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POSSIBILITY OF USING DIATOMACEOUS EARTH FROM KOLUBARA AND VESJE DEPOSITS FOR PRODUCTION OF BEER FILTER AIDS

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Abstract: Diatomaceous earth is a non-metallic mineral raw material composed of skeletal remains of single-cell water plants, known as diatomite. Owing to quite complex structure of skeletal diatomite with numerous fine microscopic pores, cavities and channels and, therefore, large specific surface area and high adsorption capacity, diatomaceous earth can be used as adsorption auxiliary material for filtration. It is suitable for production of filtering compounds used in breweries. Two of several deposits on the Balkan Peninsula, the Kolubara deposit in Serbia and Montenegro, located 60 km south of Belgrade and the Vesje deposit in the Former Yugoslav Republic of Macedonia located near Negotino, were selected for the purpose of investigating their possible application in preparation of beer filter aids. With the aim of predicting the filtration efficiency, chemical, mineralogical and structural properties of diatomite samples were analyzed and parameters of crushing, drying, calcination and classification were defined. The results showed that there are certain differences in processing technology of two investigated deposits but both types of diatomaceous earth can be used for the production of beer filter aids. Beer filtration tests proved diatomites to be satisfactory and not causing any degradation of filtration process or beer quality. Technological flow scheme for obtaining the beer filter aids is proposed in this research.

Keywords: diatomite, XRD, TEM, processing, filtration.

INTRODUCTION

Diatomaceous earth (DE) or diatomite is basically natural amorphous silica, the only biologically based natural mineral. This is a siliceous sedimentary mineral compound originating from the microscopic siliceous fossilized skeletons of diatoms remains of unicellular algae-like plants called diatoms, which are composed of rigid cell walls called frustules. Namely, when aquatic diatoms die, they sink and collect at the bottom of the ocean and lake floors to form deposits of the material known as “diatomaceous earth”. There are over 100,000 of well-known different species, each possessing a unique morphology (Martinovic et al. 2006, Ozen et al. 2015, Round et al. 1990, Ha et al. 2013).

Sizes of fossilized diatoms are in the range from less than 1 µm to more than 1 mm in diameter, typically 10-200 µm. Their morphology have a broad variety of delicate, lacy and perforated shapes varying from spheres and cylinders to discs, ladders, feathers, and needles (Martinovic et al. 2006, Ozen et al. 2015, Round et al. 1990, Ha et al. 2013, http://minerals.usgs.gov/minerals/pubs/commodity/diatomite/diatomyb03.pdf). The high porosity and low density of diatomite make it ideal for many applications such are, for example, as an insulating material, abrasive, filter, paint filler, and pesticide carrier. Diatomite is cheap and abundant in nature, possessing a high sorption ability and surface area, so it can be used for metal ions removal from contaminated wastewaters. Unfortunately, full potential of this material is far from being realized http://minerals.usgs.gov/minerals/pubs/commodity/diatomite/diatomyb03.pdf).

It was proved that filter aids produced from diatomite can improve the flow rate and quality of filtration in food and medicine industries (Ren et al. 2014, Du et al.u 2011). The particle size of diatomite affects the porosity and efficiency of filtration beds. Fine particles in the raw diatomite may give rise to low porosity and low permeability of filter materials (Ren et al. 2014, França et al. 2003). Thus, raw diatomite usually needs to be treated by calcination or flux calcination to improve its permeability and other features such as adsorption property and whiteness

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(http://minerals.usgs.gov/minerals/pubs/commodity/diatomite/diatomyb03.pdf, França et al. 2003, Bentli et al. 2004). Namely, organic and carbonate components can be removed from the raw diatomite by calcination thus improving the porosity, permeability and filtration rate which depends on opening up of diatom frustules and aggregation caused by sintering and shrinkage of the particles. Diatomite based filter aids with good filtration properties and whiteness can be easily obtained by flux calcinations using fluxes such are Na_2CO_3, NaCl, KCl, NaOH, KOH, and fluoride salts. Fluxes can be added to diatomite before the sintering or during calcination stage. They react with iron oxides at high temperatures. This can change the color and organoleptic properties of the final product in food industry, and allows the oxides in the diatomite to enter a glassy phase. They prevent coloration (when it is colorless) and form larger agglomerates of the diatom fragments (Ren et al. 2014).

This study was occupied by investigation whether a sintered diatomite can be simultaneously served as a filter aid in brewery industries. Two of these deposits, the Kolubara deposit in Serbia and the Vesje deposit in the Former Yugoslav Republic of Macedonia were selected for the purpose of this investigation.

