The 12th International Symposium on
Technetium and Rhenium – Science and Utilization

November 6–7, 2025 - Moscow - Russia

Dedicated to the 100th anniversary of the discovery of rhenium

Program and abstracts

Eds. K.E.German, I.D.Troshkina, A.V. Bardysh,
A.P.Novikov, M.A. Volkov

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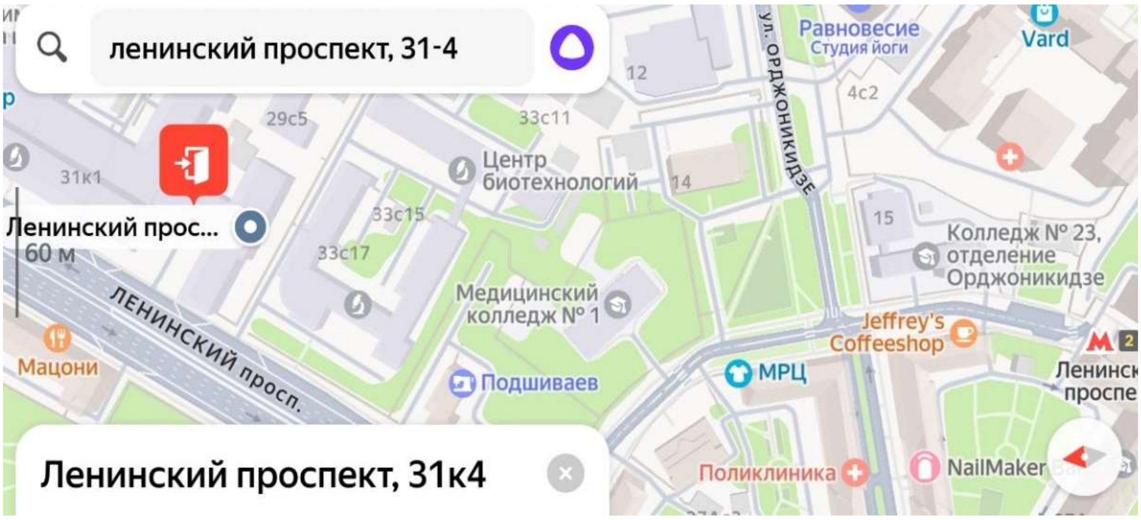
November 6 (Thursday)

Registration: 09.00 – 09.30, IPCE RAS, Moscow, Leninsky Prospekt 31



Section: Fundamental Physics and Chemistry of Tc and Re

Chair – Stepan Kalmykov, Konstantin German

09.30-10.00	Welcome address (E.N. Kablov, S.N. Kalmykov, A.Yu Tsivadze, B.F. Myasoedov)
10.00-10.40	***Sidorenko Georgy*** Coordination Chemistry of Technetium Carbonyls: Recent Advances
10.40-11.10	***Sakhonenkova Anna*** Technetium carbonyl hydrides: synthesis and reaction properties
11.10-11.40	***Maksimova Yulia*** Possibility of guanidine sorbent for extraction of perrhenate ion and comparison of its efficiency with some commercial nitrogen-containing anion exchangers
11.40-12.00	**Coffee break**
12.00-12.30	***Novikov Anton (Plenary)*** Non-Covalent Interactions Influence on the Crystal Structures Formation of Rhenium and Technetium Compounds
12.30-12.45	***Charkin Dmitri*** The fascinating chemistry of perrhenate crown ether complexes: from multi-level complexes to polyrhenates
12.45-13.00	***Lebedev Viacheslav*** Rhenium sulfide clusters formed upon laser desorption-ionization of rheniite
13.00-13.15	***Gerber Evgeny*** Structural features and thermal stability of technetium-containing triethylenediamine complexes
13.15-13-30	***Volgin M. I.*** Chemical resistance of metal phase simulants present in irradiated nuclear fuel towards oxidation in air and nitric acid
13.30 – 13.45 online	***Babitova Ekaterina*** On the way to elusive $[Tc(CO)_5]^-$

13.45 – 14.00 On line	***Brechalov Alexandr*** Technetium carbonyl hydrides with diimine ligands
14.00-15.30	***Dinner***

Section: Tc in Nuclear Fuel Cycle and in the Biosphere. Analytical chemistry of Tc

Chairs S.N. Kalmykov, K.E. German

15.30-16.00	***Vakhrushin Alexander (Plenary).*** Technetium and iodine behavior in the combined technology of SNF processing
16.00-16.15	***Miroslavov Alexander et al.*** Technetium(I) Dicarbonyl Complexes with Bidentate N,N-Aromatic Imines
16.15-16.45	***Volkov Mikhail (Plenary)*** Tc new chemistry
16.45-17-15	***German Konstantin (Key lecture).*** Technetium targets – forms and processing
17.15-17-30	***Safonov Alexey.*** Radioecology and biogeotechnology of technetium

Poster session 17.30-18.00

1. **Abramova Elena.** *The role of carbon steel corrosion products in technetium immobilization in engineering safety barriers.*
2. **Afanasiev Andrey**. *Dimeric Complex of Hydroxo-Zirconium(IV) with Tc(VII) and Re(VII) and its Extraction in Liquid–Liquid Extraction Systems.*
3. **Allabergenov Roman.** *Rhenium: hydrochemical technogenic raw material and hybrid technology of its development.*
4. **Andreeva Sofia.** *Rhenium recovery by vinylpyridine anionite Axionit VPA G2.4 from sulfuric acid uranium-containing solutions.*
5. **Artemyev Grigoriy.** *Modification of clay barrier materials with organic and mineral additives for immobilization of technetium.*
6. **Baranov Oleg.** *Synthesis and hydrolysis of binuclear halide complexes of technetium and rhenium.*
7. **Bardysh Alisa.** *Sorption of rhenium from mother liquors of non-ferrous metal precipitation in waste processing.*
8. **Belova Elena.** *Complex compounds of technetium with diethylene triamine pentaacetic acid and their role in nuclear medicine and nuclear reprocessing.*
9. **Bulatov Georgiy.** *Modeling of the technetium behavior in the gas phase over uranium–plutonium mononitride containing oxygen impurities and fission products***.**
10. **Cherkasov Denis.** *Synthesis and electrochemical properties of low-carbon technetium carbides.*
11. **Frolkova Darya.** *Hirshfeld surfaces of the components in the caffeine binary co-crystals with* $Mg(H_2O)_6[ReO_4]_2$.
12. **Frontera Antonio.** *Leveraging Theoretical XPS and NBO Analysis to Probe Matere Bonds in Perrhenate Salts.*
13. **Gakiev Adam.** *Rhenium sorption by nanocomposites based on carbon.*

14. **Grin Mikhail.** *Several features of Tc(VII) reaction with derivatives of tetrazine base.*

15. **Khanin Dmitry.** *Promising electrocatalysts based on technetium low-carbon carbide*

16. **Kholopkina Anastasiya.** *Voltammetric study of simple ion-transfer of pertechnetate anion across a polarized micro-interface between two immiscible electrolyte solutions.*

17. **Korobov Maxim.** *Recovery of rhenium from fumarole activity products.*
18. **Lyamtseva Elena.** *Radiochemical impurities in* ^{99m} *Tc radiopharmaceuticals: determination and validation (online).*
19. **Malysheva Anna.** *Design of radiopharmaceutical composition with rhenium-188 and hyaluronic acid for radiosynoviorthesis (online).*
20. **Mikheev Ilya.** *Alkoxotechnology in the production of rhenium alloys*
21. **Mokrushin Ilya.** *Structure and synthesis of potassium decacyanotechnetate and metal cyanide coordination polymer.*
22. **Panfilov Oleg.** *Transition Metal-Based Catalysts in Bio-Oil Cracking.*
23. **Pivovar Andrey.** *Investigation of the properties of cement and clay-based materials modified with biocidal additives.*
24. **Popova Nadezhda.** *Long term duration of Tc-bulk and Tc-coatings in various environmental conditions.*
25. **Safiulina Alfiya.** *Liquid-liquid extraction of zirconium pertechnetate from SNF reprocessing rafinates.*
26. **Sidorenko Georgy.** *Interaction of Technetium Tricarbonyl Triaqua Complex with Phosphoric Acid Anions in Aqueous Solution: a* ^{99}*Tc NMR Study.*
27. **Sitanskaia Anastasiya.** *Synthesis and properties of matrices for immobilization and transmutation of technetium.*
28. **Sitanskii Andrey.** *Mechanisms of autoclave methods for processing technetium-containing materials.*
29. **Solodovnikov Maksim.** *Sorption of molybdenum from acidic saline solutions in the processing of rhenium-nickel superalloy wastes.*
30. **Troshkina Irina.** *Selective advanced extraction of rhenium from uranium ore in-situ leaching solutions.*

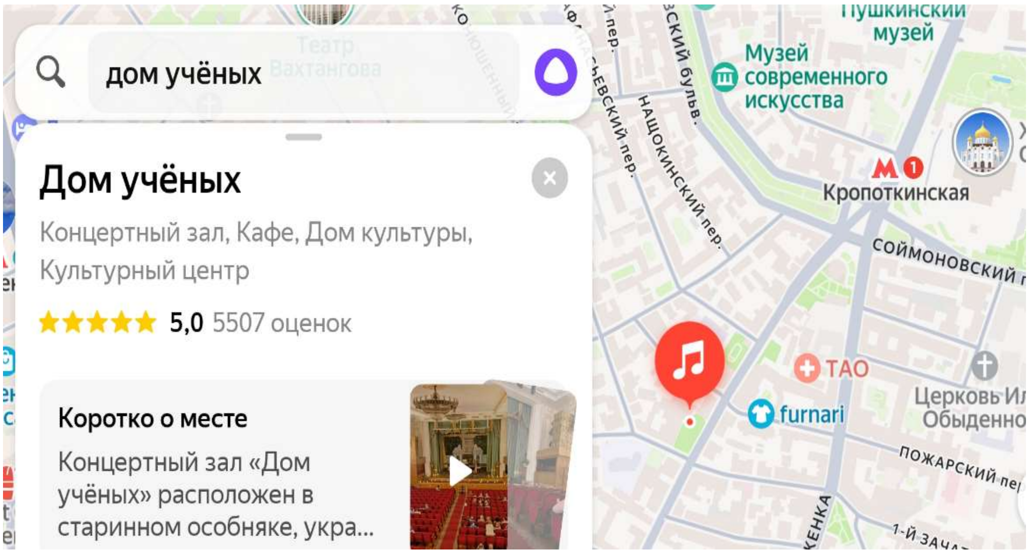
31. **Veselov Svyatoslav.** *Development of an electrochemical method for sepsrstion of 99mTc from a molybdenum tagget in the process of producing radiopharmaceutucals.*

32. **Volosnikov Semen.** *Behavior of technetium in bottom sediments of lakes at different stages of eutrophication.*
33. **Zaripov Radion.** *Reconstructing the Tc–C Phase Diagram Using a combined DFT and ML Approach.*

18.00-20.00 Welcome party

November 7 (Friday)

Central House of Scientists, Moscow, Prechistenka street, 15



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Section: Re, Geology, Metallurgy

Chair – Irina Troshkina

9.30 - 10.00	***Excursion around the Central House of Scientists***
10.00-10.25	***Troshkina Irina*** Sorption of rhenium in complex processing of primary and secondary raw materials
10.25-10.45	***Kadirov Abdusamig (online)*** Reception surface-active substances based on gossypol for the flotation enrichments of ore
10.45-11.05	***Klyucharev Dmitry*** Rhenium mineralization of insula volcanic-arc systems: from the past through now to the future
11.05-11.25	***Mikhaylenko Mikhail*** Comparative data on rhenium recovery using amphoteric ion exchange resins of various structures
11.25-11.45	***Bekbutaeva Nargiza*** Rhenium production at JSC Almalyk mining and metallurgical complex
11.45-12.00	**Coffee break**
12.15-12.30	***Targanov Igor*** Rhenium sorption in the complex processing of superalloy grinding waste
12.30-12.45	***Solodovnikov Maksim*** Kinetics of aqueous leaching of tantalum from the sintered semi-product of complex processing of rhenium-nickel waste
12.45-	***Bardysh Alisa***

13.00	Sorption of rhenium by a carbon composite modified with polytetrafluoroethylene
13.00 – 13.20	***Meshcheryakov Nikolay*** Development of new rhenium sorbents based on hyper-crosslinked polystyrenes from Sunresin (China).
13.20 – 14.00	**Coffee break**

Section: Tc and Re in Nuclear Medicine

Chair: Kodina G.E.

14.00-14.15	***Ussov Vladimir (Plenary)*** Creation of a family of pathospecific paramagnetic contrasts for magnetic resonance imaging based on quantum chemical analysis of chelation properties of ^{99m}Tc and Mn(II) and replacement of ^{99m}Tc with Mn(II)
14.15-14.30	***Tishchenko Viktoria*** Radiopharmaceuticals based on rhenium-188: the development and preclinical investigations
14.30 – 14.45	***Tyupina Margarita*** New ^{99m}Tc radiopharmaceuticals for myocardial metabolic processes
14.45-15.00	***Tyupina Margarita*** Technetium pentacarbonyl iodide as a preparation for lung diagnostics: new results.
15.00 – 15.15	***Zheltonozhskaya Marina*** Rhenium medical isotopes: new production methods
15.15-15.30	***Larenkov Anton (online)*** Design of radiopharmaceuticals for the diagnosis of neurodegenerative diseases
15.30-15.45	***Furkina Ekaterina*** Production and separation of ^{186}Re at the NRC Kurchatov Institute
15.45 – 16.00	***Rumyantsev Alexander*** Obtaining 94mTc in liquid target of medical cyclotron
16.00-17.00	***Closing ceremony*** ***Furchet***

ABSTRACTS

The role of carbon steel corrosion products in technetium immobilization in engineering safety barriers

E. Abramova[1*], A. Safonov[1], K. German[1]

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The materials of containers for the disposal of radioactive waste in deep geological formations (DGR), depending on the concept adopted in different countries, are steel (including carbon and stainless steel), copper, alloys based on: chromium, molybdenum, zirconium, titanium and nickel. The Russian concept considers carbon steel, which is a well-studied material, both in physical and chemical properties. Important characteristics of carbon steels are a good combination of strength and ductility; relative predictability of its corrosion processes; low cost. However, one of its main disadvantages is low corrosion resistance. In turn, steel corrosion products can affect the mobility of long-lived radionuclides in the system of engineered safety barriers and the geological environment after their degradation.

The purpose of this work is to characterize and model the composition of carbon steel corrosion products under DGR conditions, as well as to assess the behavior of Tc in the presence of corrosion products of this steel.

It was found that the main products of carbon steel corrosion under the model conditions of the DGR are pyrrhotite and magnetite. The main interaction of technetium occurs with the intermediate corrosion product - ferrihydrite. After 7 days of holding the steel plate of the St3 brand in the model solution, the efficiency of Tc removal from the solution was 98.7%. Addition of iron oxidation products or reduced iron powder to barrier materials is promising for increasing the immobilization of technetium in them.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation.

Rhenium recovery by vinylpyridine anionite Axionit VPA G2.4 from sulfuric acid uranium-containing solutions

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The use of rhenium-containing productive solutions of underground leaching of uranium for the production of ammonium perrhenate is a pressing task for replenishing the Russian mineral resource base of rhenium, since the demand for rhenium-containing materials used in the military industry is increasing. Obtaining pure ammonium perrhenate is complicated by its low content in productive solutions and a large number of impurities, in connection with which the technology for its production is only feasible using the sorption method of recovery [1-3].

The aim of the work is to obtain the sorption characteristics of a strongly basic anion exchanger when extracting rhenium from low-temperature sulfuric acid solutions in relation to solutions of underground leaching of polymetallic ores.

When measuring the sorption isotherms of rhenium, the variable volume method was used with a T:L (g:ml) ratio of 1:500; 1:1000; 1:2000; 1:5000; 1:10000. In two experiments, binary solutions (pH 2) with a concentration of uranium and rhenium of about 100 mg/L were used, one of which differed in the presence of impurity ions in the initial solution: Cl^{-} – 3,0 g L; Fe(II) – 0,5 g/L; Fe(III) – 0,5 g/L; $SO4^{2-}$ – 2,0 g/L. The temperature in the equilibrium experiments was 8 °C. Based on the results obtained, isotherms of rhenium sorption by gel anionite were constructed (Figure 1).

As expected, the introduction of impurity ions reduces the capacity characteristics of the sorbent used in relation to rhenium. Considering the concave nature of the rhenium sorption isotherms, their further mathematical processing was carried out using the Freundlich model.

Table 1 shows the equilibrium characteristics of rhenium sorption obtained by processing isotherms using the Freundlich equations.

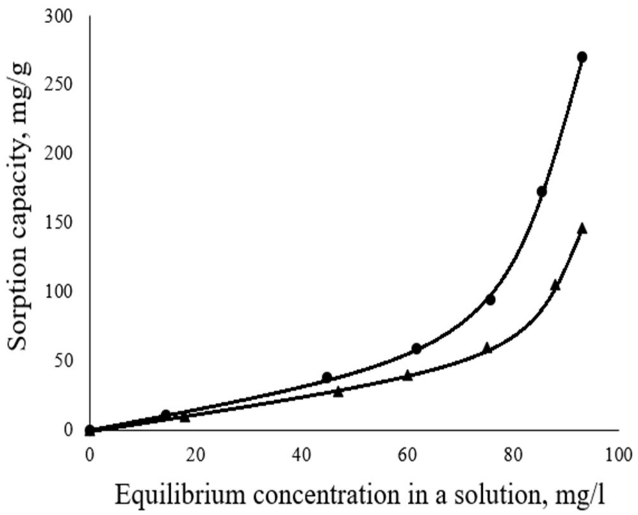

Figure 1: Sorption isotherm of rhenium with gel ion exchange resin with pyridinium functional groups (temperature 8 °C)

● – binary system; ▲ – binary system with impurities

Table 1: *Equilibrium characteristics of rhenium sorption by gel anionite with pyridine groups from sulfuric acid solutions (8 °C)*

Freundlich constant, L/mol	n	R^2
binary system		
2,0	0,3	0,9916
binary system with impurities		
5,0	0,6	0,9864

High coefficients of determination for the sorption of rhenium by Axionit VPA G2.4 anionite, as well as the concave nature of the sorption isotherms, indicate the superiority of the Freundlich model, with the Freundlich constant for rhenium ranging from 2,0 to 5,0 L/mol.

Further studies of the capacity characteristics of Axionit VPA G2.4 gel anionite were carried out under dynamic conditions. The solution flow rate was 7 column volumes per hour (c.v./h) at a temperature of 8 °C and pH 2. The concentration of rhenium in the initial solution was 26,3 mg/ L.

The total dynamic exchange capacity of the anionite under the specified conditions was 24,6 g/L, and the output curve of rhenium sorption by Axionit VPA G2.4 anionite obtained during the experiment is shown in Figure 2. Based on the data obtained, the kinetic sorption coefficient of rhenium by gel anionite was calculated, which amounted to 0.029 h.

The experimental data were described using the most common models of extraction kinetics: Thomas, Young-Nelson, and bed depth-specific time (BDST) [4].

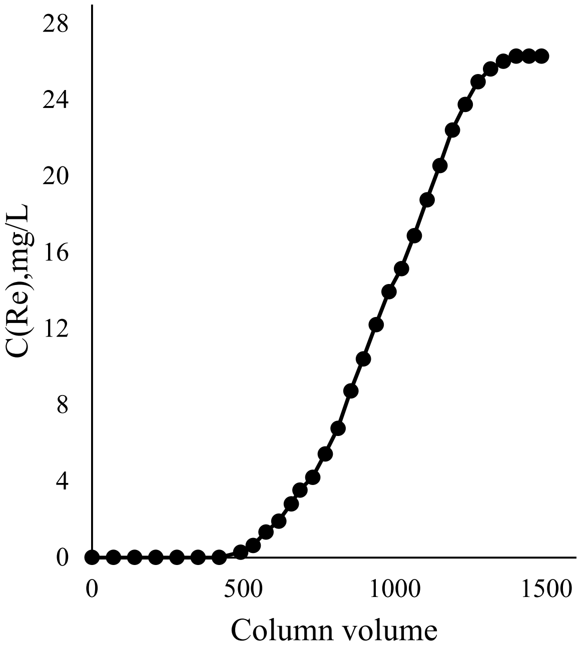

Figure 2: *Sorption curve of rhenium by gel anion exchanger from sulfuric acid solution*

The results of processing the experimental data using the models are presented in Table 2.

Table 2: *Parameters of sorption dynamics models*

Model	Parameters	Value	R^2
Thomas	K_T, ml/(mg·min)	0,0389	0,9727
	q_0, mg/g	12,1	
Yun-Nelson	K_{YN}, 1/min	0,000492	0,7769
	τ, hour	84,7	
BDST	K, cm^3/(mg·min)	0,00238	0,9727
	N_0, mg/cm^3	4,13	

The output curves are best described by the Thomas and BDTS models. Based on these values, it is possible to determine the parameters of rhenium sorption under dynamic conditions using Axionit VPA G2.4 gel ion exchange resin with pyridine functional groups from sulfuric acid solutions.

[1] Palant, A.A., Troshkina, I.D., Chekmarev, A.M., Kostylev, A.I. Technology of rhenium. Moscow: LLC "Galleya-Print", 329, (2015).

[2] Tatarnykov, A.V., Taltykin, S.E., Meshcheryakov, N.M. (2016). *Field tests of sorption technology for obtaining ammonium peroxide from productive solutions of underground leaching at the Briquetno-Zheltukhinsky deposit.* Proceedings of the scientific and practical conference “Rhenium, Tungsten, Molybdenum-2016. Scientific research, technological developments, industrial implementation, 81-84.

[3] Sharafutdinov, U.Z., Kurbanov, M.A., Alikulov, Sh.Sh., Ganieva, D.S. (2021). *Study of the sorption properties of anion exchangers during the joint sorption of uranium and rhenium in the process of underground uranium leaching*. Mining Information and Analytical Bulletin, 3-1, 136-146.

[4] You, X., Farrana, A., Guaya, D., Valderrama, C., Soldatov, V. (2016) *Cortina J.L Phosphate removal from aqueous solutions using a hybrid fibrous exchanger containing hydrated ferric oxide nanoparticles*. Journal of Environmental Chemical Engineering, 4.,388-397.

K.E. German, E.S.Abramova, I.D.Troshkina, A.V. Afanasiev, A.V. Safonov at the Central House of Scientists - session of local organisers and excursion

Dimeric Complex of Hydroxo-Zirconium(IV) with Tc(VII) and Re(VII) and its Extraction in Liquid–Liquid Extraction Systems

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The rhenium(VII) and technetium(VII) behavior in extraction systems is known to be strongly affected by the presence of zirconium. Recently the hydrolyzed form of zirconium perrhenate and pertechnetate were shown to form the dimeric $\{Zr_2(OH)_2\}$ core surrounded by six permetallate anions acting as monodentate ligands and six coordination water molecules [1,2]. It was shown [1, 2] that usually very stable tetramer $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ undergoes dissociation in the presence of TcO_4^-/ReO_4^- yielding isostructural dimers, $[Zr_2(\mu\text{-}OH)_2(MO_4)_6(H_2O)_6]\ 3H_2O$ (M = Tc, Re) that is very close to zirconyl in view of Zr:O ratio. In this frame the formation of Tc(VII)-Zr(IV) species in nitric acid and their extraction in kerosene/tributylphosphate (TBP) phases was re-examined. The technetium distribution coefficient (D_{Tc}) was evaluated as a function of nitric acid concentration (1-7 M) and is in the range of 25-37, which is significantly higher compared to solutions that do not contain zirconium and confirms the synergism of their coextraction.

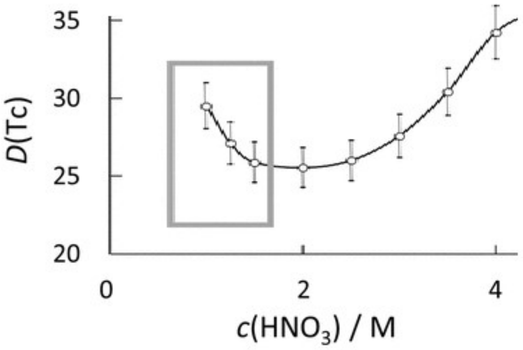

Figure 1. Technetium coextraction with zirconium: D(Tc) as a function of $[HNO_3]$ (M) in 0.5 – 4 M region. $[Tc(VII)] = 10^{-4}$ M, [Zr (IV)] = 0.11 M). Nitric acid concentrations applied within the Purex process spent fuel reprocessing are highlighted with a grey frame.

