CHARACTERIZATION OF CLAYS FROM “MINES MARITSA IZTOK” AS RAW MATERIALS FOR CERAMIC INDUSTRY

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ABSTRACT

The chemical and phase compositions of the clays from coal mining were evaluated by XRF and powder XRD method, respectively. Hot Stage Microscope was used to estimate the thermal behaviour. In addition, the thermal losses of the clays after 1 h thermal treatment at different temperatures were measured.

This preliminary analysis elucidates potential prospects for using some of clays as raw materials for ceramic industry. It seems that samples which are montmorillonite type are more plastic, while the others, where higher sand content is observed, and the drying shrinkage is negligible could be characterized as less plastic.

The initial results for the thermal behaviour and the structure of a brick sample (obtained by mixing two types of clays) and a foamed geopolymer are also reported. The first sample shows a beginning of the firing shrinkage at about 1000°C, while the second demonstrates intensive bloating after 950°C, leading to specimen with about 56 % closed porosity. Finally, X - ray Computed Tomography and SEM was used to highlight the structure of some test samples.

Keywords: industrial clays, ceramics, thermal behaviour.

INTRODUCTION

The lignite coal is the main energy source used in Bulgaria. The total coal geological resources in the country are estimated at 2.2 billion t while the lignite are about 1.9 billion t and hard coal are 0.3 billion t. In 2021, the country ranked 3rd in Europe in terms of lignite production. In fact, according to data from the Euracoal 45 % of electricity in Bulgaria is produced by the thermal power plants [1].

Most of lignite reserves are in the central part of the country (East - Marishki coal basin). The deposit is exploited by „Mini Maritsa Iztok” EAD Mines since 1953.

The company has three open - pits with total output of lignite - 35.5 million tons annually in 2021. The average mined overburden is from 80 to 100 million m^3 per year [1, 2]. Mini “Maritsa Iztok” EAD Mines uses high - performance mining equipment, including bucket chain and bucket wheel excavators, conveyor belts and spreaders. The mined lignite is burned in three nearby thermal power plants.

The clayey sediments covering the lignite are mined, transported and disposed on internal and external overburden disposal facilities. From the start of mining operations in the East -Mariski basin in 1953 to the end of 2019 were excavated, transported and disposed a total of 4.78 billion m^3 overburden and a total of 1.21 billion t lignite were mined [2, 3].

Type of wastes in mini “Maritsa Iztok” EAD mines.

The overburden in the deposit consists of a soil layer and different types of clays, which represent waste from lignite mining (Fig. 1) [4]. Depending on their type and composition, clays are distinguished as black to grey - black highly organic clays with coal inclusions and layered clays forming the coal seams of the coal - bearing horizon (Fig. 1). The coal horizon is presented grey - green, blue - green to grey - yellow and yellow - brown coloured clays, finely dispersed too powdery and dusty - sandy. Hard carbonate inclusions and sand lenses with accumulated are found in them leads. In the uppermost parts of the section, in white earthy limestones are found on the terrain heights [2].

These clays are of Neogene age. The main clay minerals for the black clays are montmorillonite from 15 % to 38 % and kaolinite from 3 % to 23 %. For supercoal clays, montmorillonite is from 13 % to 54 % and kaolinite from 3 % to 19 %. Apart from these minerals, also contain the hydromics hallusite and illite, as and feldspars and quartz. As accessory minerals anatase, pyrite and siderite are found. The total thickness of the outcrop is 30 m in the southern part of the basin and reaches over 100 m in the north [2].

The aim of current report is to describe the mainstream of wastes from lignite mining in Mini "Maritsa Iztok" EAD Mines and to give a recommendation or examples for their possible usage as row materials for high volume production of building industry.

EXPERIMENTAL

The object of research are different types of waste generated during the lignite mining from different mine's horizons. The chemical compositions of the waste materials were evaluated by XRF analysis (Zetium Spectrometer - Malvern Panalytical).

