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# INVESTIGATION OF THE STRUCTURE AND SORPTION PECULIARITIES OF COBALT AND URANIUM IONS BY NANOCOMPOSITES BASED ON MONTMORILLONITE AND TETRAETHOXYSILANE

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*Досліджено структуру та адсорбційні характеристики нанокомпозитів на основі кремнезему та монтморилоніту. Тетраетоксисилан був використаний в якості джерела кремнезему. Поруватa структура досліджувалась методом низькотемпературної адсорбції азоту.*

*За результатами досліджень встановлено, що незначна кількість кремнезему в зразках нанокомпозитів (14 % $SiO_2$) сприяє утворенню матеріалу з більшою питомою поверхнею і більшою кількістю мезо- та макропор у порівнянні з вихідним монтморилонітом. Це, в свою чергу, приводить до кращої дифузії іонів різної природи в структуру нанокомпозиту. Збільшення вмісту кремнезему (до 57 % $SiO_2$) дозволяє отримати мікропористі зразки з великою питомою поверхнею.*

*Визначено, що збільшення вмісту монтморилоніту в досліджуваних зразках сприяє покращенню адсорбційних властивостей нанокомпозитів по відношенню до вилучення іонів кобальту (II) з водного середовища. При оптимальному вмісті кремнезему (3–14 % $SiO_2$) експериментальні зразки зберігають високі значення граничної адсорбції кобальту (14 мг/г), як і вихідний монтморилоніт. Також встановлено, що збільшення концентрації кремнезему в зразках сприяє зростанню ефективності вилучення іонів урану (VI) з водного середовища (від 12 мг/г у вихідного монтморилоніту до 25 мг/г для нанокомпозитів з вмістом кремнезему 57 %). По-перше, це пов'язане зі збільшенням питомої поверхні зразків, а по-друге – підвищенням кількості поверхневих гідроксильних груп, які більш селективно вилучають уран з розчинів. Таким чином, підбір хімічного складу нанокомпозитів на основі силікагелю та монтморилоніту дає змогу регулювати порувату структур та хімію поверхні, а отже і збільшити ефективність сорбенту в залежності від поставленої задачі.*

*Ключові слова: порувата структура, безтемплатний синтез, алюмосилікатні адсорбенти, модифікація структури, адсорбція кобальту, адсорбція урану*

## 1. Introduction

Pollution of surface and ground water by heavy metals and radionuclides is one of the most urgent environmental problems of today. These toxicants constitute the greatest threat in soluble form, since they are thus able to migrate over long distances and subsequently accumulate in living organisms. One of the most dangerous heavy metals and radionuclides are uranium and cobalt compounds. Uranium compounds are widely used in the nuclear fuel cycle. They get into the environment mainly with the wastewater of hydrometallurgical plants processing uranium ores and also are components of liquid radioactive waste of nuclear power plants [1]. Pollution by cobalt compounds is possible due to the activities of galvanic productions and radioactive cobalt – when applied in medical practice [2].

Among possible methods of removing toxicants from the aquatic environment, sorption methods hold a special place due to simplicity and efficiency, especially when high levels of purification are needed. For removal of heavy metals and radionuclides, sorption materials based on natural silicate raw materials – clay minerals and zeolites, being cheap and readily available are widely used. Owing to structural features, the surface of these minerals can easily be modified to improve sorption and other technological characteristics. Thus, development of methods for modifying the surface of clay minerals to obtain cheap and effective enough sorption materials for the removal of heavy metals and radionuclides from polluted waters is promising.

Among such methods, template-free synthesis of highly porous sorption materials based on montmorillonite and silica with tetraethoxysilane as a source of silica is relevant today.

## 2. Literature review and problem statement

Removal of uranium (VI) from aqueous media presents significant difficulties, since uranyl ions are prone to hydrolysis and formation of various compounds, including anionic, which are hardly removed from aqueous solutions [3]. Cobalt, namely its isotope $^{60}$Co, is also one of the dangerous toxicants, the source of which can be radioactive waste of various origins [4]. Sorption materials based on natural raw materials, including clay minerals, are effective in removal processes [3, 5].

