

# Synthesis of new mesostructured cellular foams (MCFs) with NaY zeolite and their application to sorption of thorium ions

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The paper presents the new way of preparation of MCF foams with NaY zeolite. Significant changes in the amount of micro and mesopores in relation to the amount of NaY zeolite and 1,3,5-trimethylbenzene (TMB) added during the synthesis was observed. It suggests the possibility of controlling the micro/mesopores ratio by applying the proposed method. Environmental aspects of using new MCF/NaY foams is related to the adsorption of thorium ions ( $\text{Th}^{+4}$ ). The term of “MCF/NaY materials” refers to the general name of the material without referring to the content and state of zeolite. The obtained materials were highly effective in relation to  $\text{Th}^{+4}$ . The adsorption capacity was greater when the number of micropores was lower. The dependence of adsorption capacity of  $\text{Th}^{+4}$  ions on aluminum atoms content was also confirmed.

Keywords: *mesostructured cellular foams; zeolites; thorium ions; composites*

## 1. Introduction

Synthesis of classic MCF structures has been known for many years but still, these materials are intensively studied due to possibilities of their use in many physical and chemical processes [1–7]. Despite significant progress, there are many possibilities of changing the general procedure of their preparation to obtain materials with new features and properties. The classic process of their synthesis requires using some typical components including structure-directing agents (for example Pluronic P123), silica source in the form of tetraethyl orthosilicate as well as pore expander molecules responsible for foam structure (1,3,5-trimethylbenzene TMB). As a result, a highly porous material with a large specific surface area, high amount of mesopores and rather a small amount of micropores can be obtained [8–17]. Quite often, the final materials require further modification and adaptation to specific requirements. Without additional surface

modification, the resulting foams have a relatively small number of adsorption sites. Introduction of a component possessing expected properties is a way to reduce these limitations. Using natural zeolites as a modifier and micropore directing element can be an interesting idea in this field. Zeolites are crystalline aluminosilicates often used as molecular sieves or as catalysts due to their strong Brønsted acidity, hydrothermal stability, high surface area, and uniform microporous structure. On the other hand, the presence of micropores in the zeolite structure as a general type of porosity generates some limitations and causes that molecules with a size above 1 nm cannot diffuse into their interior. Mesoporous materials seem to be better adsorbents for adsorption of larger molecules. However, they have worse stability, catalytic activity, and acidity than zeolite structures. Hence, the idea to incorporate zeolites to the mesoporous structures seems to be promising. As a result, attractive micro- and mesoporous materials could be obtained. Previous attempts of synthesis of mesoporous materials, both mesoporous ordered materials (SBA-15) and mesoporous foams (MCF) with zeolites

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consisted in using zeolitic aluminosilicate nano-clusters also known as “zeolite seeds” [18–21] as zeolite type additions. For this purpose, “zeolite seeds” from ZSM-5, beta zeolites and faujasite-type zeolites (zeolite Y) were used. This synthetic procedure was used to change the unfavorable properties of mesoporous materials. They have some limitations in using as catalysts due to their weaker acidity and poorer hydrothermal stability, which can be attributed to the amorphous nature of the pore walls. The use of “zeolite seeds” in the synthesis of mesoporous materials improved their unfavorable surface properties and increased hydrothermal stability but did not change the number of micropores in the final materials. For increasing the number of micropores, Zhang et al. [22] have developed another procedure of synthesis a new type of zeolite/SBA-15 composite by creation a mixture of HY zeolite and Al-SBA-15. In this paper, we propose an entirely different method of synthesis of mesoporous and microporous materials modified by NaY zeolite. The new materials based on the classical synthesis of MCF, where besides the traditional silica source (tetraethoxysilane (TEOS)) NaY zeolite was added during the synthesis, were fabricated and characterized. The assumptions of the procedure are as follows: in the synthesis environment (highly acidic conditions) the structure of the zeolite is probably destroyed but initially, the matrix effect enables formation of micropore structure. The general aim of this work was to find a cheaper replacement with improved properties (containing Al atoms) than commonly used TEOS. The NaY zeolite comprises aluminum ions which may generate a positive effect on surface properties by increasing the number of adsorption sites. However, the replacement of TEOS by zeolite gives a relatively expensive product for large-scale applications. It seems that this type of material can be used to remove the actinides. For these reasons, the adsorption properties of the obtained materials in relation to thorium ions were investigated. The adsorption of thorium ions on zeolites and mesoporous materials is a widely studied subject [23–27]. Thorium seems to be the element broadly applied in the future, therefore, the sorption properties of the new MCF/NaY foams