The phase compositions were evaluated by powder XRD analysis by automatic powder diffractometer system Philips, generator PW1830 and goniometer PW1050, equipped with: X - ray tube Cu anode and secondary graphite monochromator.

HOT Stage microscope (MISURA 1400) was used to estimate the thermal behaviour. Small samples, suitable for direct measurements, with standard cylindrical shape of 5 mm height and 2 mm diameter have been prepared by manually pressing with a manual plunger and distilled water as a binder.

Additionally, to demonstrate the possible application of some of clays laboratory ceramic and geopolymer samples were obtained.

The batch for brick ceramic were humidified (6 wt.%)

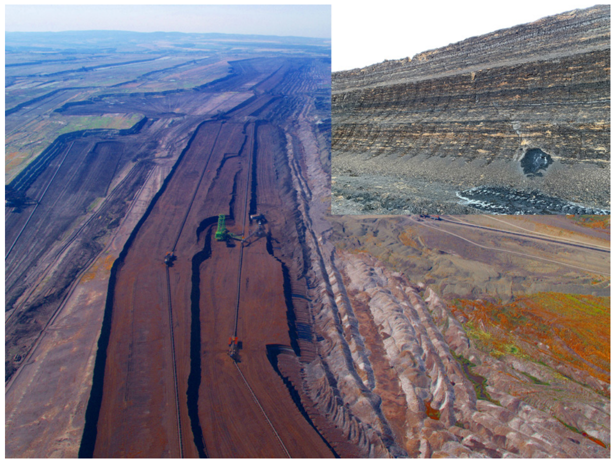


Fig. 1. Coal mining in Mini "Maritsa Iztok" and a horizon.

and pressing at 40 MPa using a uniaxial hydraulic press (Mignon C, Nannetti, Italy) to obtain bar samples (50x5x4 mm), suitable for firing in horizontal optical dilatometer (Expert System Solutions, Misura HSML ODLT 1400).

Then the sintering trends were studied by non - isothermal treatment up to 1000°C using at heating and cooling rates of 10°C min^{-1}.

The structure of this obtained samples, both surface and fracture, was studied by SEM (JEOL JSM 6390).

Alternatively, the geopolymer sample was obtained by identical pressing procedure using mixture of clay and 12M NaOH solution.

The bulk structure of the newly formed sintered material was studied by μCT analysis. The sample was scanned with the Bruker SkyScan 1272 X - ray scanner. The tube voltage and current were 80 kV and 125 μA, correspondingly. The voxel size was 4 μm. Sample rotation on 360° was performed with a step of 0.2° to result in 1800 x - ray projections A tomographic reconstruction was performed with a dedicated software NRecon, version number 1.7.4.2. delivered by Bruker. A ring artefact and beam hardening corrections were applied. The porosity was determined by the Bruker dedicated software CTAn version 1.20.8.

RESULTS AND DISCUSSIONS

Clays - wastes from lignite mining

Maritsa East deposit is built of Pliocene clays, clayed sands with a thickness of up to 300 m, lying directly on a variegated substrate of Palaeozoic and

Triassic rocks [4].

The construction of the overburden is quite diverse. About 22 layers of soil and geological materials are distinguished, differing in colour, mechanical composition, carbonate content, etc. The thickness of the layers is as follows:

- 1.70 m - soil (surface layer);
- 8.00 m - yellow - brown clays;
- 60.00 m - blue - green to grey clays;
- 70.00 m - grey - black clays.

Several samples were taken during the study: clays from overburden mining in Mini "Maritsa Iztok" EAD Mines (labelled Sample 1, Sample 2, Sample 3, Sample 4 and Sample 5, respectively).

The most significant difference between the grouped geological materials is the content of clay, which has a decisive influence on the structure and water regime.