EXPERIMENTAL

Characterization of diatomaceous earth deposits

Diatomite ores were subjected to chemical, mineralogical, and structural analysis.
Chemical compositions are shown in Table No. 1. Content of SiO_2 was determined by gravimetric analysis, while contents of Al_2O_3, Fe_2O_3, Na_2O and K_2O were determined by atomic absorption spectroscopy (AAS 703-Perkin Elmer and AANALYST 300, USA). Since the samples from Kolubara deposit contained high amount of carbon i.e. coal (up to 20 %), they were fired prior to chemical analysis. On the other hand, the Vesje diatomaceous earth did not contain organic impurities and therefore it was only dried.

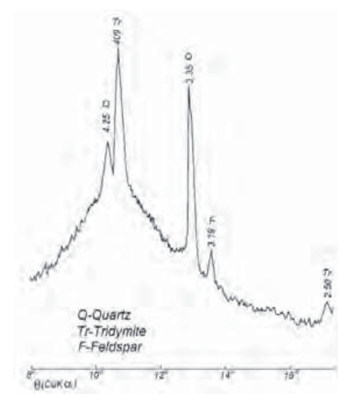
The Vesje sample has higher content of SiO_2 compared with the sample from the Kolubara deposit and therefore lower contents of other present oxides. Hence, diatomaceous earth from the Vesje deposit is considered as raw material of better quality because of its the exceptionaly high content of SiO_2. It is also evident that content of Fe_2O_3 in Kolubara sample is higher than in Vesje sample, but it has no effects on beer quality. Loss of ignition is considerable in the Kolubara sample due to high content of coal.

Table 1, Chemical composition of diatomite from the Kolubara and Vesje deposits.

Content (%)	Kolubara	Vesje
SiO_2	82.0	90.0
Al_2O_3	11.0	2.9
Fe_2O_3	2.5	1.5
CaO	1.7	0.8
MgO	0.8	0.1
TiO_2	0.6	-
K_2O	0.4	0.1
Na_2O	0.3	0.2
LOI*	0.3	4.4

*LOI- Loss of ignition; Kolubara- fired; Vesje- dried

X- ray diffraction analysis was performed by X-ray diffractometer (type Philips PW-1820/00) using monochromatic CuK_α radiation in order to determine mineral analysis of raw materials, Figure No. 1.



Kolubara

Vesje

Figure 1, XRD mineral analysis of diatomaceous earth.A

It is obvious that the samples mostly consist of amorphous phases with traces of quartz, feldspar, cristobalite, and tridimite. Analysis show that content of skeletons and shells is approximately 80 % while the rest are impurities of organic and inorganic origin.

Microstructure analysis provides reliable information about shape, structure, porosity, and size of diatomaceous earth particles. Transmission electron microscope (TEM) observations were made using a microscope of the type JSM T-20, JEOL Japan, equipped with an energy dispersive X-ray analyser (EDAX). Transmission electron microphotographs of diatomaceous earth samples are presented in Figure No. 2.

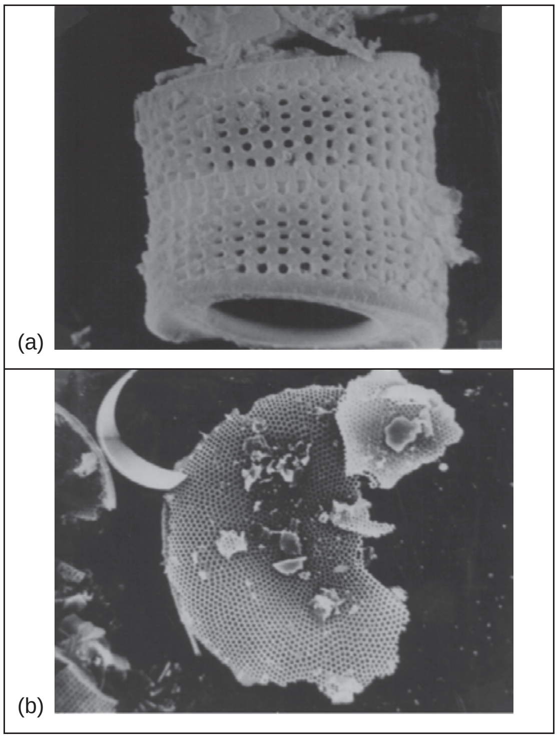


Figure 2, TEM of diatomaceous earth:

(a) Kolubara deposit (magnification of 4000 X);

(b) Vesje deposit (magnification of 4000 X).

Undamaged forms of Kolubara diatomaceous earth with extremely clean pores are obviously visible in Figure 2a. Insignificant content of the impurities originating from coal can be noticed at the surface of diatomaceous earth. The impurities are outside pores, so during the calcination, complete combustion of coal is obtained.

Vesje diatomaceous earth particles have cylindrical shape with all accompanying ingredients on its surface, Figure 2b. Considerable content of small crystals (impurities) such as quartz, feldspar and cristobalite are detected at the surface of diatomaceous earth and this sample belongs to gray diatomaceous earth.