[1] Novikov, A.P., Zagidullin, K.A., Kuznetsov, V.V. et al. Speciation and Complex Formation of Zirconium(IV) with Tc(VII) and Re(VII) in Liquid–Liquid Extraction Systems. ACS Omega, 2025, V. 10.Is. 33. 38064-38072. doi: 10.1021/acsomega.5c05158

[2] Shohel, M.; Bustos, J.; Roseborough, A.; Nyman, M. Pertechnetate/Perrhenate-capped Zr/Hf-Dihydroxide Dimers: Elucidating Zr−TcO 4 Co-Mobility in the Nuclear Fuel Cycle. *Chem. – A Eur. J.* **2024**, *30* (10), e202303218. https://doi.org/10.1002/chem.202303218.

Modification of clay barrier materials with organic and mineral additives for immobilization of technetium

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Being a transition element technetium (Tc) is exclusively interesting for investigations as it has 8 states of oxidation (between -1 and +7) and other specificities. The main source of Tc accumulation is the nuclear power industry. Today the management of radioactive waste containing Tc still causes the range of problems coming from its long half-life and high mobility in the form of a pertechnetate ion. There are also many complications with the radioactive waste containing Tc disposal since it has a low ability to immobilize in matrices and barrier materials and has high risks of uncontrolled migration in the environment. Bentonite clay is one of the most promising natural barrier materials for a multi-barrier system in radioactive waste disposal sites due to its low water permeability, high plasticity, and high sorption capacity (for Cs, Sr actinides) properties. Nevertheless, if the clay contains little of dissolved humic substances, reduced iron, sulfide sulfur, which have reducing properties, immobilization of technetium does not occur. Therefore, one of the promising areas of research for many groups today is the creation of a barrier material based on clays and concretes capable of immobilizing technetium. For this purpose, reducing additives are traditionally used, for example, ZVI, fly ash and others, which promote the immobilization of technetium in the +4 form.

This study investigates bentonite clay from the 10th Khutor deposit (Khakassia) as a promising barrier material for the "Yeniseisky" deep geological repository for radioactive waste in the Krasnoyarsk Region. The clay was modified with both organic (thiourea) and mineral (reduced iron, ferrihydrite, etc.) additives. The experiments demonstrated that the addition of 5 wt.% iron powder resulted in a technetium sorption degree of 99%. Quantitative removal of technetium was achieved within 8 hours, with a residual content of no less than 36% of the technetium retained in a strongly fixed form.

Furthermore, the incorporation of thiourea into the clay also led to the quantitative immobilization of technetium from the solution. Thiourea acts by effectively modifying technetium speciation, reducing it from the highly mobile pertechnetate ion [Tc(VII)] to immobile forms of Tc. Structural analysis of the resultant technetium-thiourea compound confirmed a reductive immobilization mechanism.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation

Synthesis and hydrolysis of binuclear halide complexes of technetium and rhenium

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Variuos technetium binuclear chloride complexes can be formed in a molten salt reactor (MSR) and, therefore, be one of the spent nuclear fuel (SNF) components. They will inevitable hydrolyse during the hydrometallurgical reprocessing of SNF. The chemical state of technetiun is essential for predicting the chemical behavior of technetium species in the course of this process. At present, the hydrolysis products of binuclear halide complexes of technetium and its chemical analog rhenium have not been identified.

Two synthetic routes, namely hydrogen reduction using 5% H_2 + 95% Ar gas mixture under evelated pressures in autoclave [1] and chemical reduction with benzoylchloride [2] were tested for synthesis of binuclear rhenium and technetium complexes ($(NH_4)_2Re_2Cl_8$ and $(NH_4)_2Tc_2Cl_8$). Ammonium perrhenate or ammonium pertechnetate were used as precursors. It was found that at the internal pressures in the autoclave of 30 and 50 atm, the reduction of ammonium perrhenate is imcomplete, and $Re(VI)OCl_5^-$ and $Re(V)OCl_5^{2-}$ are formed, respectively. On the other hand, the reaction with benzoylchloride results in the formation of $(NH_4)_2Re_2Cl_8$, which was proven by both spectroscopic and XRD data.

The product of $(NH_4)_2Tc_2Cl_8$ hydrolysis in 1.0 M solution of sodium hydroxide leads to the formation of a dark precipitate. According to the element analysis, its chemical formula is close to Tc4O5. The XRD pattern was indicateted in the tetragonal syngony, parameters of the elemental cell is a = 15,58 Å, b = 9,15 Å, c = 8,42 Å.

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Towards the elusive $[^{99}Tc(CO)_5]^-$

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Spectroscopically pure $[^{99}Tc(CO)_5]^-$ was obtained for the first time by reduction of $^{99}Tc_2(CO)_{10}$ with an excess of anthracene radical anion in THF. The IR spectrum is consistent with literature data: IR ($Na[^{99}Tc(CO)_5]$, ν(CO), cm^{-1}, THF): 1910, 1862 [1]. Considering the experimental conditions of NMR measurements, the signal at –2603.7 ppm can be tentatively assigned to $[^{99}Tc(CO)_5]^-$.

IR spectroscopy demonstrates ion-pair formation via coordination of Na^+ to the carbonyl oxygen atoms of $[^{99}Tc(CO)_5]^-$ in THF solution. A similar behavior has been reported for $Na[Mn(CO)_5]$ [2]. According to DFT calculations $[^{99}Tc(CO)_5]^-$ adopts a trigonal bipyramidal geometry. The calculated IR spectrum (1940, 1865 cm^{-1}) is in good agreement with the experimental data. AIM analysis yields a charge of 1.13 on technetium, comparable to that calculated for $^{99}Tc_2(CO)_{10}$ and $^{99}TcH(CO)_5$. The excess electron density is localized predominantly on the carbonyl oxygen atoms, consistent with the observed Na^+ coordination to these sites.

Treatment of $[^{99}Tc(CO)_5]$– with a 20-fold excess of anthracenide leads to the formation of a finely dispersed bronze precipitate. EXAFS analysis revealed that the nearest coordination surroundings of technetium in the resulting compound corresponds to $[^{99}Tc(CO)_4]$. Comparison of its X-ray absorption near-edge structure with those of $^{99}Tc_2(CO)_{10}$ and $^{99}TcH(CO)_5$, that are similar, demonstrates a substantial difference in the effective charge on the technetium. A similar trend is observed in AIM-calculated charges for the series $[^{99}Tc(CO)_4]^{3-}$ (0.89) < $^{99}Tc_2(CO)_{10}$ (1.13) ≈ $^{99}TcH(CO)_5$ (1.28). The reaction of $[^{99}Tc(CO)_5]^-$ with naphthalene dianion radical in THF afforded an analogous bronze precipitate exhibiting properties consistent with those reported for $[M(CO)_4]^{3-}$ (M = Mn, Re) [3].

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Sorption of Rhenium by a carbon composite modified with polytetrafluoroethylene from nitric acid media

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Rhenium is a strategic rare metal, more than 80% of which is used to manufacture heat-resistant alloys for aircraft engines [1]. Relatively low-cost activated carbons are used to extract microconcentrations of rhenium from solutions [2], but carbons have disadvantages, such as low sorption capacity and mechanical strength, and the rhenium desorption stage is difficult, which can be improved by introducing a modifying agent onto the carbon surface. Modified activated carbons are a promising alternative that allows reducing operating costs by simplifying the desorption stage.

The aim of the work is to study the sorption properties of a new carbon material in nitric acid environments, which are typical for many industrial processes.

The effect of pH on the sorption of rhenium by a carbon composite based on VSK grade activated carbon was studied (Figure 1).

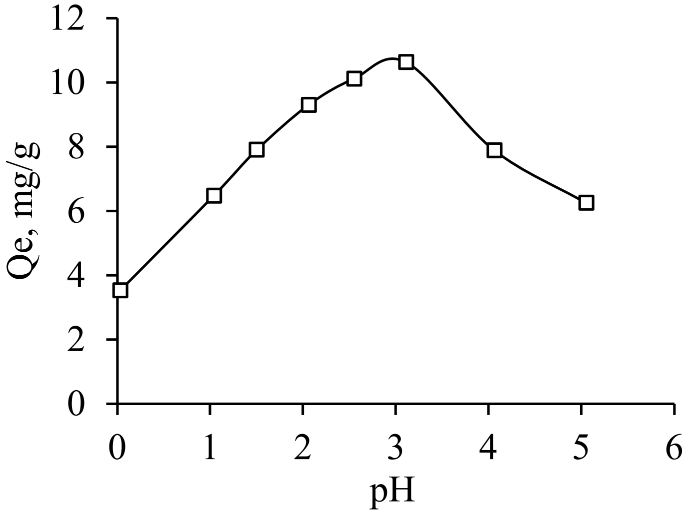

Figure 1: *Effect of pH on the capacity of a carbon composite for sorption of rhenium from a nitric acid solution*

The pH value of the solutions was adjusted with nitric acid. The sorption capacity (Qe, mg/g) was calculated using formula 1:

$$Qe=((C_{initial}-C_{fin})\cdot V_{solution})/m \qquad (1)$$

where $C_{initial}$ and C_{fin} are the concentration of rhenium in the initial solution and in the solution after sorption, respectively, mg/dm^3; $V_{solution}$ is the volume of the solution, dm^3; m – mass of the sorbent sample, g.

The optimum pH value of the solution for rhenium sorption from nitric acid media, at which the maximum sorption capacity of the carbon composite is observed, was established; it was 3.1.

At the selected pH value, the isotherm of rhenium sorption by the carbon composite was obtained by the limited volume method (Figure 2).

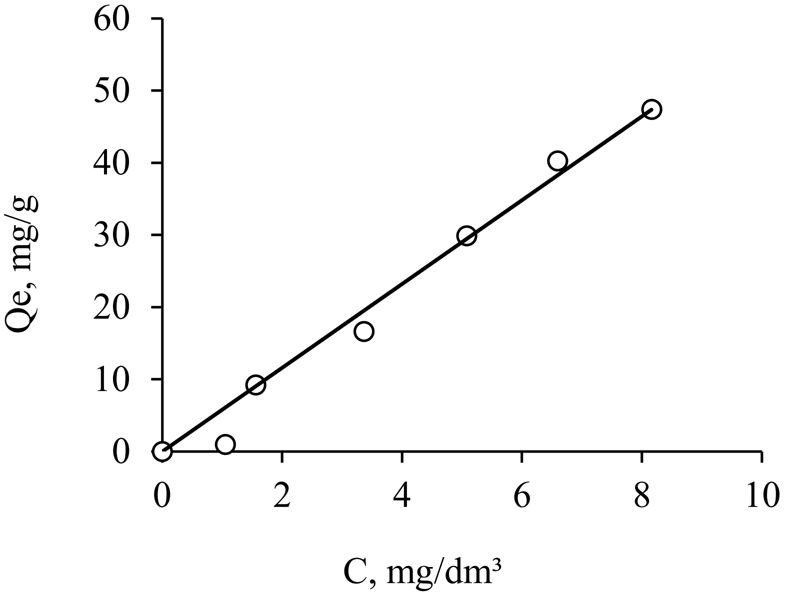

Figure 2: *Figure 2. Isotherm of rhenium sorption by the carbon composite from a nitric acid solution*

The isotherm is described by the Henry equation due to the linear correlation within its initial section. The Henry constant is Kg – 5900±200 cm^3/g.

Determined equilibrium characteristics of the carbon composite based on activated carbon VSK modified with polytetrafluoroethylene indicate the effectiveness of the obtained material for extracting rhenium from dilute nitric acid solutions.

The kinetics of rhenium sorption was studied by the limited volume method. The carbon composite samples were transferred to flasks with a model nitric acid solution (pH 2) with a rhenium concentration of C(Re) – 21.3 mg/dm^3 at a sorbent:solution phase ratio of 1:1000. The highest value of the determination coefficient (R^2 0.9924) when describing the kinetic data of rhenium adsorption from a nitric acid solution by a composite based on VSK carbon using the pseudo-second-order model may indicate a multi-stage process and the presence of a large number of active centers on the surface of the carbon composite [3], the constant K_2 is equal to $1.553 \cdot 10^{-2}$ g·mg^{-1}·min^{-1}.

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Sorption of rhenium from mother liquors of non-ferrous metal precipitation in waste processing

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Recovery of valuable components during processing of heat-resistant superalloy waste involves sorption operations using alternative materials as sorbents, such as modified activated carbons. The carbon modification stage improves characteristics, enabling effective extraction of the target element [1].

The aim of this study is to determine rhenium sorption conditions from mother liquors of nickel-cobalt concentrate precipitation using a new carbon composite based on VSK grade activated carbon, developed at D.I. Mendeleev University of Chemical Technology [2]. For comparison of sorption properties, the widely used macroporous weakly basic resin Puromet A170 was employed in rhenium technology.

The equilibrium and kinetic characteristics of rhenium sorption by the carbon composite were determined. The isotherm has a linear form and is described by Henry's equation with a constant Кg 2100±600 cm3/g. The pseudo-second-order model with rhenium sorption rate constant K2 1,73–2,83·10-3 g/(mg·min) best describes the kinetic data. The limiting stage of the process is external diffusion.

Sorption was carried out under static conditions. The stability of sorption characteristics of the carbon composite and reference sorbent was evaluated over three sorption-desorption cycles during rhenium extraction from mother liquor. The total degree of rhenium desorption from the carbon composite over three consecutive contacts after the first sorption cycle was more than 80%, and after the third cycle ~97%, which is comparable to that when using basic resin Puromet A170.

The conducted studies on the sorption characteristics of the carbon composite based on VSK grade carbon with respect to rhenium demonstrate the prospects of their use for solving technological problems related to its extraction from dilute, compositionally complex solutions.

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Experience of rhenium production at JSC Almalyk Mining and Metallurgical Complex

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The availability of a raw material base and the introduction of modern technologies have contributed to the development of rhenium production in Uzbekistan. The main producer of rhenium in the country is JSC Almalyk Mining and Metallurgical Complex (AMMC). With the involvement of the Yoshlik-I field, the introduction of effective rhenium extraction technology becomes a strategically important task for AMMC.

Rhenium is extracted as a by-product during the processing of copper-molybdenum ores from the Kalmakyr deposit. According to the technology existing at the Copper Smelter, rhenium is extracted from molybdenum concentrate.

At a rare metals production facility, rhenium is captured from sulfur gases generated during the oxidative roasting of molybdenum concentrate. This is followed by hydrometallurgical processing. The sulfuric acid solutions from the furnace's gas cleaning systems are then filtered.

The dominant technology for extracting rhenium globally is the processing of absorption solutions formed during the purification of exhaust gases from burning molybdenum concentrates. However, existing methods, particular ion-exchange sorption, face a number of difficulties. The efficiency of rhenium extraction at AMMC using ion-exchange sorption is limited by several factors: an insufficient number of effective ion-exchange resins, a high concentration of related elements, especially molybdenum (Mo 4-6 g/dm^3), in process solutions.

Since 2000, AMMC has used ion-exchange sorption to extract rhenium from solutions. Initially, "ChFO" Brand resin (Ukraine) was used. This resin was replaced by Sim-202 resins from Purolite. Due to its good sorption characteristics the Sim-202 resin is still used in rhenium production at AMMC.

AMMC employees are conducting research on various types of ion-exchange resins from foreign manufacturers to extract rhenium from process solutions and identify the most effective resin.

Table 1: Chemical composition of sulfuric acid solution, mg/dm^3

Al	**As**	**Bi**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**K**
262	24,1	13,5	106	1,5	1,3	5,3	471	1270	90
Na	**Ni**	**Os**	**Re**	**Si**	**Ti**	**Zn**	**Mg**	**Mn**	**Mo**
90,2	3,4	<1	**549**	75	8,5	30	205	2,4	**6700**

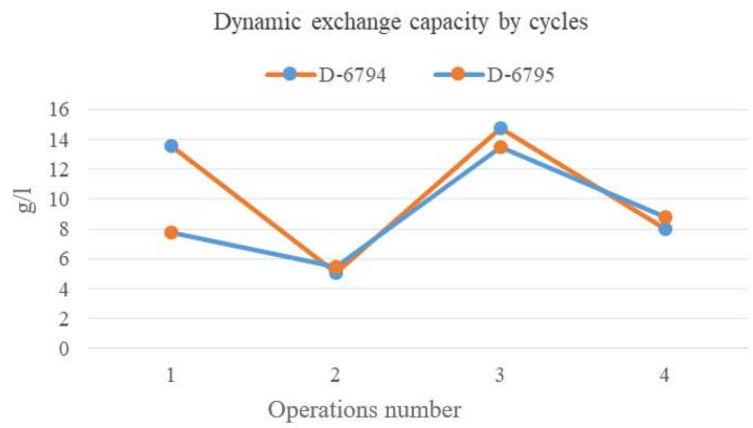

Figure 1: Dynamic exchange capacity of Purolite Ecolab ionites.

The sulfuric acid content was 276 g/dm^3, the rhenium content 0,549 g/dm^3, and the molybdenum content 6,7 g/dm^3. The rhenium concentration was slightly lower than in the Sim-202 experiments (0,7-1,5 g/dm^3), which could affect the total sorption load. At the same time, the molybdenum content was significantly higher (3,7 times), making the sorption conditions more difficult in terms of selectivity. The D-6794 Ecolab anionite generally showed higher dynamic exchange capacity values before breakthrough (14,74 g/dm^3 in cycle III) than the D-6795, which had a best value of 13,45 g/dm^3. The average values for all cycles were also higher for D-6794. This indicates a higher efficiency at the initial stage of sorption (fig.1).

In the desorption step, both ionites showed generally high efficiency. Desorption of rhenium in all cycles exceeded 86%, and in the first it achieved almost complete removal of rhenium from the sorbent 99,5%. In cycle III, some decrease in the desorption rate (up to 53-69%) is possibly due to partial compaction of the resin structure or the formation of poorly soluble forms of rhenium inside the pore space. The concentration of rhenium in rich eluates ranged from 5,3 to 16,8 g/dm ^{3}, which is close to the values Sim-202 the range is from 3 to 50 g/dm^3. However, it should be noted that the initial rhenium content of rhenium was higher in Sim-202 experiments.

In conclusion, Ecolab resins have a high rhenium capacity under conditions of high acidity and in the presence of a significant amount of molybdenum. It is worth noting the D-6794 sorbent, which consistently demonstrated higher values in key parameters: dynamic exchange capacity, recovery rate, desorption rate. Although both sorbents are still inferior to Sim-202 in terms of recovery and stability of desorption, the results for Ecolab, can be considered quite successful.

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Complex compounds of technetium with diethylene triamine pentaacetic acid and their role in nuclear medicine and nuclear reprocessing

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Hydrophilic complexes of technetium with polyaminocarboxyl ligands (NTA, EDTA, DTPA, etc.) have been known and widely used in radiopharmaceuticals for over 40 years. A number of these compounds are formed directly upon the reduction of technetium with hydrazine or tin(II) in the presence of a complexing agent. Diethylenetriaminepentaacetic acid dianhydride is one of the first bifunctional chelating agents used for conjugation with reduced technetium-99m. DTPA interacts with the terminal and/or amino group of the peptide, forming strong amide bonds. In this process, the anhydride rings open to form polyvalent groups capable of chelating metals, including Tc-99m. The bond between the metal and the organic ligand in such complexes is donor-acceptor in nature (via the lone pairs of oxygen and nitrogen in DTPA) and is quite strong. The DTPA molecule has eight potential coordination sites for metal binding (three N and five O atoms). Furthermore, DTPA can modify amine-containing polymers, such as poly-L-lysine. The resulting chelating polymers have a greater number of sites than those obtained by DTPA attachment to a peptide. This method is the most convenient and widely used in medical practice. One example is the optimization and development of a lyophilized kit for the instant preparation of ^{99m}Tc-DTPA-LSA, consisting of technetium-99m-labeled neolactosyl-human serum albumin (DTPA-LSA). A single-photon emission computed tomography (SPECT) study demonstrated that the promising biological properties of ^{99m}Tc-DTPA-LSA, combined with the development of a reliable and rapid lyophilized DTPA-LSA kit, enable liver receptor imaging for routine clinical assessment of liver function.

DTPA, in turn, has found application in the extraction technology of spent nuclear fuel reprocessing, which involves the combined extraction of uranium and plutonium from nitric acid solutions with 30% tributyl phosphate in a hydrocarbon diluent. Reprocessing high-burnup SNF significantly increases the yield of fission products (FPs). An increased FP yield increases the likelihood of process deviations and failures during the key operation of the reductive separation of uranium and plutonium. These failures include the accumulation of interphase formations and precipitates in the extraction apparatus stages, which disrupt the normal hydrodynamics of the phases within the stages. These deposits have high reactive and catalytic activity toward the components of the reprocessed solutions and the reagents used, and they also absorb significant quantities of gamma-active FPs. Extraction of a sample of the above-mentioned precipitate from the extraction equipment demonstrated that it was a poorly soluble compound of technetium with DTPA, which is one of the complexing agents used in the Purex process to stabilize target components in specified oxidation states.

To optimize the conditions for SNF extraction reprocessing, information on the composition, structure, and properties of the poorly soluble technetium compound with DTPA formed in the "Tc – $N_2H_5NO_3$ – DTPA – HNO_3" system is necessary. Due to the impossibility of synthesizing single crystals, we used X-ray absorption spectroscopy (EXAFS) and XANES at the K-edge of Tc, in combination with other physicochemical methods, to obtain structural data on the technetium complexes with DTPA.[1]

The synthesis and isolation of the test compound were carried out from model nitric acid solutions simulating, in a number of respects, the aqueous component of the extraction system characteristic of the uranium and plutonium separation stage. The kinetics of the Tc(VII) reduction reaction were studied spectrophotometrically using 1.2 ml quartz cuvettes at a temperature not exceeding 25°C. The resulting precipitates were separated from the mother liquors on a 200 µm Millipore GS membrane, washed with an alcohol solution (4:1), and dried in a desiccator. [2] Based on the analytical data obtained using various methods, it can be concluded that the precipitate formed in nitric acid Tc-containing solutions in the presence of N2H5NO3 and DTPA is a Tc-DTPA complex compound with a polynuclear and polymeric nature. Both amino and carboxyl groups of the complexone participate in the formation of this compound, which can coordinate to various technetium atoms. The latter can form complex assemblies in which both Tc-Tc bonds exist, and the presence of bridging oxo groups is also detected. The solubility value of the Tc-DTPA complex lays in close range as technetium sulfide [3] and tetrapropylammonium pertechnetate [4].

The resulting compound does not provide a definitive answer to the question of the structure of Tc in medical complexes, since the technetium concentration there is very low and polymerization is impossible. However, it does allow us to understand the type of coordination environment within them. The low solubility of the Tc-DTPA complex polymer determined in this study is of significance for nuclear technologies, as it allows us to propose a method for isolating technetium from these solutions.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation

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Comparative data on rhenium recovery using amphoteric ion exchange resins of various structures

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In rhenium hydrometallurgy, ion exchange sorption processes based on the use of weak base anion exchange resins have become widespread. The synthesis of weak base anion exchange resins with high selectivity to rhenium, from which rhenium can be quite easily and completely desorbed by ammonia solutions, has been mastered. However, weak base anion exchange resins are unsuitable for recovery rhenium from alkaline solutions. To recover rhenium from alkaline solutions, only strong base anion exchange resins can be used. However, the desorption of rhenium from strong base anion exchange resins causes significant difficulties. Relatively recently, evidence has emerged that zwitterionic resins, the functional groups of which include structural fragments with opposite charges, namely quaternary ammonium base groups and carboxyl groups, also exhibit the ability to sorption of rhenium from alkaline solutions. Although they are inferior to strong basic anion exchange resins in rhenium capacity, rhenium from them can be desorbed by water. It is also possible to synthesize ion exchange resins containing both quaternary ammonium base groups and carboxyl groups using the "snake in a cage" method, that is, by impregnating a strongly basic anion exchange resin with a solution of acrylic acid, followed by polymerization of acrylic acid with the addition of a catalyst.

The company Sunresin has synthesized two types of amphoteric ion exchange resins, the first of which, Seplite SCF904, is a zwitterionic ion exchanger, the composition of which functional groups includes both carboxyl groups and quaternary ammonium base groups, the second resin, Seplite LAC211, is synthesized using the "snake in a cage" method. It has been established that both of these ion exchange resins are similar in capacitive characteristics with respect to rhenium during sorption from multicomponent solutions, with some advantage of LAC211 resin. It has been shown that SCF904 and LAC211 resins practically do not sorb rhenium from distilled water and from a dilute ammonia solution, but when total salinity increases as ammonium sulfate is introduced into solutions, they begin to sorb rhenium, and with an increase in the concentration of ammonium sulfate, their capacity for rhenium increases. From both resins, rhenium can be desorbed with demineralized water, preferably at elevated temperatures.