composites relative to thorium(IV) ions were examined in this work. The general aim of the adsorption step of thorium ions was the confirmation that aluminum ions were incorporated into the structure of MCFs/NaY materials and participated in the adsorption process.

## 2. Experimental

### 2.1. Synthesis of MCF/NaY foams

The NaY zeolite has been delivered by Zeolyst International ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.1$ ,  $\text{Na}_2\text{O}$ , w/w 13.0 %, unit cell size  $24.65\text{\AA}$ ,  $S_{\text{BET}} \sim 900\text{ m}^2/\text{g}$ ). MCF/NaY foams were prepared by a direct synthesis method. In the preparation procedure, 2.0 g of triblock copolymer Pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ,  $M_w = 5800$ , Sigma-Aldrich) as a structure-directing agent was dissolved in 72 mL of HCl (2 M). The mixtures were stirred at  $40\text{ }^\circ\text{C}$  for 4 h. Then, 1,3,5-trimethylbenzene (TMB, Alfa Aesar, 98 %) was added to the solution dropwise and heated to  $40\text{ }^\circ\text{C}$  with rapid stirring for 2 h to synthesize the microemulsion. The resultant composites were prepared with a different ratio of TMB/Pluronic (0.5 and 1.0 which required using of TMB in the amount of 1.16 mL and 2.32 mL). In the next step, 4.65 mL of tetraethyl orthosilicate (TEOS, Sigma-Aldrich, 98 %) was added to the solution dropwise. Finally, NaY zeolite (three different masses: 0.5 g, 1.0 g, 1.5 g) was added to the mixture solutions. The solutions were stirred for 24 h at the same temperature. Next, the mixtures were aged at  $100\text{ }^\circ\text{C}$  for 48 h without stirring. The solid products were filtered two times and washed with distilled water. Organic components were removed by calcination at  $550\text{ }^\circ\text{C}$  for 5 h with  $3\text{ }^\circ\text{C}/\text{min}$  heating rate. Designation of individual samples is shown in Table 1.

### 2.2. Sorption of thorium ions

The sorption of thorium ions was carried out as follows: 0.2 g sample of MCF/NaY foam was dissolved in 50 mL of  $\text{Th}(\text{NO}_3)_4$  ( $5 \times 10^{-1}\text{ mmol}/\text{dm}^3$ ). This concentration of  $\text{Th}(\text{NO}_3)_4$  was prepared by dissolving an appropriate amount of  $\text{Th}(\text{NO}_3)_4$  in deionized

water. The mixture was stirred at room temperature for 48 h. Next, the precipitate was filtered and washed in distilled water. The amount of adsorbed thorium ions was assessed by XRF technique from solution phase as the loss of thorium ions in the solution removed by adsorption. First, the calibration curve for XRF investigation of solutions with different concentrations of thorium ions was determined. XRF measurements (Table 1) were performed for powdered samples using a PANalytical algorithm (Table 2).