Natural clay minerals, for example montmorillonite, are promising adsorbents due to the layered structure, large specific surface area and rather high cation exchange capacity [6]. However, due to the high dispersion and ability to form stable colloidal systems, application in sorption technologies is limited. Montmorillonite is used mainly in the purification of nonpolar (organic) systems from polar compounds and water [7], or as an adsorbent-coagulant in aqueous solutions [8, 9].

For selective removal of heavy metals and radionuclides, new silica-based materials (MCM-41, SBA-15), obtained by the so-called “template” method using various surfactants and, as a rule, tetraethoxysilane as a source of silica, are effective [10]. Such materials are characterized by a rather narrow pore size distribution and large specific surface area (up to 600–800 m$^2$/g). In the processes of template synthesis, clay minerals (most often montmorillonite) are also used, which makes it possible to obtain materials with high structural and sorption properties.

The paper [11] shows the possibility of obtaining porous heterostructures on the basis of bentonite and silica by the template method using zirconium compounds. A rather high efficiency of such materials in the removal of anionic dyes from aqueous solutions is demonstrated. However, the use of expensive reagents (surfactants) and complex technological operations of template removal significantly increases the cost of the resulting adsorbents.

Similar problems are observed with the materials described in [12]. Considering the complexity of synthesis operations and the large amount of organic reagents, which can reach 50 % of the total mass, the method of template synthesis for the production of general-purpose adsorbents is not economically feasible.

At the same time, additional organic reagents for the synthesis of silica- and montmorillonite-based sorbents are not used [13], which greatly simplifies the synthesis process and reduces the cost of the material. Similarly, the method of synthesizing a montmorillonite-silica nanocomposite by a simplified technique is described in [14].

The use of template-free synthesis to obtain mesoporous sorption materials is described in [15]. The authors propose to use kaolin as a starting mineral. However, the use of hydrothermal synthesis also complicates the process of obtaining the end material. In [16], the authors proposed the method of synthesis with additional treatment of the material with a solution of hydrochloric acid. However, the application of the above methods is inferior to direct synthesis with clay minerals and tetraethoxysilane hydrolysis products as a source of silica. Thus, the possibility of obtaining sorption materials by the template-free sol-gel method, which does not require complex technological operations and reagents is revealed.

For this reason, synthesis and study of sorption properties of semisynthetic sorption materials based on montmorillonite and silica by the template-free method for application in water treatment processes are the promising area of research and the aim of this work.

## 3. The aim and objectives of the study

The aim of the study was to determine the texture characteristics of synthesized nanocomposites based on tetraethoxysilane and montmorillonite, to study the efficiency of adsorption of cobalt and uranium ions as one of the most dangerous toxicants among heavy and radioactive metals.

To achieve the aim, it is necessary to accomplish the following objectives:

– to study the texture characteristics of the samples obtained by low-temperature nitrogen adsorption;

– to determine the dependence of the chemical composition of nanocomposites on the adsorption properties in relation to cobalt and uranium ions.

## 4. Materials and methods of the study of texture and adsorption properties of synthesized nanocomposite materials

### 4. 1. Materials and equipment used in the work

For the synthesis of samples, montmorillonite clay mineral of the Cherkassy deposit (Ukraine) with the general structural formula $(Ca, Na)_{0.2}(Al, Mg, Fe)_2[(Si, Al)_4O_{10}](OH)_2 \times nH_2O$ additionally treated by sedimentation was used. The mineral was converted to the Na-form (Na-MMT) before use. As a source of silica, tetraethoxysilane (TEOS) produced by Sigma-Aldrich was used. Sulfuric acid ($H_2SO_4$, 5N), sodium hydroxide (NaOH, 5M) and ethyl alcohol ($C_2H_5OH$, 96 %) of AR grade were used.

For the study, samples with the montmorillonite content from 100 to 23 wt % of dry sample were synthesized. Description of the sample synthesis method was given earlier [17].

To study the adsorption properties of synthesized nanocomposites, different concentrations of salts $UO_2SO_4 \cdot 3H_2O$ and $CoCl_2 \cdot 6H_2O$ with respect to U(VI) and Co(II) ions were used. Adsorption experiments were conducted in static conditions with a sample weight of 0.1 g per 50 cm$^3$ of the solution. The contact duration was 60 minutes, which corresponds to the establishment of the adsorption equilibrium in the studied systems. The equilibrium concentration of uranium and cobalt in solutions was determined by the spectrophotometric method using the UNICO-UV 2100 (USA) spectrophotometer. Coloring reagents were as follows: for cobalt – Nitroso-R-salt at a wavelength of 520 nm, and for uranium – Arsenazo III at a wavelength of 665 nm.