Carbonyl hydride complexes of technetium-99 with diimine ligands

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Carbonyl hydride complexes of manganese and rhenium are known intermediates in numerous catalytic processes; therefore, both their methods of generation and their reactivity are being actively investigated [1]. Complexes with nitrogen-containing heterocyclic ligands have proven to be particularly interesting in this context [2]. These complexes have been studied in considerable detail for manganese and rhenium. In contrast, carbonyl hydride complexes of technetium remain virtually unknown to date. Consequently, exploring the feasibility of their synthesis and properties is relevant for establishing structure–property relationships within Group VII elements.

An attempt to synthesize $[^{99}Tc(bpy)(CO)_3H]$ by reducing $[^{99}Tc(bpy)(CO)_3(MeOH)]ClO_4$ with $NaBH_4$ in methanol, by analogy with the synthesis of $[(Re(bpy)(CO)_3H]$ [3], afforded instead an air-stable binuclear complex $[(^{99}Tc(bpy)(CO)_3)_2(\mu\text{-}H)]ClO_4$. IR (ν(C=O), cm^{-1}, CH_2Cl_2): 2041 (m), 2024 (m), 1916 (s). ^1H NMR ($CDCl_3$, δ, ppm): 8.44 (m, 2H, bpy), 8.21 (m, 4H, bpy), 7.40 (m, 2H, bpy), –11.35 (s, 1H, Tc–H–Tc); ^{99}Tc NMR (CDCl3, δ, ppm): –1235 (s). XAS measurements indicated that, upon dissolution in THF, this compound presumably undergoes a conformational change: the linear Tc–H–Tc arrangement transforms into a bent geometry. In an analogous reaction of $[Tc(phen)(CO)_3(MeOH)]ClO_4$ with $NaBH_4$, an unidentified, unstable compound was obtained. IR (CH_2Cl_2, cm^{-1}): 2039 (s), 2007 (br), 1939 (s). The weak band at 2007 cm^{-1} may be attributed to Tc–H vibrations (for comparison, ν(Re–H) in $[ReH(bpy)(CO)_3]$ appears at 2018 cm^{-1} [3]).

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Modeling of the technetium behavior in the gas phase over uranium–plutonium mononitride containing oxygen impurities and fission products

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According to our model estimations with ASTRA-4 complex, the production of technetium in the nitride fuel $U_{0.8}Pu_{0.2}N$ during irradiation with fast neutrons of the experimental demonstration nuclear reactor with lead coolant - BREST-OD-300 with an electric power of 300 MW - (burnup 13.6% t.a. U + Pu) will be 0.25 wt% (a record accumulation among light FPs under these conditions, equal to 1.023 wt%, will be demonstrated by ruthenium) [1], while the partial pressure Tc in the gas phase in the region of operating temperatures of the reactor will not exceed 10^{-18} atm and will remain below 10^{-10} atm even at 2000 K.

Modeling methods have shown that the gas phase above U0.8Pu0.2N0.995O0.005 irradiated with fast neutrons consists of the following main components: alkali and alkaline earth metals (Cs, Ba, Sr) and their iodides, nitrogen and atomic iodine, volatile Te and Pd, monoxides of Ba, Nd, La, Sr and Ce, low-volatile metals Nd, Mo, Y, Tc, La, Ce, Zr and their nitrides, with the exception of Mo and Tc, as well as metals, oxides and nitrides of Pu and U – Pu, PuO, PuN, U, UO, UN.

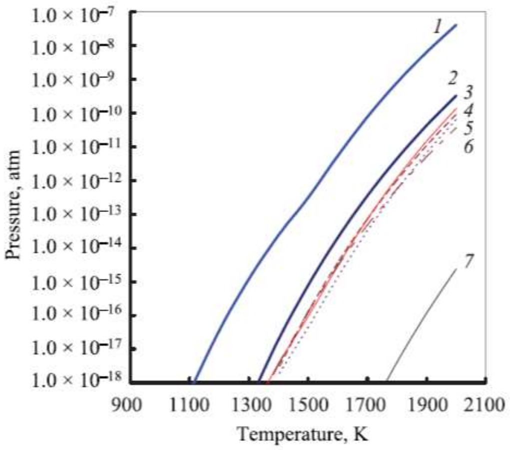

Figure 1: *Temperature dependences of the partial pressures of low-volatile metallic fission products in the gas phase over stoichiometric uranium–plutonium mononitride containing an oxygen impurity (0.032 wt % O) at a burnup of 13.6% h.a. (1) Nd, (2) Mo, (3) Y, (4)* ***Tc****, (5) La, (6) Ce, and (7) Zr.*

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Reference

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Synthesis and electrochemical properties of low-carbon technetium carbides

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Technetium is one of the major products of ^{235}U nuclear fission (yield > 6%), and the use of its compounds in the radiochemical industry seems highly desirable. Large organic cations, such as hexametyleneiminium and triphenylguanidinium use to separate pertechnetate ions form aqueous solutions. Thermal decomposition of formed precepitates leads to the formation of low-carbon technetium carbides with a cubic crystal latice [1]. The electrochemical properties of these prodicts are still unknown, although they can be successfully used as catalytically active supports for noble metals.

In this work, the redox reaction between technetium carbides Tc_xC and solutions containing K_2PtCl_4 in 0.5 M H_2SO_4 under open-circuit conditions, the so called "galvanic displacement", was used to obtain catalytically active systems. It was found that the substitution reaction proceeds very slowly comparing to molybdenum and tungsten carbides due to the more noble electrode potential of technetium and its carbides and their kinetic inertness. Nevetheless, platinum clasters are formed at the electrode surface within a few days. The electrochemically active surface area (*EASA*) of platinum was measured by the charge corresponding to the desorption of a monolayer of carbon monoxide. The prepared $Pt(Tc_xC)$/GC-electrodes exhibit high catalytic activity in the hydrogen evolution reaction (HER), which makes them promising for the electrolytical hydrogen production.

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Rhenium: hydrochemical technogenic raw material and hybrid technology of its development

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Rhenium, as an accompanying element of copper-molybdenum ores, is extracted either directly - by sublimation of rhenium heptaoxide during roasting of molybdenum flotation concentrate, or indirectly: by sintering, roasting, leaching, then rough industrial products (cinders, cakes, sludges ...) and salt solutions are used as technogenic raw material; they are processed to extract valuable components, including rhenium.

In the Republic of Uzbekistan, such technogenic rhenium-containing raw materials are industrial waste from the tailings of the Uzbek Technological Metals Plant (UzKTM, Chirchik), the former UzKTZhM, where rhenium is distributed in the pulp and liquid phase, in the form of perrhenate ions - dissociated salts of ammonium, sodium, calcium and copper. In order to increase the degree of rhenium extraction from the liquid phase of sludge, the corresponding samples were concentrated by preliminary purification from iron, copper and a mixture of sulfuric-nitric acid salts (SAS) [1,2].

The product of such enrichment is a solution with a density of 1.12-1.15 g/cm^3, pH 7-8, containing components, g/dm^3: SAS 90-120; Cu 0.58-0.60; Fe 0.027-0.03; Re 0.057-0.06; Mo 1.2-1.25; W 0.48-0.5, other elements. The known methods of extracting rhenium from such hydrochemical raw materials are considered: sorption, extraction, precipitation on lead hydroxide, sulfidization, etc. [3]: they do not solve the problem of reaching the maximum degree of efficiency, require large expenditures of materials and energy. However, there is an approach that allows increasing the degree of rhenium extraction, while reducing costs. This is a hybrid technology combining hydrothermal sulfidization of a rhenium-containing mixture [1,2] with ultrasound exposure, which activates chemical processes in the system under the influence of a mechanical and physical factor.

The approach allows providing the extraction of a collective sulfide concentrate (SAS) of rare metals from the liquid phase of the sludge: 1.99-2.00 g of dry mass from 1.0 dm^3 of solution. The SAS contains Re_2S_7, MoS_3 and WS_3 sulfides, %: Re 2.11; Mo 17.4; W 0.29. The degree of precipitation of rare metals in the sulfide concentrate is not lower than 93-95%. The hybrid technology is carried out under the influence of ultrasound in two stages: first, perrhenates, molybdates and tungstates in the initial solution are transformed into soluble thiosalts $(ReO_3S)^-$, $(MoOS_3)^{2-}$, $(WO_3S)^{2-}$; then thiosalts - into insoluble sulfide compounds. In comparison with the traditional sulfide method, the hybrid method allows to remove completely or reduce diffusion limitations of the course of chemical reactions, as well as to carry out processes at room temperature of solutions.

At the first stage of the implemented technology, to obtain soluble thiosalts, by stoichiometrically verified dosing of the sulfidizing reagent, into a neutral or alkaline solution:

$NH_4ReO_4 + (NH_4)_2S = NH_4ReO_3S + 2NH_3 + H_2O$ (1);

$(NH_4)_2MoO_4 + 3(NH_4)_2S + 3H_2O = (NH_4)_2MoOS_3 + 6NH_4OH$ (2);

$(NH_4)_2WO_4 + (NH_4)_2S = (NH_4)_2WO_3S + H_2O + 2NH_3$ (3)

Within the traditional method, this requires at least 2 hours, and under the conditions of hybrid technology - 0.5 hours. At the second stage, under the conditions of the traditional approach, in a solution of thio-salts, to obtain a well-filtered precipitate of sulfide compounds - SCS, the solution is acidified with mineral acid to pH 1.5-2.5:

$2NH_4ReO_3S + 6H_2SO_4 = Re_2S_7 + 2NH_3 + H_2S + 6H_2O + 12O_2$ (4);
$(NH_4)_2MoOS_3 + H_2SO_4 = MoS_3 + (NH_4)_2SO_4 + H_2O$ (5);
$(NH_4)_2WO_3S + 3H_2SO_4 = WS_3 + (NH_4)_2SO_4 + 3H_2O + 4O_2$ (6).

Then the solution is heated to boiling, the pulp is "twisted" (at least 1.0 h), with cooling it, and feeding it to the filter.

In the conditions of hybrid technology, thanks to ultrasound, the process is carried out without heating the solution. The hybrid method is carried out using ultrasound, with an acoustic impact frequency on the system of 22 kHz and a radiation intensity of 2 W/cm^2, for example, using an ultrasonic disperser of the UZDN-2T brand (produced at Sumy city, at "Electron" factory, 1987).

The method provides obtaining rare metal thiosalts from hydrochemical raw materials in a more energy-saving mode. This effect is achieved due to dispersion and disintegration of the medium components, facilitating the diffusion of reagents into the reaction zone and products from it, at normal room temperature. The mechanism of the processes occurring in the hybrid method, using ultrasound, is as follows: ultrasonic vibrations cause mechanical elastic vibrations in the system, which have high energy, which is the cause of ultrasonic activation of components and intensification of chemical processes in the system. As a result, physical and chemical processes are accelerated, leading to the destruction of rare metal thiosalts. The process of acoustic action on the SAS system is carried out with continuous air bubbling, preventing the turbulence of "air carbonation". Ultrasound activates the solution, initiating cavitation in it: the formation of pulsating bubbles (caverns, cavities) in the liquid, filled with gas, steam or their mixture. This process contributes to the destruction of chemical compounds, the formation of the target rhenium-containing component, increases the efficiency of the technology. The advantage of the hybrid technology is the exclusion of the use of high-temperature processes, the ability to obtain valuable primary and by-products from technogenic hydrochemical raw materials.

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Leveraging Theoretical XPS and NBO Analysis to Probe Matere Bonds in Perrhenate Salts

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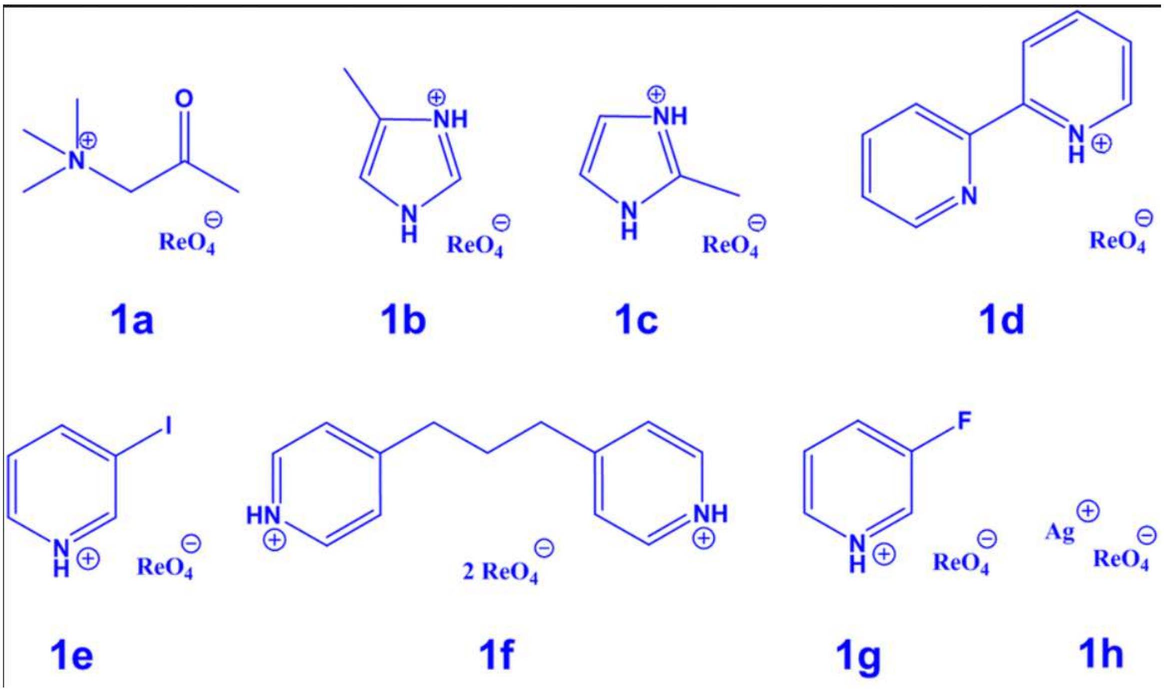
The matere bond (MaB), a σ-hole interaction where d-block elements like Rhenium act as electrophiles, is a key driver in supramolecular assembly [1-4]. While single-crystal XRD is the primary technique for its identification, a method for detecting and characterizing MaBs in non-crystalline materials is highly desirable.



Scheme 1. Structural formulae of the perrhenate salts

We combined experimental X-ray Photoelectron Spectroscopy (XPS) [5,6] with high-level Density Functional Theory (DFT) calculations to investigate a series of perrhenate salts with and without MaBs. Theoretical simulations of XPS spectra for perrhenate monomers and dimers were performed, and Natural Bond Orbital (NBO) analysis was used to quantify the charge-transfer component of the interaction.

Our theoretical models reveal a direct correlation between the MaB length (Re···O distance) and the Re 4f core-level binding energy (BE). A key finding is the strong linear correlation (Fig. 6) between the theoretically computed Re 4f BEs and the Re···O distance, demonstrating that shorter, stronger MaBs result in a lower BE. This is mechanistically explained by NBO analysis, which confirms a Lone-Pair(O) → σ*(Re-O) charge transfer that intensifies with decreasing interaction distance, increasing electron density at the Re atom and facilitating 4f electron release.

This study establishes that XPS, supported by robust theoretical modeling, is a powerful technique for not only identifying MaBs but also for extracting quantitative geometric information. The strong correlation between theoretical BEs and interaction distances provides a fundamental basis for using XPS to characterize σ-hole interactions in systems where single-crystal data is unavailable, opening new avenues for the analysis of non-crystalline functional materials.

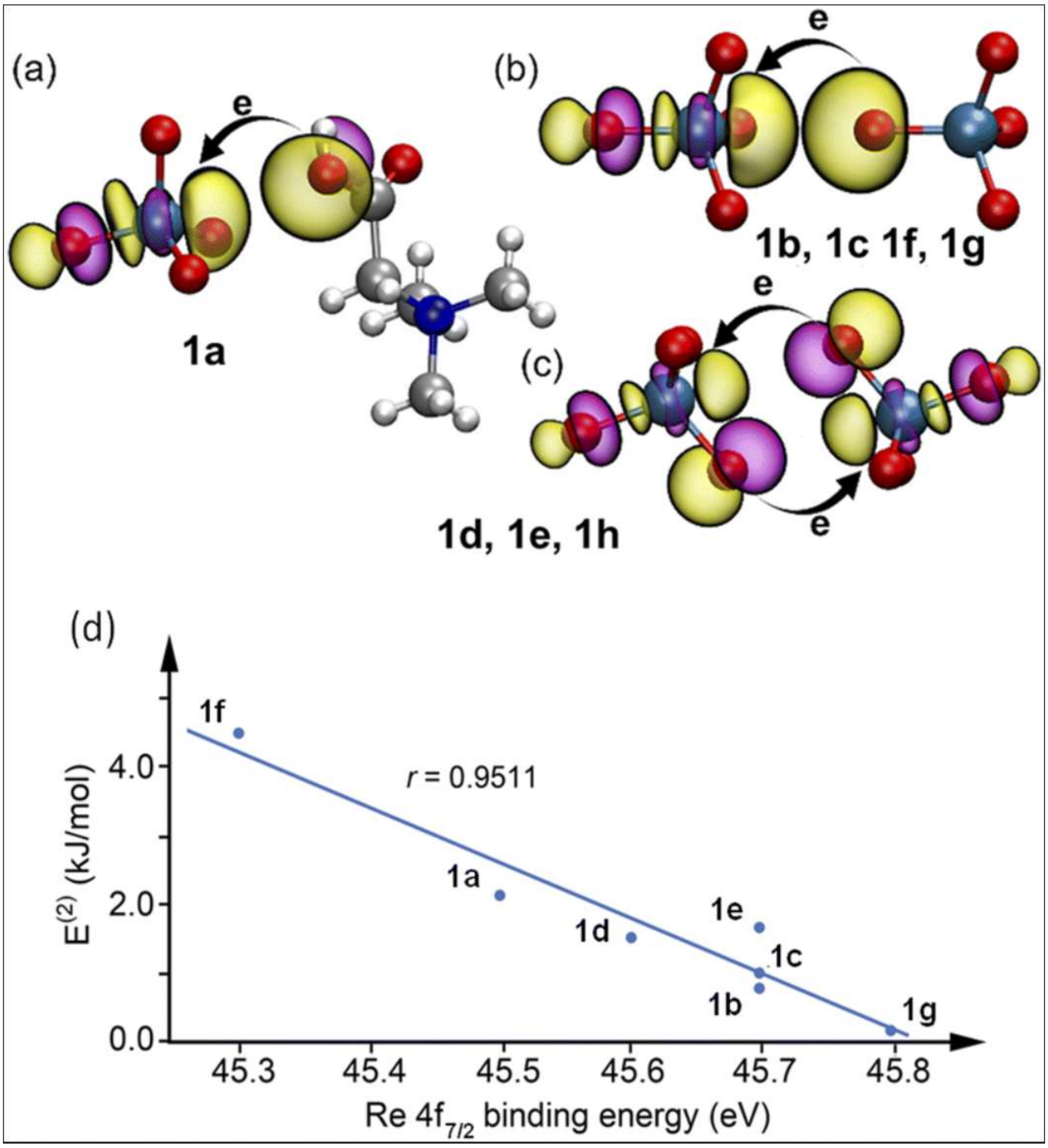


Figure 1. Plots of the NBOs involved in the three types of MaB observed in compounds **1a** (a), **1b,c,f,g** (b) and **1d,e,h** (c). Regression plot (d) of the NBO stabilization energies $E^{(2)}$ and the Re 4f7/2 BEs derived from XPS the value 45.8 have been used for 1g.

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Hirshfeld surfaces of the components in the caffeine binary co-crystals with $Mg(H_2O)_6[ReO_4]_2$

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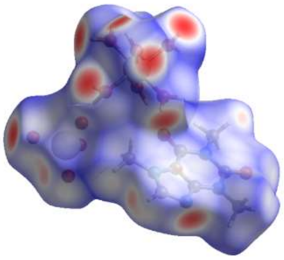
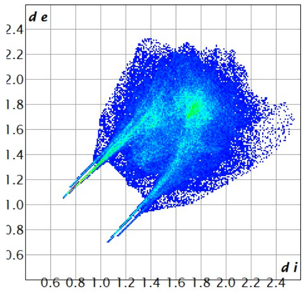
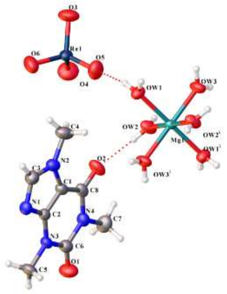
In recent years, the development of new methods for synthesizing biologically active transition metal compounds with bioorganic molecules has enabled the creation of a number of new complexes promising for targeted drug delivery in nuclear medicine, as well as for the diagnosis and treatment of severe diseases. In this study, caffeine binary co-crystals with Mg perrhenate were studied. The divalent metal atom coordinates six oxygen atoms of water molecules, forming a highly symmetrical hydrated cation in which the positive charge is distributed evenly across the 12 hydrogen atoms of the water molecules. The compound $Mg(H_2O)_6[ReO_4]_2.2C_8H_{10}N_4O_2$ consists of hydrated metal cations, perrhenate anions ReO_4^-, and caffeine molecules. Each divalent metal atom in the $Me(H_2O)_6^{2+}$ cation is coordinated by six oxygen atoms of water molecules, forming a centrosymmetric cation. The average Me–O(w) bond length is 2.0529(2) Å.



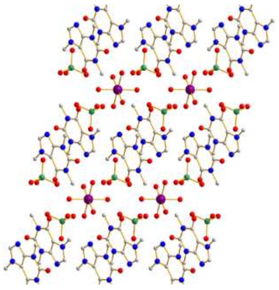
Hirshfeld surface of the compound



2D fingerprint plot



Non-covalent bonds



Crystal packing of the compound

Hirshfeld surface analyses provided evidence that the most important intermolecular interactions are due to H-bonding.

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Production and separation of ^{186}Re at the NRC Kurchatov Institute

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^{186}Re is a promising radioisotope for use in nuclear medicine due to its mild beta radiation and convenient half-life ($t_{1/2}$ = 3.72 days, $E_{\beta max}$ = 1069 keV). In addition, the soft gamma radiation (E_γ = 137 keV, 9.42%) allows for the visualization of the distribution of the radionuclide within the body. The range of β particles in tissues is approximately 3.6 microns, which makes it effective in fighting small tumors and metastases. Of particular interest is the use of therapeutic rhenium isotopes in conjunction with diagnostic ^{99m}Tc, as it is made possible by the similar chemical properties of these elements. A number of studies have been conducted on the complexation of rhenium and technetium [1,2], as well as the biochemical characteristics and distribution of these complexes within tumors [3]. These studies have demonstrated promising results when it comes to the combined use of these theranostic pairs.

This work presents methods developed at the Kurchatov Institute for the production and separation of ^{186}Re from irradiated tungsten targets. The study focuses on the use of extraction chromatographic sorbents based on quaternary amines to separate tungsten and rhenium. Distribution coefficients of these elements on the sorbents have been investigated in various media, and methods for their separation have been proposed. A semi-automatic device has been developed and tested for separating tungsten and rhenium, and a process for regenerating enriched ^{186}W from solutions after processing irradiated targets has also been proposed.

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Sorption of rhenium by nanocomposites based on carbon nanotubes

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Sorption is one of the known methods for extracting rhenium from solutions of various compositions formed during the processing of mineral raw materials.

The materials used for its implementation - strongly basic and weakly basic anion exchangers, complexing ampholytes, impregnates and Levextrel - resins have a significant cost and various limitations in use, for example, low desorption rates. Carbon materials, which are more accessible and less expensive, seem to be an alternative. The paper studies the possibility of rhenium sorption by carbon composites modified with carbon nanotubes obtained at the D.I. Mendeleyev University of Chemical Technology of Russia.

The composite is based on industrially produced activated carbons obtained from coconut shells (VSK, Taunit, etc.). Carbon nanotubes (CNTs) of the Taunit and Global CO brands were obtained at the Tambov State Technological University and AO Global CO.

The effect of the nanotube content in the carbon composite on the capacity and desorption characteristics of rhenium extraction was revealed. With an increase in the CNT content, the capacity of the VSK-CNT and Tatsorb-CNT carbon composites for rhenium slightly decreases compared to the capacity of the original activated carbon. The degree of rhenium desorption by ammonia solutions at room temperature increases up to 68 times. The sorption of rhenium by carbon nanocomposites from sulfuric acid solutions was studied under static conditions and equilibrium and kinetic characteristics were obtained.

