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CONCENTRATION OF CARBONATE ADMIXTURE FROM OPALIZED TUFF INTO ONE SEPARATE FRACTION

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A b s t r a c t: White opalized tuff (from the Strmoš locality, Probištip), as a raw silicate amorphous material, contains some quantity of admixtures. The total quantity of admixtures amounts is about 8% mass. Mine powdery ingredients are homogeneously distributed into the basic silicate mass. Carbonate material is a significant part of present admixtures, and it is possible to be separated with controlled milling. Milling parameters (type and time of milling) enables to concentrate the present $CaCO_3$ in granulometric fraction <0.032 μm, after 30 min. milling. Reliable evidence about aforementioned separation is shown with simultaneous view of the results of silicate chemical analysis, DT/TG analysis (750–850°C), and sieve-analysis. From the X-ray analysis it is evident that the present carbonate material exists in crypto crystal to amorphous state. The space where $CaCO_3$ is hidden, presents the place between basic silicate particles inside the groups, generally with dimensions about 40 to 60 μm. The concentration of $CaCO_3$ appears when this particle group goes to the process of disintegration.

Key words: white opalized tuff; admixture; milling; concentration

INTRODUCTION

Inorganic raw materials are spread in Macedonia. Raw silica amorphous minerals like tuff, trepel, diatomite, diatomaceous earth etc. are dominantly spread in some regions [1–4].

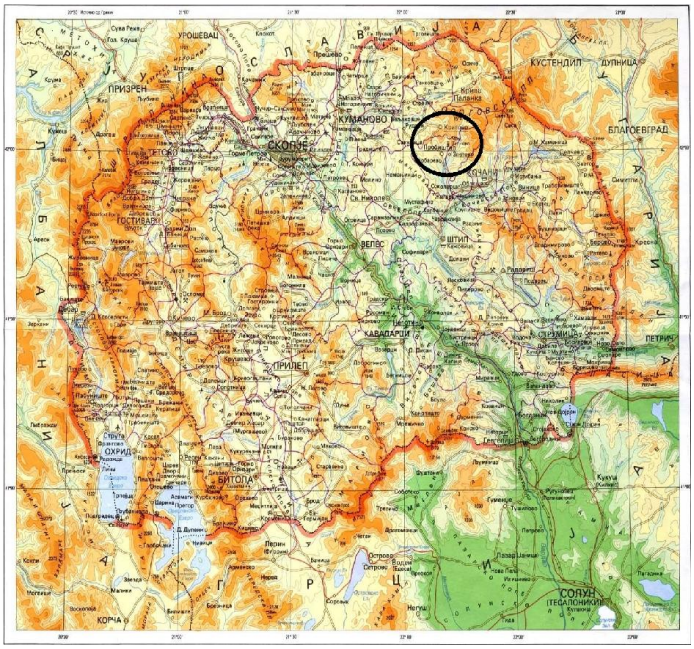

Fig. 1. Geographical location of the deposits

According to the geological origin, tuffs belong to a group of pyroclastic rocks, whose genesis is related to the volcanic activity in the region, i.e. by sedimentation of ejected volcanic mass [5, 6]. Explosive volcanic eruptions are caused by high concentration of gas and high viscosity of magma as contrary forces. Explosive eruptions of the highest intensity occur when there is grinding of solid rocks which disable exit, under the influence of increased pressure of dissolved gasses in the magma.

The magma is formed inside the Earth, under the heat influence from the parts which have not cooled yet. It is a heated liquid silicate solution consisted of a large number of components, which is rather homogeneous in early phases of forming, due to high pressure and high temperature. All known chemical elements of which oxygen and silicon are the most dominant ones, are present in the composition of the magma.

Tuffs are widely spread in almost all volcanic regions in Macedonia. The white opalized tuff, which has been the subject of this research, dominantly exists in the Kratovo–Zletovo volcanic area (Figure 1) [7, 8].

MATERIALS AND METHODS

The samples for analysis of white opalized tuff are taken from the deposit in the locality of Strmoš, Probištip (Figure 2)

White opalized tuff is a natural raw material dominantly consisted of amorphous SiO_2 [1]. Average chemical composition of the material is presented in Table 1. Variations in the chemical composition are consequence of natural changes within the deposit.