Low-temperature nitrogen adsorption was carried out on the Quantachrome Autosorb Station 4 (USA). Degassing of the samples was performed at 180 °C for 20 hours. Calculation of specific surface area and pore size distribution was conducted using specialized ASiQwin V 3.0 software with the BJH (Barrett-Joyner-Halenda) and DFT (density functional theory) models [18].

## 5. Results of studies of texture and adsorption characteristics of experimental samples

The results of the study of low-temperature nitrogen adsorption on the samples of nanocomposites produced indicate a significant change in the structural and sorption characteristics compared to original montmorillonite (Fig. 1).

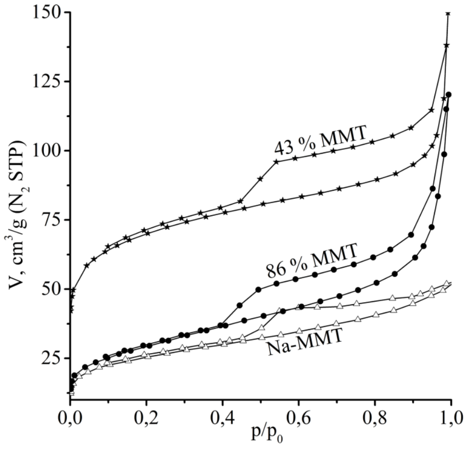


Fig. 1. Isotherms of low-temperature nitrogen ad(de) sorption by nanocomposite samples and original montmorillonite (Na-MMT)

The shape of nitrogen adsorption isotherms, for both original montmorillonite and nanocomposite samples, is typical for microporous adsorbents and refers to type II isotherms according to the Brunauer's and others' classification [18]. For nanocomposites with a branched "card house" structure, with increasing pressure to $p/p_0=1$, the isotherms asymptotically approach the straight line corresponding to the polymolecular adsorption.

However, the shape of the hysteresis loops of the studied samples in the relative pressure range of 0.4–1 $p/p_0$ differs for each sample. Thus, the hysteresis loops for nanocomposite samples are more pronounced than those of original montmorillonite. The shape of the hysteresis loops, according to the IUPAC recommendations, is close to type H3 or H4 and refers to materials with slit-like pores with plane-parallel walls [18]. The results of calculations of the characteristics of the porous structure of the original and modified samples are given in Table 1.

Nanocomposite samples are characterized by increased specific surface area (102 and 252 m$^2$/g). In addition, the values of the total pore volume ($V_\Sigma$, cm$^3$/g) for nanocomposite samples significantly exceed those of original montmorillonite (0.08 cm$^3$/g). Calculated values of the micropore content indicate differences in the structure of synthesized materials. For original montmorillonite, the micropore content is 19.8 %, which is typical for samples of this mineral. In this case, the micropore content for the 86 % MMT nanocomposite sample is only 4 %, which is associated with the formation of the "card house" structure in which montmorillonite particles contact by side surfaces between which silica gel globules are located.

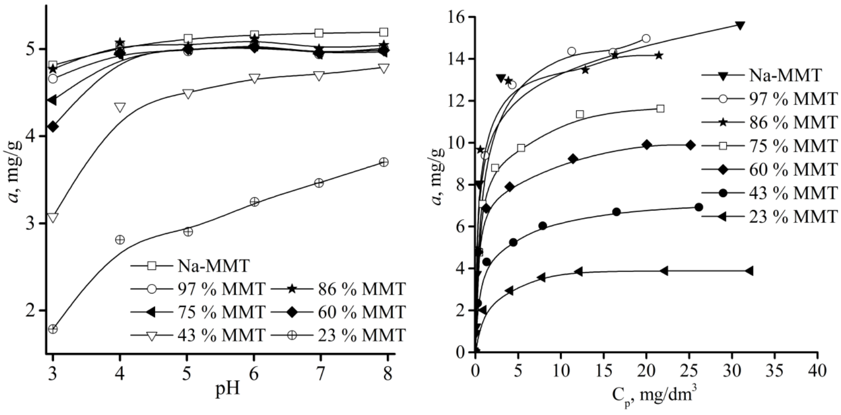
Table 1

Characteristics of the porous structure of the samples of original montmorillonite and nanocomposites on its basis

