

The effect of dispersed materials on baromembrane treatment of uranium-containing waters

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Abstract

The paper investigated a treatment process of uranium-containing waters in a membrane reactor while using natural mineral kizelgur and synthetic sorbent SKN-1K with subsequent ultra- and nanofiltration separation of the mixture. The retention coefficient of U(VI) by membrane UPM-20 under conditions of quasi-stationary equilibrium reached the levels of 0.87–0.89 and 0.89–0.91, respectively, while using natural mineral kizelgur and synthetic sorbent SKN-1K. In the case of membrane OPMN-P and natural mineral kizelgur the retention coefficient of U(VI) was 0.990–0.991 and 0.993–0.996, respectively, while using natural mineral kizelgur and synthetic sorbent SKN-1K. Data regarding the state of water in membranes formed from natural mineral or synthetic sorbent on the surface of substrate membranes UPM-20 and OPMN-P made it possible to conclude that dispersed materials of different chemical nature affect the process of baromembrane treatment of uranium-containing waters.

Keywords: Dispersed materials; Nanofiltration; Ultrafiltration; Uranium-containing water

1. Introduction

The uranium contamination of the environment is quite considerable due to anthropogenic activities. Fast growth of nuclear energy and widespread application of

radioactive materials in the national economy may pose a hazard in respect to the exposure of environment and population to radiation. That is why records and monitoring of the release of radionuclides into the biosphere

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from various sources and their migration are important [1,2].

The problem of pollution of water resources with radionuclides finding their way into them together with mine and pit wastewaters remains a critical issue.

One of the basic directions in reducing the impact of mine water on environment implies its treatment and the controlled use of the purified water for technical and household needs.

In recent years this direction has been characterized by the growing use of baro-membrane technologies. Papers are available that deal with the removal of uranium from contaminated water by the method of micellar-enhanced ultrafiltration [3]. In addition, the decontamination of uranium-containing water can be effected by the method of complexation-ultrafiltration [4,5]. Attempts were also made to remove uranium from water by ultrafiltration without introduction of any admixtures to the contaminated water [6].

Since the decontamination problem of uranium-polluted water is quite acute in Ukraine due to operation of nuclear and thermal power plants and exploitation of uranium pits, the main direction of efforts to ensure the environment protection implies further improvement of processes aimed at creating low-waste technologies. The present paper displays results of studies to purify uranium-containing waters by the method of ultrafiltration along with simultaneous application of dispersed materials having different chemical nature.

2. Experimental

Dispersed materials were used to find out their influence on ultra- and nanofiltration separation of uranium-containing waters, contribution to the purification process by forming dynamic membranes (DM) on the surface of substrate membranes. As DM

forming materials we used dispersed additions of various chemical natures: synthetic carbon sorbent SKN-1K (synthetic activated carbon produced by SE “Smoly”, Ukraine) and natural mineral kizelgur (a variety of diatomite, siliceous sedimentary rock from the Kirovograd ore deposit, Ukraine). Sorption capacity of the dispersed materials in terms of U(VI) assumed the following values: 17 mg/g for kizelgur and 47 mg/g for SKN-1K, while the size of their particles was ≤ 0.25 mm. Sorbents were initially prepared in accordance with conventional techniques [7].

As separating substrate membranes we used UPM-20 polymer ultrafiltration and OPMN-P nanofiltration membranes produced by “Vladipor”, Russia. The average size of pores of the membranes measured as follows: 20 nm for UPM-20 and up to 10 nm for OPMN-P.

Concentration of U(VI) in the initial solution was 5 mg/l. Working solutions of uranium were prepared from salt $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ of grade “chempure”. The investigations were carried out in a dead-end-type cell having volume of 1 liter and membrane area of 95 cm^2 with the magnetic mixer rotation rate of 300 rev/min. Experiments were performed at the working pressure 0.2 MPa and pH 7–8. The solution under investigation was pressed through and continuously added to the cell after the separation degree of 0.90 was achieved. In this case the sorbent in the amount of 1 g was added only to the first liter of the system under investigation, and it remained in the cell during the entire time of experiment. We used permeate samples of 100 ml and their concentration of U(VI) was determined by a photometric method [8].

