7th International Symposium on Technetium and Rhenium – Science and Utilization
July 4 -8, 2011, Moscow, Russia

BOOK OF ABSTRACTS

RUSSIAN ACADEMY OF SCIENCES, IPCE RAS, RFBR, MUCTR, ISTC, RUSNANO, TOHOKU UNIVERSITY, FMBC FMBA, ROSATOM, BRUKER ACADEMINVESTSERVICE, UNLV, CEA, PUROLITE, PHARM-SINTEZ, DIAMED, IAEA, AMPLITUDA

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Edited by
K.E. German, B.F. Myasoedov, G.E. Kodina, I. D. Troshkina, T. Sekine

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A.Ya. Maruk, Ya. A. Obruchnikova

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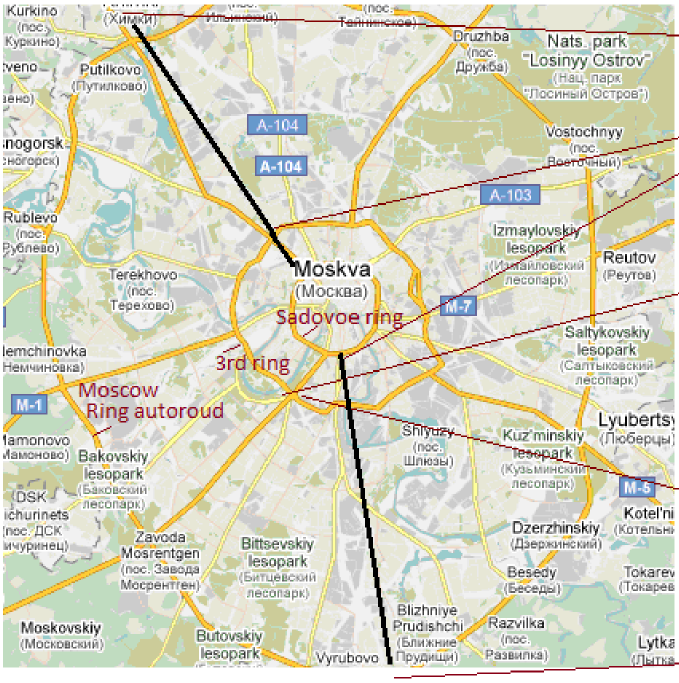

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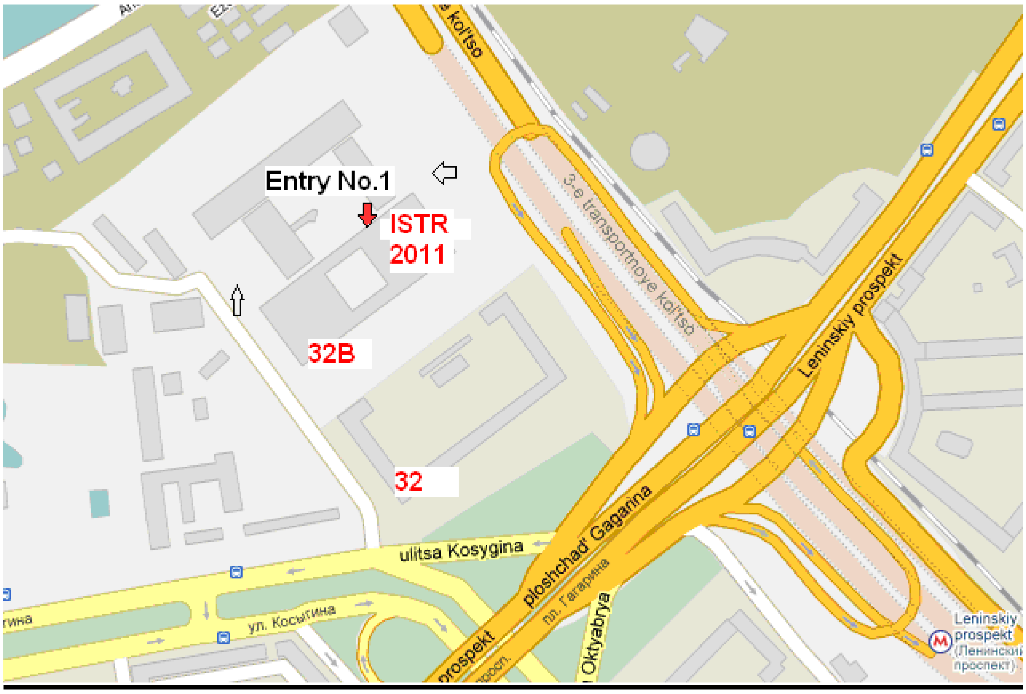

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2. Tc in the Nuclear Fuel Cycle and in the Biosphere. Analytical Chemistry of Tc and Re (in collaboration with ISTC, ROSATOM, RUSNANO)
3. Re Hydrometallurgy (in collaboration with Purolite and TMS)
4. Tc and Re in Nuclear Medicine (in collaboration with Burnazyan FMBC FMBA, ISTC, ROSATOM, RUSNANO)
5. Applications of Tc and Re, including their alloys in Modern Constructing Materials (in collaboration with Purolite, RUSNANO)
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6. I.S. Konovalov (NTC Amplituda)

TECHNETIUM: NEW TRENDS IN INVESTIGATION AND APPLICATION

K.E. German[1], F. Poineau[2]
[1] *Frumkin Institute of Physical Chemistry and Electrochemistry of RAS (Moscow, Russia)*
[2] *University of Nevada LasVegas (Las Vegas, USA)*

Technetium has a noble history of scientific community research efforts with different periods characterized by the principle interest sliding from broad general chemistry to nuclear medicine, ecology, transmutation etc... Surprisingly we could note that the last years are marked with the return to broadly understood general chemistry. This is evidently due to the improvement of the research investigating methods, now making possible to readdress the questions that were waiting the answer for many decades.

It is worth recalling the main gaps in Tc chemistry and thermodynamics having been indicated in 1999 [1]. Joseph A. Rard and co-authors have summarized the most important information needed to improve the quality of the technetium thermodynamic data base for the safety assessment of nuclear waste disposal. These items included some questions of Tc metal state, numerous oxides (also mixed-valent oxides), protonation constants for the formation of undissociated pertechnetic acid, $TcO_3(OH)(aq)$ or $HTcO_4(aq)$ and its genesis in acids, numerous inconsistence of solubility measurements (TcO_2 (s), TcS_2 (s), Tc_2S_7 (s), etc.) and the properties of TcF_6 (s).

Some of these questions were tried to be answered during the last decade and reviewed in this work. Important progress was obtained in nano-disperse Tc metal structure and properties and its dependence on the carbon impurity present [2-3]. Better understanding of Tc sulfides and their solubility was due to a combination of ultramicrocentrifugative speciation and EXAFS spectroscopic structure determination [4-5]. Another improvement gained for Tc(VII) species including TcO^{3+} and pertechnic acid evolution was due to both synthetic and spectroscopic (NMR and EXAFS) studies [6-7]. Very indicative for metal carbide and many other substance analyses are the implementations of wavelet ideas for the EXAFS results treatment that are also to be discussed at ISTR2011 [8].

It is also interesting to note that even some simple binary compounds of Tc are still to be discovered: synthesis, spectroscopic and structural characterization of several new technetium binary halides, including $TcCl_2$, $TcCl_3$, $TcBr_3$ and $TcBr_4$ and the formation mechanism of these new halides will be presented and discussed at this Symposium [9,10].

Application of Tc was critically reconsidered, with huge interest to be paid to Tc transmutation into stable Ru-100. Anyhow some other new applications were focused with the attempts providing direct usage of Tc radioactivity.

References.

1. *Rard, J.A., Rand, M.H., Andregg, G., Etc.* Chemical Thermodynamics, Vol. 3. Chemical Thermodynamics of Technetium (M.C.A. Sandino and E. Östhols, eds.), OECD Nuclear Energy Agency, Data Bank, Issy-les-Moulineaux, France 1999, 567 p.
2. German K.E., etc.// *Journ. Nucl. Radiochem. Sci. (*2006) V. 6, No.3, pp. 211-214.
3. Peretrukhin V.F., etc. // *J. de la Soc. de Chim. D.I. Mendeleiev (*2007) v.51, No 6, p.11-23.
4. German K., Reich T., Sergeant C., etc. Proceedings of OECD/NEA Workshop on pyrochemistry. 14-16 March 2000. Palais-des-Papes, Avignon (France).
5. M. Simonoff, K. E. German, C. Sergeant etc. Journee Radiochimie 2000, Gif-sur-Yvette, 28-29 September, 2000, France.
6. F.Poineau, Ph.F.Weck, K.German, etc. // *Dalton Trans.* (2010) 39 (37), pp. 8616-8619.
7. Supel J., Abram U. Hagenbach, etc. // *Inorg. Chem.* (2007) 46(14), 5591-5595.
8. V.Yu Murzin., Ya.V.Zubavichus, M.V.Chukalina, et all. *This issue*. 2011, p.172.
9. F. Poineau, E. V. Johnstone, Ph. F. Weck, E. Kim, P. M. Forster, B. L. Scott, A. P. Sattelberger, K. R. Czerwinski. // *J. Am. Chem. Soc.*, 2010, 132 (45), pp. 15864–15865.
10. F. Poineau, A. P. Sattelberger, B. L. Scott, P. Forster, Ph. Weck, E. Johnstone and K. R. Czerwinski. *This issue*. 2011, p.20.

RHENIUM IN NICKEL-BASE SUPERALLOYS FOR SINGLE CRYSTAL GAS TURBINE BLADES

E.N. Kablov, N.V. Petrushin, V.V. Sidorov

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Development of high effective materials and new technologies for their manufacture and application is the major factor of development of competitive aviation gas turbine engines. According to CIAM data in the period from 1970 to 2000 dynamics of efficiency increase of aviation engines of different generations was characterized by increase in the maximal gas temperature at the input of the turbine from 1300-1450 K (third generation) up to 1800-1950 K (fifth generation). Such growth has been attained owing to creation of new materials, basically nickel-base superalloys with high operational characteristics, perfection of cooling systems of turbine blades. In promising engines of the sixth generation the gas temperature will increase up to 2000-2200 K due to application in the turbine of single crystal blades from the rhenium and ruthenium alloyed nickel-base superalloys.

Studies carried out have shown that rhenium is one of the most effective alloying elements in nickel-base superalloys. Rhenium alloying was found to increase the incipient melting temperatures of alloys and the temperature of complete dissolution of a hardening γ'-Ni_3Al-based phase in a nickel-based γ solid solution. Rhenium decreases the self-diffusion coefficient of nickel and hinders diffusion processes in nickel alloys at operating temperatures.

The rhenium concentration reaches 3-4 wt.% in second generation single crystal superalloys and 5-6% in third generation superalloys. The superalloys designed at the All-Russian Scientific Research Institute of Aviation Materials (VIAM) contain 6-12% Re. These high-rhenium superalloys with a single-crystal structure were designed with a computer.

It is shown that for stabilization of phase structure and decrease in probability of precipitation of TCP phases it is possible to alloy with ruthenium high-rhenium nickel superalloys. Joint alloying with rhenium and ruthenium has synergetic influence on characteristics of single crystal nickel superalloys. As a result their high-temperature stress rupture and temperature efficiency considerably increases. Application in engines of developed rhenium- and ruthenium –bearing nickel superalloys having stress rupture of 120-130MPa at temperature of 1100 ºC for 1000 hours, will provide increase by 50-60 ºC of working temperature of single crystal blades made of these alloys.

The domestic sources of rhenium are examined for provision with rhenium the production of Re bearing alloys. Scientific and industrial complex on development and series production Re bearing superalloys is arranged in VIAM.

ISTR RETROSPECTIVES AND PROSPECTS

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Notes

Session 1. Fundamental Research in Physics and Chemistry of Tc and Re.

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1.1.

SPECTROSCOPIC AND PHOTOPHYSICAL PROPERTIES OF CHALCOGENIDE-CAPPED OCTAHEDRAL HEXARHENIUM COMPLEXES WITH N-HETEROAROMATIC LIGANDS

Takashi Yoshimura, Chiaki Suo, Shoji Ishizaka, Akitaka Ito, Eri Sakuda, Atsushi Shinohara, and Noboru Kitamura

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It is known that the 24 valence octahedral hexanuclear molybdenum, tungsten, and rhenium complexes with an **M_6Q_8** core **(M = Re, Q = S, Se, Te; M = Mo, W, Q = Cl, Br, I)** show photoluminescence.

In this study, the new hexarhenium complexes with N-heteroaromatic ligands were synthesized and their photoluminesent properties were characterized.

Photoirradiation of an CH_3CN solution of **$(Bu_4N)_4[Re_6S_8Cl_6]$** in the presence of 10 equiv. of pyridine (py) gave **$(Bu_4N)_3[Re_6S_8Cl_5py]$.** Emission spectroscopy in deaerated CH_3CN at 296 K was conducted at 355 nm excitation.

The mono-py complex exhibited broad and structureless emission with the maximum wavelength (λ_{em}) = 754 nm, the emission quantum yield (Φ_{em}) = 0.040, and the emission lifetime (τ_{em}) = 4.6 μs.

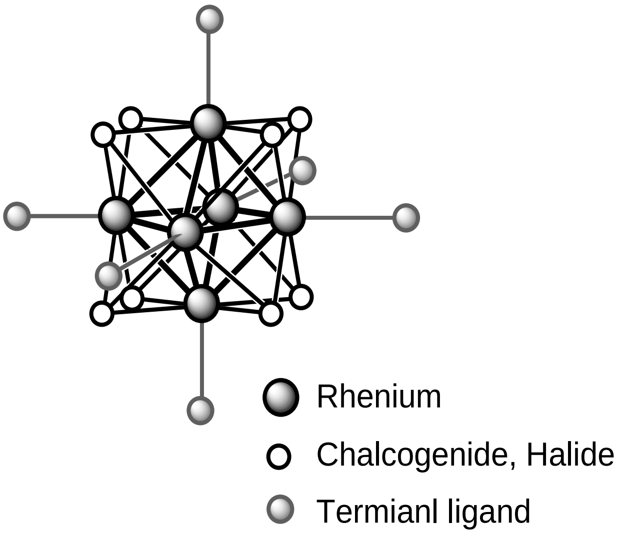

Fig.1. Octahedral Hexarhenium Complex.

The spectroscopic and photophysical data are similar to those of **$(Bu_4N)_4[Re_6S_8X_6]$** and the previously reported py coordinate complexes **$(Bu_4N)_{4-n}[Re_6S_8Cl_{6-n}(py)_n]$ (n = 2, 3)**. The present results indicate that the emissive state is the cluster core-centered excited triplet state.

A **mono-ppy** (**ppy = 4-phenylpyridine**) complex **$(Bu_4N)_3[Re_6S_8Cl_5ppy]$** were synthesized by the similar method to prepare the **mono-py** complex. The complex showed emission at 739 nm (Φ_{em} = 0.0089) in deaerated **CH_3CN** and at 690 nm in the crystalline phase at 296 K with an excitation wavelength at 355 nm. The emission lifetime (τ_{em}) of 0.33 μs in **CH_3CN** indicates that the excited-state is composed a triplet character. The transient absorption spectrum in deaerated CH_3CN showed a band at 410 nm. This spectral feature is well observed in the absorption of aromatic anion; the absorption spectrum of the ppy^- also shows the bands in these regions. These facts indicate that the excited-state of mono-ppy complex involves the π* character of **ppy**.

1.2.

RHENIUM OCTAHEDRAL CHALCOHYDROXO CLUSTER COMPLEXES

Y.V. Mironov, S.S. Yarovoi, K.A. Brylev, V.E. Fedorov

Nikolaev Institute of Inorganic Chemistry of SB RAS, Novosibirsk,
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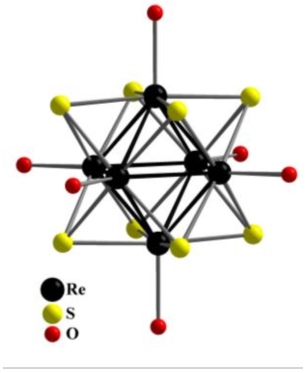
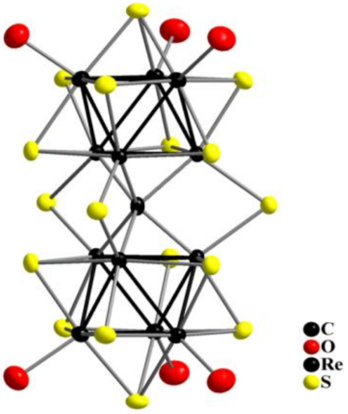
In recent years considerable research has been put into the design of solids with extended polymeric structures based on rhenium cluster cyano complexes. Here we present a new group of compounds that are also able to form polymeric compounds– anionic octahedral chalcohydroxo complexes **$[Re_6Q_8(OH)_6]^{4-}$ (Q = S or Se)** and bioctahedral thiohydroxo one **$[Re_{12}CS_{17}(OH)_6]^{6-}$.** The **$Re_6$**-based complexes were synthesized by the reaction of **$Re_6Q_8Br_2$** with molten **KOH** in the air, while the **Re_{12}** one was obtained by the reaction of **ReS_2** with **KCN** at 750°C with further interaction of the obtained product with molten KOH.



$[Re_6Q_8(OH)_6]^{4-}$ (Q = S, Se) anions consist of six rhenium atoms forming an octahedron, eight chalcogen atoms (S or Se) form a cube around the octahedron. OH terminal group coordinates each Re atom.

Cluster unit **$[Re_{12}CS_{17}(OH)_6]$** consists of two **Re_6** octahedra bonded by three **μ_2-S** bridges and one common **μ_6-C** atom. Each **Re_6** cluster is caped by 7 **μ_3-S** and additionally by **C** ligand; one might say that here the typical octahedral cluster core **$\{Re_6Q_8\}$** (where Q = **S_7C**) is formed. Such bonding and coordination allow to recognize in this structure the trigonal **μ_6-C**-centered prisms **$\{Re_6C\}$** in which the triangle faces belong to two adjacent Re_6 octahedra. Six outward **Re** atoms (tree from each **Re_6** cluster unit) are coordinated by **OH** ligands.



In this work we present the data on preparation of OH-bridged complexes based on cluster anions **$[Re_6Q_8(OH)_6]^{4-}$** (Q = **S, Se**) and cations of the II main group elements. The first example of chain structure with 3d transition metals, namely, **$[Ni(en)_2(H_2O)_2][\{Ni(en)_2\}Re_6S_8(OH)_6]$** has been also obtained. Also we present the data of study of the substitution reactions of **OH** ligands by organic and inorganic ligands.

The authors are grateful to Russian Foundation for Basic Research (grants N 11-03-00157-a and 10-03-01040-a) for financial support.

1.3.

TECHNETIUM HALIDES: FROM MOLECULAR TO EXTENDED STRUCTURES

Frederic Poineau[1*], Alfred P. Sattelberger[2], Brian L. Scott[3], Paul Forster[1],
Philippe Weck[1], Erik Johnstone[1] and Kenneth R. Czerwinski[1]

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Binary transition metal halides exhibit a rich chemistry, and the study of their structure, bonding and physical properties permits a better understanding of the physico-chemical trends across the periodic table.

Because technetium and rhenium are members of the same group in the periodic table, the occurrence of analogous coordination compounds is expected. In the case of the halides, thirteen binary phases have been reported for rhenium, but only three were, until recently, known for technetium, i.e., TcF_6, TcF_5, and $TcCl_4$.

The direct stoichiometric reactions between technetium metal and elemental bromine or chlorine as well as the reaction between the quadruple bonded dimer $Tc_2(OAc)_4Cl_2$ with HX_g (X = Cl, Br) have, to the best of our knowledge, never been reported.

In this talk, we provide details of these reactions, which have led to the synthesis, spectroscopic and structural characterization of several new technetium binary halides, including $TcCl_2$, $TcCl_3$, $TcBr_3$ and $TcBr_4$.

The structures and formation mechanism of these new halides will be presented, discussed, and compared with those of rhenium and molybdenum homologues.

Emphasis will be on $TcCl_2$ which exhibits a new solid-state structure type with metal-metal multiple bonds. Synthetic reaction using technetium binary halides as precursor will also be presented.

1.4.

SYNTHESIS OF RHENIUM ALKOXIDES VIA ANODIC DISSOLUTION

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At the first time the research of the process of rhenium anodic dissolution in absolute alcohols was carried out using the electrochemical technological complex "ECC – 1012", the measurement of potential being based on noncompensatory feed-back method. The device allows both to investigate, and to realize technological processes in optimum modes at controllable parameters.

The main application of rhenium is preparation of structural alloys with other refractory metals. These alloys possess valuable mechanical properties and stability against evaluated temperature and corrosive medium. Another application of rhenium is preparation of highly-active and selective catalysts for organic and hetero-organic synthesis. The using of rhenium alkoxides and oxoalkoxides permits to escape difficulties occurring in the traditional methods of preparation of Re-based alloys and oxide materials.

The electrochemical synthesis of rhenium alkoxides is of heightened interest, because it is flexible, less complicated in hardware design and it allows carrying out the process under maximum control via setting definite parameters. The electrochemical synthesis of alkoxides corresponds to the anodic dissolution of rhenium in the required non-aqueous alcohol in the presence of a background electrolyte. According to this method the processes of rhenium anodic dissolution in absolute alcohols ROH (R = Me, Et, i-Pr etc) with the addition of LiCl were researched and rhenium complexes $Re_4O_4(OEt)_{12}$, $Re_4O_2(OBu^n)_8{\cdot}8Bu^nOH$, $Re_4O_6(O^iPr)_{10}$, $Re_4O_6(OMe)_{12}$ etc were obtained for the first time with further investigation of their properties [1].

In order to observe the influence of electrochemical factors on the anodic dissolution the number of processes were carried out under controlled potential. The constancy of electrochemical parameters was supported by means of electrochemical complex "ECC – 1012". Besides, heteroligand complexes of common formulas $Re_4O_x(OEt)_y(OPr^i)_z$, $Re_4O_x(OEt)_y(OCH_2CF_3)_z$ were prepared for the first time. The possible mechanism of rhenium anodic dissolution and its further behavior in the solution was suggested.

The research was carryed out under the support of the RFBR grant № 09-03-00328.

1. Drobot D.V., Shcheglov P.A. Reviews, Rhenium alkoxides // Russian Chemical Bulletin, International Edition. October 2005. v. 54, № 10, p. 2177-2188.

1.5.

RHENIUM COORDINATION CHEMISTRY: OLD LIGANDS DIE HARD

Thomas Gerber[1], Kim Potgieter[1], Peter Mayer

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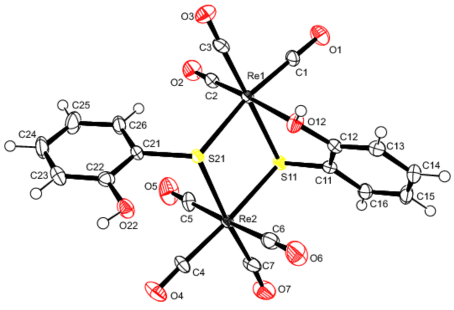
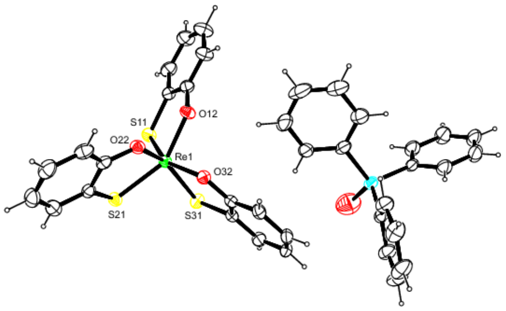
[2]Chemistry Department, Ludwig-Maximilians University, D-18377 Munich, Germany

The development of the coordination chemistry of Re and Tc has mainly focused on the +V and +I oxidation states, since they are easily accessible from the permetallates. There is currently a general notion amongst researchers in this field that there is very little scope in the the further exploration of the coordination chemistry of these oxidation states, since all routes and possibilities have been exhausted, and the new focus has shifted to the states +II, +III, +IV and +VI.

We have used relatively simple and common organic molecules, like 2-aminobenzenethiol, 1,2-diaminobenzene, 2-aminophenol, imidazoles, thiazoles, and their derivatives, as possible ligands for rhenium(I) and (V). In many instances, surprisingly unexpected complexes were found, depending on the starting complexes used and the reaction conditions. For example, with the simple ligand 2-aminobenzenethiol, the unusual disulfide-bridged rhenium(I) complex **1** and rhenium(VI) complex **2** have been obtained.

Many other examples of unusual complexes with simple ligands will be presented and discussed in terms of their spectroscopic and crystallographic data.





1.6.

REDOX BEHAVIOUR OF THE Tc(VII)/Tc(IV) COUPLE IN DILUTED NaCl SOLUTION IN VARIOUS REDUCING SYSTEMS

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Safety assessment for nuclear waste repositories requires a reliable prediction of radionuclide solubility limits. In relevant aqueous solutions, technetium solubility will either be controlled by highly soluble Tc(VII) or rather insoluble Tc(IV) species. The amount of Tc potentially mobilized is thus closely related to the Tc oxidation state and overall redox conditions.

The behavior of the Tc(VII)/Tc(IV) redox couple was studied in carbonate free 0.1 M NaCl/NaOH solutions under the presence of various homogeneous and heterogeneous reducing agents. Eh, pH values and Tc concentration were measured up to 3 months equilibration time. In the systems with sodium dithionate ($Na_2S_2O_4$), tin(II) chloride, Lawsone (2-hydroxy-1,4-naphthoquinone), Fe powder (neutral pH range), and anthraquinone (acidic pH range), TcO_4^- was reduced and the total Tc concentration in solution decreased due to the formation of sparingly soluble Tc(IV) solid phase. The broken line in Fig.1 indicates a borderline of reduction independent of the reducing chemicals or the presence of iron solid phases and in agreement with thermodynamic model calculations. Results are systematised according to E_h/pH conditions in solution and reaction kinetics correlated to the measured redox potentials.

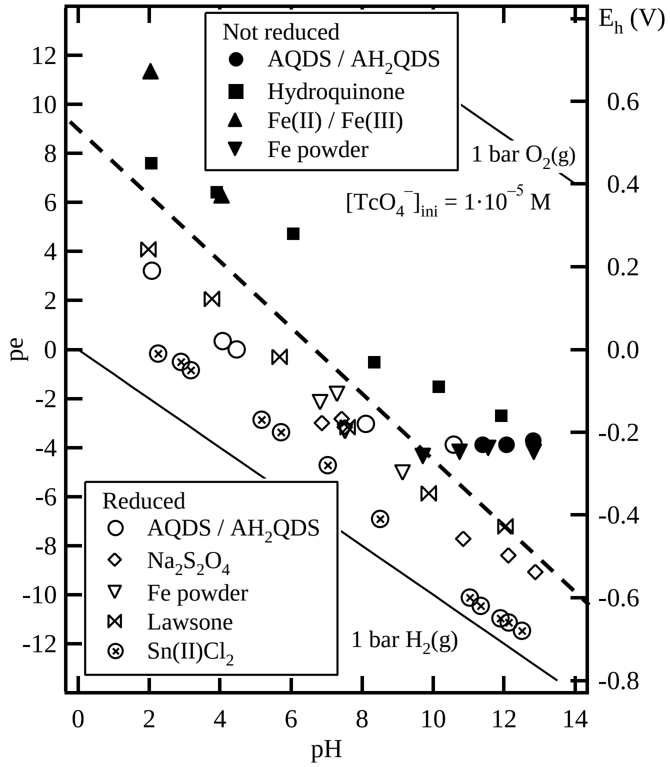

Fig.1 Reduction of Tc(VII) in 0.1 M NaCl/NaOH solutions. Open symbols indicate that Tc(VII) is reduced to Tc(IV), filled symbols indicate no Tc(VII) reduction within the time of investigation (≤ 94 days).

1.7.

TECHNETIUM(I) HEXACARBONYL CATION AND ITS REACTIVITY

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Technetium(I) hexacarbonyl cation $[Tc(CO)_6]^+$ was prepared by autoclave carbonylation of $[Tc(CO)_3(H_2O)_3]^+$ with CO at 100°C in the presence of strong acids with weakly coordinating anions ($HClO_4$, CF_3SO_3H, HPF_6). With strongly coordinating acid anions (e.g., $Cl^–$), the pentacarbonyl complex with the acid anion is formed. The $[Tc(CO)_6]^+$ cation, isolated in the form of perchlorate, was characterized by single crystal X-ray diffraction (SC XRD) and by IR (ν_{CO}, MeCN: 2095 cm^{-1}) and ^{99}Tc NMR (δ_{Tc}, MeOH: –1924 ppm) spectroscopy. The crystal structure of $[Tc(CO)_6]ClO_4$ consists of one crystallographically independent $Tc(CO)_6^+$ cation and disordered ClO_4^- anion (Fig. 1).