The maximum sorption capacity and distribution coefficient of rhenium during extraction by Tatsorb-CNT and VSK-CNT composites is observed at a solution pH of 2.

The sorption of rhenium by VSK-CNT and Tatsorb-CNT composites occurs in the external diffusion region with rate constants of $6.5 \cdot 10^{-2}$ and $6.4 \cdot 10^{-2}$ $g \cdot mg^{-1} \cdot min^{-1}$ determined by the pseudo-second-order model.

It was found that the phase stability of the Tatsorb-CNT carbon nanocomposite is maintained during 5 sorption-desorption cycles. The decrease in rhenium capacity does not exceed 5 %.

Physical adsorption and equivalent anion exchange of perrhenate ion for anions located on the carbon surface determine the sorption of rhenium on composites.

Structural features and thermal stability of technetium-containing triethylenediamine complexes

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Triethylendiamine, also known as 1,4-diazabicyclo[2.2.2]octane (DABCO) is a rigid bicyclic tertiary amine with two equivalent nitrogen atoms. Its well-defined geometry, strong basicity, and ability to form stable hydrogen-bonded frameworks make it a versatile building block in crystal engineering, supramolecular chemistry, and molecular ferroelectrics. DABCO perrhenate (dabcoHReO$_4$) is particularly interesting because it belongs to a rare class of hydrogen-bonded ferroelectrics: its spontaneous polarization originates from the collective ordering of parallel, bistable NH···N hydrogen bonds between DABCO cations [1]. This gives the material a relatively large and thermally stable polarization compared to many other molecular ferroelectrics. The crystal also shows distinct dielectric phase transitions and well-defined vibrational signatures of the ReO$_4^-$ anion [2]. Beyond fundamental interest in proton-driven ferroelectricity, dabcoHReO$_4$ has been explored in flexible piezo- and pyroelectric nanogenerators, highlighting its potential for low-cost, lightweight energy-harvesting devices [3]. However, information about it technetium analogue is missing. Moreover, one can suggest the existence of structures with second hydrogen also substituted with another equivalent of DABCO, enhancing the knowledge of technetium-containing complexes. Besides that, physico-chemical properties of these type of compound might be of additional interest, both fundamental and applied.

The current work is devoted to the structural properties of technetium- or rhenium-containing triethylenediamine complexes alongwith its thermal stability. Complexes were obtained from aqueous solutions as single crystals and investigated by X-ray diffraction, termogravimetry and IR-spectroscopy techniques. Moreover, for the compounds dabcoHTcO$_4$ and dabco(TcO$_4$)$_2$ Geometry optimization and vibrational spectra calculations were performed using the DFT method and the Quantum ESPRESSO package. Non-valent interactions stabilizing the structure were analyzed for the optimized structures using Multiwfn software.

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Targets for Tc. Fabrication

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Nuclear reactions to be effective imply different types of targets. This is well valid for the technetium nuclear reactions including reactor transmutation (n, g), or cyclotron reactions (p, n), (p,2n), (p,3n). While rapid target processing in cyclotron technologies suppose application of liquid targets [1], the reactor transmutation needs highly radiation and temperature resistant materials like metal [2, 3] or carbide [4]. Laboratory of radiochemistry – technetium chemistry – has long practical experience in processing all types of technetium targets in IPCE RAS.

The work was supported by the Ministry of Science and Higher Education of the Russian Federation.

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Targets for Tc. Processing routs

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Implying different types of targets for technetium nuclear reactions to be effective makes consequence for the processing procedures.

Cyclotron reaction (p, n) is used for Tc-94m production and is carried oud based on liquid isotopically enriched molybdenum targets. For the short-lived radionuclide processing the target material is initially liquid and direct liquid separation methods may be applied (precipitation, liquid-liquid extraction, sorption etc.).

Cyclotron reaction (p,3n) is aimed on Ru-97 production based on .

While rapid target processing in cyclotron technologies suppose application of liquid targets [1], the reactor transmutation needs highly radiation and temperature resistant materials like metal [2, 3] or carbide [4]. Laboratory of radiochemistry – technetium chemistry – has long practical experience in processing all types of technetium targets in IPCE RAS.

Basic study is supported with MINOBRNAUKI (IPCE RAS). The technical work is supported with Bauman Moscow State Technical University and Russian Foundation of Prospective Investigations. And the general study makes part of Educational Program Prioritet-2030 (MIREA).

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Excursion at the Central House of Scientists

Several features of Tc(VII) reaction with derivatives of tetrazine base

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Technetium reactions for radiopharmaceutical are still of peak interest. The by-product routs may indicate both new options and some interesting reactions. When ammonium pertechnetate reacts in hydrochloric acid and diluted alcohol with with 3,6-(2-pyridyl)-1,2,4,5-tetrazine, oxidative opening of the tetrazine ring occurs with the release and coordination of the reaction product in two groups reduced to TcOCl2 and subsequent coordination of two methanol molecules.

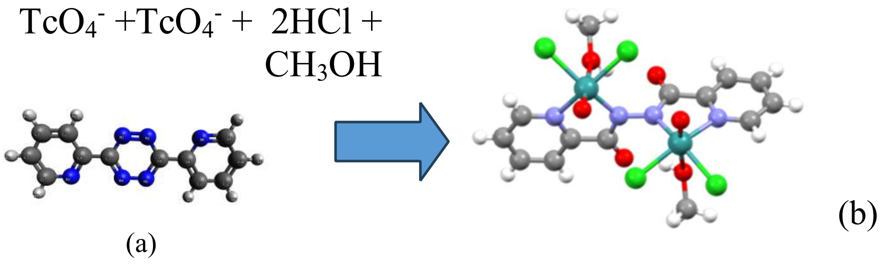

Figure 1: *Reactants (a), the reaction products (b) and its X-ray structure (b): the reduced Tc(IV) complex PyTcCl2(CH3O)-(CO)N=N(CO)-TcCl2(CH3O)Py as the product of the reaction of Tc(VII) with 3,6-(2-pyridyl)-1,2,4,5-tetrazine in methanol solution in the presence of [HCl] = 1 M*

The use of 3,6-(2-pyridyl)-1,2,4,5-tetrazine as a ligand resulted in the oxidation of the tetrazine ring and the formation of a dimeric Tc(IV) complex, the structure of which was studied by X-ray diffraction (Figure 1). Unsubstituted tetrazine is destroyed in the presence of Tc(VII) and does not lead to the formation of stable complexes.

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Reception surface active substances based on gossypol resin for the flotation enrichment of ore

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The aim of research work is to working out on effective technology for production of foaming agents of local and secondary rave material on intensification of copper, rhenium, gold ores dressing of the process for flotation's [1, 2].

Method and technology for obtaining SAS NA-1 and optimum conditions of the flotoreagent syntheses in the paste and granule forms has been elaborated.

Chemical composition of new SAS were determined and investigation of the colloid-chemical properties (adsorption, surface-active; foaming agents, micelle-formation) was carried out establishing that developed SAS NA-1 is a half-colloid, the constant of critical concentration micelle-formation were determined.

Revealed foamy forming characteristic SAS, is investigation stability, time to life's of the spumes 35-40 s. It is shown that foamy forming ability SAS NA-1 solution SAS is collapsing by polymethylsiloxane.

Investigating the stability of SAS NA-1 it is shown that foamy forming ability is directly dependent on the surface activity and lengths of hydrocarbon radical chain.

Investigation lubrication properties SAS NA-1. Direct dependency about tribology (antifriction) properties foaming agents and pH of their solution has been elaborated.

On the basis of local secondary raw materials – bottoms distillation process cotton soap stock fatty acids, water of soap production, the syntheses SAS are applied by flotation processing enrichment of non –ferrous, precious metals and rhenium by foaming agents

Flaming SAS NA-1 passed successful test in comparison with Russian reagent T-92 in central factory laboratores Almalyk and Navoi mining-metallurgical plants.

Flaming SAS NA-1 was practiced in industrial conditions at enrichment gold containing ore current ore deposit «Biran» on «Ingichka» factory (Samarkand region, Uzbekistan) of the enrichment. To account of the using SAS NA-1 is reached increase the extraction gold on 2,77%.

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Promising electrocatalysts based on technetium low-carbon carbide

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Technetium is at the limit of carbide stability in the Periodical Table. It is the critical point for carbide formation and forms only the low-carbon carbide Tc_xC ($x \geq 6$) [1]. In recent years, carbides of *d*-elements, such as molybdenum and tungsten, are considered as promising supports for catalytically clusters of active noble metals [2,3], which are deposited under open-circuit conditions in aqueous solution.

From this point of view, technetium carbide can also be used as an active support for platinum and palladium nanoparticles. In this study, an attempt was made to obtain $Pt(Tc_xC)$ and $Pd(Tc_xC)$ catalysts by the galvanic displacement method.

Techetium carbides Tc_xC were prepared by thermal decomposition of pertechnetates with large organic cations of hexametyleneiminium and triphenylguanidinium.

According to XRD data, they have a pseudocubic crystal lattice. XAFS studies revealed chemical interactions between technetium and carbon atoms, with the average Tc–C distance Tc–C estimated at 4.01±0.03 Å.

To prepare the electrodes, 0.1 mg of Tc_xC was dispersed in 1 mL of a 5 wt.% Nafion® solution, after which ~2.5 mg of the resulting mixture was applied onto both side of a glassy carbon plate ($S = 1$ cm^2).

The electrode was dried and brought into contact with solutions of 0.1 M $K_2[PtCl_4]$ or 0.1 M $PdCl_2$ in 0.5 M H_2SO_4, respectively.

Technetium carbide serves as a source of electrons for the reduction of noble metal ions through the coupled electrochemical reactions, the equations of which may be approximately written as follows:

$$PtCl_4^{2-} + 2e \rightarrow Pt + 4\,Cl^- \text{ (or } Pd^{2+} + 2e \rightarrow Pd)$$

$$Tc_xC + 2x\,H_2O \rightarrow x\,TcO_2 + C + 4x\,H^+ + 4x\,e \text{ (other oxidation products are also possible).}$$

It was found that, compared to with molybdenum and tungsten carbides, galvanic displacement of technetium in its carbides occurs relatively slowly.

It takes several days to form noble metal nanoparticles at their surface at room (~22 °C) temperature. The formation of platinum and palladium nanoparticles was confirmed by SEM and EDX studies.

The obtained Pt(TcxC) and Pd(TcxC) electrodes demonstrated excellent catalytic activity in the hydrogen evolution reaction (HER) normalized both to the electrochemically active surface area (*EASA*) of noble metal and to its mass.

The *EASA* was determined by the charge spent to a carbon monoxide monolayer desorption from the noble metal surface (the coefficient was 420 μC·cm^{-2}).

On the other hand, the low desorption potential of CO_{ads} from the surface of $Pt(Tc_xC)$ ($E \sim 0.6$ V (RHE)) electrodes suggests their high catalytic activity in the methanol electrooxidation reaction (MOR).

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Analytical chemistry and electrochemistry section:

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Voltammetric study of simple ion-transfer of pertechnetate anion across a polarized micro-interface between two immiscible electrolyte solution

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Voltammetry (VA) at the interface of two immiscible electrolyte solutions (ITIES) is a high-precision and fast electrochemical analysis method [1]. Previously, the practical use of VA on ITIES for electrochemical analysis was mainly theoretical due to the difficulty of stabilizing the electrolyte-electrolyte interface.

One solution to this problem is to use a microperforated membrane. This paper considers the use of polyethylene terephthalate (PET) film membranes with a thickness of 10 microns, one of which is perforated with a laser (**membrane I**), and the other with a microneedle punch (**membrane II**). Electrochemical sensors have been created based on these membranes.

Significant ions such as ClO_4^-, ReO_4^- in aqueous solutions have already been quantified using the developed membrane **I** sensor [2]. In this work, using membrane **II**, TcO_4^- in an aqueous solution was quantified for the first time by cyclic voltammetry at micro-ITIES. The measurements were carried out in cyclic (Fig. 1) and square-wave voltammetry according to a 4-electrode measuring circuit.

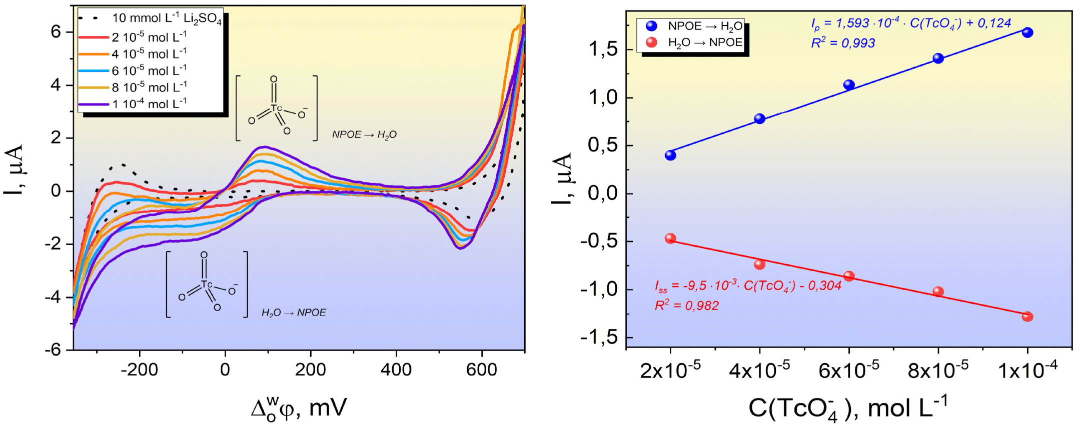

Fig. 1. Cyclic voltammograms (CVs) recorded in 10 mmol L^{-1} Li_2SO_4 in the presence of TcO_4^- in the aqueous phase. Calibration curves plotted based on the negative steady state (I_{SS}) and positive peak (I_p) ionic currents attributed to the TcO_4^- transfer from the aqueous to the organic and from the organic to the aqueous phase, respectively.

Thermodynamic characteristics such as formal Gibbs free energy of ion transfer (16.4 kJ mol^{-1}), potential of simple ion transfer (-0.169 V), and diffusion coefficient ($4.5 \cdot 10^{-6}$ $cm^2 \cdot s^{-1}$) are calculated based on the obtained voltage curves.

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Rhenium Mineralization of Volcanic Island-Arc Systems: From the Past through the Present to the Future

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In 1908, in issue 98 of the journal Chemical News, Masataka Ogawa reported the discovery of a new chemical element in the X-ray spectra of thorianite (Sri Lanka) and molybdenite from deposits of the Iwo-dake volcano (Satsuma-Iwo Jima Island, Japan). Ogawa mistakenly assigned it the element number 43 in the periodic table. This discovery was forgotten for almost a century until Kenji Yoshihara demonstrated in his research that the X-ray spectra obtained by Masataka Ogawa corresponded to element number 75 – rhenium [1].

The first confirmed finds of rhenium sulfide (ReS2) in fumarolic deposits were made by A. Bernard and P. Dumortier at Usu Volcano (Hokkaido Island) in the mid-1980s.

In 1992, rhenium sulfide was discovered in volcanic sublimates, and later in gases, of high-temperature fumarolic fields of Kudryavy Volcano (Iturup Island) [2].

In 2003, V. Ya. Danchenko summarized data on the rare metal ore potential of the Kuril Islands and identified a number of main genetic types of rhenium mineralization. Quaternary and modern – pyrite-sulfur-rare metal rhenium, sulfur-molybdenite rhenium-bearing, rhenium-bearing in deposits of mineralized springs; Neogene – epithermal of various subtypes; Mesozoic-Cenozoic sedimentogenic [3].

In 2006, a group of researchers demonstrated that the metalliferous sublimates of Kudryavy (Iturup) and Iwodake (Satsuma-Iwo Jima) volcanoes have similar mineral compositions and, consequently, genesis. Complex processes occurring in the subduction zone are considered to be the source of rhenium enrichment in fumarolic gases and metalliferous sublimates [4].

Analysis of previous studies suggests that rhenium is a typomorphic element, widespread in both space and time, for the Kuril-Kamchatka and Japanese island arcs [3].

The potential rhenium-bearing capacity of these modern island-arc structures is characterized by the following features and exploration indicators of rhenium mineralization:

1. the presence of long-lived, repeatedly activated ore-magmatic structures, often complicated by paleocalderas with post-caldera volcanic activity;

2. The evolution of volcanism, visible within activation cycles, from mafic through intermediate to felsic, with the presence of mafic and intermediate dikes and sills, and granitoid intrusions;

3. The development of a complex of interbedded volcanogenic-sedimentary, flyschoid, and effusive strata, explosive formations, and lava flows.

The identified volcanogenic manifestations of rhenium-bearing activity in modern island arcs are predominantly near-surface.

However, modeling the deep structure of fluid-supplying channels shows that at depth, these manifestations represent incompletely formed molybdenum-porphyry (porphyry copper) stockwork objects.

It can be assumed that stockwork objects of the molybdenum-porphyry, and to a lesser extent, copper-porphyry types, localized in metamorphosed volcanogenic-sedimentary strata within ancient island-arc structures, potentially harbor rhenium mineralization. Similar objects are known on the Baltic (Fennoscandian) Shield (the Aitik deposit, Sweden), in the continental part of the Peloponnese peninsula (quite numerous objects in the northeastern part – Pagoni-Rachi, Konos, Melitene, etc., Greece) [5], in the Urals [6], and in Tuva.

Thus, island-arc structures spanning the time range from the Archean-Proterozoic to the present day are a potential resource for the development of a rhenium resource base. Molybdenum-porphyry and copper-porphyry stockwork objects identified within ancient island-arc structures, localized in altered volcanogenic-sedimentary strata, require specialized study of ores for rhenium mineralization.

Massive elevated rhenium contents in samples (above 0.01 g/t) serve as sufficient grounds for establishing rhenium specialization in the object and, consequently, for studying and assessing the object's rhenium potential. In Russia, objects of this type have been noted in the Magadan region, in the Central and Southern Urals [7].

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Recovery of rhenium from fumarole activity products

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The demand for one of the rarest elements – rhenium in the aerospace and oil refining industries determines the need for continuous complex processing of its traditional and non-traditional raw material sources [1].

A unique non-traditional type of rhenium raw material in Russia is the fumarole gases of the Kudryavy volcano (Iturup Island, Kuril Islands, Sakhalin Region). The rhenium mineral, rhenite (sulfide ReS2) [2], and the first rhenium deposit proper were discovered on this permanently active Hawaiian-type volcano, which has no equal in the world in terms of power. Rhenium is released from volcanic gases with a temperature of 450–940 ºC. The concentration of rhenium in fumarole gases, a new type of unique complex mineral raw material, fluctuates from 0.5 to 6 g/t and depends on their temperature and weather conditions: the rhenium content is higher in high-temperature gas, and decreases after heavy rains. The total gas output from the crater reaches ~20–30 thousand tons per day. To extract rhenium from these gases, the Institute of Volcanology Joint-Stock Company and other organizations (JSC VNIIKhT, IPHE RAS, IMGRE) developed various process flow charts, including: precipitation of rhenium on solid carriers (zeolites), separation of rhenium as a solid product on a salt collector (soda) in a filter; separation of rhenium as a solid product (without introducing a collector) in a filter; separation of rhenium on sulfur as a solid product in a cyclone. Their enlarged tests showed that the best results are obtained using the method of capturing solid condensates as a dry product in a filter. In this case, a concentrate with a rhenium content of ~2 kg/t was obtained, which corresponds to a degree of its concentration of ~4000.

In fumarole emissions, rhenium is probably in the form of a halide and is converted into sulfide during sublimation [3].

The obtained concentrates were studied by scanning electron microscopy. It has been established that rhenium is present in them in both sulfide and oxidized forms.

Using various types of anion exchangers, as well as carbon composites, the possibility of extracting rhenium and indium from solid concentrate leaching solutions, as well as natural waters near the volcano, including lake waters, has been demonstrated.

With a confirmed average rhenium content in gases of 0.5 g / t, the emission of rhenium is about 18 tons / year.

Considering the presence of germanium, indium, palladium and other valuable elements in fumarole gases along with rhenium, as in the case of traditional raw material sources, it is advisable to extract rhenium along with these metals.

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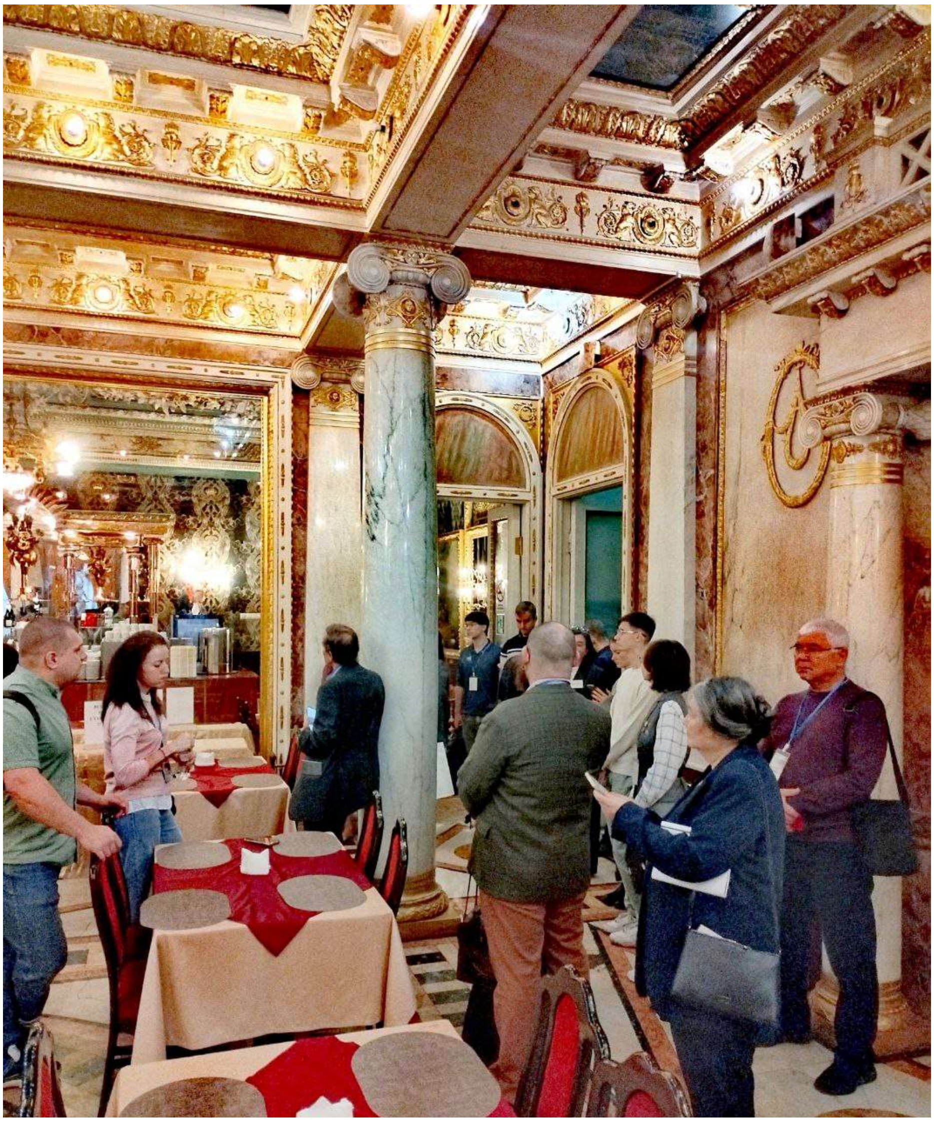

Excursion around the Central House of Scientists

Design of radiopharmaceuticals for the SPECT-diagnosis of neurodegenerative diseases

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The symptoms of Parkinson's disease are mainly associated with the formation of intraneuronal protein inclusions with Lewy bodies, and the progressive loss of dopaminergic neurons of the Substantia nigra and their axons. Existing diagnostic criteria for the diagnosis of Parkinson's disease often take into account symptoms occurring in the later stages of the disease. Thus, for a more accurate diagnosis in the early stages, it is necessary to confirm pathologic changes in brain tissue by molecular imaging methods such as positron emission tomography (PET) and single-photon emission computed tomography (SPECT). At the same time SPECT is a more accessible method of diagnostics of neurodegenerative diseases in comparison with PET, because of the possibility to obtain medical radionuclides for SPECT imaging using mobile generator systems, in particular ^{99}Mo/^{99m}Tc generator.