It is known [9,10] that at pH 7–8 uranium is mostly present in the form of hydroxocomplexes $(\text{UO}_2)_3(\text{OH})_5^+$ and carbonate complexes UO_2CO_3^0 , $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$ (Fig. 1). Therefore, we have grounds to state that in

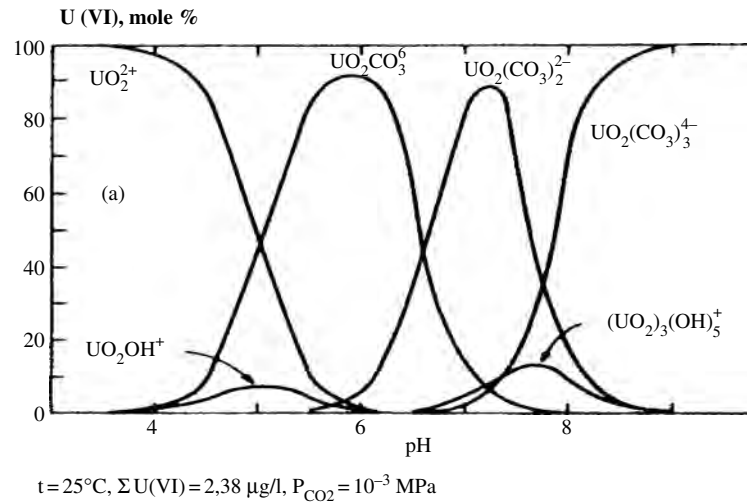


Fig. 1. Dependence of uranylhydroxide and -carbonate complexes distribution against pH.

our study the membranes used and DM formed from particles of dispersed materials on their surface retain hydroxo- and carbonate compounds rather than ions $(\text{UO}_2)^{2+}$, which primarily exist in acidic solutions at pH 3–4. Hydroxo-polymer compounds of uranium will also take part in formation of a dynamic structure on the surface of membranes UPM-20 and OPMN-P. The retention coefficient of uranium (R) and volume flow (J_v) were calculated by appropriate techniques [11].

The method of differential scanning calorimetry (DSC) was used to determine the state of water in initial (kept in distilled water for ~ 24 h) dispersed materials and membranes UPM-20, OPMN-P, and also in membranes UPM-20 and OPMN-P tested after the treatment of uranium-containing waters [12]. Endotherms were recorded using a microcalorimeter DSM-2M at the scanning velocity of 4 degr/min [13,14] in the temperature range $-50^\circ\text{C} - +20^\circ\text{C}$. A membrane under investigation having mass of 0.004/0.008 g was pressed into a container and subjected to cooling by liquid nitrogen during 1–2 min

to temperature -50°C . Next it was kept for several minutes at temperature -50°C until the equilibrium state was achieved. The accuracy of temperature measurements for DSC endotherms was $\pm 0.5^\circ\text{C}$.

Calculation of the freezing water content was conducted by endotherms of ice melting. The content of non-freezing water was determined by the difference between the total water content and the content of freezing water [12]. Water content of membranes under study was determined by drying samples to a fixed mass at temperatures 30/35°C [15]. The accuracy of data measurements was $\pm 0.001 \text{ g}_{\text{water}}/\text{g}_{\text{dry membrane}}$.

3. Results and discussion

Fig. 2 displays the results indicating the influence of kizelgur on the ultrafiltration (curve 1) and nanofiltration (curve 2) solution treatment processes for removal of U(VI). The U(VI) retention coefficient by membrane UPM-20 under the above conditions (without any use of dispersed materials) was 0.62, while that by membrane OPMN-P was 0.82.

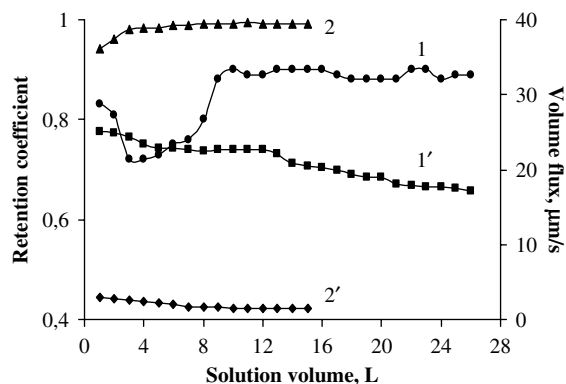


Fig. 2. Dependence of the retention coefficients of U(VI) by the UPM-20 (1), OPMN-P (2) membranes and the volume fluxes through UPM-20 (1'), OPMN-P (2') membranes against the solution volume in the process of uranium and kizelgur containing system purification

