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Clay-Based Filters for Industrial Liquid Separation

Maja Kokunešoski*

VINČA Institute of Nuclear Sciences - National Institute of The Republic of Serbia, University of Belgrade, Mike Petrovića Alasa 12-14, 11351 Belgrade, Serbia

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ABSTRACT

Sediment materials, such as clay, are attractive for application in manufacturing porous ceramics owing to their low price and high abundance. Porous ceramics possess a combination of several essential properties of clay-based materials, the most important high porosity, and high thermal and chemical stability. The combination of these mechanical and physical properties of clay-based materials is crucial for various industrial applications (filters, heat insulators, absorbents, etc.) and advanced environmental applications. Purified clay was mixed with boric acid due to its low-cost, and its eco-friendly nature for production of a porous structure. The effect of different contents of boric acid on clay-based materials was analyzed. Amounts of boric acid in 2 wt.% and 0.5 wt.%, combined with different synthesis conditions, were used for clay-based filter production. The filter medium with optimal hardness and un-uniform pore distribution was obtained.

Keywords: clay, boric acid, porosity, sintering.

1. Introduction

Clay is one of the oldest natural materials people have used since ancient times. Numerous clay ceramic vessels and other artefacts were originating from the Neolithic period. During the aforementioned period in human history, the Vinča culture was the world's most technologically advanced prehistoric culture (Garašanin, 1982). Vinča culture was named after the locality of Vinča White Hill, which is located in the village of Vinča near Belgrade, Serbia.

Over time, people increasingly discovered the importance of clay as a natural material. Clay has almost unlimited possibilities of application in synthesizing new materials with great potential for practical application. It is well known that clay, as a sediment material, is attractive for synthesizing porous ceramics due to its low price and abundance. Porous ceramics, which originated from clay, provide a combination of important properties of materials, such as high porosity and high thermal and chemical stability. This combination of properties is crucial for industrial clay uses, such as making filters, heat insulators, absorbents, catalyst supports, and advanced environmental applications like membranes and chromatography columns.

This study is a continuation of research on the development of a filter produced from clay from the Kolubara coal mine in Serbia for the purification of industrial water (Kokunešoski and Ružić, 2024). During coal exploitation from the Kolubara open-pit coal mine in Serbia, a considerable amount of clay-like material was deposited, which has a high economic potential. Boric acid was used as a low-cost, environmentally friendly chemical to create a porous structure. The modifications of the contents of boric acid in amounts of 2 wt.% and 0.5 wt.%, and various synthesis conditions, such as low compacting pressure of up to 60 MPa and low sintering temperatures of 1150 °C and 1300 °C, were applied to make a filter medium with important properties for practical application, such as optimal hardness and uniform pore distribution.

2. Materials and methods

The chemical composition of clay obtained by the inductively coupled plasma spectrometry (Spectroflame-ICP, SPECTRO Analytical Instruments) shows that its main composition includes (in wt.%) 88.00% SiO_2, 6.05% Al_2O_3, 2.06% Fe_2O_3, 0.48% TiO_2, 0.18% CaO, 0.35% MgO, 1.05% Na_2O and 1.76% K_2O (Kokunešoski et al., 2014). It should be noted that the clay from the Kolubara open-pit mine has already been characterized in detail (Kokunešoski et al., 2014; Šaponjić et al., 2022).

Raw clay granulated to a particle size of 250 µm was treated at 600 °C for 2 h in air to remove organic impurities. Then, the clay was treated in an aqueous solution of 0.5 M HCl (p.a., 37%, BDH Prolabo) (wt.%, 1:10) to reduce the iron oxide content. After decanting the liquid phase, the residual sediment was washed with distilled water to pH ~ 5.5 and dried to constant weight at 100 °C in a laboratory dryer. Dried purified clay was granulated to a particle size of 250 µm.

* Corresponding authors.
E-mail address: majako@vin.bg.ac.rs (Maja Kokunešoski).

The aqueous solution of boric acid was prepared by dissolving 5.8 g of boric acid powder (Alkaloid AD, Skopje, Macedonia) in 100 ml of distilled water at 25 °C (Lide, 2003-2004) using a magnetic stirrer. A clay mixture prepared with 2 wt.% boric acid and a clay mixture prepared with 0.5 wt.% boric acid were made by mixing boric acid aqueous solution with purified clay in a weight ratio of 98:2 and 99.5:0.5, respectively. Both synthesized powder mixtures were granulated to a particle size of 250 µm. All compacts were pressed on a laboratory uniaxial mechanical cold press using a Ø 40 mm diameter mould and a height ~10 mm, and they appeared identical (Figure 1a). Before sintering, all pressed samples were heated to 600°C in air to remove boric acid. The samples with 2 wt.% boric acid were sintered at 1150 °C. The samples with 0.5 wt.% boric acid were sintered at 1300 °C. Both synthesized pilot filters were sintered for 4 h in air, as presented in Figure 1b.

a) b)

Fig 1. a) The compacts Ø 40 mm prepared from purified clay and 2 wt.% and 0.5 wt.% boric acid, having the same colour.
b) Red pilot filter with 2 wt.% boric acid sintered at 1150 °C, and grey pilot filter with 0.5 wt.% boric acid sintered at 1300 °C.

The first bubble method tests the functional characteristics of pilot-type filters in laboratory conditions. The procedure for the bubble method test is given in the ASTM Standard F316 2003 (2019). The handmade equipment for determining the first bubble on tested samples consists of a bottle with compressed air, a glass U-tube, a bathtub, and a shell with a pilot filter melted into its upper side. Figure 2 shows the bathtub and shell with a filter as part of the handmade equipment used to determine the first bubble on the tested samples.