Among the formulations based on ^{99m}Tc and tropane derivatives proposed for dopamine transporter (DAT) imaging, ^{99m}Tc-TRODAT-1 (technetium-99m-labeled tropantiol) is the most effective. Currently, various compositions of the freeze-dried kits for the synthesis of ^{99m}Tc-TRODAT-1 have been proposed, facilitating the process of its production in situ, which, together with the availability of technetium-99m generator in a healthcare facility, as well as favorable pharmacokinetics, makes ^{99m}Tc-TRODAT-1 a drug of choice for routine use in clinical practice.

In this study various approaches to design and optimize the composition of the freeze-dried kits for the synthesis of [^{99m}Tc]Tc-TRODAT-1, including the amount and ratio of active ingredient and excipients, synthesis conditions, in particular the temperature regime, synthesis time and pH of the reaction mixture, have been considered.

Development and optimization of the composition of the freeze-dried kits for the synthesis of ^{99m}Tc-TRODAT-1 is an urgent task in the context of improving its use in clinical practice. Based on the published data, clear dependencies can be traced, which may form the basis for further development and optimization of the composition of the freeze-dried kits for ^{99m}Tc-TRODAT-1 synthesis for the diagnosis of Parkinson's disease and other neurodegenerative diseases by SPECT.

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Rhenium sulfide clusters formed upon laser desorption-ionization of rheniite

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Production of rhenium sulfide-based catalysts for petroleum reforming is the second major area of rhenium use by the amount of consumed Re. For that purpose, cluster forms of rhenium sulfides are commonly used. Rhenium may exhibit oxidation states from –III to +VII and, thus, is theoretically prone to formation of clusters.

Nevertheless, relatively few rhenium sulfide clusters are known. The information on limited number of tri-, tetra- and hexanuclear rhenium sulfide cluster structures was summarized by T. Saito in 1998, with no significantly different cluster compounds of Re sulfides being discovered or synthesized in the following years.

It is known that the formation of clusters of inorganic compounds actively occurs under conditions of laser desorption-ionization; however, such studies apparently were not conducted previously. This report attempted to describe the clusters that are formed when a sample of rheniite, i.e. natural mineral form of rhenium sulfide, is exposed to conditions of laser desorption-ionization with mass spectrometric detection (LDI-MS).

Studied rheniite sample was extracted from rock which, in turn, was collected from the fumarolic field of the volcano Kudryavy (Iturup Island, Russia) in 2002. Preliminary elemental analysis of sample by energy-dispersive X-ray spectroscopy has shown that rhenium and sulfur respectively constituted around 60% and 20% of mass of platy scaly crystals that covered the rock. The aforementioned crystals were studied by LDI-MS method using Bruker Ultraflex II low-resolution time-of-flight mass spectrometer.

The LDI-MS analysis has shown that a total of 41 $Re_xS_y^+$ type clusters containing from 1 to 10 rhenium atoms were formed and detected in the positive ion mode. Negatively charged rhenium sulfide clusters were formed less extensively and were represented by a total of 21 species containing no more than four rhenium atoms. The above number included eight $Re_xS_yO_z^-$ cluster forms that incorporated at least one oxygen atom based on their observed m/z value.

In addition, a total of 18 heterometallic rhenium – molybdenum clusters, including 12 $Re_xMoS_y^+$ and six $Re_xMoS_yO_z^-$ species, were detected during the experiment. The observed positively charged heterometallic forms contained up to seven Re atoms.

The structure of observed clusters cannot be determined from LDI-MS data alone. Nevertheless, the species that contained X + 2 and X + 3 atoms of Re were characterized by the most intensive signals, which may suggest that the detected rhenium sulfide clusters contained fragments of crystal structure of rheniite.

Majority of rhenium sulfide clusters, particularly those $Re_xS_y^+$ binary species that contained from 7 to 10 Re atoms, and isolated heterometallic Re – Mo clusters were never reported in the literature previously. In our opinion, this indicates that there exists a significant potential for development of rhenium sulfide chemistry. It is expected that at least some of Re sulfide clusters detected in this study could be isolated as stable compounds subsequently

Radiochemical impurities in ^{99m}Tc radiopharmaceuticals: determination and validation

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The development of a unified methodological approach to validation of analytical procedure of radiochemical impurities (RCI) determination in radiopharmaceuticals (RPhs) is an urgent task, since a reliable determination of RCI is responsible for the quality of radiopharmaceuticals. The current regulatory documents regulating the process of validation of the methods used to determine the quality of drugs cannot be fully applied to the validation of the analytical procedure for RCI determination. The presence of radionuclide in RPhs introduces some features in the validation process. A combination of chromatographic separation of impurities from the main complex and the radiometric measurement method were used for RCI determination. The results of the radioactivity detection do not depend on the chemical form of radionuclide, but are determined by the energy of the gamma-rays emitted by the radionuclide and detector which is used for radioactivity measurement. RCI indicators establish the relative content of impurities, a certain ratio of which in principle cannot be artificially created or changed. We believe that at validation of RCI determination the tests on specificity and precision should be carried out - tests confirming the correct application of the chromatographic separation method of components, and the tests on accuracy and linearity - tests confirming the correct use of detection equipment.

This study presents the results of the validation procedure for content determination of radiochemical impurities in radiopharmaceuticals “Pyrphotech,^{99m}Tc”, “Technephyte,^{99m}Tc”, “Tehnephore,^{99m}Tc”, “Phosphotech,^{99m}Tc”, “Rezoscan,^{99m}Tc” and “Medroscan,^{99m}Tc” at performing the “Specificity” and “Precision” (“Repeatability and “Intermediate precision”) tests. The selectivity of the chromatographic determination of sodium pertechnetate and hydrolyzed reduced technetium-99m has been proven. Coefficients of variation were 4.0–5.0% with the relative error of the methods not exceeding 11.5%. The calculated values of the Student's t-test for two samples for each chromatographic system for each radiopharmaceutical in the "Intermediate precision" tests did not exceed the table value of the Student's test, equal to 3.17 at the confidence probability of 99%. This indicates that there are no differences between the results obtained in each chromatographic system and confirms the validation of the methods for precision.

Design of radiopharmaceutical composition with rhenium-188 and hyaluronic acid for radiosynoviorthesis

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Osteoarthritis is one of the most common joint diseases. The number of patients is growing rapidly and by 2050, the number of people in the world suffering from osteoarthritis is expected to exceed 1 billion. In a number of European countries, radiosynoviorthesis is used as a treatment. It is based on irradiation of the joint synovium with intra-articular administration of various radiopharmaceuticals containing β-emitting radionuclides. Radionuclide therapy for is comparable in effectiveness to surgical therapy (72.6% and 75.2% of positive results, respectively), but it is less traumatic and dangerous, much easier to perform and does not require complex and lengthy postoperative rehabilitation. The duration of remission ranges from several months to 4 years.

This method consists in the intra-articular administration of a radiopharmaceutical (RPh) containing radionuclides with high β-energy. The injected RPh is captured by phagocytosis by the cells of the superficial epithelium of the synovial membrane, thereby exerting a damaging effect. Due to local irradiation of the inflamed synovial membrane of the joint with β-particles, the process of ablation is caused in it, i.e. death of functionally active cells responsible for inflammation. As a result of such exposure, superficial synovial fibrosis usually occurs. Clinically, in cases of a positive result, a decrease in pain and inflammation and, as a result, an improvement in the quality of life of patients is determined.

In this study ^{188}Re-Sn colloidal solution was synthesized with a radiochemical purity of more than 90%, its properties were studied, and the possibility of using hyaluronic acid to stabilize the particles formed during the synthesis was shown.

0.2% solution of hyaluronic acid is used, due to which the radionuclide is retained in the joint, preventing damage to the periarticular tissue. The average dynamic particle diameter did not exceed 10 µm. Colloidal particles labeled with radionuclide are homogeneously distributed in the intra-articular space without causing an inflammatory reaction. The bond between the radionuclide and the colloidal particle is quite strong during the entire course of radiosynoviorthesis, which is determined by the half-life of the radionuclide.

Possibility of guanidine sorbent for extraction of perrhenate ion and comparison of efficiency with some commercial nitrogen-containing anion exchangers

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Researches on guanidinium-based sorbents and ionic liquids as prospective agents for extracting ReO_4^-, including as a model of TcO_4^-, have become more common in the last years [1]. Guanidinium-based sorbents could be interesting for waste cleaning as well as for analytical preconcentration. The efficiency of sorptive preconcentration of ReO_4^-, and PGM and Au complex anions by guanidinium-based sorbent Gu (synthesised by S.E. Lyubimov) and PureResin PA202 (China) and AB-17-8 (Russia) anion exchanger resins was investigated (see Fig. 1). This focus arises because rhenium commonly occurs as an associated component with PGM in geological samples. The particle size of all investigated resins ranged beteween 400 and 1200 µm. The influence of preconcentration conditions, the presence of major components, and other anion contents in solution after preparation of different geological samples (for example, acid digestion of iron meteorites) on the rhenium preconcentration efficiency was studied.

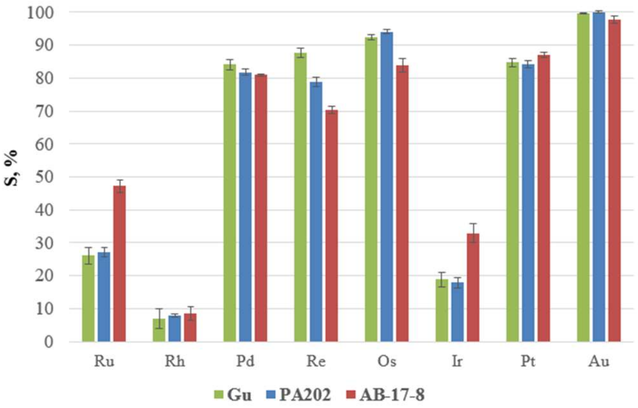

Figure 1: *The efficiency of sorptive preconcentration (S, %) of* ReO_4^-*, and PGM and Au chlorocomplex anions from 1M HCl solutions. Column efficiency volume is 150 µL.* $V_{solution}/V_{sorbent} \approx 67$*. Pump rate is 5 rpm. The concentration of each analyte is equal to 25 µg* L^{-1}*.*

This research was funded by the Russian Science Foundation № 25-23-00515, https://rscf.ru/project/25-23-00515/.

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Development of new rhenium sorbents based on hyper-crosslinked polystyrenes from Sunresin (China)

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To produce impregnated sorbents, pilot samples of hyper-crosslinked polystyrenes from Sunresin (China) were synthesized.

The physicochemical properties of the hyper-crosslinked polystyrenes were studied using a Bettersizer 2600 laser particle size analyzer and analyzed by NOVAtouch from Quantachrome Instruments. For use in the sorption extraction of rhenium from solutions of constant chemical composition, a matrix of hyper-crosslinked spherical polystyrenes with an effective diameter of 0.4–0.63 mm, a surface area of 1000–1200 m^2/g, a standard diameter of 2.5–3.4 nm, and a pore volume of 0.7–0.9 m^3/g is formed.

The matrix of hyper-crosslinked polystyrenes is impregnated with extractants using an original method developed at VNIPIpromtekhnologii. Tertiary amines (trioctylamine, tridecylamine) in polar solvents are used as extractants.

Rhenium sorption and desorption are carried out under static conditions. The composition of the model rhenium-containing solutions meets the requirements of existing hydrometallurgical production facilities: sulfuric acid – 230 g/L, rhenium – 560 mg/L, molybdenum – 6500 mg/L. 15% ammonia was used as the desorbent solution.

The capacity of the impregnated sorbents for rhenium during sorption under equilibrium conditions is 60 mg/g of sorbent.

Based on these data, it is recommended to conduct pilot tests of the sorption and desorption process under existing production conditions.

Alkoxotechnology in the production of rhenium alloys

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Rhenium-containing superalloys are a type of modern construction material used in applications involving temperatures exceeding 1000 °C. These alloys are mostly used in gas turbines, power plant engines and space applications. Rhenium is added to the composition to impart heat resistance to the alloy. However, this process is challenging due to the significant differences in density and melting point between the common superalloy-based metals, such as nickel and cobalt, as well as the high energy consumption involved. Therefore, developing a low-temperature method of producing highly homogeneous rhenium-containing alloys poses a significant scientific challenge. One possible approach is the hydrogen reduction of bimetallic rhenium alkoxides. Our research focuses on synthesizing bimetallic Re–M alkoxides (where M = Ru/Ni/Co) using electrochemical dissolution of metals in an alcohol-based electrolyte[1,2]. Electrolysis was carried out galvanostatically ($i = 0.6$ A/m²) with water cooling. We studied the quantitative indicators of the dissolution process and removed the solvent by heating at low pressure. The alloys were obtained by hydrogen reduction in an autoclave at a pressure of 10–15 atm and a temperature of 600–700 °C.We studied the synthesized alkoxides and alloys using the SEM, EDX, AAS, DTA and XRD methods. Using an electrochemical method to obtain a bimetallic alcoxocomplex enables accurate control of the metal ratio in the alcoholate composition, alloy-obtaining precursor and allows processing a temperature more than twice as low than in existing process of rhenium alloys production.

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Technetium(I) Dicarbonyl Complexes with N,N-Aromatic Imines

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Technetium(I) dicarbonyl complexes $[^{99}Tc(N,N)_2(CO)_2]OTf$ (N,N = 2,2'-bipyridine and 1,10-phenenthroline) were prepared for the first time by treatment of $[^{99}Tc(OTf)(CO)_5]$ in a melt of the corresponding imine under an argon atmosphere at 250°C for 24 h and 120°C for 2 h, respectively.The bipyridine and phenanthroline dicarbonyl complexes were isolated as red needles in relatively low yield (15-18%). The complexes were characterized by IR and ^{99}Tc NMR spectroscopy. $[^{99}Tc(bipy)_2(CO)_2]OTf$: IR in CH_2Cl_2 ($\nu_{C\equiv O}$, cm^{-1}): 1940.6 (s) and 1867.0 (m); ^{99}Tc NMR (298 K, CD_2Cl_2, δ, ppm): −48.54. $[^{99}Tc(phen)_2(CO)_2]OTf$: IR in CH_2Cl_2 ($\nu_{C\equiv O}$, cm^{-1}): 1941.5 (s) and 1867.9 (m); ^{99}Tc NMR (298 K, acetonitrile-d3, δ, ppm): −95.63. The crystal structure of the both dicarbonyl complexes was determined by SCXRD. The structures are similar and characterized by the cis arrangement of the carbonyl groups. The molecular structure of the bipyridine complex is shown in Fig. 1 as an example.

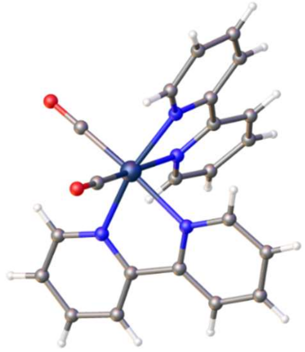

Figure 1: *The molecular structure of the technetium fragment in* $[^{99}Tc(bipy)_2(CO)_2]OTf$*.*

The possibility of stabilization of Tc(I) state with N,N-aromatic imines with weak π-acceptor properties was analyzed by DTF. It was found that ΔG of formation of $[Tc(NN)_3]^+$ (N,N = 2,2'-bipyridine and 1,10-phenenthroline) is positive both at room and high temperatures. Whereas ΔG of formation of $[^{99}Tc(NN)_2(CO)_2]^+$ is positive at room temperature and becomes negative at a temperature of an imine melt.

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Structure and synthesis of potassium decacyanotechnetate and metal cyanide coordination polymer

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Yellow solution of $K_7[Tc_2O(CN)_{10}]CN$ (Figure 1) was obtained by a reaction of a solution of KCN with freshly prepared TcO_2 in a sealed ampule and the structure was determined by single-crystal X-ray diffraction. $K_7[Tc_2O(CN)_{10}]CN$ is isostructural to its manganese analogous [1]. Crystal data: space group *Ibam*; a = 12.5766(12) Å, b = 12.7607(12) Å, c = 14.7008(13) Å; Z = 4.

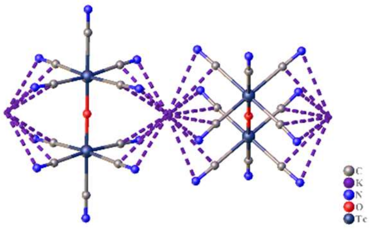

Figure 1. Structure of $K_7[Tc_2O(CN)_{10}]CN$

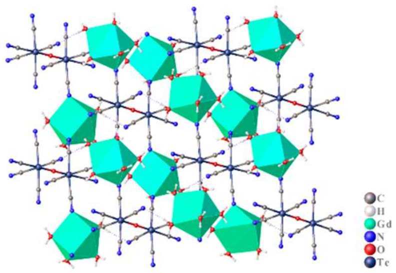

Figure 2. Structure of $[Gd(H_2O)_5]_2[Tc_2O(CN)_{10}]\cdot 8H_2O$

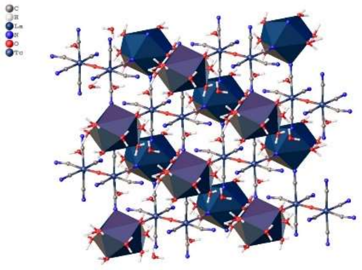

Figure 3. Structure of $[La(H_2O)_7]_2[Tc_2O(CN)_{10}]\cdot 4H_2O$

Metal-cyanide coordination polymers were obtained by adding a solution of $Ln(NO_3)_3$ (Ln = Gd, La) to a solution of $K_7[Tc_2O(CN)_{10}]CN$. Crystal data of $[Gd(H_2O)_5]_2[Tc_2O(CN)_{10}]\cdot 8H_2O$ (figure 2): space group $P2_1/n$; a = 12.6301(6) Å, b = 10.7597(5) Å, c = 13.4000(7) Å. Crystal data of $[La(H_2O)_7]_2[Tc_2O(CN)_{10}]\cdot 4H_2O$ (figure 3): space group $P1^{-}$; a = 8.6830(17) Å, b = 8.6980(17) Å, c = 11.257(2) Å; α = 67.85(3), β = 80.06(3), γ = 78.33(3). Such structures can be used in refinery of nuclear wastes from radioisotope ^{137}Cs, as it is being used on the basis of cyanoferrate salts [2].

This work was supported by the Ministry of Science and Higher Education of the Russian Federation

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Non-Covalent Interactions Influence on the Crystal Structures Formation of Rhenium and Technetium Compounds

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Non-covalent interactions play a crucial role in supramolecular chemistry, crystal engineering, and the self-assembly of functional materials. This study focuses on the synthesis and structural characterization of new rhenium and technetium compounds, revealing the contribution of weak intermolecular forces— hydrogen bonding, π–π stacking, and novel anion···anion contacts—to crystal packing and thermal behavior.

A total of 25 new compounds, including Tc(V) alkoxy complexes and Re(VII)/Tc(VII) salts with organic cations (guaninium, histidinium, and various azoles), were synthesized and characterized using single-crystal X-ray diffraction, thermal analysis, and Hirshfeld surface analysis. The obtained data demonstrate that the geometry of organic cations, protonation degree, and substituent length significantly affect the hierarchy of non-covalent interactions.

Two anion–anion motifs, C–O···Re(O_4) and Re–O···Re(O_4), were identified and shown to stabilize the supramolecular network. A correlation was established between the presence of Re–O···Re contacts and the absence of phase transitions in crystalline perrhenates. For Tc(V) alkoxy complexes, increasing the alkyl chain length reduces the onset temperature of thermolysis while preserving the coordination geometry of technetium.

Hirshfeld surface analysis confirmed that O···H/H···O hydrogen bonds dominate the molecular packing, but π- and anion···anion interactions are also important, albeit with a smaller contribution from intermolecular vasodilation. DFT calculations confirmed the experimental data, emphasizing the role of dispersion forces in structural stabilization.

The results provide a comprehensive understanding of how weak interactions govern the formation, stability, and transformation of technetium and rhenium compounds. These findings contribute to the rational design of radiochemical materials, catalysts, and potential precursors for radiopharmaceuticals.

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Transition Metal-Based Catalysts in Bio-Oil Cracking

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In the search for a sustainable alternative to fossil fuels, bio-oil produced by biomass pyrolysis is becoming increasingly important. However, its practical application is limited by its high oxygen content, which leads to low calorific value and corrosive activity.

The solution is hydrodeoxygenation – a process in which efficiency is directly dependent on the choice of catalyst. Among the many metals studied, rhenium and its compounds exhibit unique properties, making them a key component of highly efficient zeolite catalysts. Rhenium has exceptional affinity for cleaving strong C–O bonds, which are abundant in oxygenated compounds found in bio-oils. Its primary role in hydrodeoxygenation is to create active deoxygenating sites, form a bifunctional catalyst, and suppress coke formation.

While iron, zinc, and copper oxides are often used in research, rhenium often outperforms them in terms of deoxygenation efficiency and selectivity for target hydrocarbons. Its ability to operate effectively at milder temperatures (250–300 °C) makes the process less energy-intensive.

While some studies focus on more common metals such as zinc, it is rhenium's exophilic properties—its high affinity for oxygen—that make it indispensable for selectively cleaving C–O bonds without excessive hydrogenation of the aromatic ring.

This allows for the production of biofuels with high aromatic hydrocarbon content, which are of great value.

Since rhenium exhibits exceptional catalytic properties in the bio-oil recovery process, its closest chemical analogue in the periodic table—technetium—is a logical direction for further research.

Technetium has a similar electron configuration to rhenium, suggesting similar catalytic properties. Furthermore, observations suggest that a technetium-based catalyst could further reduce cracking temperatures.

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Investigation of the properties of cement and clay-based materials modified with biocidal additives

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The challenges associated with radioactive waste management significantly shape the prospects for the further development of the nuclear industry. According to the recommendations of the International Atomic Energy Agency (IAEA), one of the simple and low-cost methods for radioactive waste treatment is its solidification by incorporation into cement matrices, followed by disposal in deep geological repositories with a multi-layer system of engineered safety barriers. One factor contributing to the degradation of the structure and properties of barrier materials upon contact with the surrounding geological environment is microbiological activity. Therefore, to prevent biogenic impact, it is necessary to use biocidal additives that do not compromise the barrier properties of the materials.

The aim of this work was to evaluate the changes in the properties of cementitious and clay-based materials upon their modification with non-oxidizing biocidal additives.

The influence of eight organic biocidal additives at concentrations of 0.1, 0.5, and 1.0 wt.% on the characteristics of Portland cement matrices and clay materials was investigated. The following modifying additives with biocidal activity were considered: glutaraldehyde, sodium diethyldithiocarbamate, salicylanilide, "Polyaminol", as well as four additives based on quaternary ammonium compounds. Optimal concentrations of the considered additives for cement matrices were selected, which do not reduce their strength characteristics and also ensure a reduction in microbial activity on the surface of the Portland cement matrix. These include the "Polyaminol" additive at a concentration of 1.0 wt.% and tetramethylenediethylenetetramine at 1.0 wt.%. For clay materials, optimal concentrations of biocidal additives for reducing microbial activity were identified. For "10th Khutor" bentonite, the most suitable biocidal additives were glutaraldehyde (62% efficiency) and sodium diethyldithiocarbamate (67%). For Tagan bentonite, the effective additives were alkyldimethylbenzylammonium chloride (28%) and didecyldimethylammonium chloride (29%).

Biocidal additives of alkyldimethylbenzylammonium chloride at 0.1 wt.% and sodium diethyldithiocarbamate at 0.5 wt.% demonstrated a high immobilization capacity for pertechnetate ions in the cement matrix, with a leaching rate of less than 10%. It was established that the maximum leaching rate was observed for the control Portland cement sample without additives. The minimum leaching rates were noted for the samples with sodium diethyldithiocarbamate at 0.5 wt.% (1.8×10^{-5} g/(cm^2 day) on the 90th day of the experiment) and alkyldimethylbenzylammonium chloride at 0.1 wt.% (2.8×10^{-5} g/(cm^2 day) on the 90th day).

This work was supported Ьy the Ministry of Science and Higher Education of the Russian Federation.

Long term duration of Tc-bulk and Tc-coatings in various environmental conditions

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The contemporary method for reprocessing spent nuclear fuel entails the thorough extraction of all fission products, especially those with extended periods of decay. Technetium is one of the fission products of uranium, has moderate radioactivity ($E \approx 300$ KeV, A = 635 Bq/μg). An important feature of technetium is the high solubility of its oxidized form - the pertechnetate anion. This solubility presents challenges during the stages of nuclear fuel reprocessing and radioactive waste disposal.