### 2.3. Measurements and calculations

Nitrogen adsorption/desorption measurements were performed with an ASAP 2020 Micromeritics Inc. In the first step, the samples were degassed at 393 K for 24 h. X-ray diffraction measurements were performed using Empyrean diffractometer (PANalytical) in a wide range of diffraction angles (from  $2^\circ$  to  $90^\circ$  of  $2\theta$  with the step size of  $0.013^\circ$  and scan speed of  $0.015^\circ/\text{s}$ ) as well as a small range of diffraction angles (from  $0.9^\circ$  to  $5^\circ$ ). The X-ray diffraction analysis system was equipped with the line focus of Cu LFF HR X-ray tube with generator settings 45 kV and 40 mA and PIXcel3D detector as a scanning line 1D detector mode. The measurements were performed using reflection-transmission spinner suitable for powders and solid objects in reflection geometry. X-ray fluorescence analysis (XRF) was performed using Axios MAX (PANalytical, Netherlands), a wavelength dispersive X-ray fluorescence spectrometer (WD XRF). Transmission electron microscopy with energy-dispersive X-ray analysis (TEM/EDX) was carried out on a Tecnai G2 T20 X-TWIN transmission microscope.

## 3. Results and discussion

Fig. 1A shows the XRD pattern of MCZ3 sample as an example. As can be seen, diffractogram without diffraction peaks is observed in a wide range of diffraction angles suggesting an amorphous form of the material. A similar XRD pattern was obtained for the other samples shown in Fig. 1. It means that during the synthesis of MCFs the crystal structure of NaY zeolite was completely

destroyed and transformed into the amorphous state (Fig. 1C). It can be assumed that the degraded products of zeolite took part in the final stages of the synthesis of MCF foams. In the range of small diffraction angles, the diffraction peaks were also not observed. There was no evidence of the formation of the hexagonal structure of SBA-15 material due to the addition of TMB during the synthesis process. Textural properties, mainly surface area and size, as well as the type of pores, are important properties in designing catalysts and adsorbents.

Usually, the total surface area is the first and crucial criterion considered during evaluating the usefulness of new materials prior to analysis of active sites and their catalytic activity. Fig. 2 shows the experimental adsorption-desorption isotherms for investigated MCF/NaY foams. The characteristic shape of the isotherms, consistent with type IV, is observed. Hysteresis loop appears in the pressure range from  $0.5 p/p_0$  to  $1.0 p/p_0$ , suggesting the mesoporous nature of investigated materials and occurrence of the phenomenon referred to as capillary condensation in this range of relative pressures. This shape of hysteresis may suggest that the tested materials have a regular mesoporous channel with a narrow pore size distribution. A wide hysteresis loop indicates the presence of long mesopores. The presence of pores with narrow size was confirmed by the calculated pore size distribution curve (Fig. 2B). Textural properties of all analyzed samples were summarized in Table 1.

In all cases, the MCF/NaY foams exhibit relatively high surface area. It was observed that for the samples obtained from a lower amount of TMB ( $1.16 \text{ cm}^3$ ) specific surface area decreased with the increase in the amount of NaY zeolite added during synthesis. For the samples where the double amount of TMB ( $2.32 \text{ cm}^3$ ) was applied, the specific surface area slightly increased. We observed significant differences in specific surface areas of micropores between the investigated samples (in the range from  $90 \text{ m}^2/\text{g}$  to  $250 \text{ m}^2/\text{g}$ ).

The results suggest that it is possible to change the mesopores/micropores ratio by changing the conditions of MCF/NaY foams preparation by controlling the amount of zeolite and TMB added during this procedure. Pore size distributions

Table 1. Textural properties of investigated foams.

Sample	Adsorption capacity of Th <sup>4+</sup> [mg/g]	Zeolite NaY [g]	TMB [cm <sup>3</sup> ]	S <sub>BET</sub> <sup>a</sup> [m <sup>2</sup> /g]	S <sub>mic</sub> <sup>b</sup> [m <sup>2</sup> /g]	Pore volume		Pore size distribution	
						V <sub>t</sub> <sup>c</sup> [cm <sup>3</sup> /g]	V <sub>mic</sub> <sup>b</sup> (t-plot) [cm <sup>3</sup> /g]	D <sub>h</sub> <sup>d</sup> [nm]	D <sub>mo</sub> <sup>e</sup> (NLDFT) [nm]
MCZ1	18.2±0.1	0.5	1.16	567±7	201	1.48	0.098	10.4	1.4
MCZ2	18.5±0.1	1.0	1.16	468±5	171	1.03	0.087	8.8	1.5
MCZ3	23.7±0.1	1.5	1.16	320±4	90	0.9	0.046	11.3	1.6
MCZ4	18.2±0.1	0.5	2.31	632±7	207	1.55	0.099	9.8	1.4
MCZ5	17.4±0.1	1.0	2.31	671±8	250	1.57	0.121	9.3	1.6
MCZ6	18.9±0.1	1.5	2.31	672±8	125	1.66	0.065	9.9	1.7