The results obtained in the case of using a natural mineral kizelgur in a membrane reactor (Fig. 2, curves 1 and 2) show that the U(VI) retention coefficient was equal to 0.87–0.89 after the quasi-stationary operation mode of membrane UPM-20 together with a DM on its surface had been achieved. The treatment process continued for 35 h. The 26 l of uranium-containing solution were passed during this time. We can speak about operation of the membrane proper and the layer of kizelgur particles formed on its surface only after 10 h of the plant operation following the depletion of kizelgur sorption capacity. The volume flow during the process reduced from 25.0 $\mu\text{m/s}$ to 17.0 $\mu\text{m/s}$ (Fig. 2, curve 1'). Variation of the volume flux most likely can be related to the formation of a secondary structure consisting of kizelgur particles on the surface of substrate membrane UPM-20. Particles of kizelgur may partially block the mouth of pores of membrane UPM-20 reducing thereby a transmembrane flux through it and increasing its retention coefficient.

In the case of a nanofiltration treatment process and the use of natural mineral

kizelgur (Fig. 2, curve 2) the U(VI) retention coefficient was equal to 0.991 – 0.992 after a quasi-stationary operation mode of membrane OPMN-P together with a DM on its surface was achieved. The process of treatment continued for 245 h. The 15 l of uranium-containing solution were passed during this time. We can speak about operation of the membrane proper and the layer of kizelgur particles formed on its surface only after 85 hours of the plant operation following the depletion of kizelgur sorption capacity. The volume flux during the process reduced from 3.0 to 1.4 $\mu\text{m/s}$ (Fig. 2, curve 2'). Variation of the volume flux, similar to the case of using membrane UPM-20, most likely can be related to the formation of a secondary structure consisting of kizelgur particles on the surface of substrate membrane OPMN-P. Particles of kizelgur may partially block the mouth of pores of the membrane reducing thereby transmembrane flux through it.

As can be seen from the results presented in Fig. 3, the process of baromembrane separation using ultrafiltration membrane UPM-20 and synthetic sorbent SKN-1K

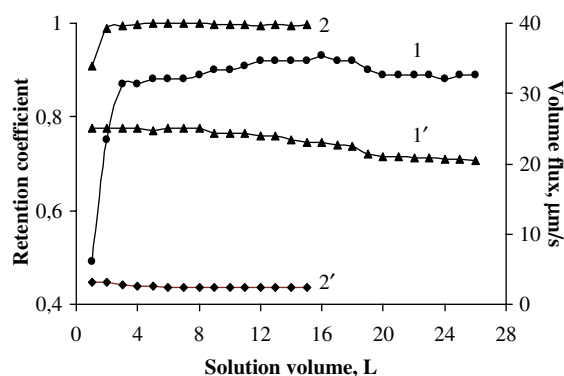


Fig. 3. Dependence of the retention coefficients of U(VI) by the UPM-20 (1), OPMN-P (2) membranes and the volume fluxes through UPM-20 (1'), OPMN-P (2') membranes against the solution volume in the process of uranium and SKN-1K containing system purification.

(Fig. 3, curve 1) is characterized by the U(VI) retention coefficient of 0.89–0.91 under conditions of the steady-state mode of quasi-stationary equilibrium. Saturation of a sorbent with U(VI) proceeds for 15 h during the plant operation. The treatment process continued for 31 h. The 26 l of uranium-containing solution were passed during this time. After expiration of this period we can speak about operation of the membrane UPM-20 proper and the secondary layer of sorbent SKN-1K particles formed on its surface.

Volume flux during the process reduced from 25.0 to 20.5 $\mu\text{m/s}$ (Fig. 3, curve 1'). Such an insignificant change of value J_v can be explained by the fact that the layer of SKN-1K particles formed is rather loose resulting in less hindrance to the flux through DM and membrane UPM-20 proper than in the case of using kizelgur.