| Sample | $S_{spec.}$, m$^2$/g | $V_\Sigma$, cm$^3$/g | $V_\mu$, cm$^3$/g | $V_{\mu\%}$, % | $r$, nm | Pore radius distribution, nm | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | BJH dV ($r$) | | DFT dV ($r$) | | |
| | | | | | | $r_1$ | $r_2$ | $r_1$ | $r_2$ | $r_3$ |
| Na-MMT | 89 | 0.081 | 0.016 | 19.8 | 1.84 | 1.41 | – | – | 1.911 | 2.821 |
| 86 % MMT | 102 | 0.402 | 0.016 | 4.0 | 7.88 | 1.89 | 46.79 | 0.663 | 1.252 | 2.543 |
| 43 % MMT | 252 | 0.232 | 0.084 | 36.4 | 1.85 | 1.91 | – | 0.637 | 1.252 | 2.643 |

*Notes: $S_{spec.}$ – specific surface by BET; $V_\Sigma$ – total pore volume; $V_\mu$ – micropore volume; $V_{\mu\%}=(V_\mu/V_\Sigma)\cdot 100$ – micropore content; r – average pore radius*

Such branched structure has a larger content of meso- and macropores. With increasing silica content in the composite, the formation of denser structures, in which pores between montmorillonite particles are filled with silica gel globules, is observed. The high micropore content (36.4 % for the 43 % MMT sample) is associated with a significant content of silica gel, which is usually a microporous material, in the sample [19].



*a* *b*

Fig. 2. Cobalt sorption by nanocomposite samples: *a* — dependence of cobalt sorption on the pH of initial solutions; *b* — cobalt sorption isotherms

Considering the difference between the specific surface area, total pore volume and average pore radius, one can conclude that the nanocomposite samples have a higher mesopore content, in contrast to original montmorillonite. This, in turn, allows various molecules and ions to diffuse easily into the nanocomposite structure.

The results of the studies show that the dependence of the adsorption amount of cobalt ions on the pH of initial solutions (Fig. 2, *a*) changes with the silica content in the samples. So, for original montmorillonite, the adsorption amount depends little on the pH of the solution. For nanocomposite samples, an increase in absolute adsorption values with increasing montmorillonite content is observed. The decrease in the maximum adsorption with increasing silica content is due to the partial overlapping of the clay mineral surface with silica gel globules both on the basal surface and on the lateral faces on which the hydroxyl groups =Al–OH and ≡Si–OH are located. Adsorption of cobalt ions occurs due to the formation of monodentate surface complexes with ion exchange centers (X) or surface hydroxyl groups (≡Si–OH) [20]:

$$\text{X–Na}+\text{Co}^{2+}=\text{X–Co}^{+}+\text{Na}^{+}; \tag{1}$$

$$\equiv\text{Si–OH}+\text{Co}^{2+}=\equiv\text{Si–OCo}^{+}+\text{H}^{+}. \tag{2}$$

At the same time, a variation of the pH, based on the above reactions, affects only the second type of interaction, namely with surface hydroxyl groups (≡Si–OH). In the acidic medium, the hydroxyl groups (≡Si–OH) are protonated and become positively charged, which prevents the addition of cobalt ion. In the alkaline medium, hydroxyl groups (≡Si–OH) are deprotonated and become negatively charged, which contributes to the removal of cobalt ions. Since the surface complexes formed are positively charged, further adsorption of cobalt ions is complicated by the change in the charge of the material surface and, accordingly, electrostatic repulsion.

The isotherms of cobalt adsorption by nanocomposite samples (Fig. 2, *b*) indicate a rather significant change in the maximum adsorption amount with increasing montmorillonite content. At the same time, samples with insignificant silica content (97 and 86 % MMT) have almost the same sorption capacity as original montmorillonite, which indicates the optimum composition of the nanocomposite in the range of silica concentrations of 3–14 %. In addition, as shown in the previous paper [17], samples of nanocomposites have better technological properties, namely lower sedimentation stability. In this case, the solid phase is easier separated from the liquid one.