Filter aid preparation

The method of mechanical and thermal sample preparation consisted of the following phases: natural draught drying of crude raw materials, primary ore crushing and cutting, drying, flux calcinations, disintegration of calcined materials and finally air classification. Natural draught of raw materials was simulated in laboratory under the conditions normally applied in industry. Crushing of raw materials air-dried to the moisture content of 30-50 % was performed in a laboratory mill with cutters. During the crushing, the cuts of 0-16 mm were obtained. The main goal of primary processing is to avoid sticking of ore to the parts of mill if moisture exceeds 30 %. For this reason, it is necessary to dry the Vesje ore to the moisture level lower than in the Kolubara ore. Drying was performed in a laboratory drum drier. Calcination was realized according to the flux calcination regime. During calcination, the additives supporting the formation of agglomerated diatomite particles were applied. The experiments of the calcination process were performed in electric laboratory drum furnace. Technological parameters of drying and calcinations are presented in Table No. 2.

Table 2, Technological parameters of drying and calcination.

Parameter	Drying	Calcination
Revolution (rpm)	5	3
Temperature (°C)	180-250	900-950

Drying and calcination are the most important phases of the process. Powder with maximum moisture content of 7 % is obtained after drying process. The agglomerates are always present in dried powder. During the calcination, these agglomerates tend to slow down the combustion of coal present in dried diatomaceous earth samples. Therefore, it is necessary to disintegrate the agglomerates prior to calcination. The method of moving layer flux calcination of real powders is applied. This method was selected due to high ratio of very fine primary diatomite particles (1-5 µm) in dried semi-product. The fine particles decrease the flux because of high resistance to flow. Hence, it is necessary to provide size distribution of the filter aids particles that have its maximum in the range of 5-40 µm. Particles of diatomaceous earth of the Vesje deposit are characterized by high proportion of particles smaller than 5 µm or bigger than 30 µm. On the other side, particles of diatomaceous earth of the Kolubara deposit are characterized by high ratio of particles in the range of 5-10 µm and 25-30 µm.

General processing flow scheme of diatomaceous earth from the Kolubara and Vesje deposits for beer filter aids preparation is developed, Figure No. 3.

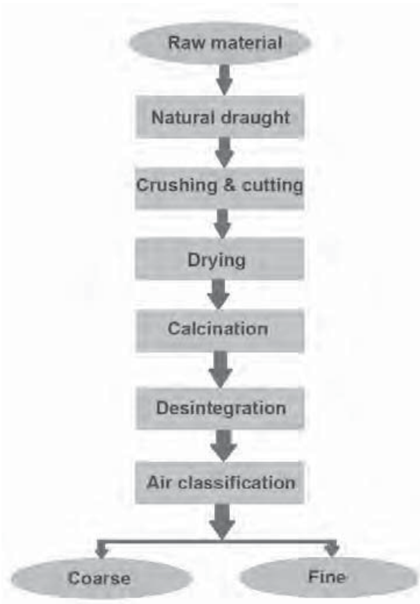


Figure 3, Processing flow scheme for preparation of filter aids.

Beer filtration test

Bulk density, moisture content, loss of ignition and influence of diatomaceous earth on organoleptic characteristics of beer were determined according to the recommended method for testing the filter aids used in breweries. Membrane filtration test, also called the Esser test (standard filterability test), was used for determination of beer filtration rate. On the basis of the laboratory tests, influence of diatomaceous earth on beer quality is presented in Table No. 3.

Laboratory tests proved the absence of adverse effects of diatomaceous earth on the beer characteristics. According to the data, it could be concluded that the particles of diatomaceous earth from the Kolubara deposit are coarser and therefore provide shorter filtration time and larger capacity of filtration. On the other hand, the smaller size and shape (cylindrical and plateaus) of diatomaceous earth particles from the Vesje deposit result in longer filtration time and consequently lower capacity of the filtration.

Table 3, Results of laboratory filtration test.

Parameter	**Test beer before filtration**	**Test beer after filtration Kolubara**	**Vesje**
pH	4.42	4.47	4.45
Beer colour (EBC)	9.0	9.0	9.0
Beer turbidity (EBC)	8.6	3.2	2.6
Beer taste and flavour	normal	normal	normal
Fe_2O_3 (mg/dm^3)	0.06	0.361	0.362
Filtration time (s)	-	94	112
Bulk density (g/dm^3)	-	240	210

CONCLUSION

Microstructure analysis shows that all impurities of either organic or inorganic origin are outside diatomite pores, which had significant influence on technological process design. The proposed technological processing procedure provides complete combustion of finely dispersed particles of coal present in the Kolubara deposit.

Fine and coarse beer filter aids can be produced from both types of diatomaceous earth. The laboratory tests of filtration proved that there is a possibility to replace the currently imported beer filter aids with domestic product, which causes no degradation of filtration process or beer quality.

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