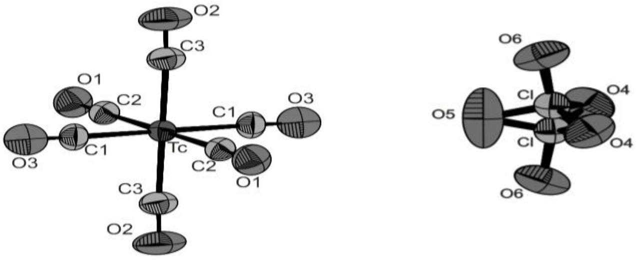

Fig. 1. $[Tc(CO)_6]^+$ cation (left) and disordered perchlorate anion (right) in the structure of $[Tc(CO)_6]ClO_4$.

Since $[Tc(CO)_6]^+$ is an analog of MIBI, it was of interest to study its cardiotropic properties. For this purpose we examined the resistance of this complex to substitution of carbonyl groups in solution. As an incoming ligand, we tested acetonitrile (mild σ donor). As seen from the IR data, $[Tc(CO)_6]^+$ slowly reacts with MeCN to form $[Tc(CO)_3(MeCN)_3]^+$. As in the case of pentacarbonyl halides [1], the rate-determining step of decarbonylation is detachment of carbonyl group. The rate constant of this reaction (2.83×10^{-7} s^{-1}, 304.4 K) is more than 1.5 orders of magnitude higher than that of decarbonylation of the most stable complex among pentacarbonyl halides, $[TcI(CO)_5]$ (76×10^{-7} s^{-1}, 303.1 K, in CCl_4 [1]). Thus, the $[Tc(CO)_6]^+$ cation is fairly resistant to thermal decarbonylation, despite relatively large lengths of the Tc–CO bonds. However, $[Tc(CO)_6]^+$ is instantaneously hydrolyzed in an aqueous solution in the presence of an alkali to form an unidentified yellow precipitate, which is probably a mixture of different compounds. Vacuum sublimation of this product yielded $Tc_2(CO)_{10}$ and $Tc_3H_3(CO)_{12}$, identified by SC XRD. We suggest that in this case decarbonylation involves nucleophilic attack of $OH^–$ anion at the carbonyl carbon atom, followed by decarboxylation of the intermediate and secondary transformations of the decarboxylation product.

We also prepared $[^{99m}Tc(CO)_6]^+$ by autoclave carbonylation of $[^{99m}Tc(CO)_3(H_2O)_3]^+$ in aqueous solutions of HPF_6 or CF_3SO_3H with a yield of 40 and 15%, respectively. The key point of the synthesis is complete removal of halide ions from the reaction mixture. $[^{99m}Tc(CO)_6]^+$ is stable in acidic aqueous solutions and in the presence of histidine for a day.

1. A.E. Miroslavov, G.V. Sidorenko, A.A. Lumpov, V.A. Mikhalev, D.N. Suglobov, *Radiokhimiya* **51:** 6–10 (2009).

1.8.

STRUCTURAL CHEMISTRY OF TECHNETIUM CARBONYL COMPOUNDS

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The results of structural studies of Tc carbonyl compounds are summarized. By now, crystal structures have been determined for approximately 100 Tc carbonyl complexes, of which 17 complexes were studied by the authors. Most of the data refer to octahedral Tc(I) complexes, with some Tc(III) and Tc(0) compounds [including $Tc_2(CO)_{10}$] also studied.

Representatives of practically all the theoretically possible mononuclear Tc(I) carbonyl complexes have been prepared and structurally characterized (here and hereinafter: M, monodentate; B, bidentate; T, tridentate ligands; Cp ligands are conventionally considered tridentate by the number of π-electron pairs): $[Tc(CO)_6]^+$, $[Tc(CO)_5M]$, $[Tc(CO)_4B]$, $[Tc(CO)_3T]$, $[Tc(CO)_3BM]$, $[Tc(CO)_3M_3]$, $[Tc(CO)_2M_4]$, $[Tc(CO)_2BM_2]$, $[Tc(CO)_2TM]$, $[Tc(CO)TM_2]$. All the di- and monocarbonyl complexes studied contain other π-acceptor ligands apart from CO (most frequently phosphines).

The *trans* effect makes preferential mutual *cis* arrangement of carbonyl ligands. Therefore, the most stable (and the most numerous) are *fac*-tricarbonyl complexes with σ- or π-donor ligand in *trans* position to each CO group {$[Tc(CO)_3T]$, $[Tc(CO)_3BM]$, $[Tc(CO)_3M_3]$}.

Numerous polynuclear Tc carbonyl complexes with bridging coordination of ligand donor atoms are known, in particular, a series of dimers $[Tc(CO)_4M]_2$, $[Tc(CO)_3B]_2$ and cubane-like tetramers $[Tc(CO)_3M]_4$. Binuclear complexes of type $[Tc(CO)_3P]_2$ are also formed when the geometry of polydentate ligands P is unfavorable for *fac*-tridentate coordinatoin. The structure of $[Tc(acac)(CO)_3]_2$ deserves particular mentioning: the dimer is formed not via $Tc–O_{acac}–Tc$ bridging similarly to other $[Tc(CO)_3B]_2$ compounds but by binding of the Tc atom with the C^3 atom of the acetylacetonate ligand of the second $Tc(acac)(CO)_3$ fragment with the formation of a cage dimer. Carbonyl compounds with Tc–Tc bonds and with bridging CO ligands (in combination with Tc–Tc bonding) are also known.

Owing to the *trans* effect, the Tc–CO bonds in *trans* position to each other [$Tc–CO_{trans}$] are longer by 0.05–0.1 Å than the Tc–CO bonds in *cis* position to each other and *trans* position to σ- and π-donor ligands [$Tc–CO_{cis}$]. In $[Tc(CO)_5M]$ complexes, the difference in the lengths of these bonds decreases in the series M = Cl, Br, I and is practically leveled off in going to π-acceptor ligands M (PPh_3, Bu^tNC). The reactivity of Tc carbonyl complexes in dissociative carbonylation reactions does not correlate with the Tc–CO bond length and decreases in the order M = Cl, Br, I, CO, which should be attributed to the stabilization of the five-coordinate intermediate formed by CO elimination. The complex $[Tc(CO)_6]^+$ is particularly inert in CO substitution, despite the fact that the Tc–CO bonds in it are even longer than the $Tc–CO_{trans}$ bonds in $[Tc(CO)_5M]$ complexes. On the other hand, $[Tc(CO)_6]^+$ is very reactive in a nucleophilic reaction (base hydrolysis).

The reactivity of $[Tc(CO)_5M]$ complexes can also be influenced by the *cis* interaction OC···M revealed by quantum-chemical calculations, which increases in going from M = Cl to M = I. Such interaction is also suggested by angular distortions of the $[Tc(CO)_5M]$ octahedra [M = halogen, $Tc(CO)_5$]. Namely, the equatorial carbonyl groups "lean" toward ligand M to the extent increasing in going from Cl to I, despite an increase in the ligand size.

1.9. Plenary lecture

"SOFT" CHEMISTRY METHODS APPEAR AS AN EFFECTIVE WAY FOR PRODUCTION OF SUPERDISPERSIVE (NANO-SIZED) MATERIALS BASED ON RE AND D-ELEMENTS OF V-VIII GROUPS

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The report is devoted to generalisation of research results concerning to the synthesis of mono-, heterometallic and heteroligand alkoxoderivatives of rhenium and d-elements of V-VIII groups and to their application as precursors in the production processes of superdispersive (> 100 nm) and nano-sized (< 100 nm) materials.

Different variants of electrochemical (anodic dissolution of metals in nonaqueous ROH (R = Me, Et, Pr^i, Bu^n) synthesis of $Re_xM_yO_z(OR)_m$ (M = Mo, W, Nb, Ta, Ni, Co) (I) [1,2] and the ways based on interaction between $M_x(OR)_y$ and Re_2O_7 were developed.

It was shown that thermal decomposition of (I) in different atmospheres (H_2, N_2, O_2) allows to obtain various functional Re-based materials under low (< 500°C) temperatures.

The catalytic activity of bimetallic (Re-W) and (Re-Ta) catalysts produced with the use of heterometallic complexes (I) as precursors was stated to be high enough in the processes of petrol (and its additives) production.

1. Drobot D.V., Shcheglov P.A. Reviews, Rhenium alkoxides // Russian Chemical Bulletin, International Edition. October 2005. v. 54, № 10, p. 2177-2188.
2. Drobot D.V., Seisenbaeva G.A., Kesler V.G. a.o. Cluster and Heterometallic Alkoxide Derivatives of Rhenium and d-Elements of V-VIII groups // J.Cluster.Sci. 2009. v. 20, № 1, p. 23-37.

The authors show their gratitude to professors G.A. Seisenbaeva and V.G. Kesler (Department of Chemistry SLU, Uppsala, Sweden) for creative collaboration on the different steps of the work and to the RFBR (projects 06-03-32444 and 09-03-00328) for the financial support.

1.10.

STRUCTURE AND MAGNETIC PROPERTIES OF POLYNUCLEAR COMPLEXES CONTAINING Re(IV)

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One of the major goals in inorganic supramolecular chemistry today is the design of polynuclear coordination arrays and the study of their magnetic properties. With the generation of well-defined architectures it is possible to understand the different factors which determine the exchange coupling between spin carriers. Most of the results found in the literature are focused on polynuclear complexes containing metal ions belonging to the first transition series. With this information the study of those systems containing 4d or 5d metal ions becomes very interesting. In this presentation we revise the structure and magnetic properties of Re(IV) mononuclear and polynuclear complexes.

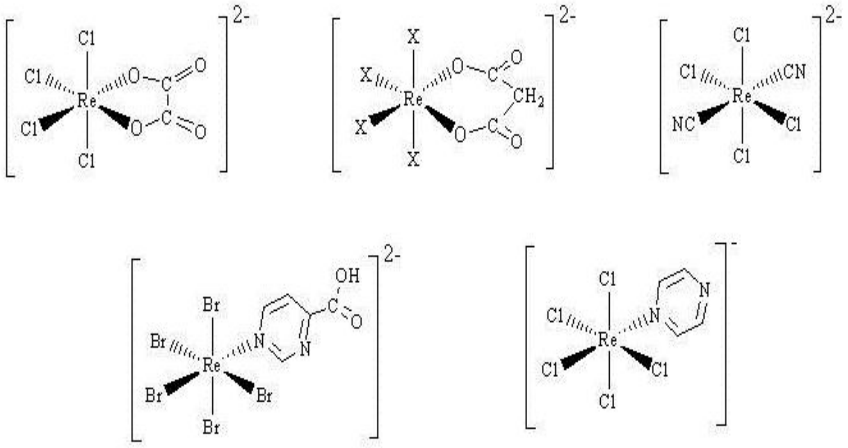

Fig. 1. Some Re(IV) mononuclear complexes used as building blocks.

Rhenium(IV), a $5d^3$ ion with a $^4A_{2g}$ electronic ground state, usually forms octahedral complexes which are reasonably stable against redox processes and inert to ligand substitution. Complexes containing dicarboxylic ligands, $[ReX_4(ox)]^{2-}$ and $[ReX_4(mal)]^{2-}$ (X = Cl, Br; ox = oxalate; mal = malonate), N-donor ligands, $[ReCl_5(pyz)]^-$ (pyz = pyrazine), $[ReBr_5(Hpyzc)]^-$ (Hpyzc = 2-pyrazinecarboxylic acid), and $[ReCl_4(CN)_2]^{2-}$, are some examples of mononuclear rhenium complexes that have been prepared and fully characterized. The presence of ligands which can act as donors toward a second metal ion (Fig. 1) is a common structural feature that has allowed the "complex as ligand" approach for the design of higher nuclearity compounds. Their structures range from discrete binuclear complexes (for example in $[ReCl_4(\mu\text{-ox})Mn(dmphen)_2]$, dmphen = 2,9-dimethyl-1,10-phenanthroline)) to extended chain-like compounds (for example in $[ReCl_4(\mu\text{-mal})Mn(dmphen)(H_2O)_2]$) are presented in this work. In addition, the magneto-structural studies of these mono- and polynuclear complexes are also discussed.

1.11.

POLYFLUORINATED β-DIKETONATES OF RHENIUM

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Fluorinated β-diketonates of metals possess a number of properties useful for technology, the most valuable properties are good solubility in organic solvents and high volatility. Therefore they can be used for solving two important problems: preparation of catalysts and film coatings by CVD. In recent years rhenium has become one of the most in-demand metals for both these problems.

We have prepared the earlier described complex $ReOCl_2(OEt)\cdot 2PPh_3$ and studied its reactions with β-diketones HL ($CH_3COCH_2COCH_3$, $CF_3COCH_2COCF_3$, $C_2F_5COCH_2COC_2F_5$, $C_3F_7COCH_2COC_3F_7$, $C_4F_9COCH_2COC_4F_9$, $C_3F_7OCF(CF_3)COCH_2COCF(CF_3)OC_3F_7$). A number of new rhenium complexes $ReCl_2L\cdot 2PPh_3$ were obtained. We have studied thermal properties and spectral characteristics of the synthesized compounds. The fluorinated rhenium complexes were shown to have high volatilities and vaporize without decomposition, this can be used in preparation of rhenium-containing films.

The details of the synthesis and physicochemical properties of the complexes will be considered in the presentation.

The work was financially supported by the Russian Foundation for Basic Research (Grant no. 09-03-00328a).

1.12.

PREPARATION OF TECHNETIUM METAL-METAL BONDED ACETATE DIMERS VIA HYDROTHERMAL ROUTE

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Recent results of hydrothermal reactions with pertechnetate, Tc(VII), have produced various low-valent compounds such as dication hexahalotechanate (IV) and Tc-Tc dimers.

The reaction of potassium pertechnetate in acetic acid /hydrochloric acid in an atmosphere of hydrogen gas yields red hexagonal crystals of known tetraacetatodichloro ditechnetate(III), $Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$ and blue triacetatodiaquadichloro ditechnetate (II)(III) hydrate.

Single crystal XRD analysis on both Tc dimers has been determined and the unit cell parameters will be presented.

Additional characterization of the $Tc_2(\mu\text{-}O_2CCH_3)_3Cl_2(H_2O)_2{\cdot}H_2O$ including UV-Vis, and FT-IR will shown. DFT calculations will be given for the $Tc_2(\mu\text{-}O_2CCH_3)_2Cl_4$ $Tc_2(\mu\text{-}O_2CCH_3)_3Cl_2(H_2O)_2{\cdot}H_2O$, and $Tc_2(\mu\text{-}O_2CCH_3)_4Cl_2$.

Currently, work explores *in situ* hydrogen generation via Zn or sodium borohydride, as well as the use of alternative reducing agents, allowing for many more reactions to be carried out in conventional autoclaves.

Results of the Zn and sodium borohydride reactions will be discussed. These one step reactions of reducing Tc(VII) to low valent technetium provides high yield intermediates for potential waste forms and use in nuclear fuel cycle separations.

Acknowledgments: SISGR-Fundamental Chemistry of Technetium-99 Incorporated into Metal Oxide, Phosphate and Sulfide: Toward Stabilization of Low-Valent Technetium Contract No. 47824B Basic Energy Sciences, DOE

References:

1. L. I. Zaitseva, A.S. Kotel’nikova and A.A. Reszvov, *Russ. J. Inorg. Chem.* 1980, **25**, 1449.
2. Cotton, A.F., C.A. Murillo, R.A. Walton.; *Multiple Bonds Between Metal Atoms,* Springer Science and Business Media, Inc.: New York, 2005, p. 257-259.
3. V. I. Spitsyn, B. Baierl, S.V. Kryuchkov, A.F. Kuzina and M. Varen, *Dokl. Akad. Nauk.* 1981, **256**, 608.

1.13.

PHYSICOCHEMICAL PRINCIPLES OF THE DEVELOPMENT OF RHENIUM-BASED AND RHENIUM-CONTAINING ALLOYS

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Rhenium (Re) is a hcp transition metal belonging to Group VII of the third long period of the periodic table (atomic number 75). The melting/boiling points (3453/6173 K), density (21.04 g/cm^3), and elastic modulus (479 GPa) of Re are higher than those of the most refractory metals. The maximum operating temperature, at which the weight loss by evaporation is ≤1% per 10 hours, reaches 2950 K.

Rhenium belongs to rare metals (its clark is ~10^{-7} - 10^{-6}%) and is difficult to manufacture (because of strong strain hardening) and expensive metal.

The unique properties of Re and some its alloys, which can be used in the environments impossible for operating of other materials, determine high interest in them. For example, in short-term and long-term strength at temperatures above 2400K, Re surpasses the best high-temperature cold-brittle tungsten alloys and, unlike them, has a plasticity reserve at temperatures down to cryogenic ones, high resistance to thermal shock and thermal cycling (290-2500K), low gas permeability, and does not form any stable interstitial phases.

The physicochemical approaches to the design of structural alloys with Re are developed.

Use of Re as an alloying element (AE) or as an alloy base is determined by two factors: the mutual solubility of Re and AE and four "rhenium effects", which have no analogs. A high solubility of Re in bcc Group VI metals (W, Mo and Cr) has allowed the development of a new class of high-temperature alloys and the alloys with special physical and chemical properties (W-Re, Mo-Re, and W-Mo-Re), in which the addition of 25-35 at. % Re simultaneously increases low-temperature ductility and strength of cold-short Group VI metals (“Re effect-1”).

The ability of Re to drastically increase the strain hardening rate of W and Mo alloys (“Re effect-2”) allowed the development of the alloys with σ_B of up to 6000 MPa for elastic members.

A substantial increase in low-temperature ductility of W and Mo alloys at 2-7 at. % Re (“Re effect-3”) allowed the development of cost-effective high-temperature rhenium alloys for bulk products.

The ability of Re to increase the high-temperature strength and service life of modern nickel-base superalloys is widely used as ”Re effect-4”.

1.14.

SYNTHESIS AND CHARACTERIZATION OF LOW-VALENT BINARY TECHNETIUM CHLORIDES

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Binary transition metal halides (BTMH) are an area of fundamental chemistry that exhibits an array of unique chemical and physical properties. Of the Group V, VI, and VII elements, the binary technetium halides for many years were considerably lacking in comparison with only three isolated and characterized in the solid state (TcF_6, TcF_5, and $TcCl_4$) [1]. More recently, the discovery of $TcBr_4$ and $TcBr_3$ has generated interest in pursuing low-valent binary technetium chlorides [2].

In this work two novel binary technetium halides $TcCl_2$ and $TcCl_3$ were synthesized in quantifiable amounts in the solid state and analyzed using various physicochemical characterization methods including single-crystal and powder X-ray diffraction (XRD), UV-Vis, X-ray absorption fine structure (XAFS), and elemental analysis, as well as density functional theory calculations (DFT).

Technetium dichloride was synthesized from the stoichiometric reaction of technetium metal and elemental chlorine at elevated temperatures as a novel compound with new structure-type consisting of an eclipsed conformation of $[Tc_2Cl_8]$ units containing a Tc-Tc triple bond [3].

Technetium trichloride was prepared from the reaction of $Tc_2(O_2CCH_3)_4Cl_2$ with passing HCl (g) at elevated temperatures and characterized as a novel compound isostructural to $ReCl_3$ with a triangular Tc_3^{3+} core structure containing metal-metal double bonds [4]. The low-valent technetium chlorides synthesized exhibit new and interesting chemical structures and properties, and even show potential as waste forms or use in separations for the nuclear fuel cycle.

Acknowledgments: SISGR-Fundamental Chemistry of Technetium-99 Incorporated into Metal Oxide, Phosphate and Sulfide: Toward Stabilization of Low-Valent Technetium Contract No. 47824B Basic Energy Sciences, DOE

References:

4. Schwochau, K. *Technetium: Chemistry and Radiopharmaceutical Applications*, Wile-VCH: Weinheim, 2000, p. 113.
5. F. Poineau, E. Rodriguez, P.M. Forester, A.P. Sattelberger, A.K. Cheetham, and K.R. Czerwinski, *J. Am. Chem. Soc.* **131**, 910-911 (2009).
6. F. Poineau B.L. Scott, P.F. Weck, E.V. Johnstone, P.M. Forester, E. Kim, K.R. Czerwinski, and A.P. Sattelberger, *J. Am. Chem. Soc.*, submitted
7. F. Poineau, E.V. Johnstone, P.F. Weck, E. Kim, P.M. Forester, B.L. Scott, A.P. Sattelberger, and K.R. Czerwinski, *J. Am. Chem. Soc.* **132**, 15864-15865 (2010).

1.15.

RECENT RESULTS IN RHENIUM CLUSTER CHEMISTRY

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Metal cluster compounds are very interesting and important representatives in rhenium chemistry. Authors of this paper carry out the systematic investigation of rhenium cluster complexes during long time. The results of this study are preparation of more then two hundred of new cluster rhenium compounds of different nuclearity - Re_4, Re_6, Re_9, Re_{12}, discovery of some key cluster complexes, among of them several compounds have original crystal structures and very interesting physical and chemical properties.

The systematic studies of tetrahedral $[Re_4Q_4(TeY_2)_4Y_8$ (Q=S, Se, Te; Y=Cl, Br) and octahedral $Re_6Q_8L_6$ cluster compounds opened the possibility for synthesis of complexes with diverse compositions and structures. Study of octahedral chalcocyanide complexes $[Re_6Q_8(CN)_6]^{4-}$ (Q=S, Se, Te) was shown that using high temperature reactions it is possible to substitute inner μ_3-Q ligands in cluster core with formation of mixed ligand units $\{Re_6Q_{8-x}Q'_x\}$. Similar reactions give the equilibrium between different chemical forms $[Re_6Q_{8-x}Q'_x(CN)_6]^{4-}$ that is in common with classical reactions of stepwise ligands substitution which are typical in coordination chemistry.

Experimental conditions of reactions bringing to condensation of cluster fragments into complexes having more high nuclearity were found: for example, octahedral $[Re_6Se_8Br_6]^{4-}$ and bioctahedral $[Re_9Se_{11}Br_6]^{2-}$ complexes were prepared from triangle compound Re_3Br_9; and twelvenuclear complexes with inserted carbon atom $[Re_{12}(\mu_6\text{-}C)S_{17}(CN)_6]^{8-/6-}$ were synthesized in the process of further condensation of octahedral clusters. The latter is unique complex in the cluster chemistry of transition metals.

Chalcocyanide cluster complexes $[Re_4Q_4(CN)_{12}]^{4-}$, $[Re_6Q_8(CN)_6]^{4-}$ (Q=S, Se, Te) and $[Re_{12}CS_{17}(CN)_6]^{6-}$ were studied broadly and carefully. Due to ambidentate nature of CN ligands these complexes are very suitable building blocks in design of coordination cyano-bridge polymers of different dimensionality with structures of chain-like, layered and framework types.

The methods for synthesis of hybrid tetrahedral and octahedral complexes coordinated organic N- and P-donor ligands were developed. Some rhenium complexes possessing bright red luminescence are synthesized; similar complexes are perspective preparation in procedure of photo-dynamic therapy. It was found that emission properties of cluster complexes may be regulated by modification of their electron structures via substitution of inner or external ligands in complexes.

Broad studies of chemistry of rhenium cluster complexes of different compositions, nuclearity and structures have expanded essentially a fundamental knowledge in the field of coordination chemistry of not only rhenium but also transition metals integrally.

Obtained regularity can be used as fundamental base in design of new cluster compounds and materials with complex of necessary functional properties.

Acknowledgment. Authors thank Russian Foundation for Basic Research (grants N 09-03-92004-HHC and 10-03-01040-a) for financial support.

Notes

1.16.

HETEROLIGAND ALKOXIDES OF RHENIUM CONTAINING O-Et AND O-^{i}Pr LIGANDS

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The similarity of $Re_4O_6(OPr^i)_{10}$ and $Re_4O_4(OEt)_{12}$ alkoxides structures (the metal-cluster frames of them have the same structure (similar to the initial structure of $Ti_4(OMe)_{16}$)), enables the synthesis of heteroligand complexes, containing O-Et and O-^{i}Pr ligands.

This report covers the electrochemical synthesis technique development of heteroligand complexes with the general formula of $Re_4O_n(O\text{-}Et)_x(O\text{-}Pr^i)_y$. The initial molar ratio is:

EtOH and Pr^iOH = 1:1, 2:1, 1:2 in electrolyte respectively.

The report also brings you up-to-date about the studies of physicochemical properties of obtained heteroligand complexes and the products of their thermal decomposition by means of IR, DTA-DTG, X-ray and Chemical analyses.

Quantum-chemical calculations according to the program «Computer Aided Composition of Atomic Orbitals» (C.A.C.A.O.) have been done. The findings have shown that the structures with general cluster frame Re_4 can exist and received compounds can not be related definitely to one or another structure, because the forming of complexes based on $Re_4O_6(OPr^i)_{10}$ structure and one based on $Re_4O_4(OEt)_{12}$ is equiprobable.

The thermal decomposition of $Re_4O_n(OEt)_x(OPr^i)_y$ complexes in oxidative atmosphere under 255°C is followed by the formation of oxide Re(VI) nanopowder.

The authors express their gratitude to the RFBR (project 09-03-00328) for the financial support.

1.17.

STATUS AND PROSPECTS OF STUDIES ON THE CHEMISTRY OF COORDINATION COMPOUNDS OF RHENIUM (V)

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Summarizes the results of targeted research on the synthesis and study of complexation of rhenium (V) with sulfur and nitrogen containing organic ligands in solution and at the interface. Established composition of the resulting complex compounds of rhenium (V) has an impact, as the ratio of initial regents, and the concentration of halo carbon acids. It is shown that in concentration 6 M of acids (HX) its formed oxo complexes structures $[ReOLX_3(H_2O)]$, $[ReOLX_3]$, $[ReO(L\text{-}H)_2X]$, $[ReOL_2X]X_2$, $[ReOL_2X_3]$, $[ReOL_4X]X_2$.

In the concentration range of 4 mol/l to 6 mol/l of acids (HX), depending the nature of coordinated ligands form either monomeric or dimerism oxo complexes with a bridging oxygen compounds $[ReO(OH)LX_2(H_2O)]$, $[ReO(OH)L_2X_2]$, $[ReO(OH)L_2]X_2$, $[Re_2O_3L_2X_4]$, $[Re_2O_3L_4]X_4$, $[Re_2O_3L_2(H_2O)_2X_4]$, $[Re_2O_2(OH)_2L_2X_4]$. In environments with acids (HX) concentration below 4 mol/l are mainly formed dimerism complexes with bridging oxygen. With the use of complex physical and chemical methods (IR spectroscopy, thermogravimetry, spectrophotometry, chromatography, potentiometry, magnetochemistry) and by elemental analysis to identify the composition and structure of the resulting complex compounds and proposed the reaction of their formation. Developed a universal method for the synthesis of complexes of rhenium (V) in environments with low concentrations of acids. A study of thermal decomposition process of the ligands and complexes detected a significant increase in thermal stability of some ligands with coordination. Revealed that the process thermogravimetry monomeric complexes rhenium (V) proceeds with the formation of dimeric compounds. According to the thermogravimetric studies found that the temperature of the onset of intensive decomposition of the complexes of rhenium (V) depends on the nature of the alkyl radical, which are part tioamides ligands.

On this basis, proposals from the respective series of thermolysis of complexes of rhenium (V) depending on the nature of the heterocyclic ligands. Investigating the equilibrium constants effect the ammonia on the complexes rhenium (V) with amide and thioamides ligands. A number of liabilities of the acidic ligands within the domestic sphere complexes of rhenium (V). Relevant to the laws established by the influence of the ionic environment, temperature and nature thioamide ligand on the stability of complexes of rhenium (V) in solutions of acids. Revealed some aspects the practical use complexes of rhenium (V).

We formulate promising directions of research in coordination chemistry of rhenium(V).

Notes

Poster session 1

Chair : Poineau F.

1.P1.

EFFECT OF THE RHENIUM(V) COMPLEX OF 3,4-DIMETHYL-1,2,4-TRIAZOL-5-THIOL ON THE DIACETATE CELLULOSE LIGHT FASTNESS

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The effect of various concentrations of 3,4-dimethyl-1,2,4-triazol-5-thiol and the complex compound [$ReOL_2(OH)Cl_2$] (L-3,4-dimethyl-1,2,4-triazol-5-thiol) light fastness diacetate cellulose (DAS) has been studied. As an example, the table shows the experimental data depending on the tensile strength of the DAS complex concentration and time of UV irradiation.