The use of a nanofiltration membrane OPMN-P and synthetic sorbent SKN-1K (see Fig. 3, curve 2) yields the U(VI) retention coefficient of 0.994–0.996 under conditions of the steady-state mode of quasi-stationary equilibrium. The treatment process continued for 172 h. The 15 l of uranium-containing solution were passed during this time. Saturation of a sorbent with U(VI) proceeds for 115 h during the plant operation. After expiration of this period we can speak about operation of the membrane UPM-20 proper and the secondary layer of sorbent SKN-1K particles formed on its surface.

Volume flux during the process reduced from 3.0 to 2.4 $\mu\text{m/s}$ (Fig. 3, curve 2'). Such an insignificant variation of value J_v can be explained by the fact that the layer of SKN-1K particles formed, similar to the use of membrane UPM-20, is rather loose resulting in less hindrance to the flux through DM and membrane UPM-20 proper.

The DSC method was used to find out contributions and roles of sorbents having

different nature: synthetic sorbent SKN-1K and natural mineral kizelgur. The resultant endotherms of initial ultra- and nanofiltration membranes UPM-20 and OPMN-P, clean sorbents, and also membranes after the uranium-containing water treatment process are presented in Figs. 4 and 5. The appearance of membrane endotherms both after the process of uranium-containing water treatment with a layer of sorbents on the surface of the membranes and after removal of layers is somewhat changed as compared with endotherms of the initial membranes (see Figs. 4 and 5). The use of sorbents having different nature during water purification results in emergence of “arms” on endotherms at lower temperatures. This is a proof of the fact that the modification of porous space of substrate membranes does take place, i.e., bigger pores can be blocked and smaller ones can be formed owing to creation of DM on the surface of substrate membranes. Water in these pores will freeze at lower temperatures. It should be noted that endotherms of membranes investigated after the purification do not return to the initial appearance (Figs. 4 and 5). After sediments of kizelgur and synthetic sorbent are removed from the surface of substrate membranes, the “arms” on endotherms in most cases remain at lower temperatures.

On the basis of endotherms obtained we calculated the amount of free and bound water in membranes before and after the treatment of uranium-containing waters (Tables 1 and 2). As can be seen from the results presented in the Tables, total water content of kizelgur is higher than that of SKN-1K. It should be noted however, that the natural mineral contains water mostly in free state and its quantity is three times as high as the quantity of bound water, while the synthetic sorbent yields an inverse regularity: the amount of bound water is almost