Fig. 2. Deposit in the locality the Strmoš, Probištip

T a b l e 1

Average chemical composition of white opalized tuff (mass %)

SiO_2	90–92
Al_2O_3	2–5
Fe_2O_3	0.2–0.5
TiO_2	0.2–0.4
CaO	1.5–4
MgO	0.4–1.2
Na_2O	0.1–0.4
K_2O	0.05–0.1
P_2O_5	max 0.1
MnO	tr.
SO_3	0.4–0.8
l.w	2–4

Operations of crushing and milling are applying for the process of mechanical preparation of the material. Initially, there is single crushing of the material to a fraction of <1 mm into a roller crusher (Figure 3).

Then, there is dry milling into a porcelain mill with balls in duration time of 30 min, 1, 2, 3, 4, 5 and 6 hours. The material: ball ratio is 1 : 2.5 and the velocity of rotation is ω = 65°/min. At these conditions, the milling is combination of cataract and less cascade regime.

Wet sieve analysis have been conducted for the various milling phases. A set of standard sieves with diameter of perforation of 0.032 mm to 0.1 mm (0.032 mm, 0.040 mm, 0,063 mm,0,071 mm, 0,1 mm) have been used. Sieve analysis have been conducted on 50 g samples, which have been previously dried in the dryer at the temperature of 105°C to a constant mass.

Fig. 3. Crushed tuff: dimensional fraction –1 mm

The further analysis are realized on separated fractions of the different phases of the milling process.

Chemical composition of the various fractions of various milling phases, are determined with silicate chemical analysis.

DT/TG analysis of the raw material were performed with NETZSCH 348 472c apparatus, at temperature range 20 – 1200 °C; 10°C/min.

X-ray analysis were realized on PHILIPS PW 1010 X-ray diffractometer (2θ = 2–60°; 38 kV; 18 mA; Cu$K\alpha$/Ni).

RESULTS AND DISCUSSION

Samples for analysis are composed of grain with size fraction from 0 to 5 mm. Their chemical composition is presented in Table 2. Compared with other tuff depostits where SiO_2 content is higher then 60% [9–12], white opalized tuff from the locality of Strmoš, Probištip, represents a high purity raw material with SiO_2 content over 90 % mass. The material contains various admixtures and constitutional H_2O whose part reaches up to 10%. On macrolevel, the admixtures are homogeneously distributed throughout basic mass of amorphous SiO_2.

In order to define the effects of the mechanical destruction of the material a wet sieve analysis of various milling phases has been conducted. Obtained results are presented in Table 3 (Figure 4).

T a b l e 2

Chemical composition (mass %) of size fraction grain 0 – 5 mm

SiO_2	90.27
Al_2O_3	2.91
Fe_2O_3	tr.
CaO	2.30
MgO	0.75
K_2O	0.08
Na_2O	0.26
SO_3	0.54
l.w	2.82
Σ	99.93

T a b l e 3

Granulometric sieve analysis of various milling phases (mass %)

Fraction (mm)	30 min.	1 h	2 h	3 h	4 h	5 h	6 h
<0.1	60.30	39.75	12.19	3.62	2.70	2.37	2.01
0.071 – 0.1	11.93	9.94	11.30	9.03	5.81	4.82	4.74
0.063 – 0.071	0.89	5.49	9.57	4.16	5.27	3.72	3.35
0.040 – 0.063	6.60	10.38	11.36	13.11	11.40	12.35	10.69
0.032 – 0.040	1.63	5.05	8.13	6.47	6.81	6.93	7.37
<0.032	18.65	29.39	47.45	63.61	68.01	69.81	71.84