Table 1. The dependence of the tensile strength of DAS on the concentration of complex composition [$ReOL_2(OH)Cl_2$], where L-3,4-dimethyl-1,2,4-triazol-5-thiol and UV irradiation (λ = 254nm, I =- 0,040 Kal/cm^{2}·min)

The concentration of additives,%	Exposure time, h						
	0	2	5	10	15	20	25
0	10,6	7,2	6,0	4,7	3,0	2,6	1,1
0,01	10,2	9,6	10,2	9,4	8,3	8,0	7,6
0,05	9,5	9,3	9,9	10,8	10,0	9,3	7,0
1	9,8	10,1	9,8	9,2	6,0	5,2	4,0
3	10,1	9,2	8,4	6,8	5,1	4,6	3,0
5	10,5	9,4	8,3	5,9	4,8	4,1	2,9

The table shows that the introduction various amounts of the complex compound [$ReOL_2(OH)Cl_2$] to the DAS has little effect on its initial tensile strength. However, there is a general tendency to the coefficient increasing of light fastness DAS at the introduction into it of various amounts of complex composition [$ReOL_2(OH)Cl_2$]. In addition, the curve of the tensile strength of the UV irradiation time for the modified films at additives concentrations equal to 0.05% it is the maximum. It means, the tensile strength of modified film exceeds its initial tensile strength. Studies have shown that the coordination compounds of rhenium (V) shows great light stabilizing activity against DAS compared to uncoordinated ligand.

1.P2.

OCTAHEDRAL RHENIUM(III) CHALCOCYANOHYDROXO CLUSTER COMPLEXES

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In recent years the compounds containing hexarhenium cluster anions $[\{Re_6(\mu_3\text{-}Q)_8\}L_6]^{n-}$ (Q = S, Se; L = Cl, Br, I) have been intensively investigated. The rapid development of rhenium cluster chemistry has led to the discovery of substitution reactions of L on other ligands, including organic. Polymeric compound $Re_6Q_8Br_2$ prepared from the reaction of Re with the appropriate stoichiometry of Q and Br_2 at 800° C in sealed quartz ampoule. Octahedral rhenium(III) cluster chalcohydroxocomplexes have been prepared from the reaction of polymeric chalcobromide $Re_6Q_8Br_2$ with molten KOH at 220-250° C in air.

In this work we present our data in the synthesis and structural study of compounds with $[Re_6Q_8(CN)_n(OH)_{6-n}]^{4-}$ (n = 2, 4) cluster anions containing two type terminal ligands – OH^- and CN^-. Such clusters are interesting because CN - ligands can form bridging bonds through the nitrogen atom and OH - ligands can be easily replaced by both inorganic ligands and organic molecules and ions. For these complexes we have proposed a simple and convenient method based on the interaction of $K_4[Re_6Q_8(OH)_6]\cdot 8H_2O$ with KCN in aqueous solution. It has been found that when Q = S the cluster anion $[Re_6S_8(CN)_2(OH)_4]^{4-}$ formed; however, if Q = Se the composition $[Re_6Se_8(CN)_4(OH)_2]^{4-}$ was found.

The structure of $[Cu(NH_3)_4]_2[Re_6S_8(CN)_2(OH)_4]\cdot 2H_2O$ cluster complex was determined by single-crystal X-ray diffraction. In addition, the presence of four OH^- groups in the cluster anion was confirmed by the fact that as a result of its interaction with molten 3,5-dimethylpyrazole the molecular complex $[Re_6S_8(CN)_2(3,5\text{-}Me_2PzH)_4]\cdot 2H_2O$ formed.

The structure of $[Re_6Se_8(CN)_4(OH)_2]^{4-}$ cluster anion was confirmed by single-crystal X-ray diffraction for complex *trans*-$[Ni(NH_3)_5]_2[Re_6Se_8(CN)_4(OH)_2]\cdot 6H_2O$ obtained by reaction of $Cs_4[Re_6Se_8(CN)_4(OH)_2]\cdot 2H_2O$ with $NiCl_2\cdot 6H_2O$ in an ammonia solution.

In addition, the compounds were characterized by a set of physical-chemical methods.

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1.P3.

RHENIUM AND TECHNETIUM ORTHOCOMPOUNDS WITH KOSNARITE TYPE STRUCTURE: SYNTHESIS AND INVESTIGATION

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The major problem of inorganic technetium chemistry is its fixation from commercial nuclear wastes in ceramic matrices and also searches of useful properties and possible areas of their application. NZP-ceramics with the kosnarite mineral $KZr_2(PO_4)_3$ (sp. gr. $R\bar{3}c$, Z = 6) structure are well-known matrices for toxic components immobilization of different waste forms including highly radioactive waste. This work represents an attempt to incorporate chemically technetium and rhenium in the cationic and anionic crystallographic positions of kosnarite-type structure obtaining $AM^{4+}_2(PO_4)_3$ (A = Li, Na, K, Cs) and $K_{1/3}Zr_2(AsO_4)_{8/3}(M^{7+}O_4)_{1/3}$ (M = Tc, Re) compounds.

The phosphates $AM^{4+}_2(PO_4)_3$ were prepared by the mixing of MO_2 oxides with phosphoric acid and ACl, drying and regrinding of mixtures and their thermal treating in sealed glass ampoules at 500°C. $K_{1/3}Zr_2(AsO_4)_{8/3}(M^{7+}O_4)_{1/3}$ samples were synthesized by the mixing of amorphous $Zr_3(AsO_4)_4$ and KMO_4 and sintering mixtures at 700°C. Compounds were characterized using XRD, IR-spectroscopy and microprobe analysis.

The phosphates $ARe^{4+}_2(PO_4)_3$ with A = Na, K and arsenates were phase-pure NZP-samples. $ATc^{4+}_2(PO_4)_3$ samples contained two phases: kosnarite-type phase in larger part and TcP_2O_7. In $AM^{4+}_2(PO_4)_3$ (A = Li, Cs) systems kosnarite-type phosphates forming was not observed. $NaRe_2(PO_4)_3$ (a = 8.4541(1), c = 22.3320(3) Å, R_{wp} = 4.33%), $NaTc_2(PO_4)_3$ (a = 8.4091(1), c = 22.2602(3) Å, R_{wp} = 6.92%), TcP_2O_7 (sp. gr. $P\bar{a}3$, a = 7.8643(2) Å, R_{wp} = 6.92%) crystal structures were determined by the Rietveld refinement. In the three-dimensional structures $[(Tc,Re)_2(PO_4)_3]^-$ units consisting of two ReO_6- or TcO_6-octahedra and three PO_4-tetrahedra are linked to form the ribbons parallel to the c axis (Fig.). These ribbons are linked together by PO_4-tetrahedra. The framework cavities are populated by Na^+ ions. It was shown that Tc^{4+} and Re^{4+} enter the Zr-type octahedral positions and Tc^{7+}, Re^{7+} occupy the P-type ones of the kosnarite-type structure framework.

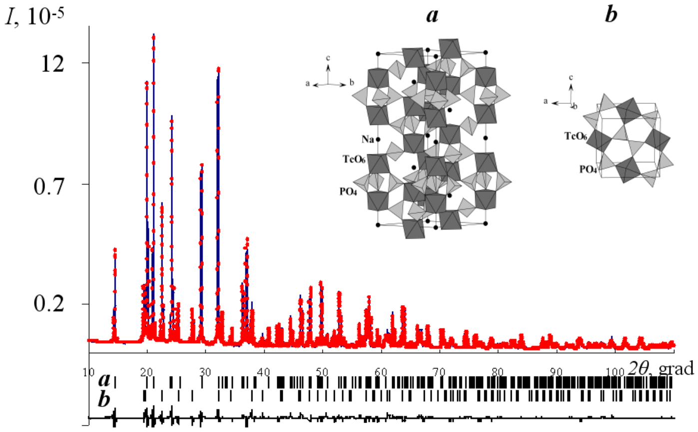

Fig. Experimental (solid line) and calculated (asterisks) X-ray diffraction pattern of the synthesized sample of $NaTc_2(PO_4)_3$. Crystal structure and the positions of the reflections in the calculated X-ray diffraction pattern: (a) $NaTc_2(PO_4)_3$ and (b) TcP_2O_7.

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1.P4.

DEPTH DISTRIBUTION OF D-IONS WITH 25 KEV ENERGY IMPLANTED INTO PURE Mn, Tc* AND Re FOILS UP TO HIGH FLUENCIES (1÷2)×10^{18} D^+/cm^2, MEASURED BY ERD METHOD

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Metal hydrides are very useful systems for hydrogen, deuterium and tritium storage and other application. As well known rhenium can create very unusual transition metal hydride as $\mathrm{Re}\,H_9^{2-}$ [1] (one example of such composition is $K_2\,\mathrm{Re}\,H_9$ [1]).

Also it is known that behavior of all metals of VBth group as V, Nb and Ta is similar concerning its properties as metal hydrides and hydrogen/deuterium diffusion coefficients. The results of depth distributions of deuterium ions implanted into some pure metals were published at [2-4].

The purpose of made experiments and presented here results was the study of depth concentrations of deuterium as “mark” atoms at VIIBth group elements. Samples of Mn and Re metallic foils with the sizes 10mm×15mm×(220÷250 μm) were polished and implanted by deuterium ions at room temperature up two fluences $F_1=1{,}0\times10^{18}$ and $F_2=2{,}0\times10^{18}$ D^+/cm^2 homogeneously. Some parameters of D^+ ions with the energy of 25keV in Re, Tc and Mn are presented in Table, together with parameters of these elements with the use of SRIM-2007 [5].

Material	Mass density, g/cm^3	Atomic density, at/cm^3	R_p, Å	N_D/N_M at $F_1=1{,}0\times10^{18}$	N_D/N_M at $F_2=2{,}0\times10^{18}$
Rhenium	20,53	$6{,}639\times10^{22}$	1369±654	~0,73	~1,46
Technetium	11,5	$7{,}139\times10^{22}$	1230±444	~1,25	~2,50
Manganese	7,434	$8{,}148\times10^{22}$	1924±631	~0,81	~1,62

The measured results of D^+ ion concentrations are presented and discussed.

References

1. Transition metals hydrides. Ed. Earl L.Muetterties, N.Y. 1971, 311p.
2. Didyk A.Yu., Kulikauskas V.S., Wiśniewski R. et al.// Elementary Particles and Nuclei-EPAN (letters), 2011 (in press).
3. Didyk A.Yu., Wiśniewski R., Wilczynska T. et al.//Elementary Particles and Nuclei-EPAN (letters), 2011 (in press) and JINR Preprint E-14-2011-8, Dubna, 2011,18 p.
4. Didyk A.Yu., Wiśniewski R., Wilczynska T. et al.//Elementary Particles and Nuclei-EPAN (letters), 2011 (in press) and JINR Preprint E-14-2011-6, Dubna, 2011, 28 p.
5. Ziegler J.F. SRIM-2003, Nucl. Instr. and Meth.in Phys.Res. B219-220 (2004) 1026-1036; http://www.srim.org.

1.P5.

COORDINATION COMPOUNDS OF BIOLOGICALLY ACTIVE N-CONTAINING HETEROCYCLIC LIGANDS

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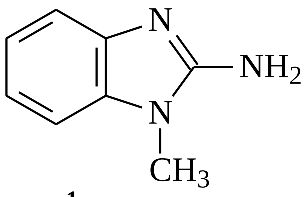
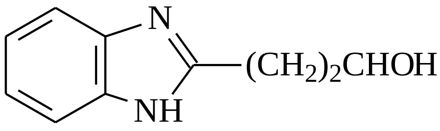
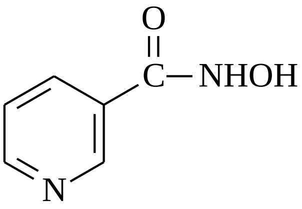
The synthesis of rhenium coordination compounds strongly depends on reaction conditions, metal precursor and ligand nature. The rhenium compounds with some biologically active heterocyclic ligands were prepared and characterized by spectral methods and thermal analysis. The 2-amino-1-methyl-1H-benzimidazole-2 ($\mathbf{L}^1$), 3 (benzimidazole-2-yl) - propanol-1 ($\mathbf{L}^2$), N-hydroxy-3-pyridinecarboxamide ($\mathbf{L}^3$), 7-methoxy-1-methyl- 4,9-dihydro-3H –pyrido [3,4-b] indole ($\mathbf{L}^4$) ligands contained the 5- and 6-membered heterocycles are existed in stable protonated forms in acid solution.



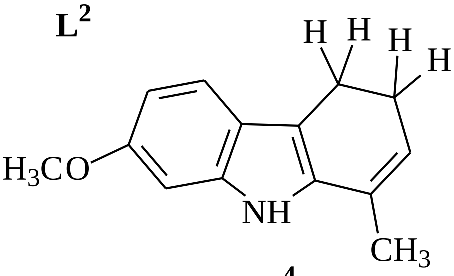
$\mathbf{L}^1$



$\mathbf{L}^2$



$\mathbf{L}^3$



$\mathbf{L}^4$

The reaction of hexachloridorhenate (IV) with L^1-L^4 yields to formation hexachlororhenates (IV) consisted from the complex metaloanions and the protonated molecules of organic ligands as cations.

These salts have poor solubility in water and can exist in the concentrated acid solution that can have application in extraction of rhenium by precipitation.

The synthesized compounds showed the solid-phase dehydrogalogenation and the temperatures of thermal effects depended on structure of organic cations.

The Re(V) precursor $ReOCl_3(PPh_3)_2$ is reduced by PPh_3 in the presence of L^1, giving good yields of rhenium(III) complexes. Good solubility of complexes in organic solvents is used for rhenium extraction.

The composition and structure of complexes were established on the base of elemental and thermal analysis, IR, NMR- data.

1.P6.

CHELATION OF RHENIUM (V) WITH 3-ETHYL-4-METHYL-1,2,4-TRIAZOL-5-THIOL IN 3 MOL/L HCL MEDIUM

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The process of complexation of rhenium (V) in medium 3 mol/l HCl in the temperature range 273-338K potentiometric method using a redox system consisting of 3-ethyl-4-methyl-1,2,4-triazol-5-thiol and its oxidizing forms. Established that in the medium 3 mol/l HCl enhanced the process of replacing the molecule 3-ethyl-4-methyl-1,2,4-triazol-5-thiol which located in the trans position to the oxygen groups with water molecules. As a consequence, there is a decrease in the equilibrium potential of the redox system in titration system with $\bar{n}$<1.The calculated values formation constants by method of Bjerrum, for oxochloro-3-ethyl-4-methyl-1,2,4-triazol-5-thiol of rhenium(V) (table 1) which used to estimate the thermodynamic characteristics of these complexes (table 2).

Table 1. Values pKi oxochloro-3-ethyl-4-methyl-1,2,4-triazol-5-thiol complexes of rhenium (V) in medium 3 mol/l HCl at 273-338K

№	T,K	pK_1	pK_2	pK_3	pK_4	pK_5
1	273	3,61	3,82	3,12	2,69	3,00
2	288	3,59	3,70	2,99	2,54	2,25
3	298	3,01	3,63	2,89	2,41	2,16
4	308	2,83	3,60	2,84	2,36	2,13
5	318	2,80	3,40	2,75	2,18	2,10
6	328	2,66	3,25	2,67	2,26	2,06
7	338	2,50	3,10	2,58	2,21	2,03

Table 2. Thermodynamic functions of the educational process oxochloro-3-ethyl-4-methyl-1,2,4-triazol-5-thiol complexes of rhenium(V) in medium 3 mol/l HCl

№	The compound	ΔH, kJ/mol	ΔG, kJ/mol	**ΔS,** J/mol·K
1	$[ReOL_2Cl_3]$	-21,27	-20,71	-1,88
2	$[ReOL_3Cl_2]^{+}$	-14,18	-16,49	9,26
3	$[ReOL_4Cl]^{2+}$	-11,49	-13,75	7,58
4	$[ReOL_4]^{3+}$	-8,51	-12,32	12,8

From table 2 shows that an increase in the number of coordinated molecules of 3-ethyl-4-methyl-1,2,4-triazol-5-thiol increases the value of ΔG, which is probably due to increased strict hindrance when entering the next molecule 3-ethyl-4-methyl-1,2,4-triazol-5-thiol into the inner sphere complex.

1.P7.

COMPLEXATION IN THE SYSTEM Re (V) – 1-METHYL-2-MERKAPTOIMIDAZOLE – 8 MOL/L HCL

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By potentiometric titration investigated the process of chelation of rhenium (V) with 1-methyl-2-mercaptoimidazole in 8 mol /l HCl at 308 K. A comparison of the pKi for oxochloro-1-methyl-2-mercaptoimidazole complexes of rhenium (V) in the medium 8 mol/l at 308 K with similar values obtained in the medium 7 mol/l HCl shows that increasing the concentration of hydrochloric acid leads to a decrease in the value of all stepwise formation constants.

Reducing the formation constants increase HCl concentration can be explained by an increase in competition between chloride ions and molecules of 1-methyl-2-mercaptoimidazole for a place in the coordination sphere. Formation constants oxochloro-1-methyl-2-mercaptoimidazole complexes of rhenium (V) defined by the curves of education (Table 1) were used to estimate the thermodynamic characteristics of complexation by the temperature coefficient (table 2).

Table 1. Formation constants of oxochloro-1-methyl-2-mercaptoimidazole complexes of rhenium(V) in 8 mol/l HCl at 273-338K

T,K	K_1	K_2	K_3	K_4	K_5
273K	$1,1\cdot10^6$	$7,4\cdot10^4$	$9,3\cdot10^3$	$1,9\cdot10^3$	$3,1\cdot10^2$
288K	$5,6\cdot10^5$	$4,4\cdot10^4$	$6,4\cdot10^3$	$1,3\cdot10^3$	$2,6\cdot10^2$
298K	$3,5\cdot10^5$	$3,6\cdot10^4$	$4,6\cdot10^3$	$1,0\cdot10^3$	$1,6\cdot10^2$
308K	$2,1\cdot10^5$	$2,5\cdot10^4$	$3,2\cdot10^3$	$7,5\cdot10^2$	$1,4\cdot10^2$
318K	$1,1\cdot10^5$	$1,4\cdot10^4$	$2,3\cdot10^3$	$3,5\cdot10^2$	$9\cdot10^1$
328K	$9,1\cdot10^4$	$9,3\cdot10^3$	$1,9\cdot10^3$	$1,1\cdot10^2$	$6\cdot10^1$
338K	$3,3\cdot10^4$	$6,9\cdot10^3$	$8,5\cdot10^2$	$8\cdot10^1$	$3\cdot10^1$

Table 2. The values of thermodynamic functions of the educational process oxochloro-1-methyl-2-mercaptoimidazole complexes of rhenium(V) in the medium 8 mol/l HCl

The compound	ΔH, kJ/mol	ΔG, kJ/mol	**ΔS,** J/mol·K
$[ReOLCl_4]^-$	-39,37	-31,36	-26,89
$[ReOL_2Cl_3]$	-28,79	-25,55	-10,84
$[ReOL_3Cl_2]^+$	-26,82	-20,74	-20,41
$[ReOL_4Cl]^{2+}$	-36,48	-16,45	-67,20
$[ReOL_5]^{3+}$	-26,39	-12,53	-46,55

Using the estimated values of the formation constants were calculated distribution curves of all complex forms, resulting in a system $[ReOCl_5]^{2-}$ - 1-methyl-2-mercaptoimidazole-8mol/l HCl at a temperature of 308K.

1.P8.

SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF TRIPHENYLGUANIDINIUM TETRAOXIDORHENATE HEMIHYDRATE

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Triphenylguanidinium tetraoxidorhenate hemihydrate was synthesized ($[(C_6H_5NH)_3C]ReO_4 \cdot 0.5H_2O$) and studied with X-ray diffraction. Also a number of physical properties were studied. Compound under study crystallizes in the triclinic system (space group P-1, Z = 4, at 293 K: a = 9.8716(17), b = 14.093(2), c = 15.439(3) Å, α = 99.632(9), β = 101.802(9), γ = 95.361(10) deg). The compound has no isostructural analogues. In all structures containing triphenylguanidinium cation, found in the Cambridge Structural Database (CSD version 5.31, August 2010), the position of the phenyl rings corresponds to the conformation that differ from that observed in the known compounds (p.e. [1, 2]). In the ($[(C_6H_5NH)_3C]ReO_4 \cdot 0.5H_2O$) structure phenyl rings in triphenylguanidinium cations occupy the position corresponding to high-symmetry (C_{3h}) conformation that has been never before observed, and this conformation is being realized in both crystallographically independent cations.

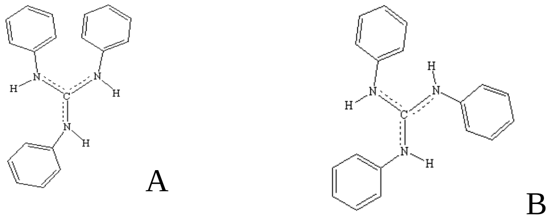

Fig. Cation conformations known from literature (A) and found in this study (B)

Perrhenate anions are in the form of weakly distorted tetrahedra and do not differ from those anions described in the literature. The system of hydrogen bonds is presented by infinite branched chains in the [110] direction, combining the two independent formula units.

The compounds under study is promising for conversion into a metal rhenium. In this connection thermal studies were carried out. The following physical properties were identified: the upper limit of thermal stability of triphenylguanidinium tetraoxidorhenate hemihydrate (393 K) and its enthalpy of dehydration ($\Delta H_{degidr}^{(393\ K)}$ = 10,0(3) kJ/mol), the melting point of anhydrous triphenylguanidinium tetraoxidorhenate (448 K), and its enthalpy of melting ($\Delta H_m^{(448\ K)}$ = 31,0(9) kJ/mol).

If the thermolysis is conducted in an atmosphere of inert gas (argon) and the sample is subjected to recrystallization annealing at a temperature above 1250 K, the solid product is *nanodimentional metal rhenium* dispersed in a matrix of amorphous carbon. Chemical analysis showed the dependence of the ratio of rhenium to carbon in the solid phase of process macrokinetic options (the rate of temperature increase, the rate of inert gas flushing, water content in the system and in the gas phase). If the thermal decomposition is carried out in an atmosphere of a reducing gas (eg. hydrogen), the solid product is almost pure metallic rhenium.

The work was supported by RFBR grant 09-03-00017-a.

1. *Silva, P.S.P., Domingos, S.R., Silva, M.R. et al.* // Acta Crystallogr. E.. V. 64. P. o1082 (2008).
2. *Polyanskaya, T.M., Il’inchik, E.A., Volkov, V.V. et al. // Journal of Structural Chemistry. Vol. 49, No. 3, pp. 494-503, 2008*

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1.P9.

SYNTHESIS AND CRYSTAL STRUCTURE OF $[AnO_2(HMPA)_4](MO_4)_2$ (An = U, Pu; M = Cl, Tc, Re)

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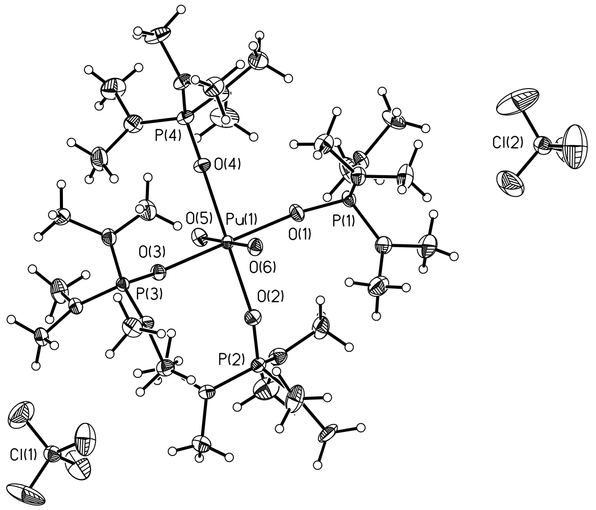
Synthesis was performed by using UO_3 or $PuO_3 \cdot H_2O$ as starting material, which was dissolved in stoichiometric amount of aqueous solution of corresponding acid HMO_4 with concentration less than 0.1 *M*. Obtained solutions were dried at heating up to temperature less than 100°C and solid residue was dissolved in excess of hexamethylphosphortriamide (tris(dimethylamino) phosphine oxide, HMPA). Large elongated crystals were obtained during slow evaporation of reaction mixture in a flow of air.

All the compounds crystallize in an orthorhombic space group *Pbca* and are isostructural with earlier studied uranyl HMPA complexes with periodate [1], perbromate [1] and perclhorate [2] anions. Full structural data were available only for $[UO_2(HMPA)_4](ClO_4)_2$.

Crystal data for $[PuO_2(HMPA)_4](ClO_4)_2$ (Bruker KAPPA APEX II autodiffractometer, MoK_α radiation): $a = 13.9939(4)$, $b = 15.0970(4)$, $c = 45.7102(13)$ Å at 100 K, $Z = 8$, $R1 = 0.0463$.



Molecular structure of $[PuO_2(HMPA)_4](ClO_4)_2$

Interatomic distances in a series of isostructural compounds will be discussed.

References

1. Gusev Yu. K., Lychev A.A., Mashirov L.G., Suglobov D.N. Radiokhimiya (1985) **27**, 412.
2. Nassimbeni L.R., Rodgers A.L. Cryst. Struct. Commun. (1976) **5**, 301.

1.P10.

TRANSFORMATION OF Tc(VII) IN ACIDS: $TcO_3(OH)(H_2O)_2$ and $TcO_3(H_2O)_3^+$ in $HClO_4$ AND POLYMERIC SPECIES IN SOLIDS AND ACETONITRYLE SOLUTIONS

K.E. German [1], A.Ya. Maruk [1], F. Poineau[2], Ph.Weck[2],
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In course of our pertechnic acid investigation the common Tc(VII) – pertechnetate ionic form - was recently shown to decompose in 7-18M concentrated sulfuric acid solutions producing the octahedral $TcO_3(OH)(H_2O)_2$ species [1]. It was worth studying if other acids could make any similar effect. Perchloric acid and nitric acid were chosen for this study. The results differed considerably: in perchnloric acid (Fig.1) the transformation of Tc(VII) was similar to the observed in sulfuric acid [1], while no notable changes in UV and NMR spectra were seen for Tc(VII) in nitric acid. Some similarity of Tc(VII) speciation in sulfuric and perchloric acids was seen by EXAFS, although the Tc(VII) solutions in $HClO_4$ were not that resistant to synchrotron radiation. The solid $HTcO_4$ and its solutions in CH_3CN were analyzed by ^{99}Tc and ^{1}H NMR in a field of 7.04 T. $HTcO_4$ and its deuterated analog $DTcO_4$ were prepared by oxidizing Tc metal in O_2 at 500°C, dissolving Tc_2O_7 in H_2O or D_2O, the solution brought to dryness with $Mg(ClO_4)_2$. The samples were dark red crystalline powders. Elemental analysis gave the ratio H/Tc ≈ 1. The ^{1}H NMR spectrum of a fresh $HTcO_4$ powder at 259 K showed two splitted signals: a strong signal at 5.6 ppm with the width at half-maximum of 400 Hz and a weak signal at ~0 ppm (relative to the external H_2O reference). Decreasing temperature to 120 K resulted in the broadening of the spectrum to 4 kHz; however, the expected fine structure of the spectrum (as the Pake doublet) was not observed. This permits a tentative conclusion that the compound under study is not a crystal hydrate and the lattice hydrogen is highly mobile. The extremely informative is the ^{99}Tc NMR spectrum of red pertechnetic acid powder (Fig.2) The spectral pattern and resonance parameters indicate that technetium has two states in the structure, *none of them corresponding to the* TcO_4^- *ion*.

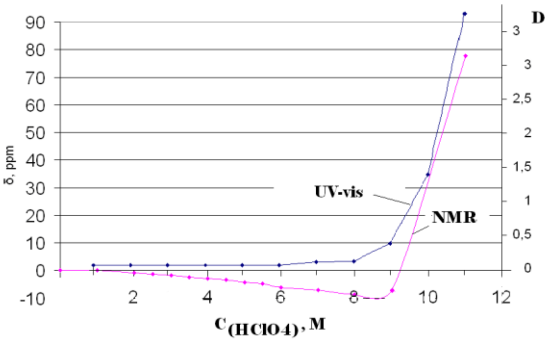

Fig. 1. NMR-Tc^{99} shift (δ, ppm), and UV-vis spectra evolution (D at 350 nm) for Tc(VII) in 1-11M $HClO_4$

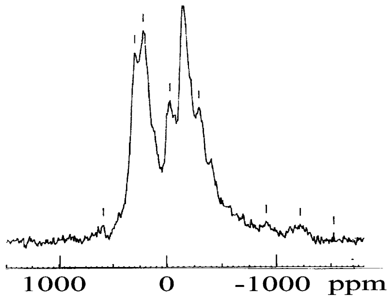

Fig.2. Solid state Tc-99 NMR spectrum of pure red $HTcO_{4\,(solid)}$

The spectrum of a fine powder of red pertechnetic acid (figure) showed two signals at $\delta_1 = +213(5)$ and $\delta_2 = -147(5)$ ppm (referenced to the external standard, a 0.1 M $KTcO_4$ solution; reported in part in [2]; the integrated intensity ratio was $I_1 : I_2 = 2 : 3$. Each of the signals had a multiplet structure due to first-order quadrupole interactions: the quadrupole coupling constants were $C_Q(1) = \sim 0.25(1)$ and $C_Q(2) = 0.43(1)$ MHz and the asymmetry parameter of the ^{99}Tc EFG tensor was $\eta = 0$ in both cases.