Mathematical processing of the isotherms of cobalt adsorption by nanocomposite samples with different montmorillonite contents (Table 2) indicates that the Langmuir equation, which is based on the monomolecular adsorption model, better describes experimental data, which is confirmed by higher values of correlation coefficients $R^2$ in comparison with those of the empirical Freundlich model. Freundlich model better describes experimental data in the field of low concentrations, and rather high values of the correlation coefficients can indicate the presence of various adsorption centers, namely cation exchange centers with hydroxyl groups of the lateral surface of the mineral and hydroxyl groups on the surface of the deposited silica gel.

Table 2

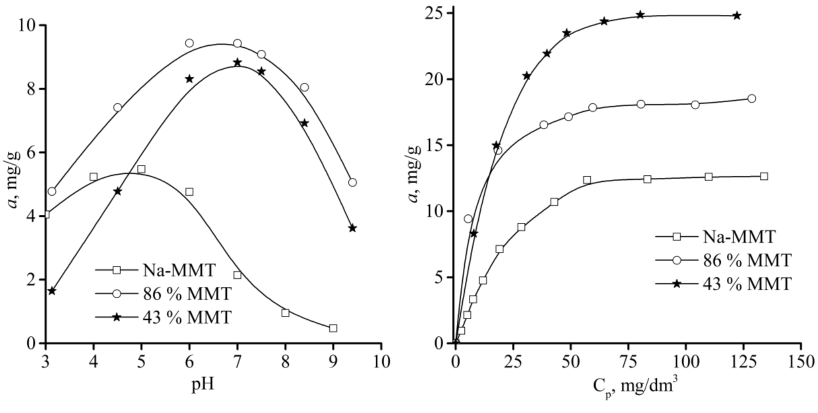
Coefficients of the equations of cobalt adsorption by nanocomposite samples at pH 6

| MMT content, % | By Freundlich | | | By Langmuir | | |
|---|---|---|---|---|---|---|
| | $K_F$ | n | $R^2$ | $K_L$, $dm^3/mg$ | $a_\infty$, mg/g | $R^2$ |
| Na-MMT | 7.2 | 4.0 | 0.857 | 1.9 | 15.8 | 0.990 |
| 97 | 8.4 | 4.8 | 0.967 | 1.5 | 15.1 | 0.998 |
| 86 | 9.1 | 6.3 | 0.951 | 3.3 | 14.2 | 0.998 |
| 75 | 6.9 | 5.4 | 0.973 | 1.6 | 11.6 | 0.991 |
| 60 | 6.3 | 6.6 | 0.993 | 2.5 | 9.6 | 0.980 |
| 43 | 3.8 | 5 | 0.983 | 1.5 | 6.7 | 0.980 |
| 23 | 2.3 | 5.9 | 0.972 | 0.9 | 4 | 0.992 |

The results show that uranium adsorption by composite samples is also effective. Thus, the dependence of the adsorption amount on the pH of the initial solution (Fig. 3, *a*) indicates the rather complex nature of the adsorption processes on the surface of the samples. It is known [21] that adsorption of uranium by natural montmorillonite significantly depends on the pH of the solution. The curve has a clearly pronounced maximum at pH 4–6. This dependence is due to the complex chemistry of uranium in the solution and surface properties of the mineral itself at various pH values.

In the acidic medium, uranium is in cationic form, with the adsorption of uranyl cations suppressed due to protonation of cation exchange minerals and surface hydroxyl groups. With increasing pH, the concentration of hydrogen ions decreases and, correspondingly, uranium adsorption increases. However, with further increase of pH, uranium hydrolyzes and passes into anionic forms as hydroxyl and carbonate, mostly polynuclear complexes. Such negatively charged uranium compounds are practically not sorbed on negatively charged montmorillonite particles. For nanocomposite samples, the maximum shift (Fig. 3, *a*) to a more alkaline region to pH 6–8 is observed, which is characteristic of silica gels [22].

Adsorption isotherms (Fig. 3, *b*) indicate better adsorption properties of nanocomposites in comparison with the original mineral (Na-MMT).