<sup>a</sup>BET surface area calculated using experimental points at relative pressure  $p/p_0$  from 0.035 to 0.31, where  $p$  and  $p_0$  denote the equilibrium and saturation pressure of nitrogen;

<sup>b</sup>Surface area and pore volume of micropores calculated by t-plot method with fitted statistical thickness in the range of 3.50 to 5.00 Å;

<sup>c</sup>Total pore volume of nitrogen adsorbed at  $p/p_0 = 0.99$ ;

<sup>d</sup>Hydraulic pore diameters calculated from the BET surface areas and pore volumes according to equation:  $D_h = 4 V/S$ ;

<sup>e</sup>Pore diameter estimated from PSD of non-local density functional theory.

calculated according to NLDFT theory suggest that the width of the micropores slightly increases with increasing the amount of NaY zeolite, while the width of mesopores does not show such a trend. The ratio of TMB/Pluronic from 0.5 to 1.0 causes changes in the pore volume. When the TMB/Pluronic ratio equals 0.5, pore volume decreases with the amount of zeolite, whereas in the case of the TMB/Pluronic ratio of 1.0 the trend is the opposite. In both cases, the largest pore size is observed for samples containing the largest amount of zeolite (1.5 g). In general, these results suggest that the number of micropores in the MCF obtained foams can be adjusted by the addition of different amounts of zeolite and TMB expander during the preparation procedure.

Chemical composition of investigated samples, as well as the size of pores, were confirmed by TEM/EDX analysis. Fig. 3 shows the TEM images and TEM-EDX spectrum for MCZ3 sample. The sizes of pores visible as a brighter areas within the darker silica walls are mostly in the range from 10 nm to 25 nm and it is consistent with the data obtained from gas adsorption measurements. For other samples, the results are very similar. TEM images show the structure of the foam of MCF with

a characteristic open three-dimensional structure. The uniform spherical pores are connected to the windows. This structure resembles in appearance aerogels. Detailed analysis of the composition indicates the presence of a small amount of aluminum (approximately 0.7 %) in the tested materials.

Table 1 shows the total sorption data for thorium from aqueous solutions onto the novel MCF/NaY foams. For all samples, the sorption is very high but there is some difference between the synthesized MCF foams. It is worth noting that unexpectedly, the lower number of micropores resulted in greater sorption capacity of thorium ions.

The highest value of thorium (IV) ions adsorption capacity was obtained for the MCZ3 sample which exhibited the lowest specific surface area and also the smallest specific surface area of micropores. However, the MCZ3 sample was synthesized with using the largest amount of NaY zeolite (1.5 g). This suggests the influence of the amount of added zeolite on the sorption level of Th<sup>4+</sup>. The greater amount of aluminum ions the more thorium ions can be immobilized by MCF/NaY foams. Table 2 shows the results of quantitative analysis of three MCF/NaY foams after Th<sup>4+</sup> ions adsorption. The data indicate that the synthesis process