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1. F. Poineau, P. Weck, K. German et all. *Dalton Trans*., 2010, 39 (37), pp. 8616.
2. G.Kirakosyan, K.German, V.Tarasov, M. Grigoriev. *3-d Russian-Japanese Seminar on Technetium, Book of Synopses*, (2002) pp. 49-51.

Notes

1.P11.

NEW COMPOUNDS BASED ON THE CLUSTER ANIONS $[Re_4Q_4(CN)_{12}]^{4-}$ (Q=S, Se, Te) AND CATIONS (1,10-phenH)$^{+}$, Nd^{3+}, Er^{3+}

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Coordination polymers of rhenium tetrahedral cluster cyanides where Q is either sulphur, selenium or tellurium, have been intensively investigated in the past decade. The strong covalent Re–C≡N–M interactions have allowed numerous polymeric coordination compounds to be obtained with transition, post-transition metals and lanthanides.

High coordination numbers inherent to the lanthanide(III) ions lead to many structural variations in resulting compounds. The type of structure depends mainly on the number of cyano groups of the cluster anion involved in interaction with lanthanide cations.

In this work we present five new compounds based on the anions $[Re_4Q_4(CN)_{12}]^{4-}$ (Q=S, Se, Te). Three of them adopt ionic structrure, while two others are polymeric. Slow evaporation of acidic water solutions of $K_4[Re_4Q_4(CN)_{12}]$ (Q=S, Se, Te) and ten-fold excess of 1,10-phenanthroline results in ionic compounds of composition $(1,10\text{-phenH})_4[Re_4Q_4(CN)_{12}]\cdot nH_2O$ (Q=S, Se, n=6; Q=Te, n=8). In case these solutions were mixed with $LnCl_3$ (Ln=Nd, Er) without acid, amorphous brown precipitate has dropped. Polymeric compounds $[Ln(OH)(phen)(H_2O)_2][Ln(OH)(phen)(H_2O)_3][Re_4Q_4(CN)_{12}]$ (Q=Se, Te) were crystallized by heating of this precipitates in a sealed glass ampoules in a mother solution.

In the structures of ionic compounds the 1,10-phenanthroline cations, phenH^{+}, are packed in an infinite stakes. Shortest distances between aromatic rings are about 3,3 Å, that is a typical value for π-π stacking interactions. All structural units, phenH^{+} cations, $[Re_4Q_4(CN)_{12}]^{4-}$ anions and crystallization water molecules, are involved in the system of hydrogen bonds.

Structures of polymeric compounds consist of endless chains, in which every cluster anion $[Re_4Q_4(CN)_{12}]^{4-}$ gives three cyano groups for bonding interactions with lanthanide atoms. The full coordination environment of lanthanide atoms also includes phenanthroline molecule, water molecules and two OH^{-} groups. These OH^{-} groups bridge two lanthanide atoms into dimers with the distance among Ln atoms of about 3.7 Å. The polymeric chains are linked together by hydrogen bonds between coordinated water molecules and cyano groups.

All compounds have been characterized by different physico-chemical methods.

1.P12.

MUTUAL SUBSTITUTION OF LIGANDS IN COMPLEX COMPOUNDS OF RHENIUM (V)

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For the chemistry of rhenium(V) focused studies of the processes of natural substitution of the ligands have not previously been carried out. The studies we have established several types of chemical reactions, according to which there are processes of mutual substitution of ligands in rhenium (V). The first type includes the reaction occurring on heating the complexes in the absence of solvent. In the process of heating the outer-sphere complexes **(AmH)2[ReOCl5]** is replacing inner-outer-sphere ligands. In reactions of this type of proton transfer occurs on the inner-sphere chloride ligand. The second type includes reactions that occur in solution in accordance with the equation

$$\mathbf{H_2[ReOX_5] + nL \leftrightarrow [ReOG(5\text{-}n)L_n]^{-2+n} + 2HX}.$$

The third type of reactions are those reactions in which one replaces the other acidic ligands and liabilities acidic ligands being in trans position to it, then the organic ligand interacts with the formed complex. The fourth type of reaction includes the reaction of solvated. By the fifth type of reaction are reactions occurring in the interaction of ammonia with solid complexes of rhenium (V), ie at the interface:

a) Reactions which occur only with the displacement of halide ions from the inner sphere complexes;

b) The dimerization reaction of monomeric complexes with the replacement of halide ligands;

d) Reaction, which resulted in the coordinated thiocyanate ions become thioamides groups.

By the sixth type of reaction include the processes of interaction of acids with the ammino complexes of rhenium (V). By the seventh type of reaction include the reaction of the parent compounds such as H2[ReOX5] c two substituted complexes of [ReOL2X3], which resulted in the formation of mono substituted complexes of rhenium (V).

On the basis of studies on the process of mutual substitution of ligands in complex compounds of rhenium (V) was proposed following a number of mutual substitution of the ligands:

L ≈ P $(Ph)_3$> SCN> Cl-, Br-> S> H_2O, where L-thioamide connection, **S-DMF, DMSO, Py, Xin, CH_3CN.**

1.P13.

RHENIUM AND ITS POSITION IN THE PERIODIC TABLE

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The discovery of rhenium by Ida Noddack *et al.* in 1925 was a result of an intensive study of the Periodic Table.

The search for the missing elements which were predicted by Dimitri Mendeleev between 1869 and 1891 was intensive especially when the prediction came true after the discovery of gallium, scandium, and germanium between 1875 and 1886.

Ida Noddack's scientific career centered around her intensive study of the Periodic Table. This resulted in two major discoveries.

The first was based on her realization that the missing element dvi-manganese should have properties similar to its neighbours in the horizontal period of the Periodic Table and not to members of the vertical group of which manganese was the only member known. In this way she was able to look for and discover the metal rhenium.

Thus Noddack introduced the concept of a horizontal similarity for the elements titanium to manganese while the vertical similarities still existed but only for Zr – Hf, Nb – Ta, and Mo – W below this horizontal group.

The second discovery was a daring hypothesis that the so-called element 93, a trans-uranium element that was supposedly formed by bombarding uranium (element 92) by neutrons, and was put under rhenium in the manganese group (in the old Periodic Table) was not correct. Instead, she suggested that the uranium atom might have split into two fragments - a phenomenon that later became known as fission.

1.P14.

MACROCYCLIC RECEPTORS FOR PERTECHNETATE AND PERRHENATE ANIONS

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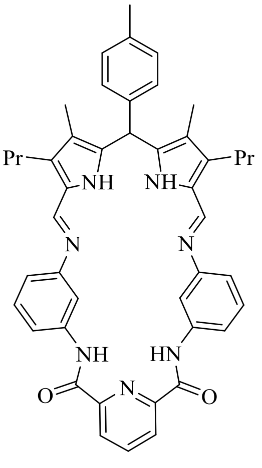
The design and synthesis of receptors capable of selective recognition of **MO_4^- (M = Re, ^{99}Tc)** are of great interest because they can greatly benefit the development of efficient extractants, sensors and materials for these anions as well as new approaches for labeling of organic compounds without any reduction step of **Re(VII)** and **Tc(VII).** Neutral receptors are known to be promising in the sense of high binding selectivity for target anions.

The neutral macrocyclic dipyrromethane based hosts capable of **MO_4^- (M = Re, ^{99}Tc)** recognition were synthesized. When in protonated form, **1** binds perrhenate with strong **H**-bonds from pyrrole and imine **NH**'s, weak – from amide **NH**'s and benzene **CH**'s, according to the X-ray analysis. The **H**-bond network of **2** is similar to that of $[\mathbf{1H_2}]^{2+}$, and the coordination mode of **2** with **ReO_4^-** was found to be equal, according to the DFT studies. The nonprotonated form of **1** binds to **ReO_4^-** using only pyrrole **NH**'s, amide **NH**'s and benzene **CH**'s, according to the DFT studies.



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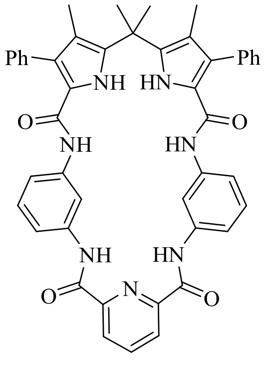

2

Affinities of the receptors towards both **MO_4^- (M = Re, ^{99}Tc)** were acquired by direct UV-vis titrations and towards **$^{99}TcO_4^-$** specifically by reverse **^{99}Tc** NMR titration. Binding constants were found to be one of the largest known to date ($K_{MO4} \approx 10^3$-10^5 M^{-1}). Receptors possess selectivity towards target anions.

We gratefully acknowledge Russian Academy of Sciences program "Chemistry and Physico-Chemistry of Supramolecular Systems and Atomic Clusters".

Session 2.

Tc in the Nuclear Fuel Cycle and in the Environment.

Analytical Chemistry of Tc and Re

Chairmen :

Ph. Moisy, S.N. Kalmykov,
M.Ozawa, V.F. Peretrukhin

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2.1.

HOW TO MANAGE TECHNETIUM (NUCLEAR RARE METAL) AND ACTINIDES, TOWARD FUTURE REPROCESSING SYSTEM PROVIDING NON-PROLIFERATION

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Aiming at utilization of elements/nuclides (*i.e.*, nuclear rare metals including technetium) in spent fuel and minimization of long-term risks (due to mainly actinides) of rad.wastes, a new fuel cycle concept has been progressed during the phase-I period (FY2005-2010).

The strategy is based on a Trinitarian research as such separation, transmutation and utilizaiton, especially relied upon advanced radiochemical separation technologies like ion exchange and electrochemistry in conbinatorial mannner.

A catalytic electrolytic extraction (CEE) method, utilizing under potential deposition (UPD) by Pd_{adatom}/Rh_{adatom}, is advantageous for separation and utilization (and/or stockpile) of light platinum group metal (PGM) and Tc. Their co-deposits showed highly catalytic ability for electrolytic production of hydrogen.

Tertiary pyridine resin (TPR) will not only strongly adsorb (separate) PGM but also generate co-products of U/Pu/Np, Am and Cm, thereby strengthen the non-proliferation character of recycled plutonium.

2.2.

COMBINED SEPARATION OF Pd AND Tc FROM THE RAFFINATES OF THE SPENT NUCLEAR FUEL REPROCESSING

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A small amount of "reactor" Pd, Ru, Rh and Tc metals is needed for investigation of the possibility of production and use of electrodes in hydrogen energetics covered by a composite made of these "reactor" metals. One of the sources of these metals is the raffinates of the first extraction cycle of the spent nuclear fuel (SNF) reprocessing.

The purpose of this study was to investigate the Tc and Pd sorption behaviors, to search the agents for their desorption, to test the determined conditions of the metals separation with use of real SNF reprocessing solutions.

The examples of individual Pd and Tc sorption by anion exchange resin from nitric acid solutions are well-known. However, their combined separation wasn't mentioned earlier.

In this study the strongly basic anionite ВП-1АП, which had been previously applied to separate a "reactor" Pd, was used as a sorbent.

Tc and Pd sorption under static and dynamic conditions were studied. It is shown that the combined sorption should be carried out at a HNO_3 concentration not more than 2 M. When passing through the sorbent at least 50 column volumes (c.v.) of the model solution (C_{HNO3} = 2 M; C_{Pd} = 100 mg / l; C_{Tc} = 100 mg / l) almost 100% of Pd and 30% of Tc were sorbed on the resin.

The conditions for 100% Pd and Tc separation from the feed solution were found.

The desorption with DTPA solution in the wide range of acidity allows to achieve both combined 100% yeild of Pd and Tc in 15 c.v. and individual desorption of these metals (Pd in 8 c.v., Tc in 15 c.v.).

An example of the combined separation of Pd and Tc from the SNF was given in the study. Distribution of Pd and Tc by fractions of experiment solutions, factors of purification of these metals from gamma impurities and obtained dynamic exchange capacities are shown.

2.3.

SPECIATION OF TECHNETIUM IN NON COMPLEXING ACIDIC MEDIA / ANIONS EFFECT

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The speciation of technetium in the non complexing acidic media HTFMS has been performed. Electro-chemical reduction of pertechnetate in HTFMS from 1 M to 6 M leads the formation of tetravalent polymeric species while the dissolution of TcO_4^- in 9 M indicates the formation of a new reduced complex.

Characterization of this specie by spectroscopic techniques (EXAFS, UV-Visible) has been performed and results will be presented.

Notes

2.4.

THE ELABORATION OF TECHNOLOGY BASES FOR THE ARTIFICIAL STABLE RUTHENIUM PREPARATION FROM TECHNETIUM-99 TRANSMUTATION PRODUCTS

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The bases of technology have been elaborated for the artificial stable ruthenium preparation from the ^{99}Tc transmutation products. The process includes the following steps: the isolation technetium from spent fuel with additional purification of Tc from actinides, the manufacture of technetium targets, their irradiation with high flux of thermal and epithermal neutrons, the exposure of irradiated targets for the short-lived radionuclides decay, chemical separation of ruthenium from technetium and the exposure of prepared ruthenium up to the fission product ^{106}Ru decay.

The metallic targets have been prepared from technetium which contained $\sim 5 \cdot 10^{-8}$ g actinide impurity per gram Tc. The irradiation of the targets has been carried out with thermal neutron flux $6.8 \cdot 10^{14} – 1.14 \cdot 10^{15}$ $cm^{-2} \cdot s^{-1}$ (epithermal neutrons part is 0.06 – 0.1) during 73 – 425 eff. days and burn up has been achieved 19 – 70% (for 3 different groups of Tc targets).

The dissolution of irradiated targets has been carried out in KOH solution in presence of excess of KIO_3 at 70 – 80°C. Volatilization of RuO_4 from $KTcO_4$ solution and other chemical methods have been applied for the isolation of ruthenium.

Total Ru separation factor has been achieved 10^{12}. The exposure of prepared artificial ruthenium during 10 years needed for the diminution of the ^{106}Ru, ^{106}Rh radioactivity of the metal up to the level required for its any application.

About 5 grams of stable ruthenium have been prepared in this work from 10 g of the technetium. This artificial ruthenium was nearly monoisotopic and contained 97.5 – 99.7% ^{100}Ru depending on ^{99}Tc burn-up. The achieved ^{99}Tc transmutation rate and targets burn-up value are records for today and may be increased by the rise of the epithermal component in the neutron flux.

2.5.

TECHNETIUM CATALYTIC EFFECT AND SPECIATION IN NITRIC ACID SOLUTIONS IN PRESENCE OF Np(V), Th(IV) and Zr(IV) AND REDUCING NITROGEN DERIVATIVES

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The technetium species develop the catalytic effect being of high importance for the reprocessing of the spent nuclear fuel [1]. One would just mark that the large-scale reprocessing in UK was delayed by 5 years in the start up stage due to the harmful Tc-effect [2]. An important item of Tc separation from the reprocessing solutions is the mutual effect of a number of redox stable (Zr) and redox sensitive elements (especially Tc, see p.e. [3-6] and Np) present in these wastes. Recently we have demonstrated the catalytic effect of Tc(VII and V) on the reduction of Np(V) to Np(IV) with hydrazine in nitric acid resulted in Np(V) disappearance and in the accumulation of Np(IV) different species, so that the free ionic form of Np(IV) accumulated in lower concentration, compared to decrease in Np(V) concentration [7-8]. This fact indicated the possible Np(IV) complex formation with some of the reaction product. The Tc(VII) participation in this reduction process was anticipated taking into account the common catalytic properties of technetium, while the interaction of An(IV) with Tc reduced species was difficult to predict and needed some additional experimental study that was demonstrated in [9-10] with simulated waste solutions with Th(IV) taken for typical example of An(IV). The existence of such species was difficult to predict based only on the accepted thermodynamic data [3], although the possibility of deep Tc reduction even to Tc(II) species in nitric acid was already demonstrated in [12], and the importance of hydrolyses and polymerization in aqueous solutions of different acids were shown in [8-11]. Anyhow such questions as the influence of the Tc valence state in the catalytic action on Np behavior remained unclear as only Tc(V) and Tc(VII) species were tested in [7-10] and the corresponding study of the Tc(IV) species is being undertaken in this report. Because of the possible interference of the Tc(V and IV) and Np(V,IV) optical spectra, the procedure of spectra analyses elaborated in the previous report was used for the optical separation of individual Tc and Np species before the kinetic treatment of the experimental data aiming the determination of the reaction orders in Np(V), Tc(IV), $N_2H_5^+$, H^+.

The experimental procedures was based on the conventional spectrophotometric methods for the kinetic measurements of Np(V) and Tc(IV). For the determination of Np(V) concentrations the NIR absorption peak at 980 nm was used. The constant initial concentrations of Np(V) and $N_2H_5NO_3$ were used in all the experiments, while C_0(TcIV) varied as $(0.24 – 1.2)*10^{-3}$ mol/l. The temperature interval from 25 to 55°C was set-up in different sets. Tc(IV) concentrations were measured at the 400 nm (after the Np(IV) spectra contribution corrections), while Tc(V) was determined according to the development of the shoulder at 470-500 nm with similar corrections for Np and Tc(IV).

Earlier it was demonstrated [8-9] that when Tc(VII) is added to the Np(V) solution containing hydrazine, the induction period is needed for the start up of Np(V) catalytic reduction. In case when Tc(V) was added no induction stage was observed [8]. We studied the kinetics of Np(V) reduction catalyzed with Tc(IV) ions in aqueous solutions of nitrogen compounds was studied. We found that the previously prepared Tc(IV) being added to Np(V) in 1.5- 3.5 M nitric acid – hydrazine nitrate solutions causes the Np(V) catalytic reduction with hydrazinium to Np(IV) without any induction period. The Np(V) reduction with $N_2H_5^+$ is catalyzed by Tc(IV) ions and follows the kinetics being zero order in [Np(V)], 1-st order in [Tc(IV)], 2-nd order in [HNO_3], with $\Delta E_{activ} = 41.9(3)$ J/M. When the reduction of Np(V) is complete, the latter is stable for 0,5-1,5 hours depending on the temperature of the solution. The further reduction of Tc (probably to Tc(III) causes the hydrazine catalytic decomposition and then – partial back oxidation of Np(IV). The kinetic mechanism of Np(V) reduction catalyzed with Tc(IV) ions is discussed.

Also technetium reduction by hydrazine nitrate and hydroxylamine chloride in the presence of Th(IV) and Zr(IV) was investigated. The conditions providing intermediate Tc species stabilization in presence of four valence actinides were found giving an evidence that at least three reduced Tc species (Tc(IV), TcX and Tc(V)) are appearing and disappearing in the course of the consequent reactions. The final complex of Tc with Th (Zr) at 470 nm by hydrazine and at 500 nm by hydroxylamine reduction has the ratio of two to one accordingly and is stable for several days. The reaction of Tc(V) complex formation in presence of Th(IV) can be turned back to Tc(IV) formation when new portion of hydrazine is added.

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References

1. Campbell D.O., Burch W.D. The chemistry of fuel reprocessing: present practices, future trends. J. Radioanal. Nucl. Chem., Art., 1990, v.142, No. 1, p.303 - 320.
2. Phillips C. Uranium - plutonium partiotionning by pulsed column in the first cycle of the three cycle thermal oxide reprocessing plant. Waste'92, Proceedings (1992) 1041- 1045.
3. J. A. Rard, M. H. Rand, G. Anderegg, H.Wanner. Chemical thermodynamics 3. Chemical Thermodynamics of Technetium. Edited by M.C.A. Sandino and E. Östhols, OECD NEA - Data Bank. 1999, Elsevier Pbl.
4. V.S.Koltunov, R.J.Taylor, T.V.Gomonova, O.A.Savilova, G.I.Zhuravleva, I.S.Denniss // Radiochim. Acta 88, 425-430 (2000).
5. N.Boukis, B.Kannellakopulos // Radiochimica Acta 49. 141-145, (1990).
6. Zelvert A.: Rapport CEA-R-5443, (1988).
7. D.N.Tumanova, K. E. German, Ph. Moisy, M. Lecomte, V. F. Peretrukhin. In: Abstracts of the 6-th International Symposium on Technetium and Rhenium – Sciences and Utilization. NMMU - Port Elizabeth, 7-10 October 2008, p.46.
8. K. E. German, Ya. A. Obruchnikova, Ph. Moisy , M. Lecomte, V. F. Peretrukhin. *In: 6-th International Symposium on Technetium and Rhenium.* NMMU-Port Elizabeth, 7-10 October 2008, p.29.
9. K.E.German. *The Fourth Adv.-ORIENT Cycle Seminar. "New Resource Strategy Pioneered by Advanced Nuclear Science and Technology". Rokkasho-mura, Aomori, Japan, July 30, 2010. Abstracts and presentations,* 2010 - Rokkasho-mura Nuclear Research Centre. Pp.1- 6.
10. K. German, A. Melentiev, V. Misharin et all. *Nucl. Med. Biol.* V. 37, No 6, (2010), P. 678.
11. K. German, A. Melentiev, V. Misharin et all. Tc-DTPA sediments formed in Tc-hydrazine-DTPA-nitric acid solutions. *Proceedings of the International Symposium on Technetium* and Other Radiometals in Chemistry and Medicine – Forum Brixen – Bressanone Congress Center (Italy) September 8-11, (2010). pp. 47 - 50.
12. C. S. Gong, W. W. Lukens, F. Poineau, K. R. Czerwinski. *Inorg. Chem.*, (2008), 47 (15), pp. 6674–6680.

2.6.

COMPOSITION AND CATALYTIC PROPERTIES OF TECHNETIUM-BASED SEDIMENTS AND INTERPHASE SUBSTANCES FOUND IN THE URANIUM-PLUTONIUM SEPARATION STAGE OF THE PUREX PROCESS

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In the process of extraction reprocessing of VVER-440 and BN-600 spent nuclear fuel (SNF) on the RT-1 facility a sedimentation problem was encountered on the stage of uranium-plutonium reductive separation with sediments formed at the interphase boundaries and at the bottom of the extraction apparatus.

Probes of these sediments and interphase substances (IFSs) were obtained and analyzed. It was found that the inorganic part of sediments and IFSs is mainly composed of such fission products, as ^{99}Tc and ^{107}Pd. The content of these elements in samples was found to be up to 30 g/l and 6g/l respectively. The sediments and IFSs concentrate the absorbed beta- and gamma-active nuclides (^{106}Ru и ^{106}Rh, ^{125}Sb и ^{125m}Te, ^{137}Cs и ^{137m}Ba, and some others) with the accumulation factors as high, as 10^3.

Due to the high Tc and Pd content (both elements being well known for their catalytic activity), the study was carried out for catalytic reactions of oxidation of the reducing agents used in the extraction reprocessing of SNF in presence of simulated and really isolated sediments and IFSs.

The frequency factors for the oxidation of reducing agents were obtained at variable temperatures and HNO_3 content. It was found that the catalytically active components may be leached from the sediments and the IFSs into the solution adding the homogeneous factor to the heterogeneous catalytic process.

Along with the rapid changes of temperature or HNO_3 content, the Tc (Pd) transfer to liquid phase becomes significantly more intensive, although the complete dissolution of sediments does not occur at the extraction process operating conditions. The studied catalytic processes became more active upon heating as well. The rise of temperature from 40 to 60 ^{o}C increased the reaction rate constants by a factor of ten.

The described effects occurring in presence of sediments and IFSs may be one of the possible reasons for the malfunctioning of the extraction process characterized by rapid destruction of reducing agents and the rise of temperature.

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2.7. Plenary lecture

INTERACTION OF MICROORGANISMS AND RADIONUCLIDES

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Pollution of environment by toxic materials such as heavy metals and radionuclides is an important problem facing the postindustrial society. The radioactive wastes were intensively produced in course of fission materials production and application during 50 past years and it will being increasingly generated by various plants of nuclear fuel cycle. Safe treatment of the wastes of this type is an imperative to further nuclear cycle development. The laboratory studies show that during underground storage of waste 95-97% of radionuclides (Sr, Ru, Cs, Ce) are immobilized. Remained solution contains long-lived elements (Tc, Pu, Np, U), which can migrate with pore water and therefore radioactive contaminated area enlarged. Microbial metal reduction results in the precipitation of a low valence, reduced form of the element, and have therefore been proposed as a strategy to treat contaminated waters.

There are many papers about using of biotechnological techniques for purification from uranium, strontium, cesium and iodine. In this study we paid attention to radionuclides of higher importance with respect to long-term radioactive waste control. Technetium-99, neptunium-237, plutonium-239, curium-244 are long-lived and mobile radionuclides and have high potential for biological uptake. The cases of penetration of those radionuclides to the environment were reported. However, published data on biological and physico-chemical mechanisms of actinide sorption by lake sediments and on kinetics of these processes are incomplete. We chose two lakes with different trophic types to test behavior of radionuclides (^{99}Tc, ^{237}Np, ^{239}Pu, ^{244}Cm) in case of its penetration of water reservoirs as a result of catastrophes. Several low-valence forms of radionuclides are possible and it is important, therefore, to identify the products accurately so that the long-term stability and environmental mobility of microbially reduced species can be predicted.

Two typical fresh water lakes were chosen according to different biological productivity: highly productive eutrophic lake (Beloye Kosino, Moscow region, Russia) and a dystrophic lake (Shatura region, Russia) where organic matters present as humic and fulvic acids. The initial concentrations of radionuclides were 10^{-5} - 10^{-4} M. Our laboratory model experiments indicate that uptake of radionuclides reached 98-99% during one summer season and biological processes play the significant role [1,2]. Our results shown that uptake of actinides from water should be considered as two-phase process – physico-chemical and biological phases [2]. First phase was very fast (during 1-2 hours) and could be described as a sorption of actinides on the sediment particles. Neptunium sorption had fast uptake during first hour when 60% and 50% of initial input was sorbed by sediment of eutrophic and dystrophic lakes, and a slow bioaccumulation period when neptunium uptake was completed in 1 and 2 months for eutrophic and dystrophic lakes, respectively [3, 4]. In case of plutonium and curium, the first phase takes in 1 hour also, but sorption of radionuclides reached only 34-38% [2, 5]. The Tc uptake rate was almost constant, the time of half-uptake being 0.5-0.6 and 1 month for eutrophic and dystrophic lakes [2, 6-9]. The complete Tc accumulation by sediment took place after 1 and 2,5 months, respectively. Temperature dependence of radionuclides uptake was investigated also [3, 10]. Temperature dependence of Tc uptake rate was not very high, the uptake halftimes increasing from 16 to only 18 days with the temperature decrease from 15 ^{o}C to 6 ^{o}C. The microflora of lake played important role in the accumulation and reduction of some radionuclides [6, 11]. The additional donor or acceptor of electron can change uptake rate of Tc. Lactate or cut reed as the electron donors increase technetium bioaccumulation rate in case of sediments from eutrophic lake. The time of half-uptake take place in 10 days instead of 20. Addition of sulfate or nitrate decreases the rate of Tc accumulation due to competition relationships between SO_4^{2-} or NO_3^- and TcO_4^- - the time of half-uptake of technetium prolong up to 30 days instead of 20 days [3, 10]. In case of dystrophic lake organic matter decompose very slowly and not complete and form a lot of humic and fulvic acids. These acids have very high molecular weight, complex structure and can made complex with many elements, with heavy metals in particularly. Our experiments show that being added to water phase of dystrophic lake finally about 3% of Tc and 30% Np were bounded in water soluble complexes with natural humic acids precipitating on acidifying water to pH 1 (concentration of humic acids was up to 0,5%) [10, 12]. In the eutrophic lake water, the humic acid concentration was below 0,005% and the fraction of Np bound to them was no more than 1% [10, 13, 14]. Also, the sediments of eutrophic lake have a great sorption capacity. During long-term experiment (6 months) technetium-99 was added three times and every time sorption was completes (99%) [10,15]. This fact is very important for development effective, environmentally safe methods of purification of radioactive solutions. The desorption of technetium was carried out with H_2O, 1M HCl, 1M $NaClO_4$ or 15% H_2O_2. The desorption factors were 0.05, 0.05, 0.08 and more 0.99 thus indicating the technetium was sorbed by sediments as a reduced forms, which were generated by microorganisms. Thus, bacterial reduction of Tc is the main mechanism controlling the Tc transport to bottom sediments.