The Metallic technetium, which is particularly well-suited for transmutation and containment matrix in long-term burial systems, shows promise as a solution to the technetium disposal problem. In this study, the resilience of the metal technetium and its two derivative coatings (amorphous and crystalline) was assessed under various conditions, including fresh groundwater and sea water. The multifunctional strain *Shewanella xiamenensis* DCB-2-1 was used to investigate the possibility of microbial biofouling of metallic technetium. Laboratory experiments have demonstrated that amorphous electrodeposited technetium is more susceptible to oxidation processes compared to its crystalline counterpart. Ultimately, the most durable form of technetium was metal foil. It has been established that biofouling of Tc becomes possible primarily due to the heterogeneity of the specimens' surface. Research conducted in the Barents Sea has revealed that the accumulation of iron, calcium, and magnesium mineral phases within the microbial biofilm may shield beta radiation, resulting in the establishment of macro-fouling (*Balanus* and *Mutilus*).

The outcomes of this study hold immense potential for the design and production of storage tanks intended for the containment of radioactive waste, which are to be buried in geological formations. Notably, the exceptional resistance of technetium to oxidation makes it a viable candidate as a storage matrix for radioactive waste, including those that contain technetium in its metallic form [45]. Moreover, the stability of metallic technetium in the face of micro- and macro-fouling conditions renders it highly promising in terms of predicting its long-term behavior over hundreds and thousands of years. The electrolytic method employed to apply uniform and thick layers of metallic technetium proves to be convenient when coating containers for radioactive waste with this metal. It is imperative, however, that technetium or technetium-covered containers undergo annealing in a reducing atmosphere to eliminate the amorphous phase of technetium and obtain a hexagonal close-packed metal structure

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Obtaining ^{94m}Tc in liquid target of medical cyclotron

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The positron emitting technetium isotope ^{94m}Tc is of interest for radionuclide diagnostics. To investigate the possibility of its preparation, a series of irradiations of an aqueous solution of molybdate by protons with an energy of 11 MeV was carried out. Then the target radionuclide was isolated from the target substance and radionuclide impurities.

Experiments were performed on cyclotron Siemens RDS-111 and use of a standard target device for 13N radionuclide. The results were analyzed on a γ-spectrometer. A pronounced spectral line of 511 keV was obtained .

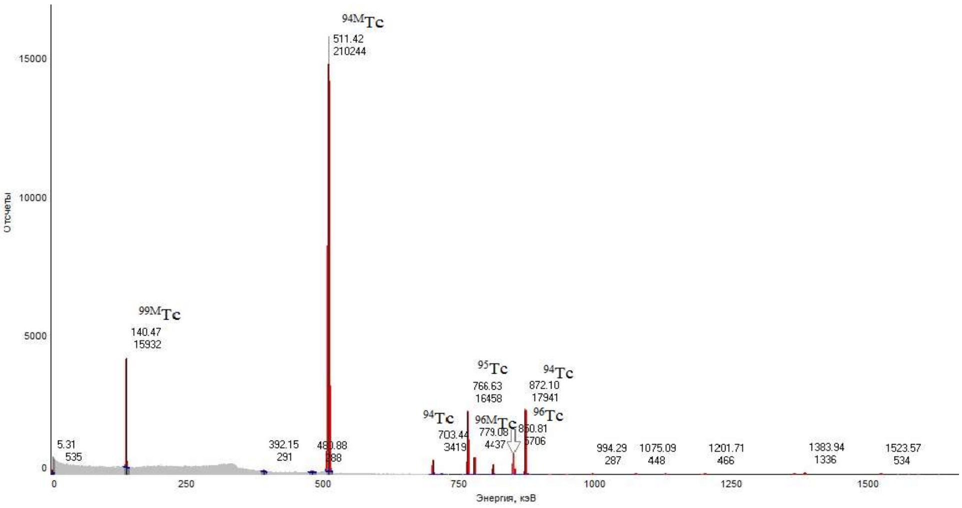

Figure 1 : *γ-Spectrum with decoding of radionuclides.*

The data obtained confirm the presence of the isotope technetium ^{94m}Tc.

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Liquid-liquid extraction of zirconium pertechnetate from SNF reprocessing rafinates

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An experimental substantiation of the possibility of extractive separation of technetium from the raffinate of the technological scheme of refining the uranium-plutonium product formed during the hydrometallurgical reprocessing of spent nuclear fuel (SNF) was carried out.

Technetium(VII) from an aqueous solution in the form of zirconium pertechnetate is extracted by 80% in 30% TBP in a hydrocarbon diluent in seven stages of a counter-current continuous cascade at a ratio of O : A = 1 : 1.

In this case, the aqueous phase contains Zr(IV) (10 g/L) in 4 mol/L HNO_3 with an insignificant content of oxocations ZrO^{b+} and $Zr_2O_3^{b+}$. By varying the phase flow ratio in the exhaustive part of the cascade, Tc(VII) is extracted into the organic phase almost completely in ten stages.

Technetium(VII) is selectively re-extracted from the loaded organic phase with 0.1 mol/L nitric acid solution almost completely in eleven stages of a continuous counter-current cascade.

To conduct the technetium extraction experiments, a model solution was used that simulated the composition of the combined raffinate of the first cycle of the extraction separation of U–Pu–Np from fission products and the raffinate of the refining operation.

Joint extraction of the pertechnetate anion with tetravalent zirconium cations occurs according to the proposed mechanism:

$$Zr^{4+} + 3NO_3^- + TcO_4^- + 2TBP = Zr(NO_3)_3(TcO_4)(TBP)_2 \qquad (1)$$

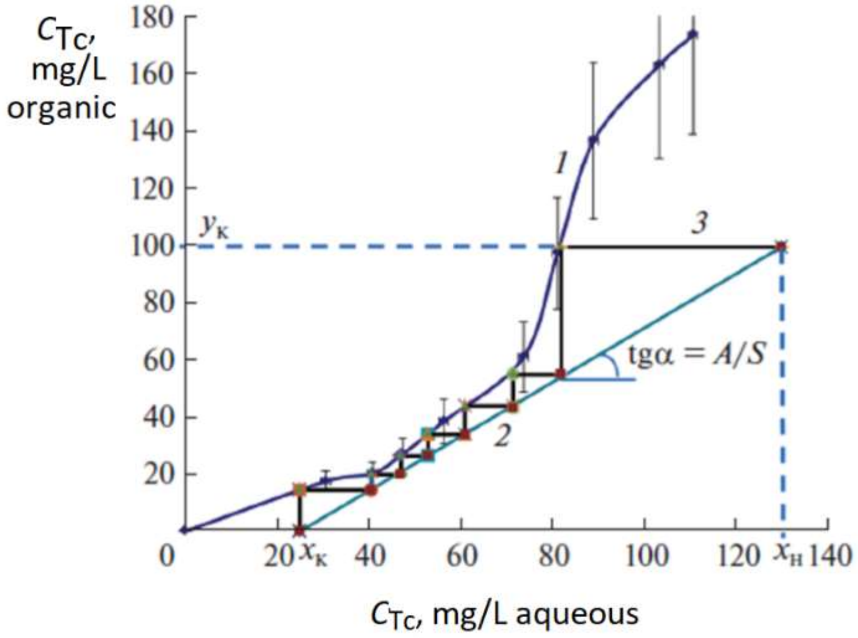

Figure 1. Extraction isotherm of Tc(VII) in 30% TBP in hydrocarbon diluent from a solution of 125 mg/L Tc(VII) in 4.02 mol/L HNO3 in the presence of 9.94 g/L Zr^{4+} and 7,58 g/L La^{3+} at 20°C (*1*), working line (*2*) and extraction stages

The working line is constructed based on the composition of the initial solution and the ratio of the organic and aqueous phase flows (O : A = 1 : 1) in the extraction cascade.

$$A(x_{\text{н}} - x_{\text{к}}) = S(y_{\text{к}} - y_{\text{н}})$$

where A is the flow of the aqueous phase; S is the flow of the organic phase ; $x_{\text{н}}$, $x_{\text{к}}$ – initial and final concentrations of technetium in the aqueous phase, mg/l; $y_{\text{н}}$, $y_{\text{к}}$ – initial and final concentrations of technetium in the organic phase, mg/L.

When oxozirconium dimeric and oligomeric species were present the formation of the third phase was observed.

A technological extraction scheme for the separation of technetium(VII) from SNF solutions is proposed.

Radioecology and biogeotechnology of technetium

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Technetium-99 compounds exhibit high solubility in aqueous media and volatility, leading to an elevated risk of environmental release and subsequent high migration mobility. Due to its long half-life and significant solubility, the environmental behavior of technetium is a subject of increasing scientific concern. This issue is of particular importance in the context of the deep geological disposal of radioactive waste.

Consequently, research efforts by numerous scientific groups are focused on the development of barrier materials capable of retarding technetium migration within geological formations.

To date, predicting the long-term environmental behavior of technetium remains a challenging scientific and practical task. Although studies over the past 30 years have accumulated extensive data on technetium accumulation in bottom sediments, soils, various minerals, and living organisms, the lack of fundamental data on its physico-chemical forms in these media impedes the development of adequate models for reliable long-term migration forecasting.

This study provides a comprehensive review of data on technetium concentrations in various environmental compartments (e.g., marine and fresh water, soils, bottom sediments, groundwater, geological formations, and biota). Furthermore, it examines prominent successful studies on technetium immobilization strategies for contaminated sites. It is worth noting that in these studies, approaches to the creation of a biochemical in situ barrier that allows for the reliable retention of technetium in a reduced form in authigenic mineral sediments show great promise.

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Technetium pentacarbonyl hydride: synthesis and properties

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Transition metal carbonyl hydrides are complex compounds containing a hydride anion and a carbon monoxide as ligands. These play an important role in many useful chemical reactions such as hydroformylation, olefin isomerization, and hydrogen exchange. Technetium carbonyl hydrides, unlike rhenium analogs, are a poorly studied class of inorganic compounds. Since $ReH(CO)_5$, which was synthesized in the 1960s, appear to be stable [1] and currently is well explored [2,3] technetium analog appears to be an exciting precursor of many reactions. Recently, we found that hydrolysis of $[^{99}Tc(CO)_6]^+$ yielded trinuclear complex $^{99}Tc_3H(CO)_{14}$ as a major product. $^{99}Tc_3H(CO)_{14}$ was characterized by single-crystal X-ray diffraction analysis and spectroscopic methods. IR (ν, cm^{-1}, KBr): 2096.5 (w), 2054.0 (s), 2034.8 (w), 2021.3 (m), 1996.2 (m), 1980.8 (w), 1971.1 (w), 1938.3 (w). IR (ν, cm^{-1}, hexane): 2096.5 (w), 2054.0 (m), 2021.3 (s), ~2015 (sh), 1996.2 (m), 1980.8 (w), 1971.1 (vw), 1938.3 (w). NMR (toluene-d^8, δ, ppm): ^{1}H: −5.48; ^{99}Tc: −2501. But when the hydrolysis of of $[^{99}Tc(CO)_6]^+$ was combined with the extraction into a hydrocarbon solvent (hexane), the major product was $^{99}TcH(CO)_5$. This compound was also prepared purposefully by the reduction of $^{99}TcBr(CO)_5$ with nascent hydrogen (reaction of zinc with phosphoric acid; $NaBH_4$ and water with simultaneous extraction into hexane). IR (ν, cm^{-1}, gas phase): 2034.8 (s, υ(C≡O)), 689.5 (w, δ(Tc-H)) (see fig. S5). IR (ν, cm^{-1}, hexane): 2021.3 (s, υ(C≡O)). IR (ν, cm^{-1}, toluene): 2021.3 (s, υ(C≡O)), 682.8 (w, δ(Tc-H)). NMR (toluene-d^8, δ, ppm): ^{1}H: −5.5, –15.3; ^{99}Tc: −2413.5, – 2473.8.

$[^{99}TcH(CO)_5]$ readily reacts with strong acids, such as perchloric and trifluoroacetic acids, forming $[^{99}Tc(ClO_4)(CO)_5]$ and $[^{99}Tc(O_2C–CF_3)(CO)_5]$, respectively. However, it shows no reactivity toward weaker acids as formic acid. When in solution, the complex demonstrates some resistance to oxidation by air, though pure $[^{99}TcH(CO)_5]$ gradually transforms into $[^{99}Tc_3H(CO)_{14}]$. Oxidation of the Tc–H bond with iodine (I_2) produces $[^{99}TcI(CO)_5]$, a process that is associated with the covalent, low-polarity nature of the compound. The carbonyl groups attached to technetium are notably resistant to substitution by donor ligands, unless the Tc–H bond is first cleaved oxidatively. Reactions involving air and ligand molecules like 2,2'-bipyridine and 1,10-phenanthroline lead to the formation of atypical technetium carbonyl complexes, such as $[(\mu_3–CO_3)(^{99}Tc(bipy)(CO)_3)]$ and $[^{99}Tc(phen)_2(CO)_2]$.

The study was financially supported by the Russian Science Foundation (project no. 22-13-00057).

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Technetium pentacarbonyl iodide as a preparation for lung diagnostics: new results

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At the present time two procedures are used for radioisotope diagnostics of the lungs: intravenous administration of a preparation intended for studying lung perfusion and inhalation of an aerosol of a radioactive preparation for studying the respiration of the lungs [1]. Previously, we synthesized technetium-99m pentacarbonyl iodide and demonstrated its high volatility and ability to accumulate in lung [2]. These complexes were characterized by HPLC using technetium-99 analogs as the reference. The biodistribution of the obtained complexes in the bodies of laboratory animals was studied healthy and with a tumor) using direct radiometry and SPECT. It was shown that the accumulation of the drug in the lungs is 50-60 times higher than in tumor tissues.

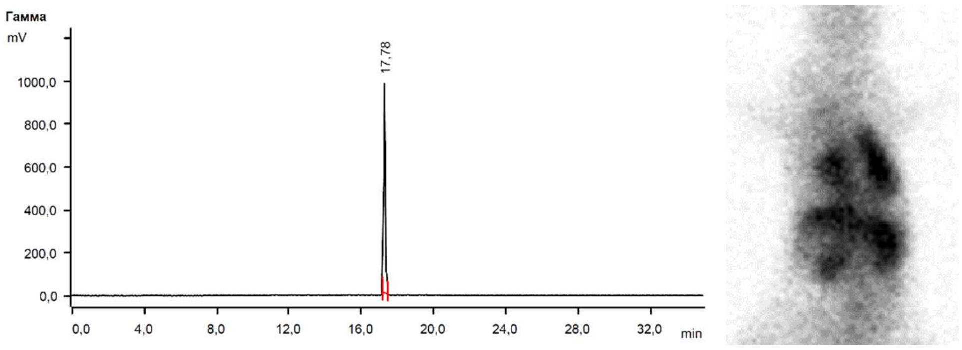

Figure 1: *HPLC .and SPECT of rat with [^{99m}TcI(CO)$_5$].*

Acknowledgements: The study was financially supported by the Russian Science Foundation (project no. 22-13-00057, prolongation).

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Interaction of Technetium Tricarbonyl Triaqua Complex with Phosphoric Acid Anions in Aqueous Solution: a $^{99\text{Tc}}$ NMR Study

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The complexation of the $[^{99}\text{Tc(CO)}_3(\text{H}_2\text{O})_3]^+$ ion in aqueous solution with phosphoric acid anions was studied by ^{99}Tc NMR. In the $\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$ system, four signals assignable to the initial complex $[^{99}\text{Tc(CO)}_3(\text{H}_2\text{O})_3]^+$ and to the 1 : 1, 1 : 2, and 1 : 3 complexes with the dihydrophosphate ions are observed at –(870–875) (signal 1), –(908–912) (signal 2), –(926–937) (signal 3), and –(940–956) ppm (signal 4), respectively (Fig. 1). The step stability constants of these complexes, estimated from the relative intensities of the signals, are 1.0 ± 0.2, 0.20 ± 0.03, and 0.07 ± 0.03 L/mol, respectively. The complexation with the HPO_4^{2-} anion at pH 6–7 ($\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ system) is complicated by the hydrolysis of the triaqua complex with the formation of $[^{99}\text{Tc(OH)(CO)}_3]_4$ (signal at –584 ppm, Fig. 2). The signal in the region of –915 ppm is assigned the 1 : 1 complex with the HPO_4^{2-} anion. Its formation constant is estimated at 10^2 L/mol. Higher-field signals observed in the spectra can be assigned to 1 : 2 (about –930 ppm) and 1 : 3 complexes with HPO_4^{2-} ions. Mixed $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ complexes can also be formed. The complexation with HPO_4^{2-} anions will significantly contribute to the "$[^{99m}\text{Tc(CO)}_3(\text{H}_2\text{O})_3]^+$" speciation in phosphate-buffered saline and should be taken into account when developing procedures for preparing candidate radiopharmaceuticals based on this core.

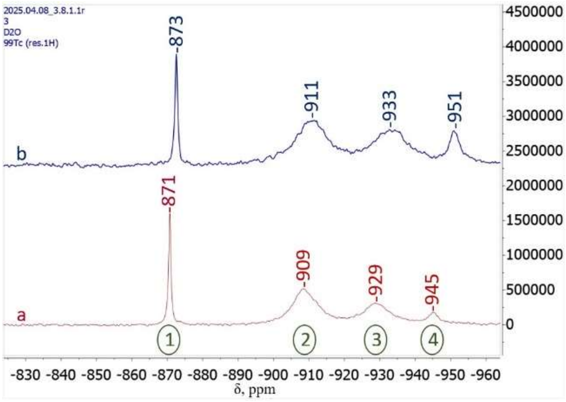

Figure 1: *^{99}Tc NMR spectra of aqueous solutions containing (M) (a) 0.023 Tc + 2.9 NaH_2PO_4 + 0.26 H_3PO_4 (pH 2.58) and (b) 0.023 Tc + 4.4 NaH_2PO_4 + 0.26 H_3PO_4 (pH 2.85).*

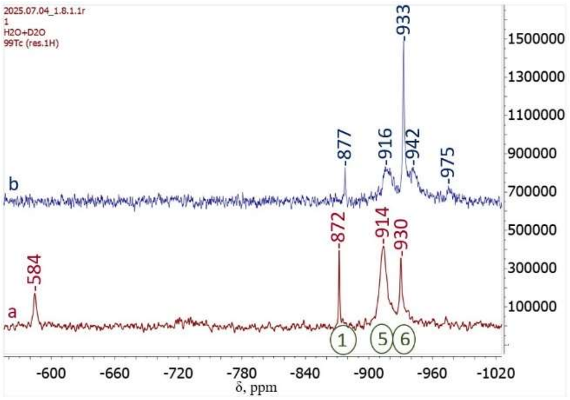

Figure 2: *^{99}Tc NMR spectra of aqueous solutions containing (M) (a) 0.009 Tc + 0.08 Na_2HPO_4 + 0.1 NaH_2PO_4 (pH 6.72) and (b) 0.009 Tc + 0.41 Na_2HPO_4 + 0.5 NaH_2PO_4*

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Coordination Chemistry of Technetium Carbonyls: Recent Advances

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The results obtained throughout the world in the past 5 years in the coordination chemistry of technetium-99 carbonyls are summarized and correlated. In the field of "traditional" (*fac*-tricarbonyl) Tc(I) coordination chemistry, a series of new 2+1 complexes were prepared and comprehensively characterized. Along with the development of the *fac*-tricarbonyl chemistry, there has been considerable progress in the synthesis and characterization of other types of carbonyl complexes.

The formation of *mer*-tricarbonyl complexes requires combination of two factors: (i) π-acceptor properties of ligands occupying the trans position in the complexes and (ii) steric hindrance to the cis arrangement of these ligands (as in the case of PPh_3) or setting of the *mer* configuration by using pincer ligands. *mer*-Tricarbonyl complexes relatively readily lose a CO group to form dicarbonyl complexes.

Technetium(I) dicarbonyl complexes can be obtained by reactions of *mer*-tricarbonyl complexes with σ,π-donor ligands or by reactions of *fac*-tricarbonyl complexes with π-acceptor ligands. For example, the π-acceptor PPh_3 ligand in *fac*-tricarbonyl β-diketonate complexes labilizes the CO bond trans to it, opening the door for the incorporation of the second PPh_3 ligand. With weaker π-acceptors such as 1,10-phenanthroline or 2,2'-bipyridine, considerably more severe conditions are required to obtain the dicarbonyl complexes.

With isonitriles, even monocarbonyl complexes and products of complete replacement of CO groups can be obtained. The reaction conditions and results depend on the electronic and steric characteristics of the isonitrile ligands.

Steric hindrance not only governs the formation of definite complexes, but also leads to stabilization of unusual Tc states. The sterically encumbering fluorinated isonitrile stabilizes Tc(–1) and even the radical 17-electron Tc(0) species. To compare, the homoleptic carbonyl analog $[Tc(CO)_5]^-$ is extremely reactive, and $[Tc(CO)_5]^\cdot$ does not exist as stable species and forms the dimer $Tc_2(CO)_{10}$.

Despite instability of $[Tc(CO)_5]^-$, success has been gained in preparation of this species in solution in the IR-spectroscopically pure form. New interesting polynuclear complexes have been isolated on the way to this species.

A procedure has been developed for facile and efficient synthesis of $[TcH(CO)_5]$. This compound behaves as a relatively robust covalent compound with weakly pronounced hydride properties, rather than as a conjugate acid of the $[Tc(CO)_5]^-$ anion. In addition, a novel trinuclear hydride cluster, $Tc_3H(CO)_{14}$, and binuclear hydrides containing diimine bases have been prepared and characterized.

To conclude, technetium occupying the central position in the d-block and in the periodic table as a whole is still poorly explored compared to its neighbors and often appears to be a lacking brick in the building of inorganic chemistry. The results obtained recently contribute to filling this gap.

Synthesis and properties of matrices for immobilization and transmutation of technetium

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One of the key challenges in improving nuclear energy safety is ensuring a closed fuel cycle [1]. Solutions include immobilization and nuclear transmutation of long-lived actinides and fissionable elements, particularly neptunium and technetium. The optimal forms of technetium that meet the requirements for its immobilization matrices are insoluble sulfides and oxides, where the element exists in the Tc(IV) form, as well as metallic, carbide phases, and alloys, where the metal has a formal oxidation state of Tc0. In addition, in rare cases, poorly soluble forms of tetraalkylammonium cation pertechnetates can be used.

Currently, metal or its carbide is considered the universal matrix for the burial and transmutation of technetium. However, methods for synthesizing technetium-based carbide materials currently do not meet radiation safety standards and are far from industrially applicable. Tc-NpO_2 cermet matrices with varying ceramic-to-metallic phase ratios were fabricated and studied. Increasing the metallic technetium content was shown to strengthen the composites and reduce brittleness. The minimum required Tc:NpO_2 ratio is 4:1. Composites with a metal content lower than 4:1 do not meet the requirements for matrix and target materials. Optimal temperature conditions for batch preparation were determined, and the necessary mechanical conditions for matrix fabrication were identified [2]. Triphenylguanidinium and hexamethyleneiminium pertechnetates were synthesized, and their crystallographic parameters were determined. The crystal structure of tetramethylammonium pertechnetate was refined. The thermal decomposition product of these compounds was shown to be cubic low-carbon technetium carbide TcxC ($x \leq 6$) with a lattice parameter of $a = 4.01 \pm 0.03$ Å.

A new method for synthesizing technetium-based carbide target material—vapor-phase cementation—has been developed.

It has been shown to yield results similar to those achieved by thermochemical reduction of triphenylguanidinium and hexamethyleneiminium pertechnetates.

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Mechanisms of autoclave methods for processing technetium-containing materials

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Technetium complexes in lower oxidation states are unstable and typically form with strong-field ligands, while complexes with weak-field ligands exist only in the presence of metal-metal bonds [1].

Thus, the chemistry of technetium complexes in oxidation states below 3^+ with weak-field ligands can essentially be considered the chemistry of cluster compounds of this element.

Research on the chemistry of technetium cluster compounds began in the early 1970s at the Institute of Physical Chemistry of the USSR Academy of Sciences after obtaining weighable quantities of this element from waste from nuclear fuel reprocessing [1].

One of the synthesis routes, used by the authors in [2], is based on the reduction of pertechnetate ions with molecular hydrogen under pressure in an autoclave.

This method has the advantage of producing well-formed crystals free of foreign impurities. The autoclave method was initially developed for the synthesis of binuclear technetium clusters with $[Tc_2Cl_8]_3$ anions and inorganic and organic cations [2].

The autoclave method for producing clusters has also proven convenient for the synthesis of more complex technetium clusters, including polynuclear ones. All currently known technetium clusters can be roughly divided into groups characterized by similar molecular and electronic structures. Acetic acid and acetic anhydride were also used as solvents in the study. Pink crystals of Tc_2Ac_5 were obtained.

