Utilization of asbestos waste in the synthesizes of “historical” yellow cobblestones of Sofia

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Keywords: ceramics, sintering, asbestos waste
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Introduction

The “yellow cobblestones” of Sofia are a historical clicker pavement, which in 1907-1908 was used to cover at about 60 decare of the central streets of the new Bulgarian capital. Today the whole reserved space is two times smaller and many of yet existing “yellow bricks” are broken or cracked.

This material was developed in Budapest and has been used as luxury pavement in various Hungarian cities and abroad. It was produced by a local Budapest marl with a specific composition. After the exhaustion of the mine in the middle of the 20th century its production was stopped.

The preliminary studies of various Bulgarian marls highlighted that somewhat similar raw materials exist also in Bulgaria, but the appropriated clays are characterised with lover MgO concentration. It can be noted that the occurrence of necessary MgO % in the batch is required because it influence positively on the sintering, phase composition and final properties.

The aim of present work is to demonstrate the possibility to synthesise a material, very similar to the original "yellow cobblestones” of Sofia, by addition of asbestos waste containing high percentage of MgO.

Experimental

The chemical compositions of used raw materials were evaluated by XRF analysis, while the phase composition of resulting ceramics by XRD.

The “green” ceramic samples were prepared after homogenization with 6-7 % water and pressing at 40 MPa. The thermal behaviour was studied with hot stage microscopy and horizontal optical dilatometer.

The structure of ceramics was evaluated by Computed Tomography and SEM.

Results and discussions

Table 1. Chemical compositions

	YB	BM	AW
SiO_2	53,0	43,5	47,3
TiO_2	0,6	0,8	-
Al_2O_3	14,5	14,3	2,3
Fe_2O_3	5,1	5,2	2,6
MgO	5,1	2,2	46,7
CaO	16,9	13,8	
K_2O	2,6	2,7	
Na_2O	1,1	1,2	
SO_3	0,1	0,6	
L.O.I.	0,5	16,2	1,1

The results for the chemical compositions of original yellow bricks (YB), used local Bulgarian marl (BM) and asbestos waste fibres (AW) are presented in Table 1. It is evident that BM doesn’t contain the necessary amount of MgO for the production of the original historical pavement, as well as that an addition of AW can compensate this difference.

Furthermore, if some Na_2O_3 is also added in the batch a decreasing of the sintering temperature can be expected. In this manner it is possible to synthesise ceramics, similar to the original clinker, by utilising valuable amount of asbestos waste and working at lower temperatures.

Here, a composition based on ~90 wt % BM and ~10 % AW plus Na_2CO_3, labelled MBM (modified Bulgarian marl), is used.

Fig. 1 shows HSM plots of YB, BM and MBM. The first curve is obtained by re-sintering of milled below 75 micron original yellow brick, while other two - by heat-treatment of ceramic bathes.

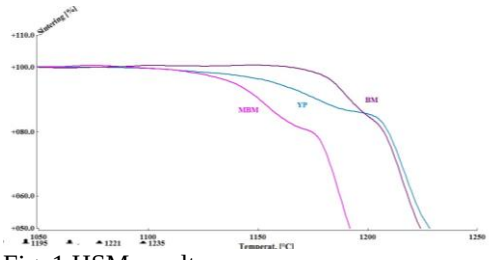


Fig. 1 HSM results

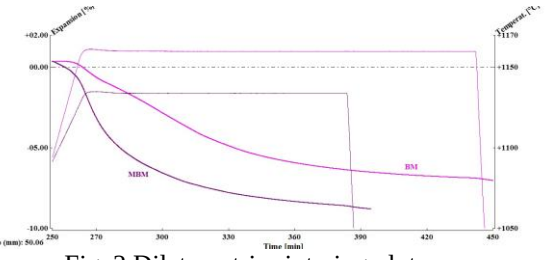


Fig. 2 Dilatometric sintering plots

It is highlighted that the re-sintering of original brick powder starts at about 1100-1110 ℃ and at 1200-1210 ℃ deformation of the sample is observed; at about 1230-1240 ℃ it is melted. The “sintering interval” is narrow (about 70-80 ºC), which means that probably working temperatures at about 1130-1150 ℃, coupled with longer holding times, were used for the production of the “historical pavements”.

The test with BM shows that the sintering starts at about 1160-1170 °C and the deformation occurs at 1200-1210 °C; than the sample melts very rapidly. Similar behaviour is problematic for eventual production. However, after the addition of asbestos waste and some Na_2CO_3 to BM very positive changes are observed. The resulting HSM plot demonstrate that the sintering and the deformation starts at about 1090-1100 and 1160-1170 °C, respectively (i.e. the sintering interval is significantly larger and the working temperature lower).

These results are confirmed by more precise dilatometric runs, presented in Fig 2. The sintering test of "as it is" BM marl at 1160 °C shows that even after 3 h holding the sintering is not completed and the firing shrinkage is at about 6 %. In addition, the crystallinity in BM sample is inferior, which is precondition for a decreasing of the mechanic properties. The colour is more brownish compared to the original clinker.