Microbial metal reduction results in the precipitation of a low valence, reduced, form of the element, and has therefore been proposed as a strategy to treat contaminated waters [16]. Sulfate-reducing bacteria Desulfovibrio desulfuricans [17], metal-reducing bacteria Shewanella putrefaciens [18] and Geobacter sulfurreducens [19], Escherichia coli [20] and thermophilic archaea and bacteria Thermoterrabacterium ferrireducens, Tepidibacter thalassicus [21] were found to be capable of reducing Tc(VII) at neutral pH. In this case very soluble pertechnetate was reduced to insoluble TcO_2 via direct enzymatic reaction. Under acidic conditions, Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans can also reduce Tc(VII) to low-valency forms with formation of brown colloid [22]. Some haloalkaliphilic bacteria (identified as Halomonas) isolated from soda lakes and soils were capable to reduce Tc(VII) under the alkaline anaerobic conditions [23]. Several reduced species, including Tc(V), Tc(IV) and Tc(III) were identified under such conditions. The results of extraction clearly show that after 4 days of incubation under anaerobic alkaline conditions, an average of 76% of the 0.25 mM of pertechnetate had been reduced by haloalkaliphilic cultures to Tc (IV) and Tc(V) species. Within the pH range from 8 to 11, the anionic complex $Tc^{IV}O(OH)_3(CO_3)$- is the dominant one.

The results of this research may be important for the fate and transport of technetium in the environment. Haloalkalophilic heterotrophic microorganisms could provide a perspective for the biotechnological treatment of low level radioactive waste. Our isolates were capable of using formate, acetate, lactate, methanol and ethanol as electron donors and pertechnetate, nitrate, selenite, selenate, tellurite, chromate and elemental sulfur as electron acceptors [23]. This wide variety of substrates and resistance to high concentration of technetium make such bacteria attractive for biotechnological applications. However, the formation of highly electronegative soluble Tc(IV) carbonate complexes indicates that it may be necessary to reassess current concepts of Tc transport in anaerobic, carbonate enriched ground waters, where Tc mobility has been considered to be controlled by the low solubility of TcO_2.

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References.

1. German K.E., Khizhnyak T.V., Lyalikova N.N., Peretrukhin V.F. In: Russian Radiochemical Conference, Dubna, Abstracts, p.144 (1994).
2. Peretroukhin V.F., Khizhnyak T.V., Lyalikova N.N., German K.E. Radiochemistry (Russ). 38/5: 471-475 (1996).
3. Khijniak T.V., German K.E., Firsova E.V., Peretrukhin V.F., Medvedeva-Lyalikova N.N. Ecological Chemistry (in Russ). 10/4: 233-237 (2001).
4. Peretroukhin V.F., German K.E., Firsova E.V., Khijnyak T.V., Lyalikova N. N. Oral presentation at the 2-d Russian conference on radiochemistry. Dimitrovgrad, 27-31 October 1997. Extended abstracts, p.144-145.
5. Firsova E.V., German K.E., Peretroukhin V.F., Khijniak T.V. Fourth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe. 1998. Abstracts, p.160.
6. German K.E., Khizhnyak T.V., Lyalikova N.N., Peretrukhin V.F. 5-th Annual Conference of the Nuclear Society, Moscow. Nuclear energy and Industry. Obninsk, 27 June - 1 July 1994, p. 498 - 499.
7. Khizhnyak T.V., German K.E., Lyalikova N.N., Peretrukhin V.F. In: Abstracts 5-th Intern. Conf. on Chemistry and migration behaviour of actinides and fission products in the geosphere. MIGRATION'95. Saint-Malo, France, Sept. 10 - 15, 1995, p.107 - 108.
8. Khizhnyak T.V., Lyalikova N.N, German K.E., Peretroukhin V.F. Papers of Russian - Japanese Seminar on Technetium, July 1-5, 1996. p.38 - 39.
9. German K.E., Khijnyak T.V., Peretroukhin V.F., German E.S., Firsova E.V. The second Japanese-Russian Seminar on Technetium. Shizuoka, Japan, Nov. 29 - Dec.2. 1999. Abstracts, pp.50-51.
10. German K.E., Firsova E.V., Peretroukhin V.F., Khijnyak T.V., Simonoff M. Radiochemistry (Russ). 45/3: 229-235 (2003).
11. German K.E., Khizhnyak T.V., Lyalikova N.N., Peretrukhin V.F. Journ. of Nuclear Biology and Medicine. 38/3: 406 (1994).
12. German E., Firsova E., Khijnyak T., Lyalikova N., German K., Peretroukhin V. Journees des actinides, 1999, 15-17 april , Luso, Portugal, Abstracts, pp.39-40.
13. Khijnyak T.V., German K.E., Firsova E.V., Medvedeva-Lyalikova N.N. Migration’99, Abstracts, Seventh International Conference on the Chemistry and Migration Behavior of Actinides and fission Products in the Geosphere. Incline Village, Lake Tahoe, Nevada, USA, September 26- October 1, 1999, p.48.
14. German K.E., Firsova E.V., Peretrukhin V.F., Khijnyak T.V. Simonoff M. Extended synopses of reports. The 3-rd Russian-Japanese Seminar on Technetium, (Dubna, June 23 – July 1). – Dubna: JINR, 2002 – ISBN 5-85165-706-5. P. 14-16.
15. Barinova F.A., Bugaeva N.G., German K.E., Peretrukhin V.F. International Symposium on Technetium - Science and Utilization - Oarai, Japan, May 24 - 27, 2005.
16. Lloyd J.R. FEMS Microbiol. Rev. 27: 411-425 (2003)
17. Lloyd J.R., Ridley j., Khizniak T.V., Lyalikova N.N., Macaskie L.E. Appl. Environ. Microbiol. 65: 26-91-2696 (1999)
18. Wildung, R.E., Gorby, Y.A., Krupka, K.M., Hess, N.J., Li, S.W., Plymale, A.E., McKinley, J.P., Fredrickson, J.K. Appl. Environ. Microbiol. 66: 2451–2460 (2000)
19. Lloyd J.R., Sole V.A., et all. // Appl. Environ. Microbiol. 66/9: 3743-3749 (2000).
20. Lloyd, J.R., Cole, J.A., Macaskie, L.E.. J. of Bacteriology 179: 2014–2021 (1997)
21. Chernyh N.A., Gavrilov S.N., Sorokin V.V., German K.E., Sergeant C., Simonoff M., Robb F., Slobodkin A.I. Appl. Microbiol. Biotechnol.. 76/2: 467 – 472 (2007).
22. Medvedeva-Lyalikova N.N., Khijniak T.V. Mikrobiologiya, 65 (4): 533-539 (1996).
23. Khijniak T.V., Medvedeva-Lyalikova N.N., Simonoff M. FEMS Microbiol. Ecol. 44/1: 109-115 (2003).

2.8.

LAYERED HYDRAZINIUM TITANATE: REDUCTIVE ADSORBENT FOR IRREVERSIBLE IMMOBILIZATION OF TECHNETIUM

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Layered Hydrazinium Titanate - 9 Å (LHT-9) is a new nanohybrid compound related to a family of lepidocrocite-type layered titanates. Its chemical composition corresponds to the formula $(N_2H_5)_{0.5}Ti_{1.87}O_4 \cdot aq$. LHT-9 combines redox functionality of hydrazine, ion exchange properties of layered titanate and high specific surface area due to its quasi two-dimensional crystallites [1]. Superposition of reductive and ion exchange properties allows using LHT-9 as effective adsorbent capable of uptake of more than 50 elements of the Periodic system, with adsorption loadings approaching 20 wt. %. Ions of completely diverse chemical behavior, like pertechnetate anion TcO_4^- and cationic cesium Cs^+ can be simultaneously adsorbed by LHT-9 involving reduction and ion exchange mechanisms, respectively. Herein we describe the adsorption properties of LHT-9 relative to the problem of ^{99}Tc fixation [2]. Reductive precipitation is considered as the best way for fixation of Tc [3]. The proposed reductants (Fe(0), Fe(II), $NaBH_4$, sulfides, bioreduction), however, possess obvious drawbacks including (1) rather narrow pH working range and (2) inapplicability of adsorption products for long-time disposal of Tc. Hydrazine is well known reductant for pertechnetate, but the reduction products have strong tendency to retain unprecipitated in the parent solution [3]. LHT-9 overcomes this problem by irreversible *in-situ* adsorbtion of Tc(IV) onto nanocrystalline layered titanium dioxide matrix. Having rather wide working range from pH 1 to 10, LHT-9 is capable of Tc uptake from acid ($HTcO_4$), neutral ($KTcO_4$) and alkaline ($KTcO_4$ + KOH) solutions, with uptake capacities up to 10 wt. %. It is even more important that adsorption products are therefore ready-to-use precursors for inexpensive one-pot preparation of stable Synroc-type titanate ceramics. Tc was found to incorporate into rutile $(Ti,Tc)O_2$, hollandite $K(Ti,Tc)_8O_{16}$ and metallic Tc phases, the latter being considered as the most durable form for long-time Tc disposal [4]. Besides of removal of Tc from concentrated HLW solutions, LHT-9 can be used as effective additive into cementous waste forms allowing long-time disposal of Tc from low-level nuclear wastes containing trace amounts of pertechnetate ion.

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References.

1. S. N. Britvin, S. V. Krivovichev, W. Depmeier, O. I. Siidra, D. V. Spiridonova, V. V. Gurzhiy, A. A. Zolotarev, *Patent Application* PCT/EP2010/001864 (2010).
2. N. N. Popova, I. G. Tananaev, S. I. Rovnyi, B. F. Myasoedov, *Russ. Chem Rev.* **72**: 101-121 (2003).
3. B. Gorski, H. Koch, *J. Inorg. Nucl. Chem.* **31**: 3565-3571 (1969).
4. N. P. Laverov, S. V. Yudintsev, B. I. Omel’yanenko, *Geology of Ore Deposits* **51**: 259-274 (2009).

2.9.

Re AND Tc IN CERMET WASTE FORMS

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Method of producing matrices for joint immobilization of actinides and Tc by self-sustaining high-temperature synthesis, SHS has been suggested. More than 20 samples consisting of REE-Al-garnet (a target phase for actinides) and alloy (host for Tc) were obtained and studied. At the first stage radionuclides were replaced by Sm or Nd (imitator of REE-actinides fraction) and Re (Tc), one experiment was carried out with addition of technetium-99 along with Re.

Main phases of these ceramic – metal waste forms (or cermets) were REE-Al-garnet (60-70 vol.%), glass (15-20 vol.%), and alloy (10–15 vol.%). Sm and Nd enter into the garnet and glass, Re forms alloys with iron group elements or molybdenum. In spite of high temperature Re and Tc did not evaporate during SHS. Compositions of the metallic inclusions in cermets and partitioning of the elements of interest (Re, Tc) between co-existing phases were analyzed.

The results are compared with published data on (Re,Tc)-containing alloys prepared by sintering or melting in high-temperature Joule-heated furnaces and by arc melting route. Compositions of the Re-containing alloys in cermets and equilibrium phases in the Fe-Re and Mo-Re systems are discussed. Alternate method for synthesis of alloys with Tc is inductive melting in a cold crucible.

Special attention was paid to analysis of conditions for the Tc-containing forms safe geological disposal. The repositories should be located in crystalline rocks at depth of 500 m or below with slightly alkaline (pH ~ 8) and reducing (Eh < 0) properties of the underground waters. Indicator of such a geochemical media is a presence of minerals of Fe (II). In these environments Tc (IV) will be stable with a very low solubility of its solid phases – $TcO_2 \times 2H_2O$ or $TcO(OH)_2$.

2.10.

ELECTROCHEMICAL AND SPECTROELECTROCHEMICAL INVESTIGATIONS OF TcO_4^- ELECTROREDUCTION IN ACIDIC MEDIA

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Despite many years of research on TcO_4^- ions electroreduction in the acidic solutions the mechanism of this process is still not fully understood [1]. Recent studies [2] indicate that in the highly concentrated H_2SO_4 solutions the TcO_4^- ions transform into $TcO_3(OH)(H_2O)_2$. Generally, in the acidic solutions multistep mechanism is postulated. As a result of the subsequent steps of the Tc(VII) ions electroreduction the different forms of Tc at lower oxidation states [3-5] are formed. The aim of our study was to elucidate the mechanism of the Tc(VII) ions electroreduction on different surfaces (Au, Pt, RVC - reticulated vitreous carbon) and in a wide range of sulfuric acid concentrations (0.5-12M). Our study were carried out using electrochemical techniques (such as cyclic voltammetry, chronoamperometry coupled with UV-Vis spectroscopy and rotating ring disc electrode technique (RRDE)). The best characterised electrochemical waves are observed for gold surface. In strongly acidic solutions are recorded two main cathodic waves. Spectroelectrochemical measurements show that in the first step of discussed process one-electron, reversible reduction of $TcO_4^-/TcO_3(OH)(H_2O)_2$ to Tc(VI) is observed. In the next step the formation of Tc(III,IV) (λ_{max}= 505 nm) is observed. The results indicate the mixed chemical(disproportionation) and electrochemical pathways for generation of Tc(IV) species. Tc(IV) ions can be reversibly reduced to the Tc(III) ions (λ_{max} = 670 nm). The stability of Tc (IV) and Tc (III) ions increase with increasing concentration of H_2SO_4 in the solution. Further measurements using the rotating ring disk electrode allowed to provide us with additional informations regarding this process. In the hydrodynamic conditions two currents were recorded. The activation energy of the electroreduction process calculated for limiting current recorded at potentials lower than 0.4V vs. SHE in 4M H_2SO_4 was 12.30 ± 1.14 kJ * mol^{-1}.

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References.

1. Rard, J. A.(ed.); *Chemical Thermodynamics of Technetium*, Elsevier: New York, 1999, pp. 74-96.
2. F. Poineau, P.F. Weck, K. German, A. Maruk, G. Kirakosyan G., W. Lukens, D.B. Rego, A.P. Sattelberger, K.R. Czerwinski, *Dalton Trans.* **39(37):** 8616-8619 (2010)
3. G. Horányi, I. Bakos, *J. Electroanal. Chem.* **370**: 213-218 (1994).
4. O.Courson, C. Le Naour, F. David, A. Bolyos, A. Maslennikov, N. Papadopoulos, *Czech. J. Phys.* **49:**, 687-694 (1999).
5. B. Pihlar, *J. Electroanal. Chem.*, **102:** 351-365 (1979)

2.11.

STABILIZATION OF RHENIUM (VI) COMPOUNDS IN SOLUTION AND USING THEM IN ANALYSIS

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Rhenium, being a typical transition element, is characterized by number of oxidation states (from +7 to –1), which it realized in its compounds, manifesting different reactivity and specific properties.

Among them a special place is occupied by Re(VI), having one unpaired electron on the next-to-last 5d- electron shell ($5d^1$, s = 1/2) - exhibiting paramagnetism and characterized by specific ESR spectra. The possibility to use the properties of the compounds with unusual oxidation states of rhenium is mainly determined by the possibility of their stabilization in solutions.

The quantitative formation of stable rhenium (VI) complexes with sulfur –containing organic ligands, such as dithionaphthol (DTN), quinoxaline-2,3-dithiol, mono-thiophenols (their derivatives) has been established in the systems, containing perrhenate- ion in acid (HCl or H_2SO_4) and organic ligands in $CHCl_3$ (CCl_4 and others) with stirring in combination with UV/ VIS-, IR-, ESR- and other methods.

Optimal conditions of complex formation in the system Re(VII) – HCl –DTN - $CHCl_3$ are the 100 – 200 – fold excess of DTN, 11.5 M HCl, $V_{org} = V_{aq}$, τ = 40-50 min (stable for 2 or more days). The composition of complex corresponding to the ratio Re : DTN = 1 : 2. The extract of this compound is characterized by absorption spectrum with the parameters - λ_{max}=505 nm , $\varepsilon_{max} = 1.5 \times 10^4$.

ESR spectroscopic study gave evidence for paramagnetic species present. It was established that the ESR spectrum of these species has the following parameters : g_{II} = 2.059 , $g_\perp$ = 1.979, A_{II} = 446 G , $A_\perp$ = 34.9 G.

System Re(VII)- HCl – DTN- $CHCl_3$ was used to develop a high selective methods of rhenium determination in the spectrophotometric and ESR version. For the determination of rhenium the main line in ESR spectrum was used.

The detection limit for rhenium is 0.15 μg / ml. The methods are applicable to the determination of rhenium in industrial sulfuric acid and several alloys (Fe-Ni-Re , Mo-Re, W-Mo-Re).

2.12.

NOVEL APPROACH TO THE MASS-SPECTROMETRIC DETERMINATION OF TRACE AMOUNTS OF RHENIUM USING ITS COMPLEXES WITH ORGANIC REAGENTS

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A new technique has been developed for the determination of trace levels of rhenium. The method is based on a formation of rhenium complexes with organic ligands and the subsequent determination of obtained complexes by surface assisted laser desorption/ionization (SALDI) from nanostructured semiconductors. In SALDI the gas-phase ions are formed from molecules deposited on a particular surface substrate that is irradiated with a pulsed laser. This process does not require the entrainment action of an added matrix compound for desorption and ionization.

The main specific feature of organic reagents used in the developed technique is that they should contain at least two essentially different functional groups. One of functional groups has the ability to form thermally stable complexes with rhenium while another one provides high effective ionization for subsequent mass-spectrometric detection. The preliminary search and investigation of such organic reagents was carried out. Two different systems were studied: 1) Re(VII)-HCl-L_1 (where L_1 are various tetrazolium salts), and 2) Re(VI)-HCl-L_2 (where L_2 are thiourea or its derivatives). The optimum conditions of synthesis were found for each studied system. The stoichiometry and structure of synthesized complexes were revealed.

All obtained compounds were studied by SALDI method. For this purpose a lab-built SALDI-mass spectrometer based on linear turbopumped time-of-flight mass spectrometer with a 0.7 m long flight tube was used. A diode-pumped YAG-laser with 355 nm wavelength (third harmonic), 0.5 ns pulse duration and 300 Hz repetition rate was used for the desorption-ionization. The synthesized complexes were dissolved in methanol-water solvent at a concentration of 10 to 500 ng/ml. A volume of solution in amount of 1-4 μl has been deposited onto the surface of nanocrystalline silicon.

SALDI mass spectra of rhenium complexes were obtained in positive and negative ionization mode. Mass spectra found to be clean and compound-specific, with several specific fragment ions. The possible pathways of fragmentation are presented and discussed. The detection limit of rhenium is at the several picograms level, with large potential improvements.

The reported results demonstrate that the developed technique possesses high analytical potential for high sensitive determination of rhenium in natural and technogenic samples.

This work is supported by RFBR (grant №11-03-01080-a)

2.13.

ANALYTICAL STUDY OF NATURAL CONCENTRATIONS AND CHEMICAL COMPOUNDS OF RHENIUM AND TECHNETIUM

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Notes

2.14.

METHOD FOR HEXAMMINECOBALT (III) PERRHENATE SYNTHESIS FROM PERRHENIC ACID

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A method for production of high purity $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ from perrhenic acid obtained by ion exchange method was presented. The perrhenic acid production is based on sorption of ammonium ions on acid cation-exchange resin – Purolite C160(H) and regeneration of the ionite with 32% solutions of nitric(V) acid. In the result of thickening of the solution, which is generated after sorption, perrhenic acid is produced, containing 300-900 g/L Re and Ca < 0.001 %, K < 0.001%, Mg < 0.0001 %, Cu < 0.0001 %, Na < 0.0001 %, Mo < 0.0001%, Ni < 0.0001%, Pb < 0.0001%, Fe < 0.0001%, NH_4^+ < 0.0003 %.

Studies into production of dihydrate of hexamminecobalt(III) perrhenate were conducted with application of $[Co(NH_3)_6]Cl_3$ (by Acros Organics) as a source cobalt compound. Also substitution of the commercial product $[Co(NH_3)_6]Cl_3$ with the produced in laboratory hexamminecobalt(III) chloride was examined as well as possibilities for direct precipitation of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ from cobalt containing ammonia solutions.

It was found out that precipitation of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ should be conducted from solution of Co content at the level of 50 g/L, in room temperature, with 60 % excess of rhenium vs. cobalt. It is important to use aqueous solution of perrhenic acid where rhenium concentration is over 100 g/L. The combined solutions should be intensively mixed for half an hour so the cobalt concentration in the solution after precipitation of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ is <0.001 g/L. Solubility of the produced compound in water and in selected organic solvents was examined. It was established that $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ is slightly soluble in water (solubility in 25 °C – 0.3 g/L, and in 80 °C – 4.1 g/L) and in classical organic solvents such as ethanol, acetone. It is, however, readily soluble in DMSO and *N*,*N*-dimethylformamide. The solubility in room temperature was 500 and 600 g/L, respectively. It was established that the examined substance is stable in the temperature range up to 60 °C. In the temperature of 80 °C some mass loss was observed which prove removal of one water molecule. The temperature increase to 100 °C resulted in removal of the next water molecule. In the temperature range 100-180 °C a stable anhydrous hexamminecobalt(III) perrhenate was formed.

Application of the developed method resulted in production of $[Co(NH_3)_6](ReO_4)_3 \cdot 2H_2O$ with efficiency of over 97 %, of following composition: 10.77 % NH_4^+, 6.22 % Co, 58.93 % Re and containing less than 150 ppm of impurities, such as sodium, chlorine, iron, nickel, chromium, potassium, magnesium and lead.

2.15.

MODERN X-RAY ANALYTICAL INSTRUMENTS OF BRUKER AXS

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2.16.

PREPARATION OF ^{95m,g}Tc, ^{96}Tc BY IRRADIATION OF MOLYBDEN WITH ALPHA-PARTICLES AND DEUTRONS

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Lomonosov MSU

A method is proposed to produce the short-lived radionuclide ^{95g}Tc via formation of the parent ^{95}Ru. To produce ^{95}Ru, the bombardment of molybdenum target of natural isotopic composition with α-particles and the irradiation of ruthenium of natural isotopic composition with bremsstrahlung photons were used.

Irradiation of natural molybdenum stack foil target for 15 min with alpha particle beam (1 μA) followed by radiochemical separation yields 140 kBq of ^{95g}Tc and 9 kBq ^{96}Tc.

The ^{95g}Tc obtained is of considerably higher purity than those formed by common ways (niobium or molybdenum irradiation with alpha particles). The main radionuclide impurity (that could not be avoided) is a small amount (9.1×10^{-2} %) of long-lived ^{95m}Tc isomer.

Attention was also paid to the production of side products such as ^{95m}Tc, ^{96}Tc and ^{97,103}Ru, in order to utilize optimally the energy of the alpha particle beam.

2.17.

MODERNIZATION METHOD FOR PRODUCTION OF FISSION Mo-99 FROM LOW-ENRICHED-URANIUM FOIL (LEU-FOIL)

S. Alwaer.
(Tripoly TNRC, Libya)

Supported by IAEA

Notes

Poster session 2

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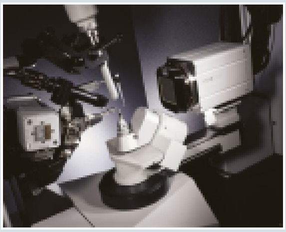

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2.P1.

^{99}Tc TRANSMUTATION TARGET HETEROGENEITY FOR THE ARTIFICIAL STABLE RUTHENIUM PURIFICATION FROM ^{106}Ru

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^{99}Tc transmutation can be the source of artificial stable ruthenium $^{100–102}$Ru. Radioactive ^{106}Ru ($T_{1/2}$ = 369 days) can not be generated by ^{99}Tc transmutation, however it will appear in the target as fission product from actinide impurities. The total (U+Pu) impurity is usually about $5 \cdot 10^{-8}$ g per gram of Tc, isolated from spent fuel by modified Purex process and selective precipitation of tetraalkylammonium pertechnetate. The fission of all actinide nucleus-impurities is complete during the transmutation, because of the cross sections of (n,f) actinide reactions are higher in 1 – 2 orders of magnitude than that of ^{99}Tc neutron capture. Therefore the artificial stable ruthenium, prepared from Tc homogeneous target, is contaminated by ^{106}Ru, which prevents the practical use of the product in non-nuclear field during ~10 year up to its complete decay.

^{106}Ru can not be removed from artificial stable ruthenium by chemical methods. However there is the possibility to remove fission product ^{106}Ru from transmutation products $^{100–102}$Ru during the irradiation of technetium by thermal neutrons using the physical phenomenon of recoil after nuclear transformations. The kinetic energy and recoil range of fission fragments, including ^{106}Ru, are higher than those of transmutation products ^{99}Tc(n,γ)^{100}Tc(β^-)^{100}Ru. If technetium target is manufactured from Tc metal powder with the particles whose size is compared with the recoil range of ^{106}Ru (about 8 mkm), this radionuclide can escape the Tc particle. ^{106}Ru yield from Tc-Ru spherical particle with radius R is following:

$$Y = \frac{3}{4}\frac{\overline{R}}{R} - \frac{1}{16}\left(\frac{\overline{R}}{R}\right)^3 \text{ if } R \geq \overline{R}/2 \text{ and } Y = 1 \text{ if } R \leq \overline{R}/2,$$

where $\overline{R}$ – path length of fission fragments in Tc-Ru alloy.

Tc particles should be surrounded with a stuff particles, whose role is to immobilize ^{106}Ru. Such heterogeneous target should be treated with diluted nitric acid. The stuff particles containing ^{106}Ru, will be dissolved and removed, whereas transmutation products $^{100–102}$Ru together with non-burned ^{99}Tc remained in solid state. Such recoil separation with Tc particles size 10 mkm provides with the removing about 95% of ^{106}Ru from irradiated technetium. The proposed recoil separation is more simple and cheap method, than additional purification of Tc from actinide impurities.

2.P2.

THE BEHAVIOR OF TECHNETIUM, AMERICIUM AND NEPTUNIUM IN THE SPENT FBR (U,Pu)N FUEL AFTER FAST NEUTRON IRRADIATION AS A FUNCTION OF THE TEMPERATURE AND BURN-UP

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The development of new generation of nuclear power reactors previews the utilization of nitride base fuel, including mixed uranium – plutonium nitride. This kind of fuel may be also used for the incineration of military plutonium, minor actinides and some fission products before the final disposal. To obtain new data on the behavior of (U,Pu)N under fast neutron irradiation thermodynamic analysis of the composition of condensed and solid phases of $U_{0.8}Pu_{0.2}N_{0.995}$ was carried out using ASTRA-4 software as a function of temperature and burn-up up to 14 %.

Irradiation brings to the formation of a complex structure including solid solution based on uranium-plutonium nitride with dissolved americium and neptunium, zirconium, yttrium and lanthanides and some separate condensed phases, namely U_2N_3, $CeRu_2$, BaTe, Ba_3N_2, CsI, Sr_3N_2, LaSe, as well as Mo metal, Tc metal and intermetallic compounds $U(Ru, Rh, Pd)_3$. The content of the mentioned and its change as a function of the irradiation temperature and burn-up values was determined. It was found that the content of Tc, Am, Np at 13.6 % burn-up was 0.253, 0.126, 0.018 wt. % correspondingly.

The values of partial pressures for certain gas phase components over irradiated $(U_{0.8}\ Pu_{0.2})N$ were calculated for the same range of temperatures and burn-up. The empiric equations describing the changes of Am, Np and Tc partial pressures (atm.) were deduced:

$$\lg(P_{Tc})=7.55 - 35194/T + 33139/T^2 \qquad (1500 – 2000K)$$

$$\lg(P_{Am})=9.43 - 38550/T + 10000000/T^2 \qquad (1000 – 2000K)$$

$$\lg(P_{Np})=6.10 -37230/T - 319050/T^2 \qquad (1500 – 2000K)$$

The presented results may be used in the design of FBR reactors using nitride based fuel, for the estimation of the risks associated with the behavior of (U,Pu)N in the accidental situation and in the development of the spent nitride fuel.

2.P3.

COMPOUNDS OF CURIUM WITH TECHNETIUM

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For the last years RIAR has pursued investigations on synthesis of the TPE compounds, specifically, curium and americium with other elements of the periodic system. The paper provides the primary results of production and identification of compounds of curium-244 with technetium which refer to the complex oxides.

The samples of the technetium compounds with curium were obtained during condensation of the curium metal vapours on the technetium substrate and investigated by the X-ray diffractometry (a DRON-7 diffractometer) at room temperature.

The investigations performed allowed us to obtain the new curium compounds which were not known before:

- complex oxide Cm_6TcO_{12} that has a hexagonal lattice of the Ho_6MoO_{12} type and the crystal lattice parameters (CLP) a = 10,552(3) Å, c = 9,879(5)Å;
- complex oxide $Cm_3Tc_2O_{10}$, the isostructural $La_3Mo_2O_{10}$, with the cubic crystal lattice and the CLP a = 5,592(1) Å.

It is noted that curium remains insoluble in the hexagonal closed-packed technetium lattice.

2.P4.

EXTRACTION-CHROMATOGRAPHIC PURIFICATION OF URANIUM EXTRACT FROM TECHNETIUM

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Uranium purification from technetium in the process of spent nuclear fuel reprocessing is one of the most complex problems.