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Sorption of molybdenum from hydrochloric acid solutions of rhenium-nickel superalloy waste processing

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Currently, one of the global problems of modern technology is the recycling of industrial waste [1]. Secondary raw materials include waste generated during the production and operation of products made of multicomponent rhenium-nickel superalloys used for the needs of various industries. During their hydrometallurgical processing, after the acid leaching of rhenium, nickel and cobalt, a solid residue containing tungsten, molybdenum and tantalum is formed.

In light of the fact that molybdenum is an indispensable material in the metallurgical industry, the optimization and introduction of new more efficient technologies for its extraction from intermediates formed as a result of the processing of rhenium-nickel superalloy waste is an urgent task [2].

The purpose of this study is to determine the conditions of sorption of molybdenum from hydrochloric acid solutions of rhenium-nickel superalloy processing on various materials.

Weakly basic macroporous anionites Purolite A100 and Lewatit MP64, as well as the solid extractant TVEX-TBP, were used as sorbents.

Table 1 shows the main capacitance characteristics of materials during the sorption of molybdenum from hydrochloric acid solutions (pH 2).

***Table 1:** Capacitance characteristics of molybdenum sorbents*

Material	Equilibrium capacity, mg/g	Distribution coefficient, mL/g	Degree of recovery, %
Purolite A100Mo	295	2042	67,1
Lewatit MP64	271	1602	61,6
TVEX-TBP	161	578	36,6

Figure 1 shows the integral kinetic curves of molybdenum sorption from a productive solution using various sorption materials.

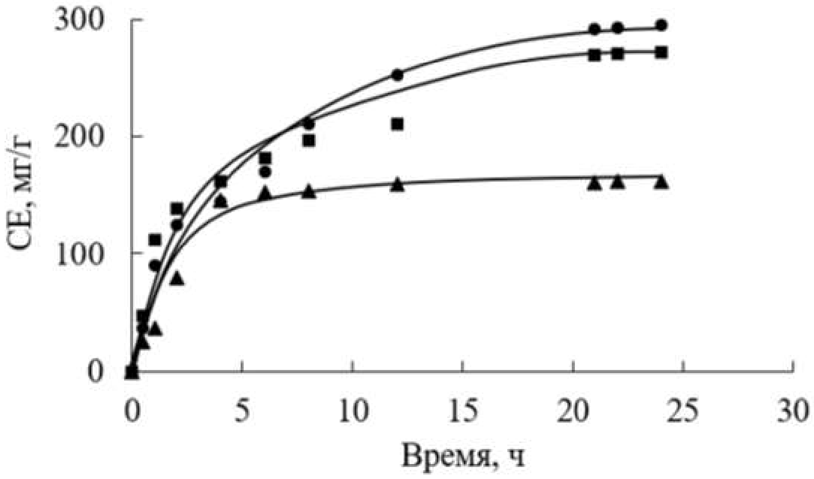

Figure 1: *Integral kinetic curves of sorption of molybdenum from hydrochloric acid solution of waste processing of rhenium-nickel superalloy:* • Purolite A100; ■ Lewatit MP64; ▲ TVEX-TBP

The results of mathematical processing of the obtained integral kinetic curves using kinetic and diffusion models are presented in Table 2.

Table 2: *Kinetic characteristics of sorbents*

Sorbents	The pseudo-first-order model		The pseudo-second-order model		The Weber-Morris model		The Boyd-Adams-Myers model	
	R^2	$k_1 \cdot 10,^{-3}$ min^{-1}	R^2	$k_2 \cdot 10,^{-3}$ g/mg·min	R^2	k_p, mg/g·min^{0,5}	R^2	$B \cdot 10^{-3}$, mg/g
Purolite A100	0,9795	4,375	0,9947	1,058	0,9255	7,816	0,9777	11,57
Lewatit MP64	0,9567	3,224	0,9947	1,054	0,9078	7,006	0,9513	17,19
TVEX-TBP	0,7902	4,145	0,9948	1,052	0,6628	6,928	0,8013	5,582

The highest value of the coefficient of determination R^2, observed when processing data on molybdenum sorption (Table 2), allowed us to conclude that the kinetic parameters of the sorption process by the materials under study satisfy the empirical pseudo-second-order model.

Figure 2 shows the processing of integral kinetic curves using the Weber-Morris model.

Kinetics of aqueous leaching of tantalum from the sintered semi-product of complex processing of rhenium-nickel superalloy waste

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Among rhenium alloys containing tantalum, nickel-based superalloys hold a special place. Rhenium-nickel superalloys are characterized by a multicomponent composition, incorporating expensive rare and non-ferrous metals. For this reason, the technology for recycling waste generated during the processing of components made from these alloys must meet the requirements of complex processing [1].

With existing methods for processing waste from various types of heat-resistant rhenium-nickel superalloys (solid lump waste, grinding sludge), which include operations such as thermal distillation, electrochemical anodic dissolution, and reagent leaching with solutions of various compositions, a tantalum-containing intermediate product is formed [2]. Information on the extraction of tantalum from this material is practically non-existent.

To convert tantalum into a water-soluble state, the tantalum-containing intermediate product was sintered with potassium hydroxide in an air atmosphere at a temperature of 800 °C, followed by aqueous leaching.

The kinetics of aqueous leaching of tantalum from the alkali-sintered intermediate product were studied at various temperatures (Figure 1).

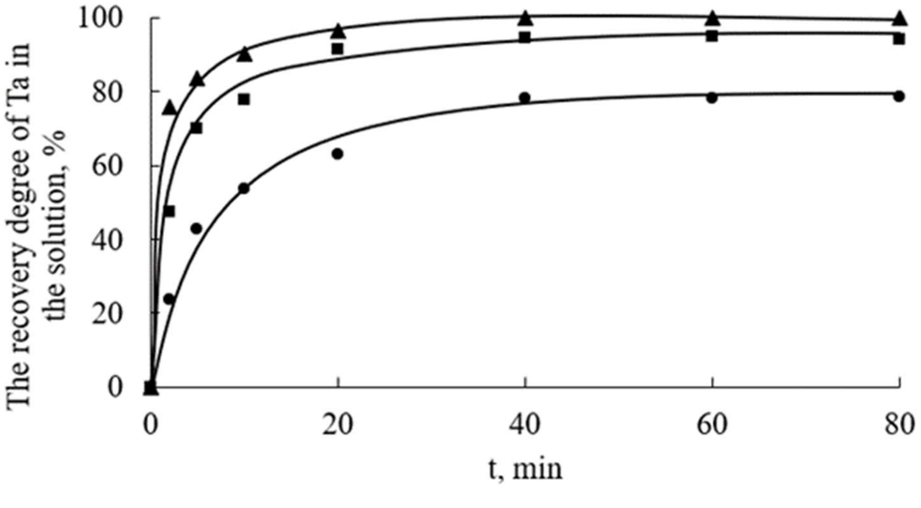

Figure 1: *Integral kinetic curves of tantalum leaching from the sintered intermediate of waste processing of rhenium-nickel superalloy with potassium hydroxide: • 20 °C; ■ 50 °C; ▲ 90 °C*

From the obtained dependencies, it can be seen that an increase in process temperature has a positive effect on the rate of water leaching of tantalum from alkaline sinter. The mathematical treatment of integral kinetic curves was carried out according to various models (table 1).

Table 1: *Kinetic characteristics of tantalum leaching from the sinter of the semi-product with potassium hydroxide*

Model name	Kinetic equation	Temperature, °C	Constants and the value of the coefficient of determination R^2
Prout-Tompkins model	$k_{ПТ} = \frac{1}{t}(ln\left(\frac{\alpha}{1-\alpha}\right))$	20	$k_{ПТ}$ = 0,0028 R^2 = 0,9407
		50	$k_{ПТ}$ = 0,0179 R^2 = 0,9214
		90	$k_{ПТ}$ = 0,0288 R^2 = 0,9011
Jander model	$k_{я} = -\frac{1}{t}(1-\left(\sqrt[3]{1-\alpha}\right)^2)$	20	$k_{я}k_{я}$ = 0,0017 R^2 = 0,9752
		50	$k_{я}k_{я}$ = 0,0179 R^2 = 0,9521
		90	$k_{я}k_{я}$ = 0,0026 R^2 = 0,9265
Gistling-Brounstein model	$k_{ГБ} = \frac{1}{t}(1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}})$	20	$k_{ГБ}$ = 0,0012 R^2 = 0,9624
		50	$k_{ГБ}$ = 0,0014 R^2 = 0,9602
		90	$k_{ГБ}$ = 0,0017 R^2 = 0,9458

The determination coefficients (R^2) for the Ginstling-Brounshtein model applied to the obtained kinetic curves have the highest values at the selected temperatures compared to the other models. Based on this, it can be concluded that the process is described by the Ginstling-Brounshtein model, and the rate-limiting step is internal diffusion.

Using the Arrhenius equation and the tantalum leaching rate constants presented in the table, the apparent activation energy of the process was calculated (Figure 2).

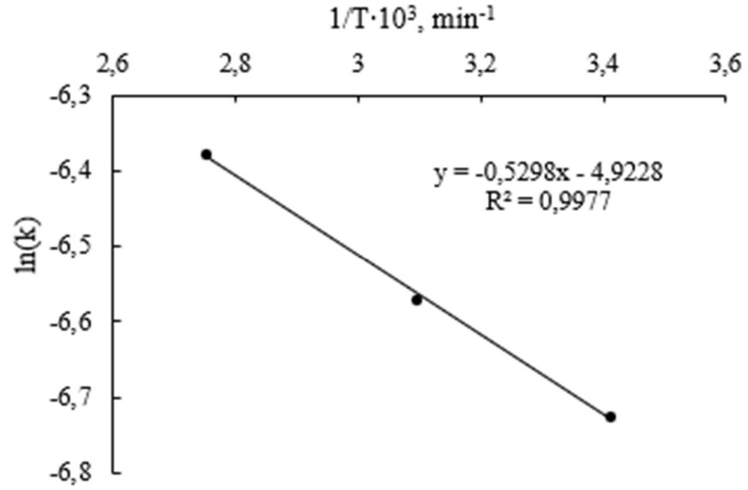

Figure 1: *Dependence of the natural logarithm of the leaching rate constant of tantalum from the sinter on the inverse temperature*

The apparent activation energy calculated using the tangent of the slope of the straight line (E/R = tgβ) was 5.30 ± 0.05 kJ/mol during the leaching of tantalum from the sinter [3]. The obtained values indicate that the leaching of tantalum occurs in the intradiffusion reaction area. The process can be intensified by increasing the area of interaction between the solid and liquid phases - by grinding the sinter, as well as by regulating the rotation speed of the mixing device.

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Rhenium sorption in the complex processing of superalloy grinding waste

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The need to provide the raw material base of the Russian Federation with the critically important rare metal rhenium is determined by the fields of its application. The production of special heat–resistant alloys for the aerospace industry, reforming catalysts in the oil refining industry, and electronics is not a complete list of them to produce products that are unique in their properties [1]. When there is a shortage of raw materials in Russia, the processing of secondary rhenium materials becomes in demand. Since ~80% of rhenium is used as superalloys, the volume of waste in the manufacture or disposal of products from them is significant, which justifies the urgency of creating and improving technologies for processing such materials [2].

The sorption and desorption characteristics of the complexing TVEX-DIDA ionite containing diisododecylamine for the recovery of rhenium from a solution of complex processing of nickel superalloy waste were studied.

The isotherm of rhenium sorption by TVEX-DIDA was obtained by the method of variable volumes, and its anamorphosis in Langmuir coordinates was constructed (Figure 1).

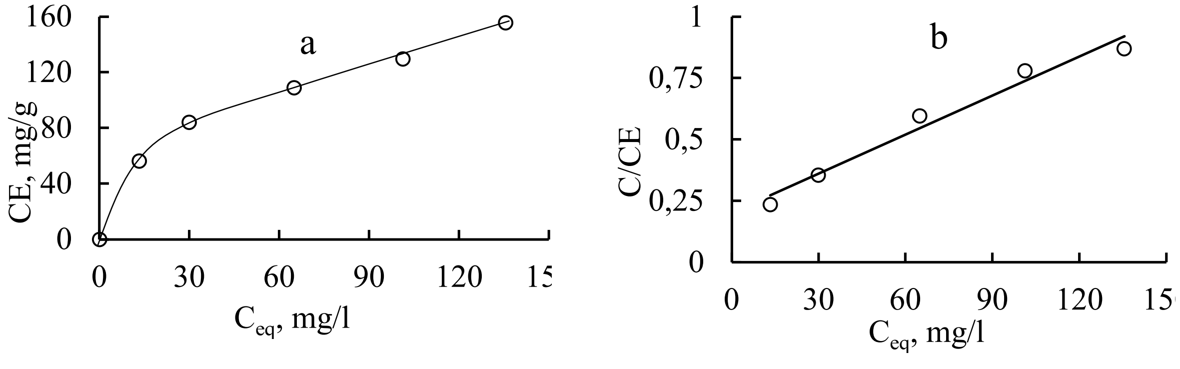

Figure 1: *Isotherm of rhenium TVEX-DIDA sorption (a) and its anamorphosis in Langmuir coordinates (b)*

Processing of the isotherm data using the Langmuir equation allowed us to determine the sorption equilibrium constant, the value of which was 0.026 ml/g.

The kinetic characteristics of the sorption of rhenium by TVEX-DIDA from a solution of rhenium leaching during the complex processing of nickel superalloy waste have been determined:

- half–absorption time – 9.90·102 s,
- rate constant – $6.70 \cdot 10^{-3}$ $g \cdot mg^{-1} \cdot min^{-1}$,
- effective diffusion coefficient – 7.57·10-12 m^2/s.

The kinetic data of rhenium sorption by TVEX-DIDA were processed according to known models (Table 1). The rhenium sorption process is characterized by a high rate and is limited in the diffusion region.

Table 1: *Values of the rhenium sorption by TVEX-DIDA rate constants*

The pseudo-first order model		The pseudo-second order model		The internal diffusion model		The Yelovich model	
k_1, min^{-1}	R^2	k_2, $g \cdot mg^{-1} \cdot min^{-1}$	R^2	k_p, $mg \cdot g^{-1} \cdot min^{-0,5}$	R^2	β, $g \cdot mg^{-1}$	R^2
0.0117	0.920	0.0067	0.998	5.05	0.867	0.042	0.949

The output curves of rhenium sorption and desorption using a TVEX-DIDA in dynamic mode were obtained at a solution transmission rate of 1 and 0.5 m/h, respectively (Figure 2).

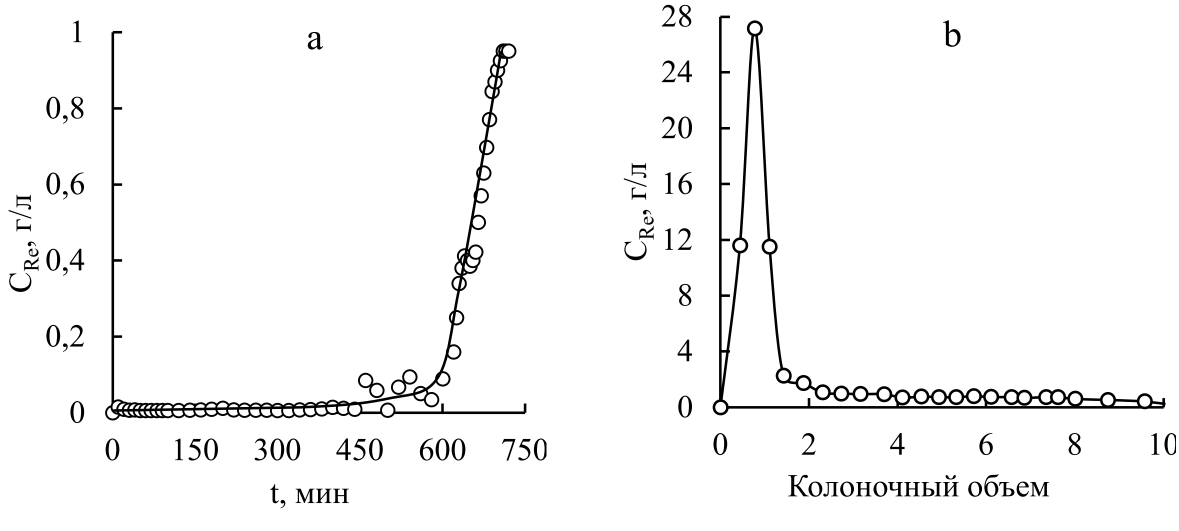

Figure 2: *The output curve of rhenium sorption (a) and desorption (b) using a TVEX-DIDA in dynamic mode*

The dynamic characteristics of rhenium sorption by TVEX-DIDA are presented in Table 2.

Table 2: *Dynamic characteristics of TVEX-DIDA during rhenium sorption from hydrochloric acid solution*

DEC		The number of bed volumes until the ionite is completely saturated	Sorption service time, h	Concentration coefficient	Kinetic coefficient β, h
mg/ml	mg/g				
55	105	70	11.8	55.0	0,05

The rhenium sorption output curve is described by the Yoon-Nelson model (R^2 – 0.916) with a constant value of 0.0091 min^{-1}.

Dynamic characteristics of rhenium desorption by 8% ammonia at a solution transmission rate of 1 m/h are obtained: the maximum concentration of rhenium in the eluate is 27 g/l, the main amount of rhenium (80%) is concentrated in two bed volumes of the eluate.

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Chairwomen of the Rhenium and Nuclear Medicine Sections :

Irina Troshkina and Galina Kodina

Radiopharmaceuticals based on rhenium-188: the development and preclinical investigations

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Rhenium-188 is considered to be a promising therapeutic radionuclide due to its nuclear properties ($T_{1/2}$ = 17 h, $E\beta^-$ = 2.12 MeV, $E\gamma$ = 155 keV) and availability from ^{88}W/^{188}Re generator [1]. Radiopharmaceuticals based on ^{188}Re can be useful and inexpensive alternatives to ^{177}Lu, ^{225}Ac, ^{161}Tb, etc. In Medical Radiological Research Centre radiopharmaceuticals based on albumin microspheres and ^{188}Re were developed.

The first radiopharmaceutical, «Albumin microspheres 20-40 µm, 188Re», or «Hepatoren-MRRC», is designed for radioembolization of hepatic tumors. Radioembolization is a procedure that combines embolization and radiotherapy to treat both primary and secondary liver tumors. Radiolabelled microspheres are injected directly into the hepatic artery to deliver high doses of radioactivity to the tumor lesions.

The other radiopharmaceutical is «Albumin microspheres 5-10 µm, 188Re», or «Artroren-MRRC», for radiosynovectomy of knee joints. When microspheres are injected into the joint cavity, the phagocytosis of labelled particles by mononuclear phagocytes (synoviocytes) is occurred. It leads to reduction of synovial membrane inflammation due to radiation damage and destruction of the synoviocytes.

The injection forms of both radiopharmaceuticals are prepared in nuclear pharmacy before injection to patients. The technological scheme of radiopharmaceuticals production is as follows: in vial 1 with lyophilizate, containing tin dichloride and ascorbic acid, ^{188}Re eluate is added and stirred for 5 min. This solution is filtered into vial 2, which contains albumin microspheres and Tween-80. Vial 2 is heated at 95 °C for 1.5 h with stirring the mixture in the vial every 10 min. Then the mixture from vial 2 is added to vial 3 with KNa tartrate and stirred for 10 min at room temperature (Figure 1). Radiopharmaceutical is ready for injection.

Microspheres are obtained from human serum albumin by emulsifying of albumin solution in vegetable oil by our own technology. ^{188}Re in the form of $Na^{188}ReO_4$ is obtained from ^{188}W/^{188}Re generator (GREN-1, IPPE JSC, Obninsk, Russia).

Preclinical investigations revealed that in rats with transplanted N1-S1 hepatocellular carcinoma, maximal uptake of «Albumin microspheres 20-40 µm, 188Re» (up to 14% of injected dose) was observed in the tumor lesions as compared with healthy liver. Also, it was shown an increase of life expectancy of «treated» animals by 15 %. The average life expectancy of animals after treatment was

62 days, whereas for «non-treated» animals it was only 46 days. In addition, «treated» animals showed stable inhibition of tumor growth during 60 days of observation.

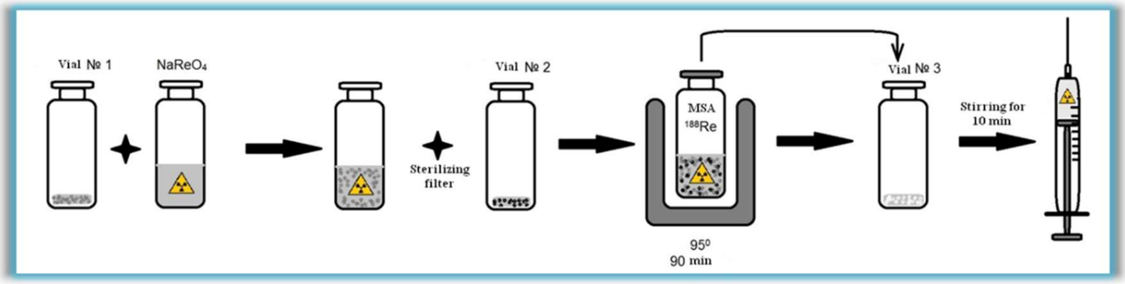

Figure 1: *The technological scheme of radiopharmaceuticals production.*

Radiopharmaceutical «Albumin microspheres 5-10 µm, 188Re» retained in the knee joint cavity (95-98% of the administered dose) both in intact rats and rats with induced synovitis. The uptake of «Albumin microspheres 5-10 µm, 188Re» in other organs and tissues did not exceed 1% of the injected dose. Therapeutic efficacy studies of radiopharmaceutical were performed on animals with a model of acute aseptic knee joint synovitis. The reduction of joint pain sensitivity and restoring the motor activity after intraarticular injection of radiopharmaceutical «Albumin microspheres 5-10 µm, 188Re» was observed.

Clinical investigations of I/II phases were also successfully carried out so far.

The developed radiopharmaceuticals based on albumin microspheres and rhenium-188 showed high efficacy and safety in treatment of liver tumors and synovitis

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Sorption of rhenium in complex processing of primary and secondary raw materials

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Complex processing of primary and secondary raw materials with relatively low rhenium content includes sorption operations using various types of materials.

The possibility of rhenium extraction using carbon materials, including carbon composites modified with various reagents, impregnates and TVEX based on amines obtained at D.I. Mendeleyev University of Chemical Technology of Russia, is shown.

Equilibrium, kinetic and dynamic characteristics of rhenium sorption by these materials are determined. Equilibrium constants, rate constants, diffusion coefficients and apparent activation energy are calculated. Losses of the mobile phase of the extractant from TVEX during operation are estimated.

Examples of using the sorption method of rhenium extraction for solving some technological problems are given.

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Selective advanced extraction of rhenium from uranium ore in-situ leaching solution

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Analysis of geological exploration materials and market conditions showed that the associated extraction of one of the rarest strategic elements of the periodic table – rhenium – is not always effective when processing the entire volume of productive uranium-containing solutions. A selective-advance scheme for rhenium extraction from productive uranium sulfate solutions of underground leaching of uranium ores using mobile units is proposed. The technology has the following features: zoning of production blocks during construction of injection and extraction wells; piping of selective extraction wells into a separate collector; implementation of advanced sorption of rhenium. Its implementation makes it possible to obtain rhenium from economically advantageous areas of a uranium deposit.

The mobile unit includes the following main units: a filter for cleaning (final cleaning) from suspended matter, a cascade of sorption devices (sorption filters or columns), connecting fittings, and control and measuring devices.

The sorption devices are filled with an ion exchanger selective for rhenium. Weakly basic nitrogen-containing ion exchangers containing functional groups of amines of various types, modified activated carbons, and fibrous materials of various compositions can be used as a selective sorbent for primary concentration. If further concentration of rhenium is required in order to unify the equipment used, materials with a mobile phase of the extractant (TVEKS and impregnates) can be used.

Economic aspects of selectively advanced rhenium technology are discussed.

[1] Rudenko, A.A., Troshkina, I.D., Danileyko, V.V., Barabanov, O.S., Vatsura, F.Y. (2021) *Prospects for selective-and-advanced recovery of rhenium from pregnant solutions of in-situ leaching of uranium ores at Dobrovolnoye deposit*. Gornye nauki i tekhnologii = Mining Science and Technology (Russia), 6(3), 158-169.

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New ^{99m}Tc radiopharmaceuticals for myocardial metabolic processes

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Previously we showed that the heart uptake of «2+1» tricarbonyl complexes of technetium with 1,10-phenanthroline and 2,2’-bipyridine is comparable to that of MIBI [1]. We also found that isocyanides form strong complexes with technetium(I) [2].