The yellow - brown clays situated below the soil profile are characterized by the lowest clay content of 20 - 28 % and a high sand content of 18 - 24 %. The carbonates in the individual layers reach up to 2 %. The bulk density is 1.77 g cm^{-3}. The total porosity is 23 % and the maximum hygroscopic moisture is 6.78 % [4].

Blue - green to grey clays are predominant. In them, the physical clay is 50 - 55 %, and the sand content is 33 - 35 %. Carbonates are about 1.5 %. The total porosity is about 35 %, and the maximum hygroscopic moisture is 8 - 10 % [4].

The main characteristic of blue and black clays is that they have „heavy mechanical composition", corresponding to bulk density of 1.94 g cm^{-3}. This has a decisive adverse effect on the water regime and structuring. Obviously, the porosity is smaller and is between 27 and 31 %, and the hygroscopic moisture is too high - about 20 %. Carbonates are absent and the organic matter (up to 26 %) consists of lignite constituents [4].

The results from chemical analysis of clays in Maritza East mines, heat treated at 1000°C are presented in Table 1. It is shown that the clays contain the following main chemical elements: silicon from 34.61 % to 40.34 %; aluminium from 13.77 % to 17.61 %; iron from 7.58 % to 13.3 %. Additionally in all samples about 3 % potassium is measured and about 1 - 2 % calcium (excluding sample 3 where the content of Ca is about 6 %). The sulphur content in clays from samples 1 to 4 is relatively low, while the content of S in sample 5 is about 4 %. The reason is forming of this clay in the lignite interlayer.

The difference in chemical composition between the different samples can be explained by various geological structure of the deposits.

The thermal losses of the clays after thermal treatment after 1 h at different temperatures were measured. The results are presented in Table 2. These analyses show that the thermal losses of clays at 120ºC are similar, while between 120ºC and 700ºC the samples 2 and 5 (blue - green to grey and grey - black clays) show significantly higher losses than the other clays. As a result, the total losses for samples 2 and 5 are about 21 % and 26 % respectively while for other three samples are in the range 12 - 14 %.

The difference in thermal behaviour corresponds to the phase XRD analyses summarized in Fig. 2. Samples 2 and 5 are characterized by higher amount montmorillonite (i.e. muscovite) type clay, whereas in the other samples the clays are mainly kaolinite types. It is well known that montmorillonite clays are characterized with higher water content. Clays from Serpentine subgroup (i.e. antigorite) are also observed in all samples. Their amount again is higher in samples 2 and 5.

In principle, the comparison of Silica and Alumina in the "pure" clay can be between molar ratio of 1:1 or 2:1 (i.e. 27:28 and 54:28 in weight). This value mainly is a result of the type of the clays (in kaolinite the structure is with two layers and the ratio is 1:1 while in montmorillonite the structure is by three layer - the ratio is 2:1 [5]), as well as of the sand inclusion. In our samples the ratio Si and Al varies between 2 - 2.2 (samples 2 and 5) to 2.5 - 2.8 (samples 1, 3 and 4). In fact, the amount of quartz is highest in samples 1 and 4 and lowest in sample 2. In addition, samples 1 and 3 are characterized by lower thermal losses which is typical for kaolinite clays.

In sample 3 where, due the presence of calcite Ca amount is 6 %, while in the other samples Ca content is below 2 %. Notwithstanding of high iron oxide content in the clays the XRD results show that in all samples magnetite and hematite are not identified. The iron in sample 3 is presented as siderite, and in the other samples probably is part of the clay structure.

The HOT stage analysis in low temperature region

Table 1. Results from chemical analysis of the clays, wt. %.