Uranium reclaim for separating plant is to be extremely decontaminated from Tc because of the problems at the sublimation stage caused by volatile TcF_6 formation during uranium recycling process.

There is a conflict between Thorp plant requirements for uranium product after the second extraction cycle (Tc content 4 mg/kg U [1]) and ASTM C787-03 standard, which requires Tc content in uranium hexafluoride less than 0.5 mg/kg U and in some cases [2] the level of uranium decontamination from Tc in this product should be less than 1.6 mkg/kg U. This conflict could be resolved by uranium reclaim additional radiochemical reprocessing for supplying purified product to the sublimation plant. It is evident that such technology makes reprocessing process rather expensive.

The aim of the research work was to find and work out such a process, that can provide effective and not expensive deep uranium purification from Tc on the basis of extraction spent fuel reprocessing technology.

The solution of mentioned problem is an extraction-chromatographic purification of uranium extract by usage of aqueous reducing agents solution as a purifying stream. These agents reduce Tc (VII) to nonextractable Tc (IV).

The process of purifying is carried out in cyclically-countercurrent feed mode of purified and purifying streams in a column filled with porous excipient (charged with aqueous purifying stream).

It is shown that depending on composition of the aqueous phase concentration factor varies from 40 and above. These conditions provide practically complete treatment of uranium extract.

References

1. Kopyrin A.A., Karelin A.I., Karelin V.A. "Technology of the production and radiochemical reprocessing of nuclear fuel" M, Atomizdat, 2006, p. 226

2. Timofeev S.V., Belyaev V.D., Karpov A.A., Shishkov S.U. " Improving the evaluation control of technetium-99 in the chemical reprocessing technology of NFC natural and recycled uranium". Youth NFC: Science, production, ecological safety, URL:http://conf.atomsib.ru/archive/conf2008/section1/17.doc, date - March 4, 2011.

2.P5.

METAL-THERMAL IMMOBILIZATION OF HIGH-ACTIVE TECHNETIUM WASTE INTO MATRICES BASED ON METAL GLASS CRYSTALLINE COMPOSITES

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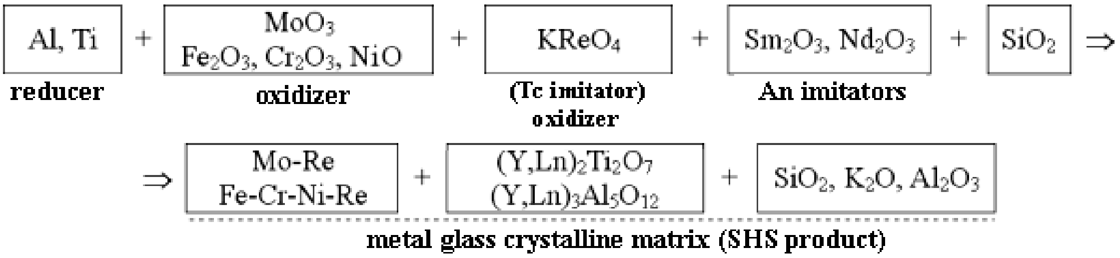
In the framework of recycling fuel cycle the problem of high-active waste (HW) treatment should involve solution of the three major process stages: liquid HW fractionation; calcination (crystallizing) of radionuclides of these fractions predominantly on inorganic sorbents and immobilization of produced dry sorption-crystal concentrates into chemically and thermally resistant mineral-like matrix materials suitable for ecologically safe disposal. To synthesize such matrices, it is recommended to use metal-thermal self-propagating high-temperature synthesis (SHS) where Al and Ti are the fuel elements (reducers), and molybdenum oxide and iron oxide are mainly oxidants.

To provide further progress in this direction, the problem of immobilization of technetium as most environmentally dangerous product of nuclear fuel fission is considered in this report. Technetium imitator representing its nearest chemical analog – rhenium in the form of potassium perrhenate is used in investigations.

When treating high-active waste, Tc-fraction can contain actinides impurities. Therefore the matrix composite materials synthesized in SHS conditions should incorporate phases efficiently immobilizing both technetium (rhenium) and actinides (An). To imitate the last-named, lanthanides (Ln) are used. SHS-produced metallic phases where rhenium-molybdenum (Mo-Re) and Fe-Cr-Ni-Re alloys are dissolved with ease have been produced as matrix material for rhenium immobilization (see the diagram). Matrix materials being simultaneously synthesized on the basis of stable aluminate or titanate complex oxides like pyrochlor $(Y,An\ldots)_2Ti_2O_7$ or Y-Al garnet $(Y,An\ldots)_3Al_5O_{12}$ are used to immobilize An.



The present authors are grateful to S.V. Yudintsev and B.S. Nikonov, IGEM RAS* experts, for identification of interaction SHS products and analysis of their structure.

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2.P6.

APPLICATION OF MODIFIED WOOD MATERIALS FOR EXTRACTION OF TECHNETIUM (VII) FROM AQUEOUS MEDIUM

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Influence of various modifying additives on sorption ability of some carbon materials in relation to the technetium (VII) is studied. As objects of research were are taken: (1) coal formed at electron beam processing of vegetative materials; (2) carbonized of wood; (3) the oxidized coal received at soft oxidation carbonized of wood by oxygen of air, and also the initial and modified (4) wood (aspen sawdust); (5) activated coal FAS-E and (6) carbon nanomaterial "Taunit".

It has been shown that oxidizing processing carbonized of wood (2) improves it sorption properties. It is possible to explain this fact, education on a surface of coal participating in anionic exchange of carbonyl and carboxyl groups at processing on air.

For improvement sorption properties concerning the Tc(VII) carbon materials have been modified by processing by phosphoric acid, urea (thiourea) and potassium thiocyanate. It is shown that in the acidic medium (pH <4) the Tc(VII) is most effectively taken by the wood modified by urea (K_d = 1,3·10^2 sm^3/g from 2M HNO_3). In the subacidic and neutral environment is the most effective than the Tc(VII) it is taken by the coal modified thiourea (K_d = 58,64 sm^3/g from 10^{-3} M HNO_3). In the alkaline environment is better the wood modified by phosphoric acid (K_d = 76 sm^3/g proves at pH 9).

It is found that samples FAS-E modified by urea and H_3PO_4 effectively takes the Tc(VII) of subacidic solutions HNO_3 with K_d equal 2,4·10^4 and 1,7·10^4 sm^3/g, accordingly. Modified by urea or H_3PO_4 samples of "Taunita" take the Tc(VII) in the same conditions with K_d equal 400 and 73 sm^3/g, accordingly.

Thus, researches have shown that as a whole modifying of wood and carbon materials improves them sorption properties in relation to technetium (VII). Important that the modified carbon materials possess concerning high sorption abilities in relation to Tc(VII) at its extraction from the natural (technogenic) objects possessing difficult salt structure. Thus, presence of extraneous impurity practically does not interfere with extraction of a purposeful element technetium the modified sorbents synthesized by us on the basis of carbon materials.

2.P7.

STRUCTURE AND PROPERTIES OF INSOLUBLE TECHNETIUM COMPOUNDS FORMED IN TECHNETIUM - HYDRAZINE - DTPA - NITRIC ACID- SOLUTIONS

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The paper presents the results of the study of low-soluble technetium compounds with diethylenetriaminepentaacetate (DTPA), which finds use as a stabilizing agent in the extraction reprocessing of spent nuclear fuel. The Tc sediments were studied by chemical analyses, XRD, IR, Raman and UV-VIS, EXAFS and ESR spectroscopy. The role of the Tc reduction process by hydrazine in mother solutions prior to precipitation was also evaluated.

It was shown, that the precipitation of Tc occurs when the reduced Tc(IV) is partially back-oxidized to Tc(VII) with a possible formation of intermediate Tc species after the most part of hydrazine is expended. The studied precipitate was defined as the Tc polyaminocarboxilate of both polynuclear and polymeric nature. Tc-DTPA ratio was found to be close to 1:1, the huge part of Tc in the polymeric sediments being in Tc(IV) valent state. Both carboxylic and amino-groups of the DTPA participate in the formation of the Tc compound and the coordination of functional groups from one DTPA molecule to multiple Tc atoms is highly possible. The Tc-DTPA chelates tend to form large and more complex ensembles with Tc-Tc bonds and bridging oxo ligands.

Possible structure of the Tc-DTPA compound was modeled (fig. 1) and some ways for exclusion of the Tc precipitation during SNF reprocessing were proposed.

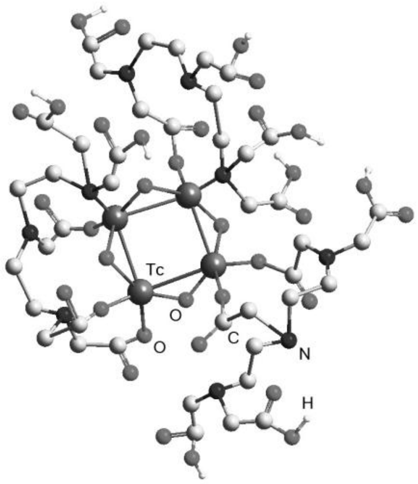

Fig. 1 - The model of the possible structure of Tc-DTPA core

The work was supported by RFBR grants 09-08-00153-a and 09-02-12257-ofi_m

2.P8.

THE BEHAVIOR OF THE TECHNETIUM - HYDRAZINE - NITRIC ACID - TBP SYSTEM IN PRESENCE OF THE COMPLEXING AGENTS

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The extraction properties of one of uranium fission products – technetium - are of a major importance for the spent nuclear fuel reprocessing by PUREX-process. Tc(VII) possess significant distribution coefficient in TBP/HNO_3 system thus following the U and Pu at the first extraction step. Later it may seriously interfere with the U-Pu reductive separation by catalyzing undesirable red-ox reactions and increasing the decomposition rate of hydrazine, used as a stabilizer. Different complexing agents may be used to reduce the negative influence of Tc and to control its extraction behavior.

This paper presents the experimental results on the extraction behavior of Tc and the decomposition of hydrazine in presence of complexing agents - DTPA and oxalic acid. It was shown that DTPA did not render significant impact on the hydrazine decomposition in the modeled hydrazine-containing nitric acid Tc solutions during the 6 hours hold out at temperature of 45 °C, but the rate of the Tc(IV) reoxidation decreased in presence of DTPA. After the hydrazine was spent, the yield of Tc(VII) as a result of reoxidation process was found to be significantly lower, compared to the DTPA-free systems. Upon increase of acidity the chelating properties of DTPA weakened, so this agent may have limited usability for stabilizing reduced technetium in fuel reprocessing.

Oxalic acid was shown to be more efficient protecting agent for both hydrazine and Tc(IV). In presence of $H_2C_2O_4$ hydrazine decomposition rate was slow; the remaining concentration of hydrazine after 6 hours exceeded 50% of the initial quantity, and only insignificant oxidation of reduced Tc(IV) was observed. It should be noted, that the initial reduction of Tc(VII) by hydrazine was slower, than in solutions not containing the complexing agents. The ability to bind Tc(IV) increased for $H_2C_2O_4$ with the rise of HNO_3 content. It was also found, that azide products of hydrazine decomposition play an important role in the process of stabilizing the systems both with and without complexing agents.

The authors are grateful to Prof. B.Ya. Zilberman for useful discussion of the results. The work was supported by RFBR grant 09-08-00153-a.

2.P9.

TECHNETIUM(VII) EXTRACTION WITH HYBRID PHOSPHOR-NIROGENATED DERIVATIVE LIGANDS

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A new simple "one-pot" synthetic method based on the reagents that are commercially available is elaborated as a rout to prepare hybrid phosphor-nirogenated derivative ligands like $Ph_2P(O)CHRCHR'R''$ (**I a-c**; **a** R = Ph, R' = R'' = CN; **b** R = Ph, R' = CN, R'' = COOEt; **c** R = R' = H, R'' = 2-pyridyl), being the substances of potential bioactivity.

The synthetic rout is given by the sequence:

$$Ph_2PCl \xrightarrow[20^{o}C\ \ MeCN]{H_2O} [Ph_2POH] \xrightarrow[20^{o}C\ \ THF]{RCH{=}CRR''} Ph_2P(O)CHRCHR'R''$$

(**I a-c**) (yield > 85 %)

Thus obtained compounds were tested with respect to technetium liquid-liquid extraction (Organic phase: 0.05 M $Ph_2P(O)CHRCHR'R''$ in CCl_3H, aqueous phase contained 10^{-5} M $KTcO_4$ in 0.05-0.5M NaOH or 0.05-5.5M HNO_3).

Very small distribution coefficients were measured for Tc(VII) extraction from the basic solutions for the 0.05-0.5M NaOH concentration range studied .

Extraction from nitric acid solutions was notable, with 2-[2-(diphenylphosphoryl)ethyl]pyridine (**I c**) being the most effective for 0.7 – 1.5 M HNO_3 range.

The data indicate that **I**-type phosphoryl-nitrirogeneted derivatives fonctionalization is prospective approach to Tc(VII) extraction.

Extraction tests for reduced Tc with the hybrid phosphor-nirogenated derivative ligands like $Ph_2P(O)CHRCHR'R''$ (**I b-c**; **b** R = Ph, R' = CN, R'' = COOEt; **c** R = R' = H, R'' = 2-pyridyl) indicate the necessity of temperature pretreatment and the importance of reducing reagent excess in the aqueous phase.

The work was partially supported by the Program P-17 (Elaboration of new methods for chemical synthesis and design of new materials) of Presidium RAS.

2.P10.

NEW MATERIALS FOR IMMOBILIZATION OF TECHNETIUM-CONTAINING WASTE FOR THE PURPOSE OF THEIR ISOLATION FROM THE ENVIRONMENT

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The possibility for immobilization of long-lived radioactive ^{99}Tc in carbon matrices was investigated.

Stable rhenium was used as chemical analogue of ^{99}Tc in the form of inorganic salts and in associated with the ion exchange resin form. We studied the physical and chemical properties of rhenium-containing carbon matrices, obtained by carbonization of the composites, which include the polyimide binder, and carbon cloth as a reinforcing component. Upon receipt of the composites as a binder used polyimide derivative ITA-31, which is a mixture of dianhydride 3,3 / 4.4 /- benzophenontetracarbonic acid and tetra-acetyl derivative of /4,4 /- diaminodiphenyl ether.

Physico-chemical properties of the resulting carbonized samples of carbon matrices were investigated. It is shown that the matrix have a set of properties that meet the requirements of the matrix for storing high level waste (HLW). They are distinguished by high thermal and chemical stability, have high compressive strength and have a high elastic modulus.

Irradiation in a research reactor WWR-M with an integral flux of neutrons in 10^{18} (estimated absorbed dose of gamma rays 10^{8} Gr) does not lead to a significant change in the above-mentioned properties.

Metal content in the matrix reaches 30%.

2.P11.

TECHNETIUM SULFIDES – ROLE IN CHEMISTRY AND ECOLOGY

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So-called technetium heptasulfide was among the first synthesized Tc compounds [1-2] because it was considered as a convenient route for Tc separation from aqueous solutions. Already in the first works its composition was established as Tc_2S_7 thus supposing that Tc is in its higher oxidation state. This experimental value was sufficiently precise although rather surprising in view of Tc redox potentials being in contradiction with those of S^{2-}. Meanwhile no explanation was available for more than 45 years [3], although Tc(IV) sulfide was also described.

Many investigations [4-8] carried out in this period indicated important Tc accumulation by different sulfide minerals. The Tc_2S_7 solubility was investigated but no reasonable value was possible to establish because of its complicated hydrolyses behavior [8], and only the formation kinetics and colloidal particle size speciation studies [9-11] provided with the reliable information on Tc concentration dependences. Reaction of Tc(VII) with sulfide was characterized with induction period and kinetic dependent on the [Na_2S] in the solution. The S/Tc ratio in the sediment was obtained by chemical analyses as 3.36(7) on a macroammount of the precipitate and confirmed by RBS (Fig.2) In the growing process of Tc-S colloid system, the size of colloid particles was shown to increases by deposition of Tc sulfide on the particle surface, not by coagulation of the particles [11].

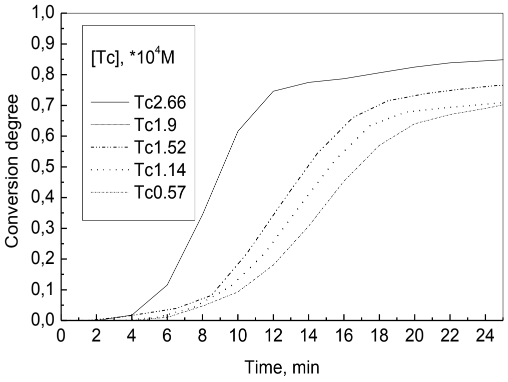

Fig.1 . Reaction kinetics of $NaTcO_4$ with 0,3M Na_2S , pH=11.2, t=20°C [9]

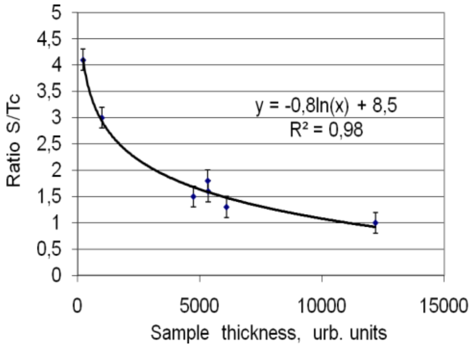

Fig.2. RBS determination of S/Tc ratio in technetium sulfide [10]

Final ideas for explanation became possible only based on EXAFS studies [12]. It was demonstrated that -S-S- disulfide ligands are present in the structure thus explaining the reduction mechamism for Tc(VII) to Tc(IV) with no notable change in Tc:S stoichiometric ratio. At the same time the presense of S_2^{2-} ligand in the compound explane some other properties that was not well understood before. The determination of the concentration of free Tc species as fractionized with separation of ionic or nanocolloidal particles with 5 kD “Sartorius” ultramicrocentrifuge tubes [10] gave evidence on the Tc_3S_{10} nanosulfide formation (Fig.3) similar to that observed in [12].

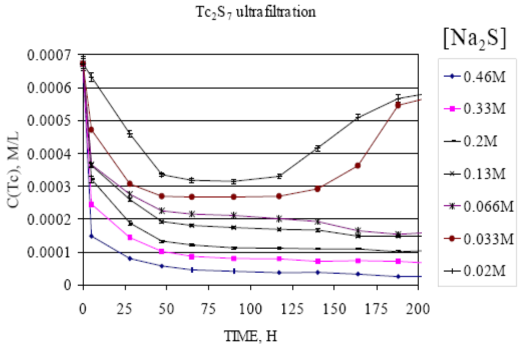

Fig.3. Concentration of free Tc species as fractionized with separation of ionic or nanocolloidal particles with 5 kD "Sartorius" ultramicrocentrifuge tubes [10]

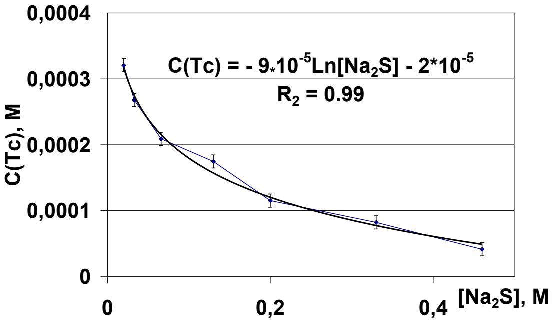

Fig. 4. Solubility of Tc sulfide at τ = 75 - 110 h as evaluated for diffesent [Na2S] by separation of nanocolloidal particles with 5 kD "Sartorius" ultramicrocentrifuge tubes [10]

The stability of Tc_3S_{10} in the resulting solution was dependent of the S^{2-} concentration in it. When higher than 0.06M Na_2S, further grouth of Ts sulfide particles occurred for $\tau \geq 150$ h similar to observations made in [11]. For $[Na_2S] \leq 0.04$ M, the Tc_3S_{10} was reoxidized by present air to Tc(VII) within 175-200 hours thus being resolubilized.

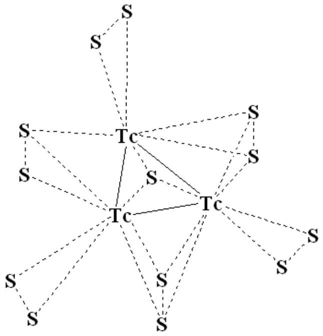

Fig.5. Structure unit fragment Tc_3S_{13} for technetium sulfide acc. to EXAFS studies[12]

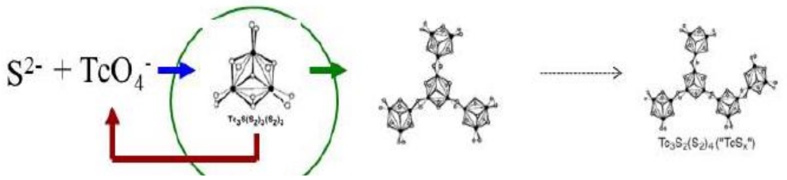

Fig. 6. The scheme of Tc reaction with sulfide follows the one drawn based on the results of Lukens et all. [12].

The determination of the free Tc species concentration with separation of ionic or nanocolloidal particles with 5 kD "Sartorius" ultramicrocentrifuge tubes [10] (Fig. 4) gave evidence on the Tc_3S_{10} nanosulfide formation similar to that observed in [12]. The equation for the Tc sulfide solubility based on these figures was evaluated.

We highly acknowledge the fruitfull discussios with Dr. W. Lukens and the provided suplimentary EXAFS and XANES data on Tc_3S_{10}.

References

1. Cobble, J. W., Nelson, C. M., Parker, G. W., et all., *J. Am. Chem. Soc.*, **74** (1952) 1852.
2. Rulfs, C. L., Meinke, W. W. J. *Am. Chem.Soc.*, **74** (1952) 235–236.
3. Rard J.A., Rard M.H., Anderegy G., Wanner H. // "Chemical Termodynamic of Technetium.", by Ed. Sandino M.C.A., Osthls E., OECD NEA, Data Bank , Issy-les-Moulineaux, France, 1999
4. Bondietti, E.A., Francis , C.W. *Science*, **203** (1979) 1337-1340.
5. Lee, S. Y., Bondietti, E. A., In: "Sci. Basis Nucl. Waste Manage. VI, held Nov. 1982 in Boston", (Brookins, D. G., ed.), New York: North-Holland, 1983, pp. 315–322.
6. Winkler A., Bruhl H., Trapp, Ch., Bock W.D. *Radiochimica acta* **, 44/45 (**1988), 183-186.
7. K.E. German, V.F. Peretrukhin, L.I. Belyaeva, O.V.Kuzina. In: "Technetium and Rhenium Chemistry and Nuclear Medicine 4, (Bressanone-Bolzano-Italy, Sept. 12-14, 1994, (Nicolini M., Bandoli G., Mazzi U.- Eds.) SGEditoriali, pp. 93- 97
8. El-Waer, S., German, K. E., Peretrukhin, V. F. *J. Radioanal. Nucl. Chem.*, **157** (1992) 3–14.
9. M. Simonoff, K. E. Guerman, G. Simonoff. In: Abstracts of the 2nd Japanese-Russian Seminar on Technetium, Shizuoka, 1999, p. 25
10. M. Simonoff, K. E. Guerman, C. Sergeant et all. *Journee Radiochimie 2000*, Gif-sur-Yvette, 28-29 September, 2000, France.
11. Y. Saiki, M. Fukuzaki, T. Sekine et all. *J. Radioanal. Nucl. Chem*. **255** (2003) 101–104.
12. W. W. Lukens, J. J. Bucher, D. K. Shuh, N. M. Edelstein. *Environ. Sci. Technol*.**, 39** (2005) 8064-8070.

2.P12.

TECHNETIUM LIMNOLOGY AS FRAME FOR ITS ECOLOGY AND THE KEY FOR UNDERGROUND STORAGE

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Radionuclides' accumulation by natural associations of microorganisms is important item for comprehension of their behavior in natural and technogenic water ecosystems. Different microorganisms are shown to exhibit different concentration factors from very low to very high, and the situation is complicated when we analyze the behavior of natural sediments composing of the association of some about 100 microbial species with some mineral. Tc transfer factors from water to sediments were analysed in some works [1-3 and ref. therein].The influence of natural water composition onto radionuclides sorption by lake sediments is not thoroughly studied.

Here we overview the results of model laboratory study of the bioaccumulation of the long-lived radionuclides [4-5]. The isotopes were introduced as pertechnetate solution (^{99}Tc (VII)) or nitrate solution (^{234}Th (IV) - as a tracer for typical behavior of four-valent actinides) into batch samples containing lake water and sediments taken from the 3 eutrophic lakes 1) Beloye Kosino (Moscow reg.), 2) l. Kezadra and 3) l. Navolok, both - Udomlya reg., near from Kalininskaya NPP). The initial concentrations of Tc have been adjusted to 10^{-6}-10^{-7} M and that of ^{234}Th (IV) to 3000 cpm per initial aliquote. Eutrophic lake Beloye Kosino sediment was mainly formless organic detritus, gray colored, H_2S odoriferous. Udomlya reg. lakes sediment were 30% organic detritus and humics, 60% sand and 10% (Fe_2O_3 and other inorganic minerals).

Table.1. Main eutrophic lake Navolok sediment and water phase content

Microorganism	Cells' number N/ml	Comments
		Ratio in batch: $V_{sediment} : V_{liquid} = 1:3$
Microalgae	10^6	Total = $2{*}10^9$ bacteria/g, pH = 7.0 (stable); Eh = -0.20V NHE (inner sediment part); water phase: [HCO_3^-] = 1 – 4 mg-C/l; [HSO_4^-] = 0 – 50 mg/l, [Cl^-] = 35 mg/l.
Bacteria:		
Sulphate reducing	10^4	
Methanogenic	$10^4 – 10^5$	
Nitrifying	10^3 - 10^4	
Denitrifying	10^5	

Two equilibration modes were modeled (overhead agitation and hipolimnionic Tc transfer to sediment). Centrifuge MPW-210 (48G, 15 min), and microfilterfuge tubes – (5 kD "Sartorius") were used for phase separation. No more than 5 % of water phase was sampled during the experiments in total. More than 95% of Tc-99 were truly dissolved species of TcO_4^- in water phase all time through the experiment. The kinetics' analysis of data from Fig.1 has shown that the half-time values of the initial content removal from the water-phase form 400h for Tc. Two different uptake rates were characteristic for Tc sorption for some samples from Udomlya reg. : fast uptake during the first 2 hours when

40% of initial input was sorbed by eutrophic river/lake sediment, and a slow bioaccumulation period when Tc uptake was completed in 11 days.

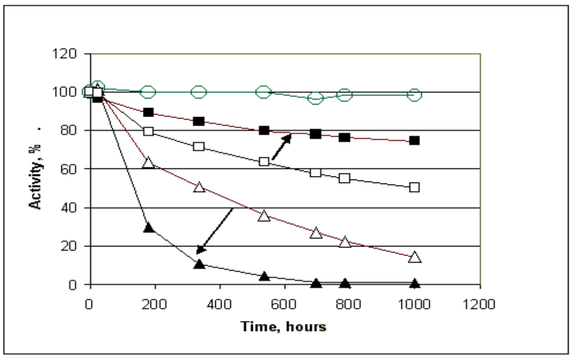

Fig.1. Tc uptake by Lake Sediments: O – steril sample; □-Torfyanoe, ∇-Beloe; white points - sedimentation; black points – agitated in overhead

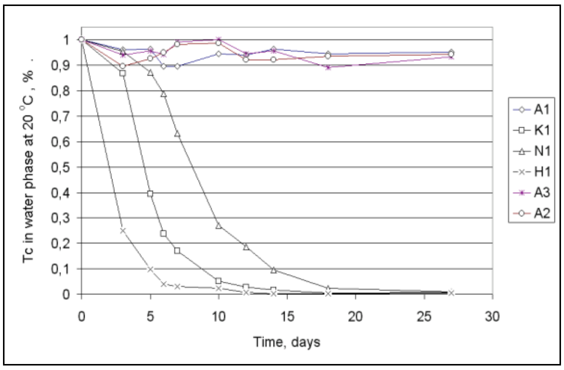

Fig.2.Tc uptake by Lake Sediments A1 – steril sample; K1 – Kezadra, N1- Navolok; H1-Homutovka

The Tc uptake rate differed for different lakes sediments, the time of half-uptake being ½ month for eutrophic lake Beloye Kosino (Moscow reg.) and much less (4-7 days) for the two lakes of Udomlya reg. Concentration factors at 1600 hours of equilibration of Tc with sediments and natural water were 1710 ml/g for eutrophic lake Beloye Kosino and 1850 ml/g for the two lakes of Udomlya reg. The complete Tc accumulation by sediment took place after 1.0 months and 0.8 month respectively. Speciation by centrifuging at 10000 rpm, ultrafilterfuging or filtration through 0.05 - 0.22 μm membranes, has shown that the Tc fraction remaining in water phase was present as truly ionic species up to 90%. The microflora of lake played important role in the accumulation and reduction of radionuclides. Some microorganisms (being able of anaerobic respiration) had competition relationships between SO_4^{2-} or NO_3^- and TcO_4^- so that the additions of SO_4^{2-} or NO_3^- decreases the rate of Tc accumulation by the sediment.