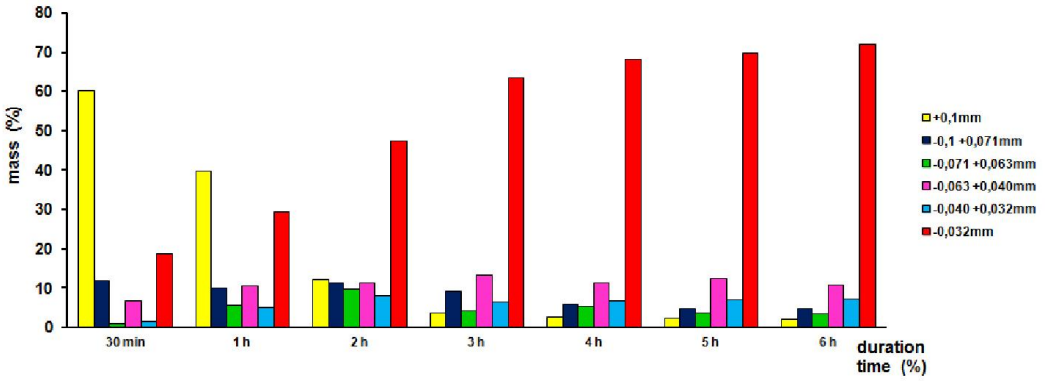

Fig. 4. Histogram of granulometric sieve analysis of various milling phases

Concentration of some of the mixtures in different fractions is determined with simultaneous review of the results of chemical, XRD, DT and TG analyses.

The results of chemical analysis of the fractions with various dimensions of the grains after 30 min of milling are presented in Tables 4 and 5.

T a b l e 4

Chemical composition of various fractions after 30 min of milling (mass %)

Fraction (mm)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	l.w	Σ
<0.1	90.62	2.84	tr.	1.95	0.65	0.09	0.38	0.42	2.93	99.88
0.071 – 0.1	91.56	2.92	tr.	1.24	0.47	0.08	0.35	0.55	2.75	99.92
0.063 – 0.071	91.81	2.95	tr.	1.07	0.42	0.08	0.26	0.63	2.63	99.85
0.040 – 0.063	90.02	3.35	tr.	1.63	0.95	0.07	0.11	0.60	3.18	99.91
0.032 – 0.040	89.48	3.18	tr.	1.84	1.08	0.08	0.13	0.68	3.46	99.93
<0.032	84.13	3.95	tr.	3.92	1.36	0.07	0.14	0.65	5.73	99.95

T a b l e 5

Chemical composition of fraction <0.032 mm of various milling phases (mass %)

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	l.w	Σ
30 min	85.13	3.95	tr.	3.92	1.36	0.07	0.14	0.65	4.73	99.95
2 h	89.72	3.35	tr.	2.54	0.5	0.08	0.12	0.51	3.12	99.94
6 h	90.48	3.31	tr.	2.17	0.47	0.07	0.09	0.44	2.89	99.92

With the results of the chemical analysis it is confirmed that white opalized tuff is a natural raw material with a basic mass of amorphous SiO_2 (which is confirmed with an X-ray analysis). Total quantity of admixtures is around 10 %.

The part of CaO in the initial material is 2.30 %. With the exception of the fraction <0.032 mm) after 30 min. of milling, its mass part in other fractions at various milling phases is within the limits of 1.07 – 1.95 %. In the previously mentioned fraction the concentration of the present CaO was 3.92 % mass. In that fraction there is significant loss of mass under thermal treatment, which points to the presumption that it is probably a carbonate admixture.

The results correlates to DT/TG analysis (Figure 5) where there is loss of mass in the temperature interval of around 750 – 800°C due to the thermal dissociation of carbonate admixtures.

Comparatively, the TGA curves of various fractions of various milling phases are presented in Figures 6 and 7.