Powders Elements	Unit	Sample 1 Yellow-brown clay	Sample 2 Blue-green to grey clay	Sample 3 Blue-green clay	Sample 4 Yellow-brown clay with organic remains	Sample 5 Grey-black clay
Si	%	40.338	35.39	36.013	38.485	34.612
O	%	23.881	30.643	23.681	31.962	25.354
Al	%	14.647	17.613	14.2	13.767	15.977
Fe	%	12.823	9.416	13.301	7.582	12.069
K	%	3.707	2.174	3.284	3.864	3.063
Ca	%	1.346	1.452	5.992	1.053	1.664
Ti	%	1.274	1.038	1.088	1.057	1.147
Mg	%	1.059	0.991	1.09	0.918	1.178
Na	%	0.297	0.301	0.268	0.565	0.375
S	%	0.025	0.522	0.201	0.258	4.032
P	%	0.144	0.054	0.193	0.052	0.042
Ba	%	0.097	0.075	0.087	0.082	0.085
Ce	%	0.056	0.055		0.063	0.054
Sr	%	0.052	0.037	0.043	0.047	0.04
Zr	%	0.042	0.024	0.029	0.036	0.026
Mn	%	0.039	0.025	0.351	0.039	0.056
Rb	%	0.038	0.032	0.031	0.034	0.036
Zn	%	0.028	0.029	0.025	0.024	0.03
Cu	%	0.027	0.041	0.022	0.019	0.035
Cr	%	0.02	0.02	0.016	0.022	0.022
Cl	%	0.019	0.033	0.02	0.039	0.03
Ni	%	0.013	0.01	0.011	0.009	0.017
Pb	%	0.009	0.01	0.01	0.009	
Y	%	0.007	0.005	0.007		
Ga	%	0.006	0.011	0.005	0.005	0.008
Nb	%	0.004		0.003	0.003	
La	%			0.029		
As	%				0.006	0.008
V	%					0.04
Sum	%	100	100	100	100	100

Table 2. Results from thermal losses analysis of clays, wt. %.

Number of the sample	At 120ºC	Between 120ºC and 700ºC	Between 700ºC and 1000ºC	Total, %
1	4.73	7.25	0.82	12.36
2	6.02	14.74	1.50	21.08
3	4.38	6.99	1.17	12.11
4	5.33	8.04	0.87	13.71
5	7.05	17.69	3.07	25.84

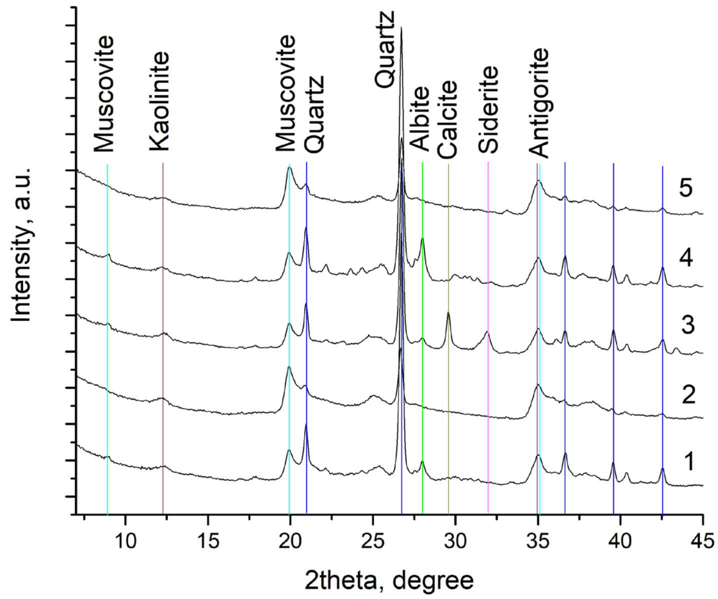


Fig. 2. Phase analysis of clays in mini Maritza East (the sample number is on the right).

is presented in Fig. 3a while a high temperature is shown in Fig. 3b. The results demonstrate that up to 1200ºC significant volume changes are not observed, excluding the shrinkage at 100ºC for montmorillonite clay type samples 2 and 5.

In samples 1, 3 and 5 some swelling above 1200ºC is noted probably due to Fe^{3+} to Fe^{2+} reduction. In other two samples, where the iron percentage is lower, this process is less intensive or take place in higher temperature.