*a* *b*

Fig. 3. Uranium sorption by nanocomposite samples: *a* — dependence of uranium sorption on the pH of the initial solutions; *b* — uranium sorption isotherms

Calculated using the Langmuir equation, the values of the maximum adsorption indicate an increase from 13 mg/g for original montmorillonite to 25 mg/g for the 43 % MMT sample, which corresponds to a nearly 2-fold increase in the adsorption capacity. The nature and shape of the isotherms and, accordingly, calculated coefficient of the Langmuir equation indicate higher selectivity of the synthesized nanocomposites compared with original montmorillonite. The coefficients of the Langmuir and Freundlich equations are presented in Table 3.

Table 3

Coefficients of equations of uranium adsorption by nanocomposite samples at pH 6

| MMT content, % | By Freundlich | | | By Langmuir | | |
|---|---|---|---|---|---|---|
| | $K_F$ | n | $R^2$ | $K_L$, $dm^3/mg$ | $a_\infty$, mg/g | $R^2$ |
| Na-MMT | 1.9 | 2.4 | 0.921 | 0.041 | 15.9 | 0.986 |
| 86 % MMT | 7.1 | 4.4 | 0.989 | 0.172 | 19.3 | 0.999 |
| 43 % MMT | 6.5 | 3.3 | 0.934 | 0.060 | 30.0 | 0.988 |

The calculated correlation coefficients indicate that the experimental data are better described by the Langmuir equation ($R^2$=0.986–0.999). For nanocomposite samples, an increase in the amount of the maximum adsorption (from 15.9 to 30 mg/g) and selectivity (from 0.041 to 0.172 $dm^3$/mg) is observed.

Better adsorption properties of nanocomposites in comparison with the original mineral can be caused by several factors. First, nanocomposite samples have a more developed specific surface area and higher content of macro- and mesopores, which, in general, improves the diffusion of various uranium forms into the material. Secondly, an increase in the silica gel content leads to an increase in the content of rather active surface groups ≡Si–OH, which more selectively remove uranium from solutions as proved by some studies [23] and the results of this work.

## 6. Discussion of the results of the study of the influence of silica concentration on structure formation processes and adsorption properties of nanocomposites

The obtained results indicate better sorption properties of the synthesized materials due to their larger specific surface area and presence of more active adsorption centers. As shown, such active centers are hydroxyl groups on the silica surface. The developed system of pores promotes the diffusion of ions of different nature into the structure of synthesized nanocomposite materials.

As a result of the study, it was found that the proposed synthesis method allows obtaining highly porous sorption materials based on tetraethoxysilane and montmorillonite. Investigations of the porous structure show that, with a small amount of silica, the nanocomposite materials obtained have a larger specific surface area and higher content of micro- and mesopores compared to original montmorillonite. The materials obtained by the template-free sol-gel synthesis are not inferior or have similar structural and sorption properties in comparison with the materials described in the works discussed above [13–16].

At the same time, the complexity of this study is the peculiarities of structure formation in sol-gel transformations, which do not allow determining the patterns of structure formation of the pores of the finite material in full.

Among the main disadvantages of this study is the complexity of the processes of hydrolysis and polycondensation of tetraethoxysilane, which greatly complicates the method of materials synthesis.

Further development of the research can be aimed at obtaining nanocomposite materials in the granular form. This will allow investigating the possibility of widespread introduction of synthesized nanocomposites in water treatment technologies.

## 7. Conclusions

1. The results of low-temperature nitrogen adsorption indicate that the use of the proposed template-free sol-gel synthesis allows obtaining highly porous materials. It was found that the largest specific surface area (250 $m^2$/g) is observed for the sample with the montmorillonite content of 43 %. The synthesized materials have a “card house” structure with a developed system of micro- and mesopores, which is confirmed by the calculated values of micro- and mesopore volume.

2. According to the results of the adsorption removal of cobalt and uranium ions, it was found that the change in the chemical composition of nanocomposite samples has a mixed effect. In the case of cobalt removal, the maximum adsorption amount decreases with the montmorillonite content, which is associated with the overwhelming ion exchange mechanism of sorption. For uranium sorption, the dependence is opposite. Reducing the montmorillonite content leads to an increase in the maximum adsorption amount (up to 30 mg/g), which is associated with more selective uranium removal due to the formation of surface complexes involving surface hydroxyl groups.

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