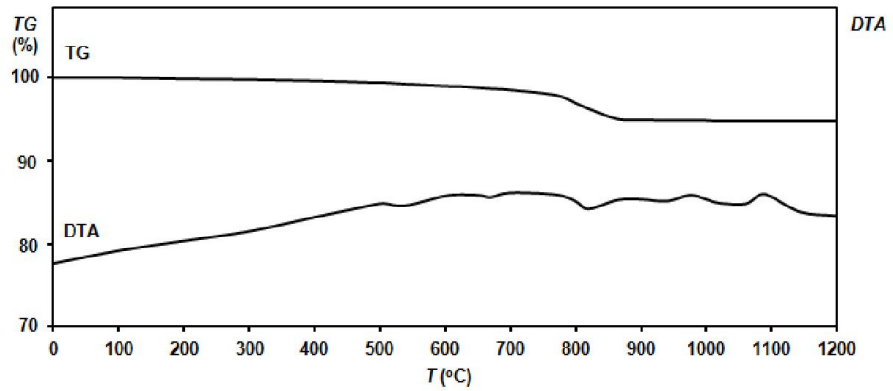

Fig. 5. DT/TG analyses of fraction <0.032 mm after 30 min. of milling

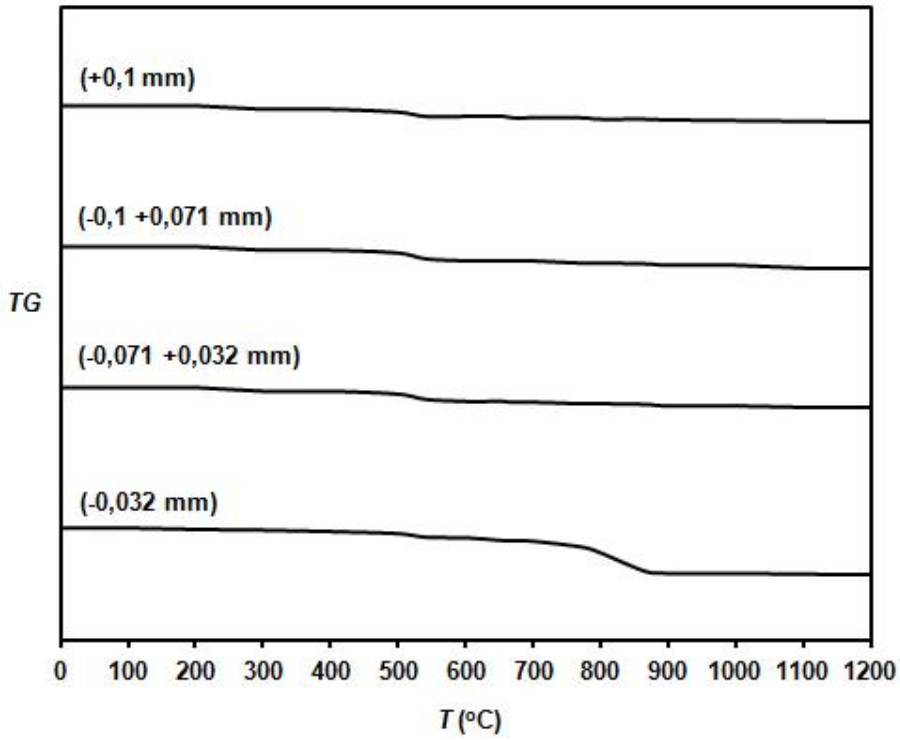

Fig. 6. Comparative TG analyses of various fractions after 30 min. of milling

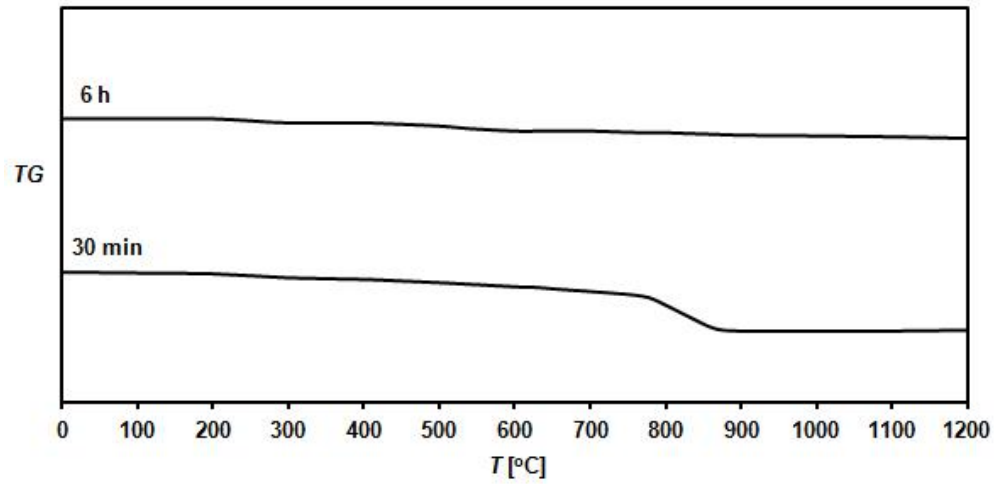

Fig. 7. Comparative TG analyses of fraction <0.032 mm of various milling phases

Thermal treatment of the material causes higher degree of structure stabilization – crystallization, depending on the temperature and time treatment. At the same time minimal change in the porosity occurs, resulting in insignificant decrease of specific surface [1].