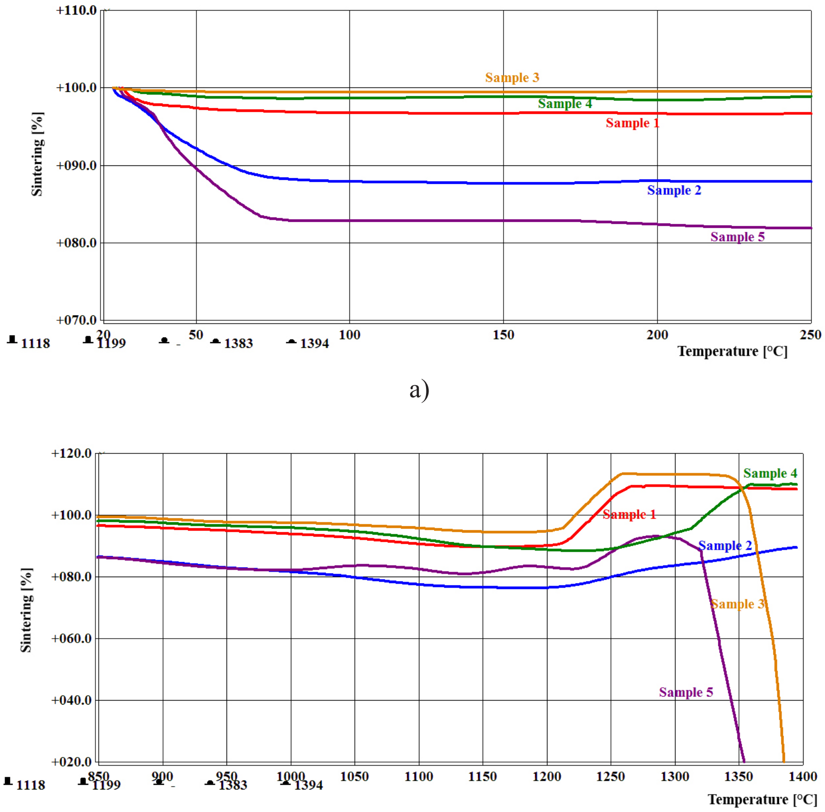
Samples 1, 2 and 4 do not show beginning of the melting to 1400ºC. In sample 3, where the content of limestone and siderite is higher the melting point is near to 1360ºC. The other clay with lower melting temperature is sample 5 where the sulphur content is the highest.

Potential usage of studied wastes

Interesting study was conducted on the content of rare earth elements in single samples of clays and coals from The Mini "Maritsa Iztok" EAD Mines [6, 7]. Some samples show high to unusual enrichment of elements relative to Clarke values for clays and shales (CE > 10): Yellow clay - Pd, Se, and Te; Black clay - Pt; Black clay 1 - Ag, Pt, Au, Se, Te, and Re. The established higher upper Clarke concentrations of the specified rare earth elements in the clays and in the coal ashes is explained by their presence in the aqueous solutions during the formation of the coal and is related to the rocks of the feeding provinces, with their petrographic and mineral composition, as well as with the presence of ore occurrences.

When comparing the established elemental contents in the samples with those according to published data, sees that the black clays and yellow clays are characterized by significantly higher concentrations (2 - 3 times) of rare earth elements, Y and Sc. This makes them interesting as a potential source for extraction of these elements by using several metallurgical and bio - metallurgical methods [8, 9]. The results reported in Table 1 also confirms the presence of rare metals in the clays.

These analyses highlight the potential usage of some of the clay as a source for rare metals. However, the main application of some of the clays can be related with the production of high-volume building materials. During the last decades some authors studied possibilities for using different wastes as a raw material for bricks and geopolymer production [10 - 16]. The



a)

b)

Fig. 3. The HOT stage analysis in low (a), and in high (b) temperature region.