The experiment starts by introducing air into the lower part of the shell previously immersed in water, and it finishes by measuring the pressure at the moment of the appearance of the first air bubble on the surface of the tested pilot filter. The bubble test indicates the size and location of the largest pores in the filter; the open bubble point pressure determines the mean pore size of the filter. The theoretical relation between this transition pressure and bubble-point pressure is the ($D=(4g\ x\ cos\ q)/P$ where P (N/m^2) is the bubble-point pressure, g is the surface tension of the liquid (72 mN/m for water), q is the liquid-solid contact angle (which for water is generally assumed to be zero) and D (mm) is the diameter of the pore. Equation (1) expresses diameter D (mm) of the pores, where K1=0.288 N/m is the empirical factor dependent on the filter material, and the form of the pores and P is the bubble point pressure, which determines the mean pore size of the tested filter.

$$D = \frac{K1}{P} \quad (1)$$

Vickers macro hardness (HV) was determined using the indentation method on sintered test tubes with 2 wt.% and 0.5 wt.% boric acid on a BUEHLER MICROMET 5101 Microhardness Tester instrument. The dimensions of the test tube on the surface of which the indentation was performed are Ø 16 mm, height ~ 16 mm. Both groups of test tubes were made in the same way, as the pilot filters with 2 wt.% and 0.5 wt.% boric acid, which have already been described. On the polished surface of the test tube, identification was performed until cracks reached a load of 0.5 kg, and the retention period was 10 s. The Vickers hardness (as $HV0.5$) was determined as the mean of measurements on 6 test tubes for both tested samples.

Vickers macro hardness (HV) is a measure of a material's resistance to the penetration of a diamond four-sided pyramid with an apex angle of 136°, loaded with a force F (N). Vickers hardness is expressed as stress on the indentation surface as done for equation $HV=F/A$, where A is the indentation area of the diamond four-sided pyramid (mm^2) and F the pressing force of indentation (N). The indentation area of the diamond four-sided pyramid can be calculated by the equation $A=d^2/2\ sin\ (136°)/2$ or approximately $A\approx d^2/1.8544$, where d is the mean value of the diagonals: $d=(d1+d2)/2$. Following that, Vickers macro hardness can be calculated from this Equation (2):

$$HV = \frac{F}{A} \approx 1.8544\frac{F}{d^2} \quad (2)$$

Pilot-type filter with 2 wt.% boric acid (60 MPa, 1150 °C).

Pilot-type filter with 0.5 wt.% boric acid (40 MPa, 1350 °C).

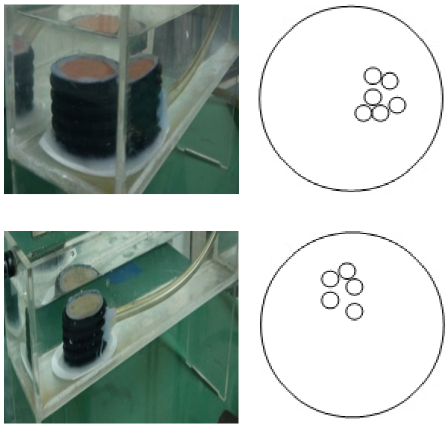

Fig. 2. Parts of the equipment for determining the first bubble (bathtub and shell with the filter) and the schemes of pore locations of the largest pores on the surface of the tested samples.

3. Results and discussion

The bubble test showed that the pores were not evenly located on the surface of both tested samples and indicated that the pores were grouped and moved toward the rim of the pilot filters (Figure 2). The tested sample, sintered at 1300 °C with 0.5 wt.% boric acid and compacted at 40 MPa, has a mean pore diameter of 0.133 mm. The tested sample, sintered at 1150 °C, with 2.0 wt.% boric acid and compacted at 60 MPa, has a mean pore diameter of 0.196 mm.

Using the indentation method on the tested samples with 2 wt.% and 0.5 wt.% of boric acid, the values of Vickers hardness of 58.58 MPa and 90.57 MPa, respectively, were determined. Further, the previously published results from the compressive tests exhibit the compressive strength of 22.64 MPa and 69.60 MPa and Young's moduli of 30.80 MPa and 71.27 MPa, for samples with content of boric acid of 2 wt.% and 0.5 wt.%, respectively (Kokunešoski and Ružić, 2024). Obtained results of the mechanical properties for samples with boric acid content of 2 wt.% and 0.5 wt.%, which could indicate their optimal mechanical stability and separation properties, originating from the pore net created in both filters. The crucial evidence for this phenomenon is that pilot filters remained stable during further manipulation as well as during long-term exposure in the water.

In earlier research, the separation functionality of synthesized filters was tested in laboratory conditions (Kokunešoski and Ružić, 2024). It is obvious that seemingly small changes in the pore size diameter of the tested samples significantly affect the separation ability of the tested filters. The plan for further investigation is to optimize the processing parameters to obtain the filter media of desirable properties.

4. Conclusion

This study is a continuation of research in the development of clay-based filters for the purification of industrial water using boric acid in amounts of 2 wt.% and 0.5 wt.% as a low-cost, environmentally friendly chemical to create a porous structure. The obtained Vickers hardness values of 58.58 MPa for the filter with 2 wt.% boric acid and 90.57 MPa for the filter 0.5 wt.% boric acid indicate good mechanical stability of the investigated sintered filters. The bubble test showed that the largest pores less than 0.2 mm were not evenly located on the surface of both tested samples.

Investigated filters showed optimal mechanical stability and separation properties due to the formation of the pore network. Due to the reached mechanical and physical properties, the produced filters show solid behaviour during long-term usage. The main goal of this research was to optimize the processing parameters to obtain the filter media for specific industrial applications in industrial water purification.

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