature, which is due to the larger amount of melt formed. At a temperature of 1130°C the water absorption is 0%, but the baking interval - 15/20°C is the narrowest.



**Fig. 3.** Radiograph of a high-temperature synthesized sample of mass №1 shows the presence of peturgical phases anorthite and diopside, which predetermine the good physico-chemical and mechanical parameters of the finished products shown in table 7.

The strength characteristics of the samples of test masses M1, M2, M3 and M4 are presented in Table 7.

**Tabl. 7.** Compressive strength and bending strength of test specimens at different temperatures

Indicators	M1	M2	M3	M4	T°C firing temperature
compressive strength, MPa	800	900	950	1000	1000
	1000	1100	1150	1250	1130
	1200	-	-	-	1160
Bending strength, MPa	116	120	125	140	1000
	140	400	420	470	1130
	460	-	-	-	1160

### 3. Conclusion

The results of the research confirm the possibility of using the marl from the Alexandra deposit to the village of Lovets, Targovishte district. However, the use of marl clay from this deposit requires a change in the technological process, which is the main goal in the present development.

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