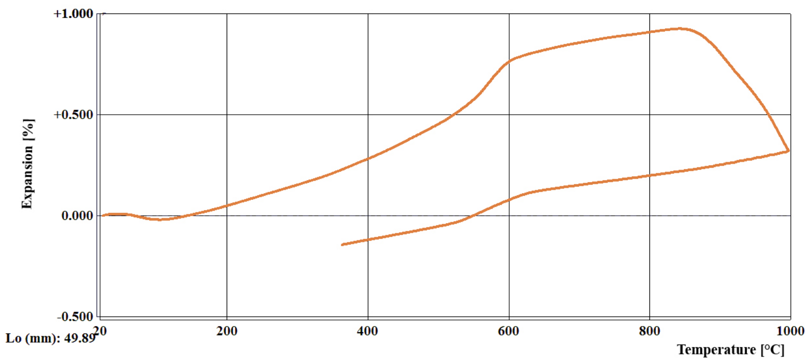


Fig. 4. Dilatometric sintering curve of brick sample.

results of chemical analysis and mineral composition of the clays in mini Maritza East show that some of these clays also can probably be used in the synthesis of bricks and geopolymers with various applications.

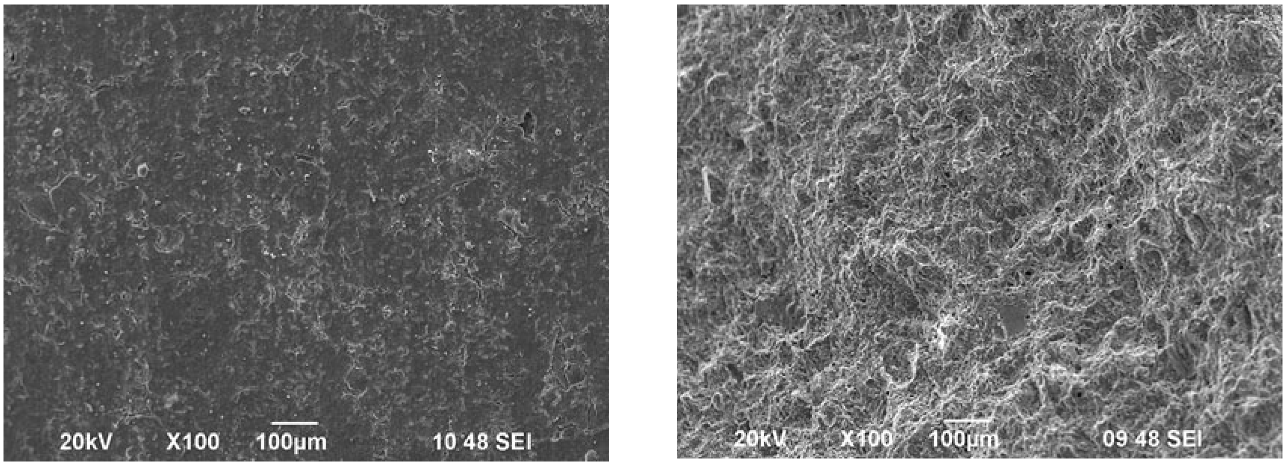
The batch for the brick sample was formed by mixing 50 wt. % of clays 1 and 50 wt. % of clays 4. After humiditation and pressing of the batch the sintering was studied by optical dilatometer. The sintering plot is reported on Fig. 4 and demonstrates a slow beginning of the sintering at about 1000°C, which is typical temperature for the brick 's manufacture, as well as the typical volume variations due to the transformation of quartz phases at heating and cooling. The scarce degree of densification is confirmed by the SEM images, presented in Fig. 5, showing a typical bricks structure with high percentages of open and closed porosities.

Obviously, the porosity in the surface (5a) is lower than one in the volume (5b).

Geopolymer sample was obtained from clay 2, previously heated to 700°C and then left at 150°C for 24 h. This calcined material is mixed with 12M NaOH, homogenized and after pressed.