Reduction of Tc(VII) to Tc(IV) and sorption of hydrolyzed species are the main mechanisms for Tc accumulation in this biosystem. We suppose that Tc(VII) reduction and further uptake by the lake sediment is due to microbial activity of the sediment components, most probably to sulfate-reducing bacteria, that are known to reduce Tc(VII) [5]. The difference in the uptake rate is associated with the higher chemical stability of TcO_4^-. This mechanism is supported by Tc uptake rate slowing down when concurrent anions like sulfate or nitrate are injected into the water phase.

The sediments from freshwater lakes have a considerable sorption capacity. The consecutive sorption runs have demonstrated only small decrease of Tc uptake rate. The desorption of technetium was carried out with H_2O, 1M HCl, 1M $NaClO_4$ or 15% H_2O_2 and gave the desorption factors of 0.05, 0.05, 0.08 and more 0.99 thus indicating the oxidative stripping mechanism and contrary - the bioreduction of technetium to be the main mechanism of its uptake.

Thorium (IV) uptake by the sediments of both types was complete in 3 to 5 hours due to much more important sorption affinity of four-valent elements. About 20 % was sorbed by microparticulated organic matter and were removed only by microfilterfuge tubes ultrafiltration (5 kD “Sartorius”).

The analyses of the new experimental results and its comparison with the literature data unambiguesly indicate that some important ideas well developed in conventional limnology could be applied with success to the modeling and the forcast of radionuclide migration in the mixed mineral-sediment-aquatic natural environment both surfacial and deep underground. The known dependencies of season variations of temperature, oxic conditions and hydrodynamics could be usefull for these purposes. Some chemosynthetic and thermophilic bacteria species impact could be discussed also with respect to the recent accidents at the seaside environments (p.e. Fukushima accident).

References

1. M.J. Keith-Roach, P. Roos. The transport of Tc to the sediments of stratified fjords. Int. Conference Migration’2001.Bregenz, Austria, Sept 2001. Abstracts, PA5-05
2. Blaylock B.G., Frank M.L., Hoffman F.O., Deangelis D.L. Behaviour of technetium in fresh-water environment. In: Technetium in Environment. Edited by G.Desmet, C.Myttenaere. Elsevier Applied Science Publishers. London, New York, 1986, p.79-90.
3. G.M. Milton, R.G. Cornett, S.J. Kramer, A. Vezina. The transfer of iodine and technetium from surface waters to sediments. Radiochimica acta, 58/59 (1992) 291-296. .
4. Lloyd, J. Khijnyak T.V., Macascie L., and Lyalikova N.N. Reduction of technetium by Disulfofibrio desulfuricans: Biocatalyst Characterisation and use in a flowthrough bioreactor. Appl. Environm. Microbiol.1999, v.65, No.6. pp.2691-2696.
5. Guerman K.E., Khijnyak T.V., Peretroukhin V.F., German E.S., Firsova E.V. Behaviour of technetium in eutrophic and dystrophic fresh water lakes. The second Japanese-Russian Seminar on Technetium. Shizuoka, Japan, Nov. 29 - Dec.2. 1999. Abstracts, pp.50-51.

2.P13.

KASSITERITE AS A DURABLE HOST-PHASE FOR TECHNETIUM IMMOBILIZATION

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Kassiterite, SnO_2, is well-known accessory mineral with high mechanical and chemical durability.

Solid solution of Tc in kassiterite, $(Sn,Tc)O_2$, was suggested as a durable host-phase for technetium immobilization. Starting precursor was obtained by co-precipitation from aqueous solution ($SnCl_2 + KTcO_4$) using ammonium hydroxide.

Reduction of Tc valence state from (7+) to (4+) was observed during precursor preparation. Then precursor was calcined in air at 800°C, ground in agate mortar and cold pressed. Ceramic synthesis was carried out at 1100°C in argon.

No essential evaporation of Tc was detected during synthesis.

Crystalline ceramic doped with 5% wt. Tc was obtained. All the samples obtained were studied using optical and scanning electron microscopy (SEM); powder X-ray diffraction (XRD) and microprobe analysis (EMPA).

Ceramic physical and chemical properties are discussed.

It was concluded that Sn-Tc-containing precursor obtained in air might be used for synthesis of Tc-doped ceramic based on kassiterite.

This is in contrast with all other precursors obtained before in reducing or inert atmosphere only.

2.P14.

ELECTROCHEMICAL INVESTIGATION OF CORROSION AND DISSOLUTION OF METALLIC TECHNETIUM AND Tc-Ru ALLOYS IN 0,5 – 6,0 M HNO_3

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The electrochemical oxidation of metallic technetium and Tc-Ru alloys in 0,5 – 6,0 mol/l HNO_3 was studied. The quantitative characteristics of the corrosion and dissolution processes were determined.

It was found that at the concentration of the nitric acid in the electrolyte less than 2,0 mol/l and at potentials less than 650 mV / Ag/AgCl the metal surface is passivated due to the formation of the slightly soluble hydrated Tc(IV) dioxide. The potential increase leads to the transition of the technetium metal into the transpassive state. In solutions containing more than 2,0 mol/l HNO_3 hydrated Tc(IV) dioxide looses its passivating properties.

It is shown that oxidation of Tc(IV)/Tc(V) is the main reaction that effects the corrosion rate. The results of the corrosion rates obtained from the measurements suggest that technetium metal can be quantitavely dissolved in nitric acid if its concentration exceeds 4,0 – 6,0 mol/l.

Comparison of the repassivation potentials of Tc-Ru alloys with the repassivation potentials using the pure Tc and Ru electrodes shows that the values of the alloy repassivation potential are intermediate between the repassivation potentials using the pure Tc and Ru electrodes. As in the case with pure metals, the values of the alloy repassivation potentials increase with increasing the HNO_3 concentration in the solution.

2.P15.

Tc-99 DETERMINATION IN CONTAMINATED GROUNDWATER

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As a result of long-term operation of industrial ponds V-9 and V-17 as reservoirs for liquid nuclear wastes at PA “Mayak” the significant contamination of groundwater system by radionuclides occur. During several years the distribution and migration of ^{90}Sr, ^{137}Cs, ^{60}Co, ^{3}H and long-lived alpha-emitting isotopes in subsurface horizons was studied while no data is available concerning the behaviour of ^{99}Tc. This study presents the first experimental results on ^{99}Tc distribution in groundwater near V-9 and V-17 reservoirs. The samples were collected from different depths.

The analytical determination of ^{99}Tc included precipitation of Fe(III) hydroxide to co-precipitate some of the interfering radionuclides that form cationic species, then technetium was reduced to Tc(IV) by adding Fe(II) and co-precipitated with its hydroxide. The precipitate was separated by centrifugation and then dissolved in diluted nitric acid with addition of H_2O_2 to oxidize Fe(II). Finally technetium containing solution was purified by anion exchange. The radioactivity of ^{99}Tc was determined using liquid scintillation spectrometry, the chemical yield was determined using ^{99m}Tc tracer.

It is shown that ^{99}Tc activity varies between 1 and 2300 Bq/l with the tendency of increase of its concentration with depth. The last fact could be explained by the high density of waste solutions in V-9 and V-17 and gravitational exclusion of groundwater by contaminated solution.

2.P16.

SORPTION OF Tc-99 AND Np-237 BY DEPLETED UO_2

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Alteration of spent nuclear fuel (SNF) upon storage in deep geological repositories under oxidizing conditions will likely result in formation of secondary phases on UO_2 surface. This may influence the solubility of SNF and release of radionuclides to the environment. On the other hand precipitated phases may limit the leaching of other radionuclides and prevent SNF from further oxidation. The goal of this work was the study solubility, secondary phase formation and Np(V) retention on the surface of UO_{2+x} sample during hydrothermal treatment in simulated oxic groundwater.

The UO_2 sample was characterized by X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to determine bulk and surface phase composition that were UO_2 and $UO_{2.25}$ respectively. The hydrothermal experiments were performed at 25°C, 70°C and 150°C during 6 months in the presence of about $1\cdot10^{-5}$ M of Tc(VII) and Np(V). For room temperature experiments the retention of Tc(VII) Np(V) by UO_2 sample was also studied as a function pH in batch mode. Solid phase and solution aliquots were taken periodically for various analyses: determination of technetium and neptunium concentrations in solutions, for XRD, XPS, SEM and TEM analyses of solid phases. Neptunium sorption was almost quantitative for all studied temperature conditions after one week of equilibration while technetium sorbed only at pH<2. Uranium solubility increased in time and reached the equilibrium values typical for U(VI) also in about one week. The progressive oxidation of the sample with formation of U(VI) alteration phases were detected by XPS, XRD and TEM for samples treated at 70 ^{0}C and 150 ^{0}C.

For Np sorption experiments that were done at room temperature the reduction of Np(V) to Np(IV) was observed at pH<4.5 while technetium stayed as Tc(VII) that explains its low sorption affinity towards UO_{2+x}. Neptunium reduction was possible either due to its interaction with the surface that had a shoichiometry close to UO_2 at low pH as determined by XPS or through the reduction by U(IV) present in solution. Upon the increase of pH the UO_2 surface became more oxidized and its stoichiometry became close to $UO_{2.25}$ as determined by XPS. At pH>4.5 neptunium was present in pentavalent and was sorbed by the surface complexation mechanism.

The work was partly supported by the ISTC project No. 2694.

2.P18.

ReO_4^- AND TcO_4^- ION-SELECTIVE BUBBLE-THROUGH FLOW CELLS

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There are two widely used techniques which are commonly regarded as flow analysis: flow-injection analysis (FIA)-methods of non-segmented streams [1-2] and continuous-flow analysis in air-segmented streams (CFA) [3]. The CFA technique includes segmentation of the pumped stream by air bubbles in order to eliminate the cross-mixing of samples and improve the mixing with the reagents. Before the stream reaches the sensor it is often passed through a debubbler to prevent erratic response. FIA utilizes a carrier stream, unsegmented by air bubbles, into which highly reproducible volumes of samples are injected. Both of these concepts have useful application, but it has been claimed that although the use of air segmentation decreases carry-over, it leads to stream irregularities owing to the compressibility of air, prevents miniaturization of the system and limits the sampling rate because of the need for debubbling of the stream. As a result, FIA has been claimed to have the advantage of a higher sampling rate. In order to eliminate the operation of removing bubbles with debubbler and to obtain the rapid sampling rates in conventional air-segmented system, bubble-through flow cells without different bubble-gating methods have been proposed in this report for Tc and Re tetraoxometallate anion determination. The feasibility of Tc determination in NSF solutions is demonstrated.

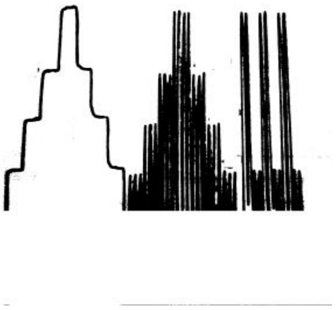

Fig. 1. *Determination of Re in standard solutions*

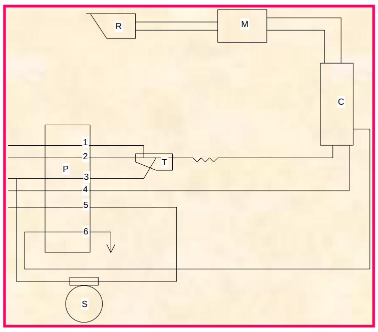

Fig. 2. *Schematic diagram of the cell response rate measuring system*

Notes

Session 3. Re Hydrometallurgy

Chairs : I.D. Troshkina, B. Bryskin
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3.1.

RHENIUM IN NUCLEAR FUEL CYCLE

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Implementation of the first stage of the nuclear fuel cycle (NFC) - uranium mining at the present stage is accompanied by a strengthening of the role of complex processing. Rhenium, an important strategic metal, has a special place among the other by-product metals due to the high profitability of its recovery.

The main rhenium-uranium deposits in the world and the data on distribution of rhenium in the processing of uranium ores are given. The basic stages of rhenium recovery from productive solution of the process of underground leaching of uranium ores are sorption on anionites, elution, the subsequent concentrating by the method of solvent extraction and the obtaining of ammonium perrhenate. The processes of rhenium recovery from solutions obtained after uranium sorption are given.

Application field of the tungsten-rhenium alloys as structural materials of equipment used in nuclear fuel cycle is discussed. These alloys operate at high temperatures (1000–1200 ^{o}C). Neutron irradiation induces significant transmutation of tungsten into rhenium and osmium. Precipitation of these alloying elements could dramatically modify the properties of the initial material. Using atom-probe tomography, it was showed that neutron irradiation could trigger the precipitation of nanoscale precipitates of the σ and χ phases in W-10 and 25 at. % Re alloy irradiated between 575 and 675 ^{o}C to 8.6 dpa. More observations of precipitation in irradiated tungsten alloys revealed the onset of phase separation at low doses.

Rhenium is intended for use in high-temperature nuclear power plants to improve efficiency and safety of their work. The interaction of nuclear fuel − uranium mononitride with the material cladding − rhenium in the temperature range 1800-2200K was investigated.

Rhenium-molybdenum alloy large tubing was developed for nuclear reactor control.

Isotope of rhenium -188 used in nuclear medicine for diagnosis is obtained in special generators from isotope of tungsten-188 as isotope production at enterprises NFC.

Rhenium is the substitute for technetium in the modeling process to generate predictions of the nuclear fuel cycle.

3.2.

RHENIUM OF KAZAKHSTAN

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The base mineral raw materials for recovery of rhenium in Kazakhstan are solid and liquid by-products of copper, lead and uranium production. Results on the recovery of rhenium from these by-products are summarized in this report.

Copper production. In pyrometallurgical processing of sulfide copper concentrates containing rhenium, this metal is concentrated in metallurgical gases. During the purification of the gas phase, rhenium is distributed between dusts, slime and wash sulfuric acid. Dusts are sent to lead smelters. At the present time wash sulfuric acid containing the basic quantity of rhenium is the only source of its industrial production in Kazakhstan. Recovery of rhenium from the wash sulfuric acid is carried out by solvent extraction. The direct recovery of rhenium was 89.1%. Technology for separate processing of mother liquor with recovery of Re and Os-187 has been implemented, and total level of Re recovery from wash sulfuric acid reaches 97.5 %. Method including slime (dust) carbonization with subsequent leaching of cake by nitric acid with production of ammonium perrhenate, tribasic lead sulfate, and osmium-, rhenium-, silvercontaining concentrate has been developed for slime processing.

Lead production. The main source for Re recovery in lead industry is the secondary dusts resulted in production of sinters from dusts of copper production together with the lead concentrates and circulating plant materials. This dust contains in % (wt.): 66.02 Pb; 0.09 Re and other elements. The method of dust leaching by solutions of sulfuric acid in a mix with the manganese concentrates produced in Kazakhstan is proposed for dust processing. Based on laboratory studies of dust leaching the optimum conditions allowing to recovery 91% rhenium, 88% cadmium, 92% zinc into solution has been chosen. For recovery of rhenium from these solutions solvent extraction technology is developed and introduced. Recovery of rhenium from the dusts into marketable products was 77%.

Uranium production. It is known that uranium ores of different deposits contain rhenium. There are a number of such ores deposits in Kazakhstan, at that rhenium resources in some of them are more than dozen of tons. Processing of uranium ores is carried out by the method of underground leaching (UL). The behavior of rhenium in the technology of uranium recovery from UL solutions has been studied at one of the enterprises in Kazakhstan. The results of studies on the development of technology for production ammonium perrhenate from UL solutions have been presented. The basic stages of rhenium recovery are sorption on anionites, and desorption with the subsequent concentrating by a method of solvent extraction. The technology of rhenium recovery from filtrates after uranium sorption has been proposed.

3.3.

DEVELOPMENT OF THE TECHNOLOGY FOR PRODUCTION OF HIGH-PURITY AMMONIUM PERRHENATE AT BALKHASH COPPER SMELTER, REPUBLIC OF KAZAKHSTAN

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The Republic of Kazakhstan is within five world's largest rhenium producers. The main source of rhenium in Kazakhstan is copper ore and Kazakhmys is virtually copper monopolist in Kazakhstan The copper concentrate is processed in electric furnace (Zhezkazgan smelter) and Vanyukov furnace (fluidized bed furnace, Balkhash smelter). During smelting and converting processes the rhenium sublimates with the gas which goes through dry ESP, cooling and washing processes and finally fed to the Acid plant to produce strong sulfuric acid. At this stage up to 70% of initial rhenium in the feed is reported to the washing sulphuric acid (weak acid).

The weak acid produced at Zhezkazgan copper smelter is supplied as a rhenium-containing feed to Zhezkazganredmet (Zhezkazgan rare metals plant) being 50% owned by Kazakhmys and 50% by the Government. The technology used at the plant is solvent extraction (SX) with followed by trialkylamine re-extraction with ammonia solution and crystallization.

The weak acid produced at the Balkhash commissioned in 2007 acid plant is the primary potential source of rhenium. It is the low rhenium grade at comparatively large flow determined the selection of the extraction method – sorption in resin-based water-insoluble ion-exchangers. The weak acid produced at Balkhash acid plant is featured by presence of selenium.

The purpose of this article is to give idea about the technology used for processing the sulfuric acid solutions produced at Balkhash acid plant, based on industry tested sorption processes featuring high rhenium and selenium recoveries and producing high-grade ammonium perrhenate and metallic selenium.

The total process flowsheet includes two stand-alone sorption sections. The first one provides for complete rhenium extraction. The rhenium-free solution containing the remaining selenium produced by the main rhenium sorption is fed to the same stand-alone selenium sorption process as well. The second stage sorption producing elemental selenium.

A special attention in the development of the sorption-based technologies should be paid to preventing the impurities from poisoning the ion exchanger as well as to development of the ion exchanger regeneration technologies.

Thus, implementation of the developed Balkhash acid plant solutions processing flowsheet will allow significant increase in high-quality APR-0 grade ammonium perrhenate production.

3.4.

USE OF ION-EXCHANGE RESINS FOR PRODUCTION OF HIGH-PURITY AMMONIUM PERRHENATE WHEN PROCESSING RHENIUM-CONTAINING ORE AND SECONDARY RAW MATERIALS

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Process flow-sheets for treatment of rhenium-containing ore and secondary raw materials differ from those for extraction of other metals by an extensive variety of techniques for production of commercial-grade ammonium perrhenate. Such a variety of technological alternatives is attributable to the small scale of production. Another aspect of this issue is selection of such an ion-exchange resin that is able to desorb easily and with a small volume of ammonia solutions the absorbed perrhenate anion up to a vanishingly low residual capacity. Such properties are intrinsic for the class of anionites or amphoteric sorbents of low basicity.

The range of ion-exchange resins for rhenium recovery is not limited to anionic resins with low basicity, which are use in acidic media. Neutral and alkaline solutions, e.g. carbonate-bicarbonate systems formed in the process of underground uranium leaching, can be processed for rhenium recovery only with the aid of strongly anionic resins. The latter have, in comparison with low-basicity ion-exchange resins, high sorption capacities for rhenium within a wide interval of hydrogen ion concentrations.

An important area of research is development of processes for rhenium extraction from materials with microconcentrations of rhenium. This would permit us, among other things, to find a solution for a problem studied since many years, i.e. recovery of rhenium from such a non-conventional raw materials as fumarole gases emitted from the Kudryavyi volcano on the Iturup Island of the Kurile island chain; according to some data, several tonnes of rhenium are emitted with those gases annually. Studies aimed at searching for ion-exchange resins suitable for use in case of rhenium microconcentrations have been carried out in the Mendeleyev State University of Technology (Troshkina I.D.) in Moscow, in the Saint-Petersburg State Institute of Technology (Blokhin A.A.), in the Gintsvetmet Institute (Gedgagov E.I.) and some other research centers.

It is obvious that in all those cases different types of apparatus should be used for processes for rhenium recovery from solutions containing as low as 0.1 to 0.2 mg Re per liter. Instead of apparatus with stationary resin beds it is required to use pressure columns with extremely high linear velocities, which have been uncommon earlier in the nonferrous metals industry.

There are significant reserves of ores in the Russian Federation containing rhenium, but careful attention is paid to techniques for processing of various types of secondary materials (waste of superalloys and spent catalysts, binary alloys, etc.) and systems with microconcentrations of rhenium (volcanic gas emissions, solutions from underground uranium leaching, etc.); at the same time, the state makes efforts to create a national sector of industry to produce ion-exchange resins, carry out comprehensive research and discuss the results obtained at conferences. All these efforts will ensure substantial progress in meeting the domestic demand for rhenium, an essential metal for future achievements in the field of aerospace technology.

3.5.

PUROLITE® ION EXCHANGE RESINS FOR RECOVERY AND PURIFICATION OF RHENIUM

Mikhaylenko, M.

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Rhenium supply in the world market is fed from two main sources: processing of different ores and recycling of secondary materials.

Hydrometallurgical methods are used for processing the rhenium feed. Often the SX, precipitation and membrane separation techniques are used to recover and purify rhenium from other elements. However in many practical cases application of rhenium selective resins provide the most direct and simplest, and consequently the most economical way to produce ammonium perrhenate of high grade.

Purolite® manufactures two rhenium selective resins: Purolite® A170 and A172. Both resins are weak base anion exchange resins made of polystyrene-divinylbenzene polymer, but the first one is macroporous and the second is gel type. Effective desorption of rhenium can be done by either sodium or ammonium hydroxide. Enrichment coefficient in desorbate can be as high as 10^3 order of magnitude.

The A170 resin is perfect for recovery of rhenium from solutions comprising of 1 to several hundred ppm of rhenium, up to several hundred grams per liter of sulfuric acid, high chloride. The rhenium recovery is very selective in regards of common alkali, alkali earth and base non-ferrous metals. Such solutions are commonly generated by copper smelters and two large smelters have already installed this resin.

The A172 resin is tailored for selective separation of rhenium from molybdenum. This technical task is quite difficult due to very similar chemical properties of perrhenate and molybdate compounds in aqueous solutions. Such solutions are obtained at processing of molybdenite concentrates.

Other application of the A170 resin is rhenium recovery from low grade solutions. An example is sulfuric uranium PLS where rhenium concentration is typically 0.5 to 3 ppm. This resin has been installed at Navoi GMK, Uzbekistan to recover rhenium from uranium barren solutions, i.e. after sorption of uranium by strong base anion exchange resin, and has been successfully operating for several years.

Finally, the A170 resin can be effective for recovery of technetium from acidic solutions.

3.6.

PHYTOMINING OF Re - AN ALTERNATIVE METHOD FOR Re PRODUCTION

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Phytomining is the uptake and preconcentration of bioavailable forms of metals from the environment into the plant biomass in a natural way. The main benefits of phytomining are low cost and environmental friendliness.

Rhenium possesses the unique property to accumulate in the green parts of a number of terrestrial and aquatic plants in amounts many times exceeding its natural occurrence. This makes the plant biosphere a natural extractor and concentrator of rhenium from soils and waters. We found that the bioavailable species of rhenium is the ReO_4^- ion. Vegetation enriched with rhenium more than 500 g Re/ t ash is considered of industrial importance and could be used as a source for rhenium production.

Our approach for Re phytorecovery from soils and waters was as follow: a) carrying out regional investigations on the Re distribution in vegetation of the copper mine “Asarel”- Bulgaria; b) locating areas with industrial importance of Re concentration in the vegetation; c) discovering plant species, which are rhenium hyperaccumulators (able to accumulate 1000 g Re/t dry mass or more; d) developing a procedure for efficient Re extraction from the plant mass and obtaining pure NH_4ReO_4**.**

Regional investigations on the degree of rhenium accumulation in various plant species from the copper mine “Asarel” in Bulgaria helped us to find an area with industrial importance of Re concentration in vegetation.

The acacia growing close to the depot for oxide Cu concentrate (obtained by bioleaching of Cu) accumulates in its leaves up to 1686 g Re/t ash. For Re phytomining it was necessary to find out the plant species, which hyperaccumulate Re and are unpretentious for cultivation and easy to harvest.

Our laboratory investigations showed that mountain-spinach (*Atriplex hortensis*) accumulates up to 3150 g Re/t dry mass, buck-wheat (*Polygonum Fagopyrum*) - 9130 g Re/t dry mass, alfalfa (*Medicago)* - 46 586 g Re/t dry mass and white clover (*Trifolium Repens*) - 35 090 g Re/t dry mass. All these plant species are Re hyperaccumulators and are suitable for real Re phytomining.

We developed two procedures for quantitative extraction of Re from the plant mass - by incineration and by ethanol extraction. After purification on a cation exchange resin, the resulting leaching solutions contained 98 % Re and only 2 % impurities of the main ash elements.

3.7.

SORPTIVE RECOVERY OF RHENIUM FROM CIRCULATING SOLUTIONS OF URANIUM IN SITU LEACHING OPERATION AT NAVOI GMK, UZBEKISTAN

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In Navoi GMK recovery of rhenium from the uranium ISL solutions was periodically made until 2002 by means of it's desorption from gel strong base anion exchange resin after desorption of uranium [1]. Due to poor technical performance of used technology its economical viability was questionable. For 15 years of exploitation of it less than 500 kg of ammonium perrhenate of AP-0 grade was produced. This old installation has been dismounted in 2008 for implementation of newer technology.

In 2003-2004 the NPO "GPS" company has undertaken laboratory investigation of the Purolite® KEP-100 and KEP-200 rhenium selective resins for sorption of rhenium from artificial solution. Being based on positive results obtained in laboratory the pilot tests of both resins were performed in the 5th RU of Navoi GMK. The resins were loaded in two similar columns by 0.7 m^3 each. Rhenium concentration in the real uranium barren solution was 0.9 – 1 mg/L. Effective desorption of rhenium was made by 2% ammonia solution.

The following results were achieved (for KEP-100 and KEP-200 accordingly):

- volumes of the solution treated for one cycle – 5500 and 7340 m^3;
- elapsing time of a sorption cycle – 735 and 790 hours;
- Re capacity achieved – 12.9 and 13.1 g/L;
- Yield of desorbates – 5.0 and 3.7 BV's;
- Re concentration in desorbates – 1.21 and 1.42 g/L.

Rhenium from the desorbate was concentrated by one-step SX followed by dialysis to produce ammonium perrhenate of AP-0 grade. Operation of existing installation has allowed to produce more than 3 tonnes of ammonium perrhenate of AP-0 grade by the end of 2010. The technology described above is defended by a patent of Russian federation [2].

[1] Zagorodnyaya, A.N., Abisheva, Z.S. et al. "Complex sorption-solvent extraction-electrodialysis technology for production of ammonium perrhenate from uranium containing solutions". Tzvetnye Metally, N8, 2010, p.p. 59-62.

[2] Volkov, V.P., Mescheryakov, N.M. et al. Patent RUS 229 4392 of 24.05.2005.

3.8.

RHENIUM(VII) SOLVENT EXTRACTION BY MIXTURES OF TERTIARY AMINE AND OXYGEN-CONTAINING EXTRAGENTS FROM SULPHATE MEDIA

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Tertiary aliphatic amines R_3N with hydrocarbon radicals of the C_8-C_{10} fraction are widely applied in rhenium technology [1]. Nevertheless, efforts are being made to develop new extracting compositions to improve rhenium recovery. In this work we have examined different parameters affecting the process of rhenium(VII) extraction from a sulphate medium by solutions of tertiary amines with different structure in a solvent admixed with octyl alcohol or ketone as modifier. The parameters essential for the process were found to be the type and concentration of both amine and modifier, as well as the aqueous phase acidity. In terms of structure and extractive ability towards rhenium, these amines can be arranged in the series: TiOA>TOA>TAA. In the case of ketone as modifier, a synergetic effect was observed, and also differently directed effects of increasing modifier concentration in the organic phase when using alcohols and ketones. In the case of increasing octyl alcohol concentration in extragent, the rhenium(VII) distribution coefficients diminished, whereas with octanon-2, these coefficients increased.

In interphase distribution studies, the pH region has revealed the presence of an extraction maximum by tertiary amines at pH=1-2. When the pH is increased to 7-9, rhenium(VII) extraction by amine-alcohol mixture is totally suppressed. Using amine-ketone mixtures, rhenium(VII) can be extracted at pH~5-7.

By increasing the aqueous phase acidity in the interval of 0.5-6 mole/l, the distribution coefficients diminish considerably. However, even admixed with octyl alcohol, tertiary amines extract rhenium at these H_2SO_4 concentrations with high distribution coefficients, that allows to recommend them for use in the complex SX technology of wet gas cleaning wastes of the copper-nickel process, providing rhenium recovery [2]. As the result, both rhenium and osmium are extracted and concentrated and some of the sulphuric acid is recovered.