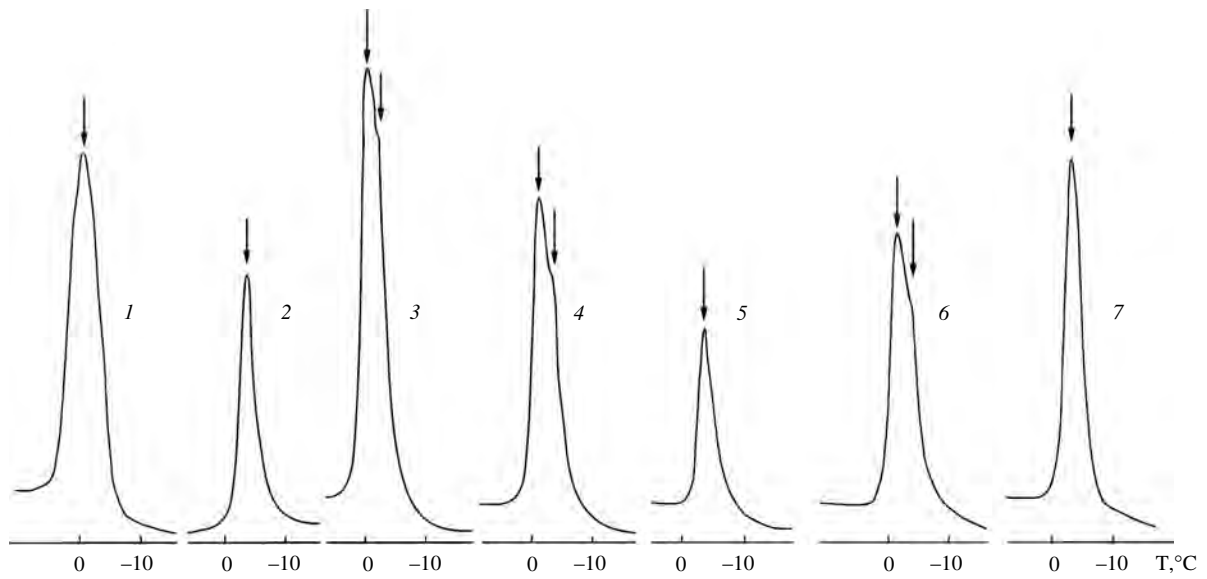


Fig. 4. Endotherms of ice melting in the natural mineral kizelgur (1), in the initial UPM-20 membrane (2), in this membrane with a kizelgur layer (3) and after washing-out of this layer from its surface (4) as well as in the initial OPMN-P membrane (5), in this membrane with a kizelgur layer (6) and after washing-out of this layer from its surface (7).

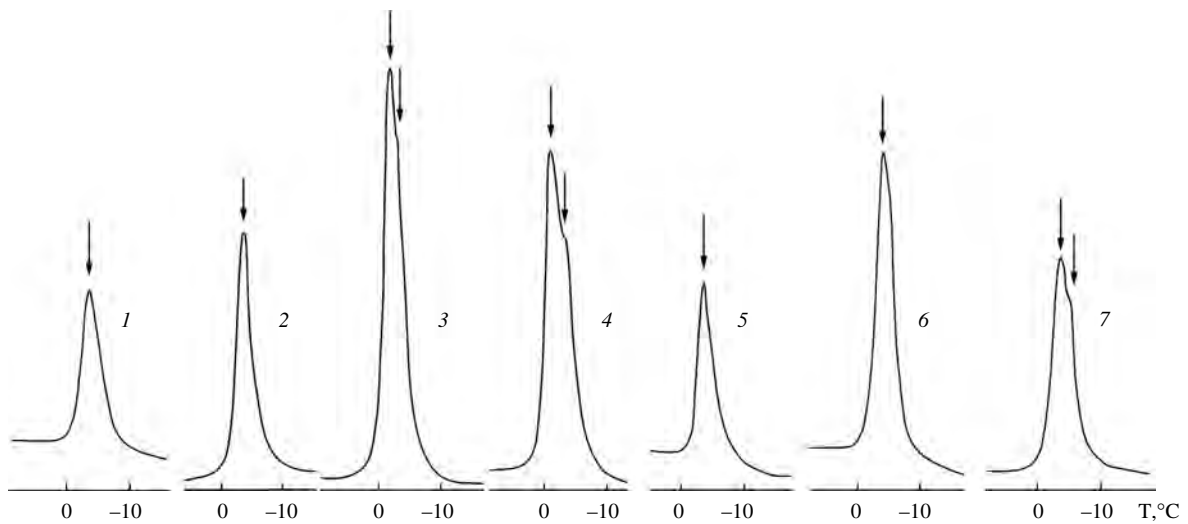


Fig. 5. Endotherms of ice melting in the synthetic sorbent SKN-1K (1), in the initial UPM-20 membrane (2), in this membrane with a SKN-1K layer (3) and after washing-out of this layer from its surface (4) as well as in the initial OPMN-P membrane (5), in this membrane with a SKN-1K layer (6) and after washing-out of this layer from its surface (7).

Table 1

Water state in the dispersed kizelgur, in the initial membranes UPM-20 and OPMN-P and in these membranes investigated after pressurizing of uranium-containing solution through the membrane reactor in the presence of dispersed kizelgur

| Parameter | Kizelgur + H ₂ O | Membrane UPM-20 | | | Membrane OPMN-P | | |
|------------------------------|-----------------------------|-----------------|------------|-------------------------------|-----------------|------------|-------------------------------|
| | | initial | + kizelgur | after washing-out of kizelgur | initial | + kizelgur | after washing-out of kizelgur |
| Moisture content, % | 43.0 | 35.6 | 41.5 | 42.3 | 50.0 | 49.0 | 49.0 |
| Free water, g/gdry membrane | 0.58 | 0.45 | 0.71 | 0.62 | 0.68 | 0.82 | 0.78 |
| Bound water, g/gdry membrane | 0.19 | 0.11 | 0.03 | 0.11 | 0.34 | 0.13 | 0.22 |