The dilatometric curve is presented in Fig. 6 and demonstrate interesting intensive bloating starting after 950°C. The corresponding HSM silhouettes at 30, 930 and 980°C are presented on Fig. 7a, 7b and 7c, respectively.

The microstructure of the newly obtained



a) b)

Fig. 5. SEM image of the surface (a) and of the fracture (b) of ceramic sample.

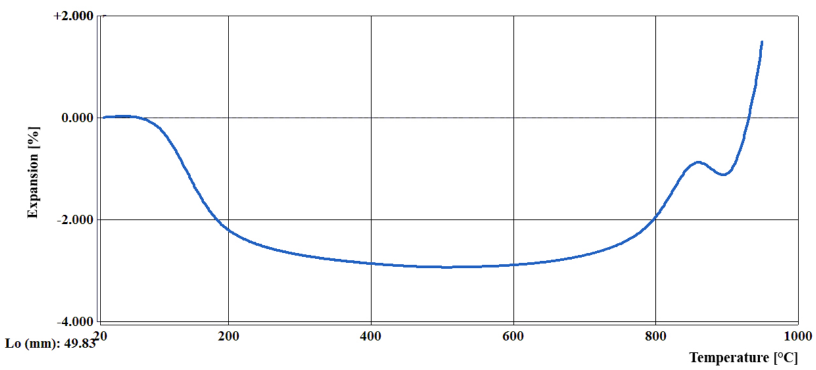


Fig. 6. Dilatometric curve of geopolymer sample.

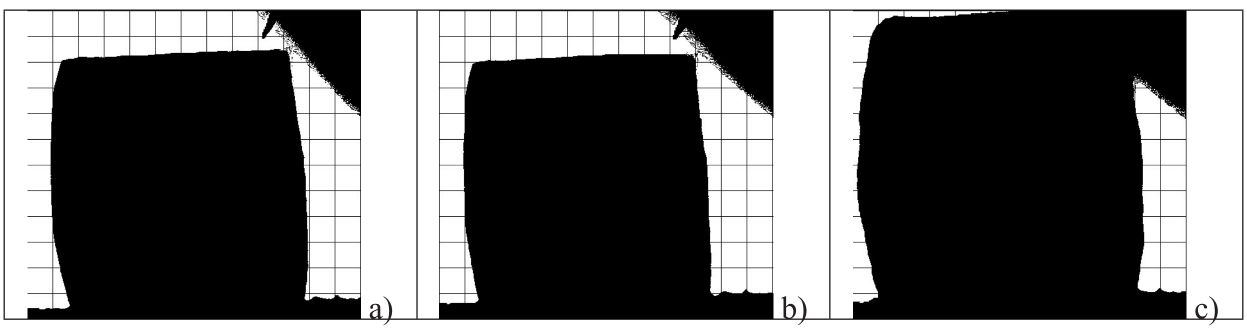


Fig. 7. HSM silhouettes at 30°C (a), 930°C (b) and 980°C (c).