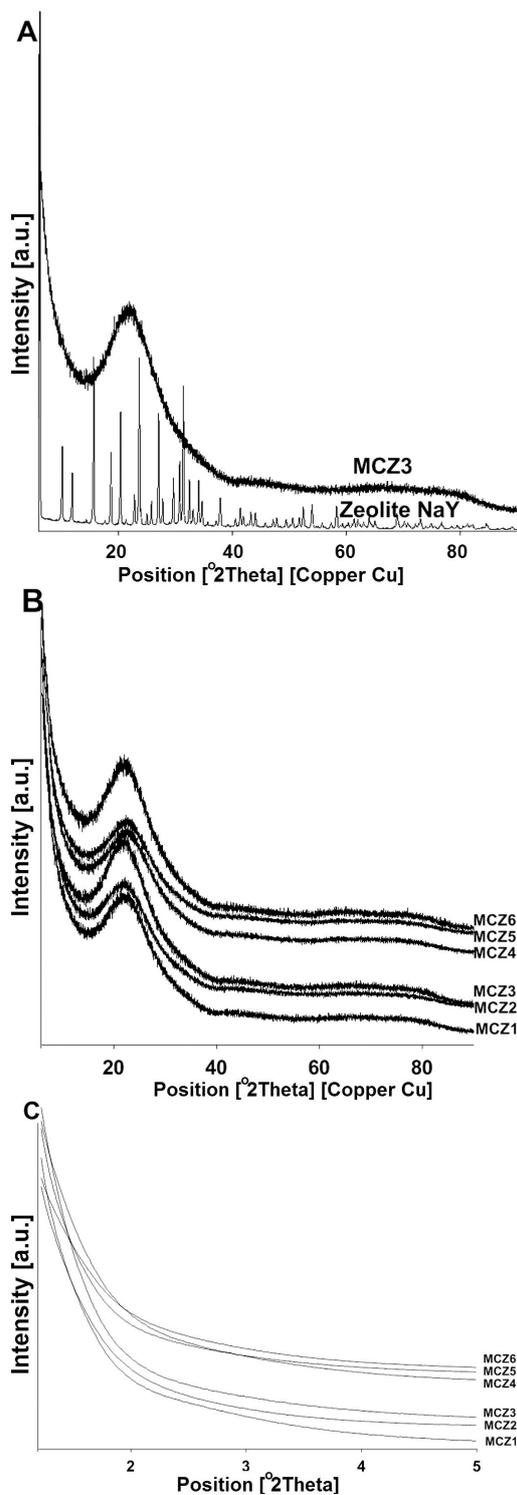


Fig. 1. (A) wide-angle XRD patterns of MCZ3 sample and pristine NaY zeolite, (B) wide-angle patterns of all MCF/NaY foams, (C) low-angle pattern of all MCF/NaY foams.