These data suggest that «2+1» tricarbonyl complexes of technetium with 1,10-phenanthroline and 2,2’-bipyridine show promise for introduction of technetium *via* the isocyanide group into fatty acids [3] with the aim to develop a new technetium radiopharmaceutical for heart metabolic process.

In this work we developed a procedure for preparing «2+1» tricarbonyl complexes of technetium-99 and rhenium with a combination of the bidentate ligands and fatty acid isocyanides ($CN(CH_2)_{10}COOMe$, $CN(CH_2)_4C(COOCH_3)S(CH_2)_9CH_3$, $CN(CH_2)_{12}CCH_3(CH_2)(COOCH_3)$).

The complexed were isolated and characterized by IR and NMR spectroscopy. The IR spectrum of the complexes contains three bands typical for the tricarbonyl fragment.

The coordination of the isocyanide group is confirmed by the ^{1}H NMR. Based on the results obtained we developed the procedure for preparing «2+1» tricarbonyl complexes of technetium-99m. These complexes were obtained and characterized by HPLC using technetium-99 analogs as the reference. The lipophilicity of the technetium-99m complexes was measured. The biodistribution of the obtained complexes in the bodies of laboratory animals was studied.

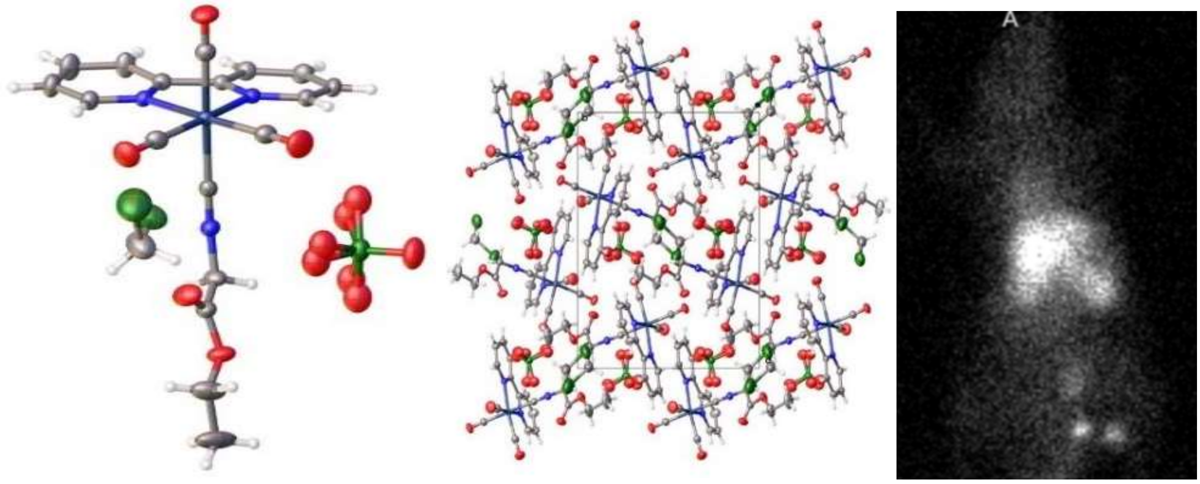

Figure 1: *Crystal and molecular structure of the complex [Tc(CO)$_3$(bipy)CNCH$_2$COOEt]ClO$_4$.and SPECT of rat with "[^{99m}Tc(CO)$_3$(bipy)CNCH$_2$COOEt]Cl".*

Acknowledgements: The study was financially supported by the Russian Science Foundation (project no. 22-13-00057, prolongation).

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Creation of a family of pathospecific paramagnetic contrasts for magnetic resonance imaging based on quantum chemical analysis of chelation properties of ^{99m}Tc and Mn(II) and replacement of ^{99m}Tc with Mn(II)

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4-Siberian State Medical University, Tomsk ,
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It has not yet been possible to create patho- and organospecific paramagnetic contrasts based on Gd complexes. **The aim of the study** was to develop pathospecific contrast compounds based on the analysis of Mn complexation with ^{99m}Tc chelators, in particular for tumor processes.

Materials and methods. Syntheses have been developed and preclinical *in vivo* studies have been carried out for a number of paramagnetic contrasts due to Mn(II) and ^{99m}Tc belonging to the same group of the Mendeleev table, the proximity of Mn(II) and ^{99m}Tc properties, and possibility of replacing ^{99m}Tc with Mn(II). **Results.**

Table 1.

Biophysical properties of paramagnetic contrasts based on complexes of Mn.

	$lgK_{Mn\text{-}Chelator}$, stability constant at pH=7,4	LD_{50} (млl/кг веса), and group of danger by GOST 12.1.007-76	Relaxivity R1, 1/(c *мМ)	Viscosity mPa*s, at 37 ºC	Osmolality, mOsmol/ (Kg H_2O), at 37 ºC
Mn-DMSA, onco-avid	17,1	16,2, Group 4 — low dangerous	3,79 ± 0,07	2,35± 0,07	1850 ± 35
Mn-DCTA, non-specific	19,6	17,5 Group 4 — low dangerous	3,68 ± 0,08	2,97 ± 0,07	1754 ± 21
Mn-Glucarate, onco-avid	17,6	15.1 Group 4 — low dangerous	4,1 ± 0,05	2.85±0.15	1550±39
Mn-Phytate, liver-avid	17,5	> 18.7 Group 4 — low dangerous	6,81 ± 0,07	-	-

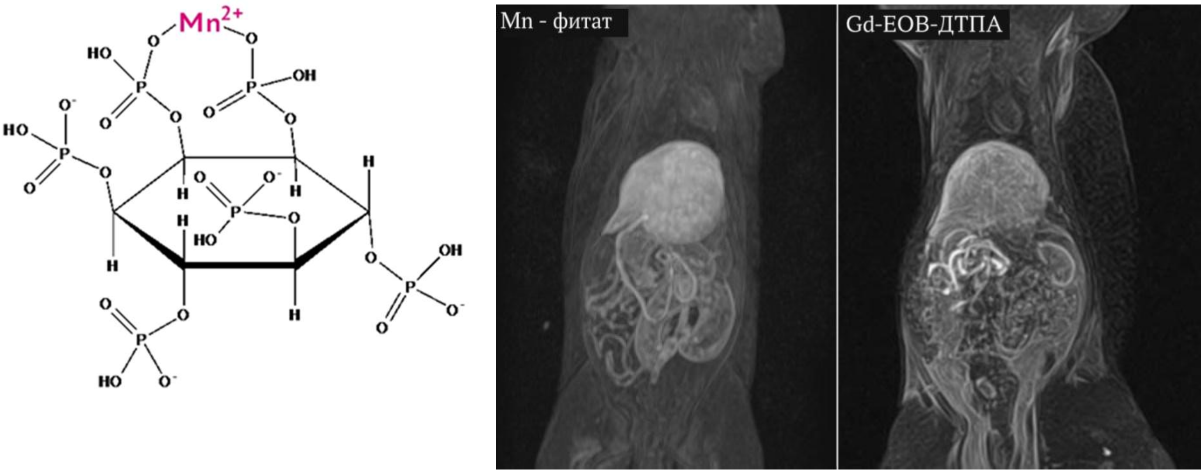

Figure 1. MRI of the rat liver enhanced with original Mn-phytate, in comparison with Gd-EOB-DTPA

Conclusion. The inclusion of Mn(II) in complexes with organo- and pathospecific complexing agents, previously tested with ^{99m}Tc in SPECT studies, makes it possible to obtain oncotropic and organotropic paramagnetic contrast compounds for MR tomography..

Technetium and iodine behavior in the combined technology of SNF processing

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Isotopes ^{99}Tc and ^{129}I are long-lived which considered as potential candidates for transmutation in the midterm perspective. Presumably, transmutation will be carried out in special targets located in suitable areas of the fast reactor. The products of transmutation in the first case are stable isotopes of ruthenium, and in the second case, xenon. The combined technology for processing spent nitride fuel of the BREST-300-OD reactor, implemented within the framework of the “Proryv” project, includes possible high-temperature fuel treatment (voloxidation), separation of fissile materials by the pyro electrochemical method in a eutectic melt of chloride salts and their extraction and crystallization refining, followed by recycling DM and americium into new fuels (refabrication). In the absence of pretreatment of the fuel, technetium and iodine will almost completely pass into the gas phase formed during the electrolysis of molten salts with a number of impurity transition metals. In the presence of an oxidation operation, technetium and iodine will be distributed in the gas streams of both operations, depending on the temperature regime of the high-temperature treatment. Possible options for handling gas streams of head-end operations of a combined nitride fuel processing flow sheet for the localization of technetium and iodine with the subsequent manufacture of transmutation targets are considered. It has been shown that commercial extraction of transmutation products is not economically feasible, and irradiated targets can be recycled together with spent fuel without any changes to the combined nitride fuel recycling technology.

The ratio of the number of targets to be recycled and the number of spent nuclear assemblies is 1:1000, which will not change the structure of the reactor-fuel recycling/refabrication complex, but will allow the recycling of Tc and I until they are completely destroyed.

Development of an electrochemical method for separation of ^{99m}Tc from a molybdenum target in the process of producing radiopharmaceuticals

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In the production of the isotope 99mTc, widely used in radiopharmaceuticals for in vivo diagnostics, one of the key tasks is to develop a method for its rapid and selective separation from the molybdenum target. Traditionally, this problem is solved using chromatographic methods, where polymeric Mo(VI) compounds are effectively adsorbed on a column packed with Al_2O_3, while pertechnetate ions (TcO_4^-) are not retained and pass into the eluate. However, to obtain a pharmaceutically acceptable form of technetium, their subsequent reduction is necessary.The electrochemical approach, although less commonly used in this field, represents a promising alternative to chromatography. Reduction of pertechnetate ions at the cathode not only enables their selective separation from molybdenum compounds but also converts technetium into a reactive oligomeric form of technetium(IV) oxide, which can be further used for the synthesis of radiopharmaceutical compounds. This study examines the electrochemical reduction of pertechnetate ions in alkaline solutions containing molybdate and pertechnetate ions. It was found that a high yield of technetium compounds was achieved with an electrolysis time of 30 minutes, confirming the effectiveness and potential of the electrochemical method for its selective separation and conversion to the target chemical form.

Table 1. Tc yield at various scan rates Ei and electrolysis times

Experiments with assumed solution concentrations and scan rates v	Before electrolysis activity, Bq/mkg	After electrolysis activity, Bq/mkg	Before electrolysis C, mmol/l	After electrolysis C, mmol/l	Separation %
0,0001 M $KTcO_4$ + 0,01 M Na_2MoO_4 + 0,5 M NaOH – 1 В/с	2523	452	0,403	0,072	82
0,0001M $KTcO_4$ + 0,01M Na_2MoO_4 + 0,5M NaOH – 0,1 В/с	817	76	0,131	0,012	91

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Chemical resistance of metal phase simulants present in irradiated nuclear fuel towards oxidation in air and nitric acid

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This work is dedicated to the investigation of «white inclusions» behavior during spent nuclear fuel (SNF) reprocessing. «White inclusions» are metallic particles formed in SNF by such fission products as Mo, Tc and platinum group metals (PGM). Mo-Tc-Ru-Rh-Pd alloy, known as ε-phase, is formed in oxide SNF. It is known that this SNF component is responsible for the precipitates formation during SNF dissolution process and can contain fissile materials.

Two samples of ε-phase - $Mo_{0.2}Re_{0.1}Ru_{0.6}Rh_{0.05}Pd_{0.05}$, $Mo_{0.2}Tc_{0.05}Re_{0.05}Ru_{0.6}Rh_{0.05}Pd_{0.05}$ were prepared.

Differential scanning calorimetry with thermal gravimetry (TG-DSC) in airflow revealed that ε-phase is resistant towards oxidation under usual voloxidation conditions (400 – 450 °C). It was found that during high-temperature voloxidation (~1000 °C) volatile MoO_3, Re_2O_7 could be effectively stopped by thermal gradient, while volatile ruthenium and technetium oxides could spread into cooler regions (<100 °C) of the furnace.

During leaching in 8M HNO_3 both compositions of ε-phase demonstrated high corrosion resistance. Nevertheless, leaching behavior of Tc-containing and Tc-absent samples differed significantly as well as leaching behavior of technetium and rhenium. The last fact makes questionable usage of rhenium as technetium simulant in leaching experiments.

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Behavior of technetium in bottom sediments of lakes at different stages of eutrophication

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The article presents a study of various mechanisms of hypolimnion technetium behavior which occur at different stages of waterbodies eutrophication. The samples of water (obtained at depth of 1m) and silt taken from Navolok and Kezadra eutrophic Lakes (see Figures 1 and 2 respectively) of Udomelsky district, Tver oblast (region), Russia, and from Khomutovka River were the objects of research. Khomutovka River is the southern tributary of Lake Udomlya, where Kalinin Nuclear Power Plant is located. Both lakes are subject to different stages of eutrophication, meanwhile the water from river was almost unaffected by eutrophication. Navolok and Kezadra Lakes belong to the category of p-mesosaprobic water bodies.

Eutrophication stage was found to be positively correlated with the rate of ^{99}Tc removal from water phase. The study identified a complex biogeochemical mechanism of technetium behavior. Planktonic phototrophic community plays a pivotal role in such a mechanism by ensuring fast oxygen consumption in hypolimnion. This creates favorable conditions for the active development of anaerobic bottom bacteria of sulfur and iron cycles given nutrients inflow. Sulfates and nitrates were discovered to have inhibitory effect on ^{99}Tc biosorption by bottom sediments due to oxidizing conditions. Apart from the shift of redox potential of the medium to reducing values, the ^{99}Tc removal and partial immobilization are also promoted by the presence of inorganic mineral phases of reduced sulfur and iron. These phases form a reducing barrier in the silt, thus preventing the oxidation and migration of technetium.

We suggest the ways of stimulating *in situ* waterbody remediation by means of various additives, which will allow irreversible immobilization of technetium in silt once several growth periods have passed.

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New chemistry of technetium

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Technetium is famous for its rich chemistry, possessing nine just integer oxidation states. The large number of redox transitions results in the high lability of its compounds and, consequently, the often-unpredictable chemical behavior in solutions, including during the hydrometallurgical reprocessing of spent fuel. Despite of more than 88 years have passed since the discovery of technetium (1937), its chemistry remains unclear and the subject to debate. Among the most unresolved issues in technetium chemistry are the synthesis and study of the properties of simple salts (complexes) of organic and mineral acids, the behavior of compounds in concentrated solutions, methods for stabilizing various forms of coordination compounds in various oxidation states, and the selection of stabilization conditions for specific types of compounds for the development of radiopharmaceutical approaches.

The progress of the recent 7 years in technetium and rhenium chemistry group resulted in:

1. Synthetic methods for a new class of rhenium compounds have been developed. Patterns of formation of Re and Tc polyoxometalates have been formulated. The first representatives of the class of polyoxorenates containing two types of anions, $Re_4O_{15}^{2-}$ and H2Re3O12–, have been isolated in crystalline form, and the structures of the resulting compounds have been studied.[1, 8] Technetic acid solutions (at acid concentrations greater than 10 M), in the absence of light irradiation, are shown to be in a dynamic equilibrium similar to perchloric acid 2HTcO4↔Tc2O7+H2O, demonstrating the formation of dimers and oligomers in solution. Using the isolated rhenium oligometallates as an example, as well as theoretical models of oligotechnetates, it has been shown that reduction processes occurring in technetic acid solutions with concentrations greater than 5 M are accompanied by oligomerization processes and are photolytic.

2. A method for the targeted synthesis of [Tc(V)O2L4]+ complexes has been developed, and the key principles of the formation process have been identified. It has been shown that oligomerization processes accompanied by reductive processes with the formation of stable Tc(V) solutions occur in concentrated technetic acid solutions (>3 M) upon irradiation with light. Based on the obtained data, a new method for the synthesis of ionic forms of technetium [Tc(V)O2L4]+ coordination compounds with ligands has been proposed, using pyrazole and 2-methylimidazole as examples. Analysis of the obtained reaction products suggests that nitrogen-containing heterocycles are oxidized by Tc(VII) compounds to form N-oxides, with technetium being stabilized in the pentavalent form.

3. A new approach to the synthesis of technetium and rhenium oligocarboxylates has been proposed [2-4]. Methods for the synthesis of technetium oligocarboxylates have been developed, and the key principles of the processes have been identified. Technetium has been shown to form polymeric and oligomeric carboxylate complexes in carboxylic acid anhydride solutions. Initially, technetium was found to be present in solutions as monomers and oligomers of Tc(VII), which is photoactive. X-ray diffraction and electron absorption spectroscopy demonstrated that the reduction of Tc(VII) proceeds stepwise, forming the carboxylates Tc(VI), Tc(V), Tc(IV), and Tc(II,III). The study revealed that at

certain points during the reaction, technetium can be present simultaneously in the anhydride solution as Tc(VII), Tc(VI), Tc(V), and Tc(IV). Reduction to Tc(II,III) compounds occurs only under hydrothermal conditions.

4. The patterns of formation of binuclear halide complexes of Tc(VI), Tc(V) and Tc(IV) were revealed. The influence of the structure of heterocyclic nitrogen-containing ligands on the formation of cis- and trans-isomers of Tc(V) complex compounds in the coordination environment of TcO2Hal2L2 was shown. It was shown that the process of formation of Tc(V) complexes depends on the change in the pH of the solution. Using electron absorption spectroscopy and DFT modeling, it was shown that the pentavalent form of technetium is stabilized in alcoholic solutions of hydrohalic acids. In aqueous solutions of hydrohalic acids, the tetravalent form TcHal62– is predominantly stabilized. It was shown that in non-aqueous solutions, under conditions of in situ formation of N3-, oligomeric and dimeric forms of Tc(VI) compounds are stabilized, the formation of which depends on the pH of the solution, the concentration of stabilizing ligands and does not depend on the concentration of water and N3-sources.

5. Methods for synthesizing Tc(III) and Tc(V) complexes with sulfur-containing ligands have been developed. The main patterns of the reaction of Tc(VII) with sulfur-containing reducing agents have been identified. It has been shown that, depending on the structure of the reducing agent, the coordination environments of CN 5 and CN 8, which are unusual or uncommon for technetium, can be stabilized. It has been shown that thiourea can be used to synthesize Tc(V) complexes of the composition $[Tc(V)O_2L_4]^+$ in the presence of N-donor ligands. Sulfur-containing reducing agents have been proposed as additives to cement and clay materials, which can be used to prevent technetium from entering the environment.

6. A method for the targeted synthesis of metallic technetium with a cubic crystal structure through the reduction of Tc(VII) with hydrogen has been developed . It has been demonstrated that metallic technetium undergoes a phase transition in the temperature range of 300-350°C. It has been shown that a pronounced reduction process of pertechnetes occurs already at ambient temperatures of 150°C. [5] The fact that a metallic phase forms at low temperatures from ammonium pertechnetate demonstrates that the reduction processes in ammonium pertechnetate crystals are not associated with autoradiolysis.

7. A selective method for the synthesis of technetium carbide by reducing pertechnetates or technetium concentrates with methane at temperatures up to 1000°C has been developed. It has been shown that the formation of technetium carbide is reversible by calcining the materials in a hydrogen stream [6,7].

8. It has been shown that the temperature of thermochemical reduction of hexahalotechnetates primarily depends on the structure of the organic cation and is independent of the nature of the halogen

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Reconstructing the Tc–C Phase Diagram Using a combined DFT and ML Approach

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Technetium carbides (Tc–C) are promising for nuclear waste immobilization and advanced reactor fuels. Here we combine density functional theory with machine learning to reconstruct the Tc–C phase diagram. By screening the complete configurational space of carbon interstitials in hexagonal and cubic technetium lattices up to 20 at.% C, we predict the Gibbs free energy landscape from 0 to 2000 K. The resulting phase diagram (see **Figure 1**) confirms and extends experimental data [1], while also allowing direct comparison with USPEX predictions [2].

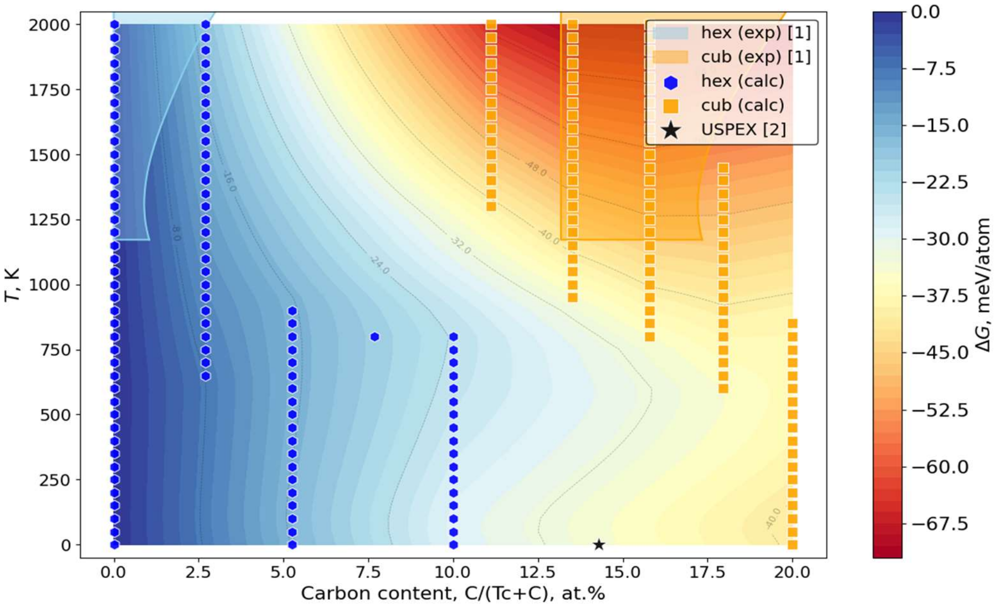

Figure 1. ΔG-derived Tc–C phase diagram for carbon contents up to 20 at.% over 0–2000 K. Hexagons and squares denote disordered hexagonal and cubic phases, stars indicate ordered structures from [2]. Experimentally observed homogeneity regions from [1] are shown for comparison.

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Rhenium medical isotopes: new production methods

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The rhenium isotopes (^{186}Re and ^{188}Re) have a wide range of applications in the diagnosis and treatment of cancer, owing to their distinctive physical and chemical properties (see Table 1).

Table 1. Radioisotopes of rhenium that are suitable for medical applications due to their nuclear physical properties.

Isotope	$T_{1/2}$	$E_{\beta max}$, keV (%)	Main γ-rays E_γ, keV (%)
^{186}Re	3.7 day	1072.7 (70.9%), 935.5 (21.5%)	137.2(9.5%)
^{188}Re	17 h	2120(70.7%), 1965(25.8%)	155(15.5%)
^{189}Re	24.3 h	1008(62%), 791(13%), 789(7.4%)	216.7(5.5%), 219.4(4.5%)

The objective of this study is to propose a method for the production of rhenium isotopes from osmium in (γ, *pXn*)-reactions at electron accelerators. In order to achieve this purpose, the irradiations of the osmium targets with a natural isotopic composition were carried out. The experiments were conducted at the Race-Track Microtron of the Skobeltsyn Institute of Nuclear Physics (MSU), with an end-point energy of bremsstrahlung 55 MeV. The weighted average cross-sections of reactions leading to the formation of ^{186}Re, ^{188}Re, and ^{189}Re were obtained. Subsequently, a comparison was made between the experimental results and the theoretically calculated weighted average cross-sections within statistical models (σ_{Talys}) using the TALYS1.96 software code (see Table 2).

Table 2. Weighted average cross sections of (γ, pXn) reactions on osmium isotopes at 55 MeV bremsstrahlung.

Nuclear reactions	Reaction product	σ_{exp}, mb	σ_{Talys}, mb
^{187}Os(γ, *p*) (<5%)+^{188}Os(γ, *pn*)+^{189}Os(γ, *p*2*n*)+ ^{190}Os(γ, *p*3*n*)	^{186}Re	0.082±0.008	0.064
^{189}Os(γ, *p*) (25%)+^{190}Os(γ, *pn*)+^{192}Os(γ, *p*3*n*)	^{188}Re	0.24±0.02	0.1564
^{190}Os(γ, *p*) (80%)+^{192}Os(γ, *p*2*n*)	^{189}Re	0.88±0.09	0.13

The irradiation of 10 g of osmium at an electron accelerator with 55 MeV bremsstrahlung at 0.1 mA results in the production of 3 GBq of ^{188}Re in a period of two hours and 3 GBq of ^{186}Re in a period of seven hours. Furthermore, a significant amount of ^{189}Re is also produced, whose nuclear properties are similar to those of ^{188}Re (see Table 1), thus rendering it a viable theranostic candidate.

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К.Э. Герман

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