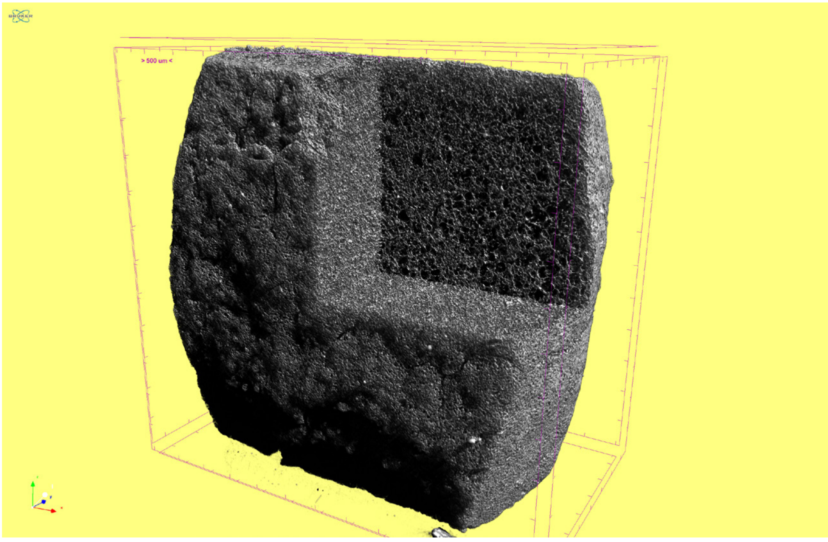


Fig. 8. 3D reconstruction of X-ray computed.

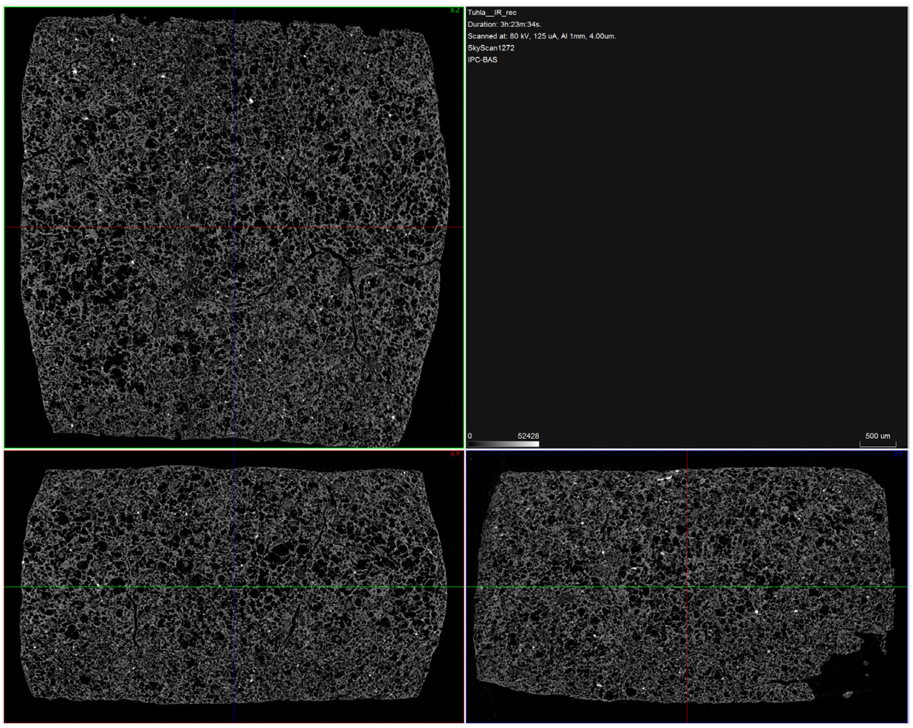


Fig. 9. 3D reconstruction of X-ray computed.

materials can be further investigated with μCT. The 3D reconstructions of X - ray computed of the samples also give the possibility to evaluate the total porosity (Fig. 8 and Fig. 9). The measurement of the volumes of the samples and that of the total solid substance produces porosity percentage is 56 %. It can be noted that the porosity is mainly closed with size between 100 - 300 μm.

CONCLUSIONS

This preliminary analysis elucidates potential opportunities for using the clays from sample 1, 2 and 4 as raw materials for ceramic industry. It seems that sample 2, which is montmorillonite type is more plastic, while 1 and 4, where higher sand content is observed, and the drying shrinkage is negligible could be characterized as less plastic.

The initial results for the thermal behaviour and the structure of a brick sample (obtained by mixing of clays 1 and 4) and a foamed geopolymer samples (based on clay 2), are also reported. The first sample shows a beginning of the firing shrinkage at about 1000°C, while the second demonstrates intensive bloating after 950°C, leading to specimen with about 56 % closed porosity.

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