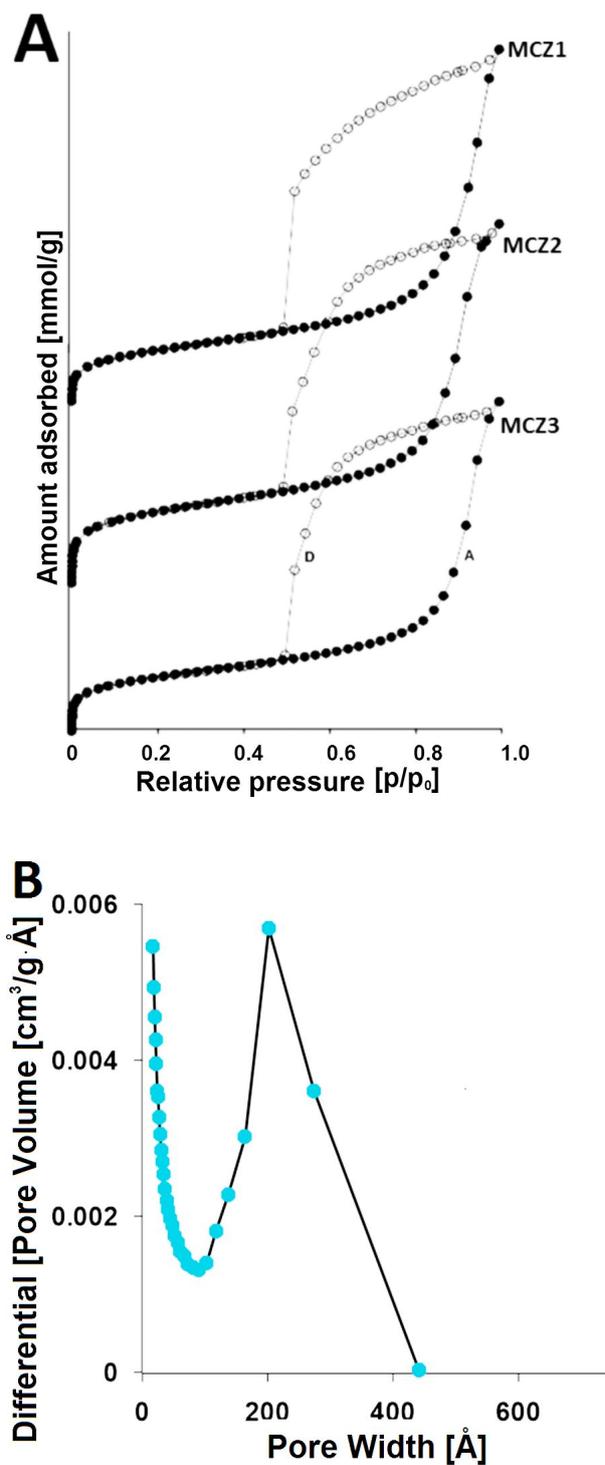


Fig. 2. (A) Experimental nitrogen adsorption-desorption isotherms of some MCF/NaY foams, (B) pore size distribution curves calculated by BJH procedure.