At the same time, the modified MBM batch riches at about 8 % shrinkage after 2 h at 1130 °C. Then the densification process practically rests without beginning of over-firing. The phase composition and crystallinity are comparable to the original "yellow cobblestones" and the of sample's colours are similar.

In Fig. 3 are presented CT images of the original YB and the new MBM clinker, which demonstrate a very good degree of sintering of both samples. The porosity is only closed and its amount is 8-10 vol %. The pores are mainly spherical, excluding some micro-cracks in the original cobblestone, manufactured a century ago. The similar microstructure of both ceramics is demonstrated in Fig. 4, which elucidate the high crystallinity of samples and the formation of tiny pyroxene and plagioclase crystals.

The good degree of sintering, coupled with so fine crystalline structure, explain the extraordinary mechanical properties of the "yellow cobblestones" of Sofia. The comparable structure and crystallinity of newly studied MBM ceramic is a precondition for eventual successful production of replicas of this remarkable pavement, which from one century is one of the "symbolc" of Sofia.

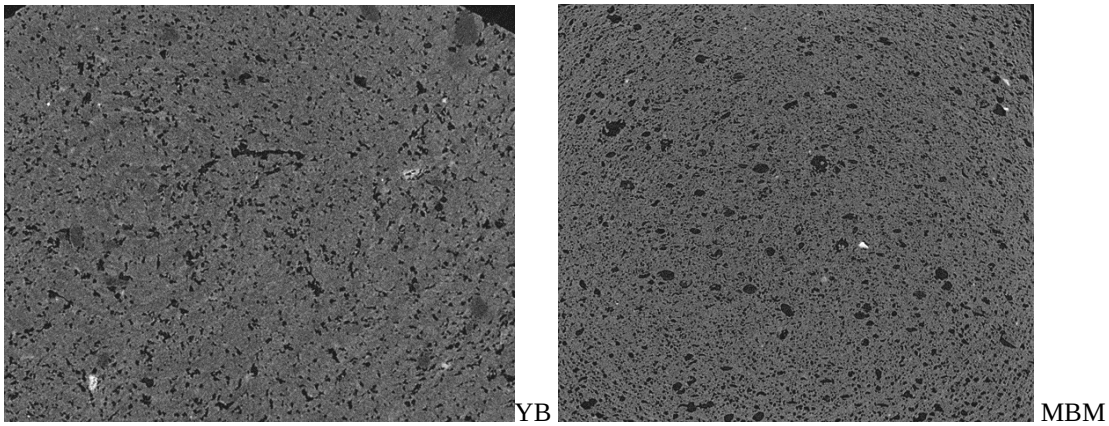
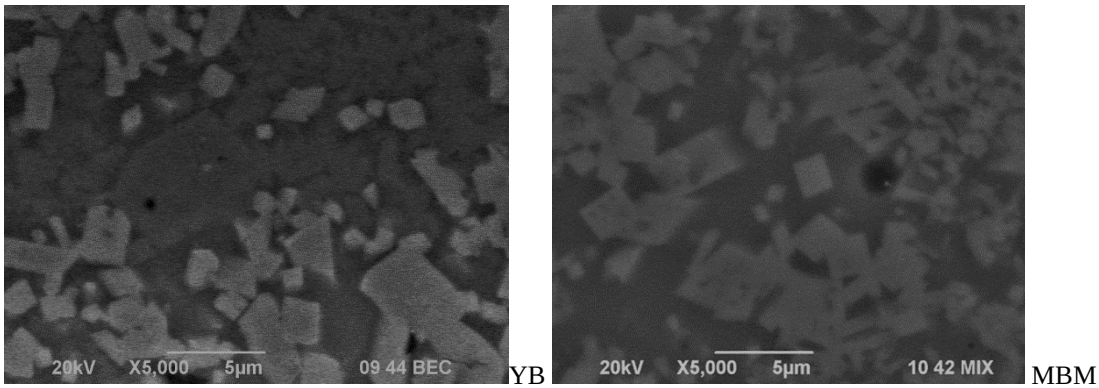

YB MBM

Fig. 3 Computed Tomography reconstructions of YB and MBM ceramics



YB MBM

Fig. 4 SEM images of polished YB and MBM ceramics

Conclusions

It is demonstrated that a ceramic, very similar to the original "yellow cobblestones" of Sofia, can be synthesised using local Bulgarian marl. The lower MgO content in used clay is compensated by the addition of asbestos waste in the batch. Thus, samples with very similar structure, chemical composition and crystallinity are obtained.

Acknowledgements: This research was financially supported by BSF project KP-06-N67/13 "Use of Bulgarian marl raw materials with additives from other natural and industrial sources for the synthesis of high-quality ceramics of the „yellow" pavers type".