Table 2

Water state in the dispersed SKN-1K, in the initial membranes UPM-20 and OPMN-P and in these membranes investigated after pressurizing of uranium-containing solution through the membrane reactor in the presence of dispersed SKN-1K

| Parameter | SKN-1K + H ₂ O | Membrane UPM-20 | | | Membrane OPMN-P | | |
|------------------------------|---------------------------|-----------------|----------|-----------------------------|-----------------|----------|-----------------------------|
| | | initial | + SKN-1K | after washing-out of SKN-1K | initial | + SKN-1K | after washing-out of SKN-1K |
| Moisture content, % | 39.0 | 50.0 | 49.0 | 49.0 | 35.6 | 41.6 | 41.2 |
| Free water, g/gdry membrane | 0.24 | 0.68 | 0.79 | 0.75 | 0.45 | 0.61 | 0.59 |
| Bound water, g/gdry membrane | 0.41 | 0.34 | 0.19 | 0.25 | 0.11 | 0.12 | 0.13 |

twice as big as that of free one (see Tables 1 and 2).

Water treatment with the use of both kizelgur and sorbent SKN-1K results in the fact that the state of water in membranes OPMN-P and UPM-20 varies as compared to the state of water in initial membranes. The amount of free water increases, while that of bound one diminishes. In this case, total water content increases for nanofiltration membranes OPMN-P and slightly drops for ultrafiltration membranes UPM-20 (Tables 1 and 2). Proceeding from the

quantitative data about free and bound water we can suggest that the mechanism of water treatment is the same and does not depend on substrate membrane. Probably, particles of kizelgur and SKN-1K settling on the surface of substrate membranes together with hydroxo- and carbonate complexes of uranium form a secondary layer and may block to a certain degree mouths of membrane pores resulting in reduction of the amount of bound water. Formation of a layer on the surface of substrate membranes in both cases yields an increased amount of

free water. Moreover, since the clean kizelgur contains more free water than sorbent SKN-1K, the quantity of free water in a layer of kizelgur on both substrate membranes will be higher than in a layer of sorbent SKN-1K. An enhanced water content of substrate membrane OPMN-P after the water treatment as compared with that of the initial membrane can be, probably, explained by a reduced size of pores of the substrate as compared with the membrane UPM-20 (Tables 1 and 2).

In case of washing-out of the sediment from the surface of substrate membranes OPMN-P and UPM-20 the amount of free water reduces, while that of bound water increases. This fact indicates that part of pores in the substrate membranes open. In this case, total water content practically does not alter (Tables 1 and 2). However, the quantitative data on free and bound water are not identical to those for initial membranes. That is why the above results indicate that particles of sorbents, perhaps, partially penetrate into pores of substrate membranes thus blocking the pores of the membranes, while the main layer is located on their surface.

Results of the water state in membranes obtained by the DSC method corroborate the above suggestions.

4. Conclusions

Hence, two factors contribute to an increased retaining capacity of membrane and a reduced volume flux: the first factor implies a possible penetration of particles into pores of substrate membranes OPMN-K and UPM-20, and the second implies formation of a layer on the surface of the same membrane that in its turn contributes to a further reduction of the size of pores of substrate membranes. Application of dispersed sorbent SKN-1K results in enhanced values of the retention coefficient and to a less

significant drop of the volume flux as compared with the use of natural sorbent kizelgur. This fact, most likely, may be related to formation of a more branched structure of SKN-1K having higher sorption capacity in terms of uranium as compared with that of kizelgur resulting in absorption of greater amounts of water despite its smaller swelling capacity in water.

Thus, on the basis of results obtained we found out the effect of dispersed materials on retaining capacity of the membranes under study in the treatment process of uranium-containing water. A membrane reactor, i.e., application of dispersed materials in baromembrane (in this case nano- and ultrafiltration) separation, can be used in the process of purification / concentration of systems containing U(VI). Application of dispersed materials in this process yields an enhanced retaining capacity of ultrafiltration membrane and enables us to obtain a high purity permeate with simultaneous concentration of U(VI) in a small volume of concentrate and dispersed material.

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