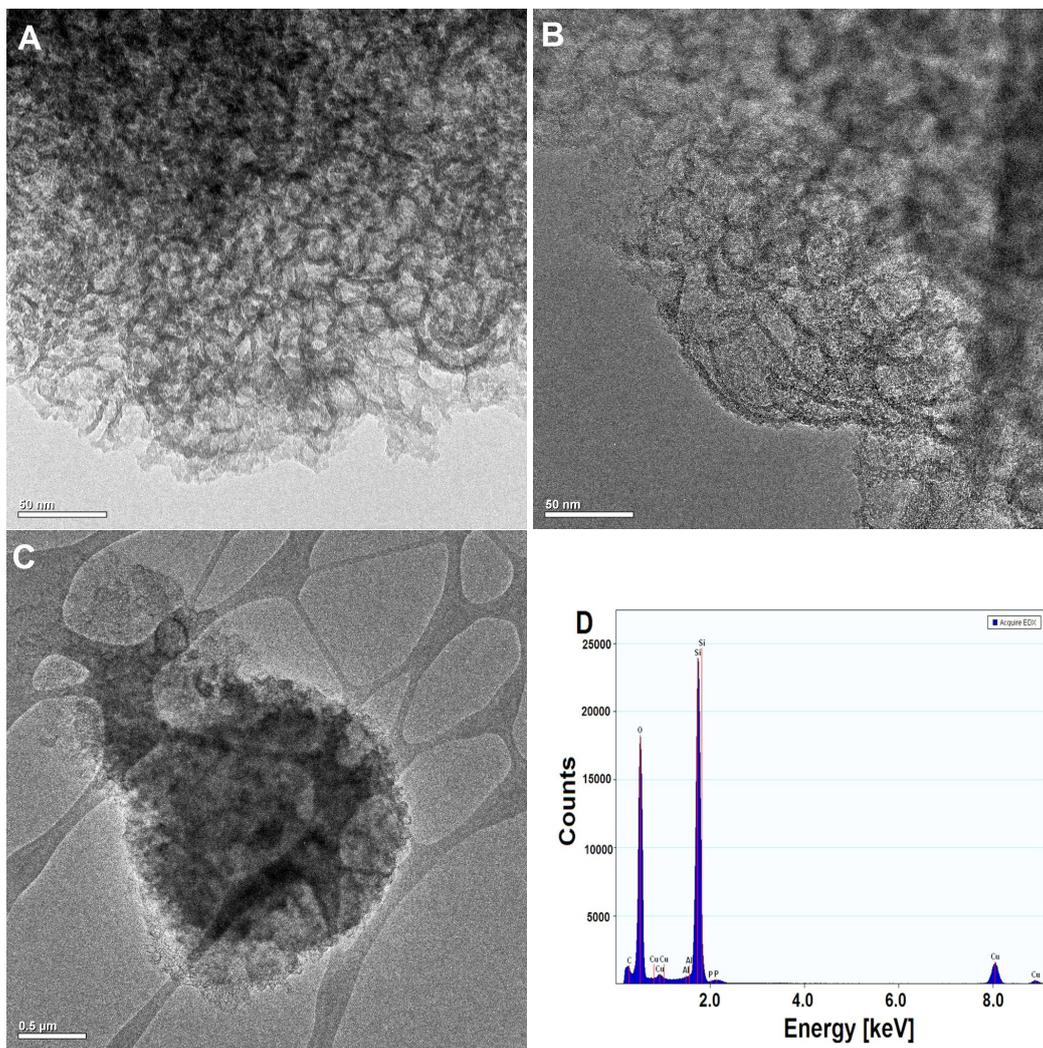


Fig. 3. (A-C) TEM images of MCZ3 as an example of MCF/NaY foam and (D) EDX spectrum of MCZ3.

of MCF from NaY zeolite is affected not only by the amount of zeolite added during the synthesis but also by the amount of 1,3,5-trimethylbenzene. This complicated synthesis process results in significant differences in the amount of aluminum in the obtained samples. Moreover, it is worth noting that all the samples (except MCZ3Th) were devoid of sodium atoms. The amount of sodium in the sample MCZ3Th was significantly lower than the aluminum content (Table 2). The aluminum content in the MCZ3Th sample determined by TEM-EDX and XRF techniques is very similar. The results indicate that aluminum in the investigated

samples is not present as a compound with sodium (as individual phase) but is in the built-in state which influences the effective adsorption of thorium ions. Generally, MCF-silica materials have many positive features. They are characterized by high surface area and chemical stability (it is almost just like silica). Unfortunately, they exhibit low adsorptive capacity due to the small number of adsorption sites. It is possible to change this limit by surface modification by incorporation of active functional groups, sometimes with complex structure [23]. However, this procedure can be expensive and complicated.

Table 2. Results of XRF analysis of selected samples.

Sample	XRF analysis			
	% Na <sub>2</sub> O	% Al <sub>2</sub> O <sub>3</sub>	% SiO <sub>2</sub>	% ThO <sub>2</sub>
MCZ1Th	–	0.19	97.5	2.06
MCZ3Th	0.082	0.86	96.3	2.53
MCZ6Th	–	0.20	97.7	1.97

## 4. Conclusions

The presented procedure of preparation of a new type of MCF allows us to obtain foams with various ratios of micropores to mesopores, aluminum ions incorporated into the surface layer of silica network and finally gain an effective tool for adsorption of thorium ions. The use of this simple procedure allows us to obtain the materials with a large diversity of microporous and mesoporous content, much higher than the most common procedures used to control their quantity (e.g. changing the synthesis temperature or time of aging). The proposed procedure not only reduces the cost of synthesis but also allows to incorporate the aluminum ions into the structure, which has a beneficial effect on adsorption capacity. Also, in this work, we present a new way of preparation zeolite/silica composites in the form of active foams for adsorption of thorium ions. We propose the procedure of preparing the foam structure composites with aluminum ions inside the silica network. Embedding aluminum into the silica matrix influenced the ability of thorium ions adsorption. Not without significance is also the possibility of using another type of silicon source (NaY zeolite) instead of more expensive tetraethoxysilane.

The mechanism of the synthesis with NaY zeolite seems to be more complicated than synthesis based on TEOS. The NaY zeolite exhibits ion-exchange properties and even if it is destroyed during synthesis, it can change temporarily and locally some synthesis conditions, e.g. pH. This phenomenon may have an effect on the properties of the final product. For example, in MCZ3 sample, the lowest specific surface area and the lowest amount of micropores do not limit the sorption of the Th<sup>4+</sup>. The higher sorption level

may be correlated with the higher content of aluminum ions in the structure than in other samples.

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Received 2018-10-28

Accepted 2019-04-23