Applying the XRD-analysis, dominant quantum of amorphous SiO_2 has been proven. Beside the amorphous SiO_2, there are minor quantities of crystalline forms of tridymite and quartz. Absence of the typical peaks of $CaCO_3$ on X-ray diffractogram confirms that the present carbonate material exists in amorphous to crypto-crystalline phase.

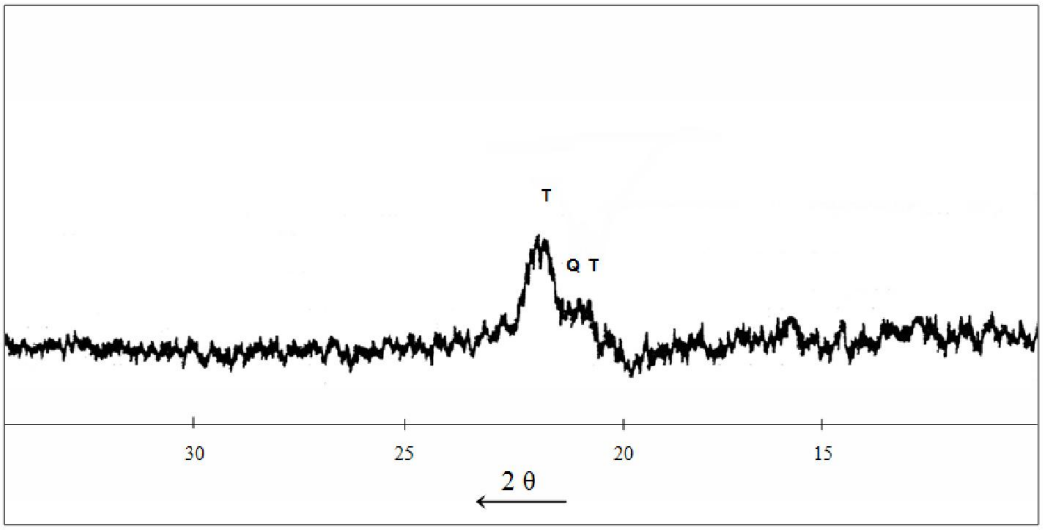

Fig. 8. X-ray diffractogram of fraction <0.032 mm after 30 min of milling

CONCLUSION

The distribution of admixtures by volume in the original material, as well as parameters of the milling process (regime and duration time) provide concentration of the present carbonate admixture in sieve fraction <0.032 mm after 30 min. of milling).

The space where $CaCO_3$ is "hidden" presents the place between basic silicate particles inside the groups, generally about 40 – 60 μm. During the process of preparation of the material (mechanical

destruction), there is a concentration of the carbonate admixture in these size fracction grains.

From the obtained results it can be concluded that depending on the used material, the milling process can be implemented at a specific regime in order to satisfy the previously set requirements from the aspect of concentration of admixtures, thus using previously obtained knowledge. The detailed characterization of different size fractions gives opportunity for their specific and selective implementation.

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Р е з и м е

КОНЦЕНТРИРАЊЕ НА КАРБОНАТНАТА ПРИМЕСА ОД ОПАЛИЗИРАН ТУФ ВО ОДДЕЛНА ФРАКЦИЈА

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Клучни зборови: бел опализиран туф; примеси; мелење; концентрирање

Белиот опализиран туф (од локалитетот Стрмош, Пробиштип) претставува аморфна силикатна суровина, која во својот состав содржи и одредени примеси. Вкупното количество на примесите изнесува околу 8% масени. Рудните прашковидни примеси се хомогено дистрибуирани во основната силикатна маса. Значаен удел во примесите претставува карбонатниот материјал, кој може да биде сепариран со контролирано мелење. Параметрите на процесот на мелење (типот и времето на мелење) овозможуваат концентрирање на присутниот $CaCO_3$ во гранулометриската фракција <0,032 μm, по 30 минути мелење. Истото се докажува со симултан преглед на добиените резултати од силикатната хемиска анализа, DTA/TG анализата (750–850°C) и ситовата анализа. Рендгено-структурната анализа докажува дека присутниот карбонатен материјал егзистира во криптокристалеста до аморфна состојба. $CaCO_3$ е скриен во меѓупросторот од групите на силикатната честички со димензии од 40 до 60 μm. До концентрирање на $CaCO_3$ доаѓа при деструкцијата на овие групи честички.