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References

1. Palant, A.A., Troshkina, I.D., Chekmarev, A.M.; *Metallurgiya reniya*, Nauka: Moscow, 2007, p. 298
2. N.S. Areshina, A.G. Kasikov, I.E. Malts, V.Y. Kuznetsov, Tsvetnaya metallurgiya (Rus). **8**: 32-38 (2008).

3.9.

INTERPHASE SUBSTANCES OF RHENIUM EXTRACTION CIRCUIT ARE A SOURCE FOR PRODUCTION OF RHENIUM AND RADIOGENIC OSMIUM

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The study of rhenium extraction from wash sulfuric acid solutions produced at one of the smelters in Kazakhstan for many years has demonstrated that a black-colored precipitate is accumulated in an extract. At the stage of the solid-phase stripping a most part of the precipitate co-precipitates with pulp of ammonium perrhenate. In the production of marketable ammonium perrhenate from this pulp, a black precipitate is recovered as an independent fat dough-like or black oil-like product (hereinafter referred to as interphase substance IS).

This product makes the procedure very complex; and as we have determined, it causes a loss of rhenium, osmium and the extraction reagent. It was a matter of considerable interest to determine the elemental composition of this product and the cause of its formation.

The distinguishing feature of this IS is the high content of valuable elements: up to 10% (wt.) of rhenium and 0.5 % (wt.) of osmium. It was established that in 3% rhenium and osmium is lost with IS (from entering with the charge in copper production).

The composition of IS, was determined by infra-red-spectroscopic, x-ray diffraction (XRD), spectrum and chemical analyses. It consists of inorganic compound of various metals, organic compounds, including trialkylamine, kerosene and humic acid, insoluble compounds of Re and Os, poorly soluble complex compounds $[Cd(NH_3)_4](ReO_4)_2$, $[Cu(NH_3)_4]CI_2$.

The reason of IS origin is the presence of the precipitate in the original solution. The precipitate is the result of chemical reactions between rhenium and osmium oxides having higher level of oxidation with SO_2 and H_2O, and as well as the formation of humic acid in the gas phase and in scrubbing of metallurgical gases.

A significant amount of IS of different consistency has accumulated in the enterprise because of lack of processing technology of IS. The technology of selective recovery of soluble TAA, rhenium, and the precipitate of insoluble compounds of rhenium and osmium from IS was developed. It is based on the ability of TAA dissolved in organic solvents, recovering it from the IS by repulpation.

A combined pyro-, hydrometallurgical method for processing of precipitate has been suggested for implementation in production. This method results in selective recovering of rhenium in solution (93%), osmium almost completely left in the cake, TAA recycled to extraction.

3.10.

ELECTRODEPOSITION OF RHENIUM ALLOYS IN FORM OF POWDERS AND COATINGS FROM WATER SOLUTIONS BY MEMBRANE ELECTROLYSIS

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Alloys on the basis of refractory rhenium have a number of unique physicochemical and mechanical properties allowing essentially improve parameters of some devices. Homogeneous structure of rhenium alloys obtained from water solutions by electrolysis under given conditions with properties essentially differ from properties of these alloys produced by thermal methods.

Electrochemical processes in water solutions differ by their high efficiency and need neither aggressive reagents nor high temperatures. The basic problem is stability of anodes. All materials, except platinum, may decompose and contaminate deposited alloys during electrolysis. Application of ionite membranes in electrolyzers allows to prevent of cathodic and anodic reactions' products mixing and to obtain a pure final product without application of expensive platinum electrodes.

The possibility of Re-W, Re-Ni, Re-W-Ni alloys deposition in the form of powders and coatings on the copper and steel base plates in membrane electrolyzer with the graphite anode has been shown. As electrolytes sulfate-ammonium and sulfuric solutions with citric acid, sodium fluoride and glycerin additives were used.

The obtained Re-Ni alloys powders contain from 31 up to 76 % Re and from 24 up to 69 % Ni depending on electrolysis parameters. According to roentgen-phase analysis they are solid solutions of Re in nickel and Ni in rhenium, having cubic and hexagonal lattices respectively.

The Re-W, Re-Ni, Re-W-Ni coatings are alloys in the form of solid solutions on Re, W and Ni base. Alloys are nanostructured because their crystallization occurs with isolation of fine-dispersed phases having 2-20 nanometers size of grains. Microhardness of the coatings deposited on copper plate can reach 8270 MPa for Re-Ni, 35000 MPa for Re-W, 14808 MPa for Re-Ni-W coatings depending on electrolysis parameters. Re-W coatings corrosion resistance is higher than Re-Ni coatings corrosion resistance.

Thus, possibility of electrodeposition from water solutions electrolytes of nanostructured alloys on the basis of refractory rare metals (rhenium, tungsten) in the form of coatings with the improved constructional and physicochemical properties was established.

3.11.

APPLICATION OF ELECTRODIALYSIS METHOD FOR HIGH PURITY METAL RHENIUM OBTAINING

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High-temperature reduction of ammonium perrhenate by gaseous hydrogen is widespread method for powdery metal rhenium obtaining. Purity of metal rhenium produced by this method is generally determined by purity of initial ammonium perrhenate obtained by re-crystallization of crude ammonium perrhenate or by electrodialysis of its solutions.

Metal rhenium produced from marketable AP-0 grade ammonium perrhenate (weight %: Re - 69,2; K - $3\cdot10^{-3}$; Na - $1{,}1\cdot10^{-3}$; S $<2\cdot10^{-4}$; P $<1\cdot10^{-3}$; Si $<4\cdot10^{-5}$; Mg - $4\cdot10^{-5}$; Mn - $2\cdot10^{-5}$; Al - $2\cdot10^{-4}$; Fe - $6\cdot10^{-5}$; Ca - $2\cdot10^{-3}$; Mo - $1\cdot10^{-4}$; Ni - $1\cdot10^{-4}$; Cu $<5\cdot10^{-5}$) by method of high-temperature reduction with gaseous hydrogen at 800-900^{o} C contained no more than 99,981 % of the basic metal.

Initial ammonium perrhenate purification was carried out on industrial electrodialysis apparatus with using specially purified water for increase of metal rhenium purity in industrial conditions. Produced rhenium acid contained, weight %: Re - 27,5; K - $4\cdot10^{-5}$; Na - $8\cdot10^{-5}$; Fe - $2\cdot10^{-4}$; SO_4^{2-}-0,01; Cl^--0,06; mechanical impurities were not determined.

Ammonium perrhenate, deposited from this acid by ammonia salt contained, weight %: Re-69,2; K $<2\cdot10^{-4}$; Na - $6\cdot10^{-5}$; S $<2\cdot10^{-4}$; P $<1\cdot10^{-3}$; Si $<4\cdot10^{-5}$; Mg - $8\cdot10^{-6}$; Mn - $4\cdot10^{-6}$; Al - $1\cdot10^{-4}$; Fe - $5\cdot10^{-6}$; Ca - $3\cdot10^{-4}$; Mo - $1\cdot10^{-4}$; Ni $<1\cdot10^{-4}$; Cu $<5\cdot10^{-5}$, that on 1-2 degree (order) lower than content of such impurities as K, Na, Mg, Mn, Fe in initial ammonium perrhenate.

Washed and dried by alcohol salt was processed in the portions on laboratory facility for reduction of ammonium perrhenate with production of metallic rhenium. Roentgen-phase analysis of the obtained metal powder showed full rhenium reduction up to metal and absence of oxides in it. Impurity content in metal rhenium powder is determined by quantitative spectral method. Rhenium content is calculated by impurities content and is not less than 99,9962-99,9970 %.

Thus, metal rhenium powder, produced by high-temperature reduction with gaseous hydrogen of ammonium perrhenate, preliminary purified by electrodialysis method, exceeds on degree (order) by basic metal content the rhenium, obtained by reduction of AP-0 grade ammonium perrhenate.

3.12.

THE ELECTROLYTIC SUBSIDENCE OF RHENIUM FROM ACID ELECTROLYTES

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The future development of science and technology is possible through the study of materials with new features and development of new equipments that would meet up-to-date requirements based on these materials. From this view point the electrochemical acquisition of rhenium covers is of great importance. The fact that rhenium has high melting temperature and anti-corrosion durability allows utilizing these covers in various fields of modern technology. There are numerous electrolytes for the subsidence of rhenium in acid solutions. The main feature of the below abstract include the methods on the electrochemical acquisition of thin layers of rhenium covers from various electrolytes, as well as the selection of the optimal regime and electrolyte for the utilization of the acquired covers in the technology. For this purpose the process of the electrolytic subsidence of rhenium from sulfate, chloride-sulfate and chloride-borate solutions has been studied through the application of modern electrochemical methods. Platinum, rhenium and copper electrodes have been utilized as cathodes and platinum electrode has been utilized as anode; silver-chlorine electrode has been utilized as comparison electrode. The affects of thickness, temperature, acidity of solution, currency density, thickness of active surface elements, change speed of the potential, stirring, etc. on the process of electrolytic subsidence of rhenium have been studied. Through the controlled potential and cycle polarization curves revealed that the rhenium reduction in sulfate and chloride-sulfate solutions happens in several stages alongside with the acquisition of interim products (Re oxides). In this regard, each stage is characterized with certain electrode potential. Because rhenium reduction happens in acid environment the potential grade of its reduction depend upon the acidity as well. The impact of the electrolytic acidity on the electrolytic subsidence process shows that as the acidity increases the interim elements passivate the surface of the electrode to certain degree which hinders the subsidence of rhenium. With the change of the acidity of the electrolyte the yield of rhenium as per currency changes as well and its value ranges between 50-60%. In order to clarify the kinetic and mechanical features of the subsidence process the cathode and anode curves of rhenium were drawn and their nature of their polarization in the given electrolytes was studied. It was determined that under smaller values of the currency rhenium subsides through electrochemical polarization, under the barrier currency through diffusion and under next densities through mixed polarization.

Poster session 3

Chairman: A.A. Blokhin

Notes

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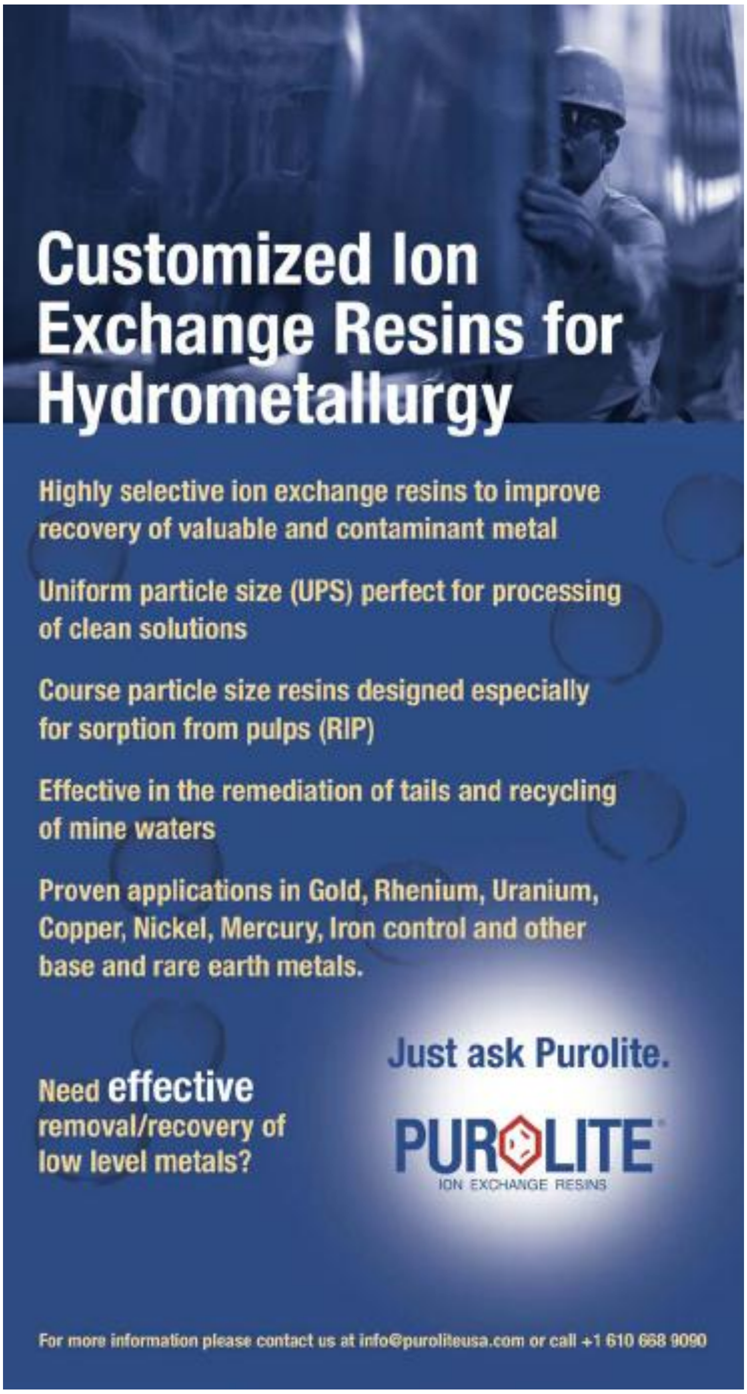

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3.P1.

SORPTION RECOVERY OF RHENIUM FROM ACIDIC SULFATE AND MIXED NITRATE-SULFATE SOLUTIONS CONTAINING MOLYBDENUM

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Molybdenites are the richest natural source of rhenium. The possibility of rhenium recovery from the molybdenite concentrates processing solutions by means of macroporous and gel anion exchange resins Purolite A170 and Purolite A172 (referred below as A170 and A172) has been investigated. Oxidizing roasting and leaching in the nitric acid (usually pressure leaching in the presence of oxygen) are the most common ways for the molybdenite concentrates processing. Acidic sulfate solutions from the roasting gas treatment system contain 0,3–0,7 g/l of Re and 4–7 g/l of Mo, while pregnant solutions from the nitric acid leaching contain 0,03–0,04 g/l of Re and 8–15 g/l of Mo.

It has been found, that A170 macroporous resin, unlike A172 gel resin, loaded both rhenium and significant amounts of molybdenum. Due to this effect, the rhenium capacity of A170 lower than that of A172 by 20–30% on terms of the sorption from the molybdenum containing solutions. At the same time, ammoniac solutions readily striped rhenium from A170 resin for any resin saturation of rhenium, as in the case of A172 resin acceptable stripping occurred only for high resin saturation of rhenium. Rhenium stripping was not complete when low rhenium saturation of A172 resin obtained. It is typical for the recovery of rhenium from the pregnant solutions of the nitric acid leaching of the molybdenite concentrates.

Therefore, A172 resin is proposed for the rhenium recovery from the acidic sulfate solutions from the roasting gas treatment system, and A170 is proposed for the rhenium recovery directly from the pregnant solutions of autoclave leaching molybdenite concentrates with nitric acid. Both A170 and A172 resins are applicable for the secondary concentration of rhenium from primary eluates if optimal pH conditions would be provided. Above recommendations have been experimentally proved on the model and real solutions.

3.P2.

RHENIUM PHYTOMINING BY ALFALFA (MEDICAGO) FROM SOILS OF ORE DRESSING REGIONS AT LABORATORY CONDITIONS

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Current technologies for the production of rhenium containing concentrates and subsequent rhenium recovery are not effective enough. During these processes, part of the rhenium is lost and dispersed as volatile Re_2O_7 in the surrounding soils and as ReO_4^- in the waste industrial solutions and waters. The unique property of rhenium to accumulate in the green over ground parts of vegetation could be used for collection of the rhenium scattered in the environment, i.e., for phytomining. The best plant hyperaccumulators of Re discovered by us at laboratory conditions are alfalfa (*Medicago*) containing 4.66 % Re in the dry mass and white clover (*Trifolium repens)* – 3.51 % Re in the dry mass.

The present work deals with the application of alfalfa (*Medicago*) for collection of the rhenium scattered in the soil near the depot of Cu concentrate of the mine Asarel - Bulgaria. Experiments were carried out as follows: a) determination of Re in an aqueous extract of the soil using the direct catalytic DMDTO method. The results of the analysis showed that C_{Re}= 5μg Re/ g dry soil, pH=8-9**;** b) planting the soil with alfalfa at laboratory conditions; c) determination of the accumulated Re in alfalfa for different periods.

The experimental results showed that 10 days after sowing the Re concentration in alfalfa was 2780 g Re/t ash while in 35 days it reached the maximum value of 4870 g Re/t ash. In this case the concentration of Re in the alfalfa was higher by a factor of 974 than that in the soil. We concluded that:

1. Alfalfa is suitable for real collection of scattered rhenium from soils of ore dressing regions.
2. Simple calculations show that 1t alfalfa ash could be obtained from 2937 m^2 alfalfa crop. With Re concentration = 4870 g Re/t ash at a current price of Re = 4 500$/kg, the profit for the producers will be 21 915 $.
3. Cultivation of alfalfa on the exhausted soils of mine regions leads to their remediation. For example, after being sowed with alfalfa for three years, 1000 m^2 soil was enriched with 7 kg P_2O_5, 12 kg Ca, 20 kg N_2 and 9 kg K_2O. This exceeds the average norm for fertilization of agriculture soils [1].
4. Application of Re phytomining in ore dressing regions would result in remediation and purification of the environment in these districts.

3.P3.

RHENIUM RECOVERY FROM GAS-PURIFICATION WASTES OF THE KOLA MINING COMPANY

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As the result of pyrometallurgical processing sulphide copper-nickel raw materials of the Kola MMC JSC, there emerge vast volumes of sulphur dioxide enriched in some volatile compounds, including Re_2O_7. During the gas purification rhenium mostly concentrates in solutions of the wet gas cleaning system (up to 10 mg/l) and, partly, in fine dust of the electric precipitators, where its content may exceed 50 g/t.

We have developed several patterns to recover the Severonikel scrubbing acid, yielding rhenium. From the point of view of comprehensive utilization of raw materials, the best pattern is the one incorporating simultaneous processing of scrubbing acid (SA) solutions and acidic flue sludges of the wet gas cleaning system, enriched in Se, Os, and Re, using solvent extraction. By this pattern, the solution with a filtered out selenium precipitate is further processed with a mixture of 20-30% TiOA and octyl alcohol to extract Re, Os and H_2SO_4. The extract is then washed with water to recover H_2SO_4 and recycled to the extraction stage. After rhenium and osmium accumulation, the part of organic phase is removed for deep alkaline stripping with NaOH. After acidifying the alkaline solution, Os distilling and further rhenium SX concentrating, a marketable Re salt is obtained.

According to another pattern, rhenium after osmium removal is recovered from scrubbing sulphuric acid either by using solvent extraction or sorption.

Rhenium from the fine dust can also be extracted with the use of several patterns, incorporating sorption or solvent extraction. Since the rhenium found in dust is in a water-soluble form, it can be effectively dissolved by aqueous leaching at 60ºC for 1 hour at S:L =1:(3-4). The leaching solutions contain 2-6 mg/l Re, the solution pH being ~2-3. To selectively isolate rhenium, we have tried sorption on Busofit carbon fibres, ion-exchange sorption on Purolite A170 resin, and solvent extraction with 15% TiOA admixed with a 10% octanol-2 as modifier. All approaches have proved satisfactory, but the highest selectivity of rhenium extraction from dust-leaching solutions was achieved with the A 170 resin.

As the result of laboratory experiments on solvent extraction and sorption of dust-leaching solutions, concentrated rhenium solutions for pure ammonium perrhenate production have been obtained.

3.P4.

SOLVENT EXTRACTION OF RHENIUM(VII) BY HIGH-MOLECULAR ALIPHATIC ALCOHOLS FROM ACID SOLUTIONS

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High-molecular aliphatic alcohols have been widely used in hydrometallurgy for solvent extraction of metals from acidic solutions. In this work, rhenium(VII) extraction by C_8-C_{12} alcohols from acidic sulphate and chloride solutions has been investigated.

It has been established that increasing of the hydrocarbon radical length diminishes the alcohols' extracting ability due to the so-called "hydrocarbon diluting effect".

For all these alcohols, rhenium distribution coefficients D_{Re} are greatly depend on the mineral acid concentration in the aqueous phase with an extraction maximum in the area of 4-7 M, depending on the alcohol type. Initially, the D_{Re} increase with increasing solution acidity is caused by the presence of H^+ participating in extraction by the hydrate-solvate mechanism; next, the D_{Re} diminish in the more acidic region in response to the competing process of mineral acid extraction by alcohol. Besides, at very high acid concentrations rhenium(VII) may change its ion species [1]. On transition from primary to secondary alcohols their extractive ability to rhenium(VII) enhances. Simultaneously, this dependence on the alcohol structure is observed when extracting single charged complex anions from sulphate and chloride solutions, whereas the doubly charged anion complexes were found to be better extracted by primary alcohols [2].

Apparently, the obtained dependencies are associated with steric problems arising when extracting multiply charged complexes with secondary alcohols. The dissimilar ability of primary and secondary alcohols to extract different-charged metal complexes was used to separate rhenium(VII) from platinum(VI) and molybdenum(VI) in processing of secondary rhenium-containing raw materials [3].

It should be noted that, notwithstanding the high performance of C_8-C_{12} alcohols in rhenium(VII) extraction from acidic solutions, increasing hydrocarbon radical length promotes the alcohol tendency to etherification with mineral acid, forming in the organic phase of compounds with surfactant properties. This hinders phases separation in the aqueous-organic systems. Therefore alcohols like decanol-1 and dodecanol-2 can hardly be unacceptable for extraction from acidic solutions.

References

1. A.G. Kasikov, A.M. Petrova. Zh. Prikl. Khimii (Rus). 82, **2**: 203-209 (2009).
2. A.G. Kasikov, A.M. Petrova. Abstr. Intern. Symp. on Sorption and Extraction "ISSE-2008", 29 Sept.-4 Oct. 2008. Vladivostok. – Vladivostok, 2008, p. 34.
3. Kasikov A.G., Petrova A.M., Bagrova E.G., Serba N.V., Kalinnikov V.T. RF pat. 2412267, 2011.

3.P5.

PRODUCTION OF THE HIGH PURITY NH4REO4 USING ELECTRODIALYSIS METHOD

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At the last years in Europe it was passed new high standards to the NH_4ReO_4 quality.

Our long-termed experience shows that standard method of recrystallization doesn't produce NH_4ReO_4 of high quality. The objective of this work was the investigation of the ability of the ultra pure NH_4ReO_4 producing. For this problem solution the process flowsheet was used: NH_4ReO_4 – electrodialysis synthesis – NH_4ReO_4 by ammonia precipitation.

In this paper NH_4ReO_4, which contains next impurities, %: Na, Mg, Mn, Al, Ni, S – 0.002, Mo – 0.01, Cu, Fe – 0.01, was studied. The investigations were carried out in the three-cell electrodialysis apparatus, which have included two membranes: the first was MA-41IL and the second was MK-40. At the first time it was added 5 g/l of the HNO_3 to the anodic cell, where bidistilled water was, and 100 g/l of the HNO_3 to the cathodic cell. NH_4ReO_4 was periodically added to the middle cell. It was producing the pregnant solution of the $HReO_4$ with C_{Re}=400 g/l as a result of electrodialysis. From this solution NH_4ReO_4 was precipitated by NH_4OH using standard method.

The process conditions were: I=2.5-5.0 A, U=18-25 V, temperature in the anodic cell was 20-30°C, in the middle cell 25-40°C.

NH_4ReO_4 crystals contain next impurities, %: Fe – 0.00008 (0.0005), Al – 0.0001(0.0001), Cu – 0.00005 (0.0001), Mo – 0.00005 (0.0005), Ni – 0.00005 (0.0001), Mn – 0.00005 (0.0001), Mg – 0.00005 (0.0001), Ca – 0.00016 (0.0005), Na – 0.00006 (0.0005), K – 0.00004 (0.0005), Cr – 0.00005 (0.0001) (in parentheses it are maximum permissible concentration of the impurities in accordance with new European regulations).

3.P6.

POSSIBILITIES OF OXIDATIVE LIXIVIATION OF RHENIUM SULPHIDES BY LOW PRESSURES

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By processing of tail salt solutions of molybdenum industry by means of hydrothermal sulphidizing sediment of geptade sulphide renium-Re_2S_7 is received. It is necessary its to utilize [1,2]. In this connection stadying appropriatenesses of lixiviation of this form is urgent.

Oxidative lixiviation of raw materials has been carried out in the following way: water- sulfate pulp of raw materials has been prepared and has been loated in to hermetic reactor supplied by fast-acting stirring rod, pipe of hydroblock and cylindrical diffuzer. Oxygen is given directly under stirring rod with qoal of effective its disperse. Due to intensive exchange of gas phase liquid environment and hard raw materials simultaneous oxidation components of raw materials and regeneration oxides of nitrogen is provided in the reactor. His possible to characterize behavior of rhenium into solution in the form of above rhenium $H_4Re_2O_9$ and rhenium $HReO_4$ acids:

a) $2Re_7+ +4,5\ O_2*- +4H+ = H_4Re_2O_9$;

b) $Re_2S_7+NO++2H++3e-+4,5O_2^{-}* = 2HReO_4 +NO_2 + 7\ S$;

c) $Re_2S_7 + H_2NO_2+ + 4O_2*- + e- = 2HReO_4 + NO_2 + 7\ S$;

d) $Re_2S_7 + 2H_3O^{+} + 4O_2^{*-} = 2HReO_4 + 7S + 2\ H_2O$.

The radicals-nitrozonium (NO^{+} or $H_2NO_2^{+}$) superoxide oxygen ($O^{2—}$ *) and H_3O^{+} ions are by active beginning and motive are generated in work zone of reactor of lixiviation and serve for extraction rhenium into solution through mechanism of oxidation-reduction. The last consists in the fact that sulfur is oxidized up to element S^{2-} -2e- = S, ion of nitrozoniy is reduced up to dioxide NO + ½ $O^{2—}$ * + 1e- = NO_2, which in the water environment forms nitrous acid- source of active radicals.

So far as reactor of regeneration of nitrous acid is irreversible, its speed with lowering absolute pressure increases, and, therefore, speed of consumption of oxygen increases with formation active radicals. Oxydative catalytic of nitrite sodium permits to reach maximum full rhenium extraction into solution to 98-99%.

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1. Аллабергенов Р.Д. Автоклавный азотнокислотный способ переработки медных концентратов.- Автореф….к.т.н. –Алма-Ата, 1983. – 25 с.

2.Евтифьев В.М., Беляев Ю.М. Способ окислительного выщелачивания сульфидного и металлического сырья - Авторское свидетельство СССР, №1295760, 13.04.1984 г.

3.P7.

SORPTION OF RHENIUM FROM URANIUM SOLUTIONS BY NANOSTRUCTURED IONITES

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Rhenium is traditionally obtained as by-product in the processing of molybdenite and copper ores concentrates. Limited resources of traditional raw materials in Russia are responsible for the searching of new sources of rhenium. Uranium polymetallic raw material is additional source of rhenium. For the first time rhenium was recovered from uranium ores in the USA from 1969 to 1974 (Texas, Susquehanna Corporation).

Effective method of uranium ores processing is the underground leaching. Rhenium concentration in uranium productive solution is 0.1-0.5 mg/l. Rhenium is recovered by sorption from these solutions.

The aim of this study is the rhenium sorption by nanostructured ionites from model productive solution obtained in the process of underground uranium leaching.

Used nanostructured ionites on styrene-acrylate-based (B-62, B-510) were synthesized in Federal State Unitary Enterprice Leader Research Institute of Chemical Technology. These ionites have different types of functional groups and porosity. In micrographs of grain cleavage the resin obtained by electron microscopy, there are spherical microgranules that have the size of 200-400 nm. The channels between microgranules (pores) have a diameter of 100 nm.

The model solution contains: rhenium – 20 mg/l, uranium – 20 mg/l; sulfate-ion – 10 g/l; chloride-ion – 1 g/l.

The equilibrium and dynamic characteristics of sorption are studied. Calculated Henry's law constant K has the following value for selected resins, ml/g: $(1,48 \pm 0,13) \cdot 10^3$ (R^2 - 0,91) (the resin B-62) and $(1,88 \pm 0,13) \cdot 10^3$ (R^2 - 0,93) (the resin B-510).

Degree of rhenium concentration calculated according to data on the dynamics of sorption and eluation reached 600 - 700.

Nanostructured ionites are recommended for rhenium recovery from productive uranium sulfuric acid solution obtained in processing of ores by underground leaching.

3.P8.

SORPTION OF PALLADIUM FROM THE RHENIUM CONTAINING SULPHURIC ACID SOLUTION

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Rhenium raw of Uzbekistan has high complexity with known in recent years a significant share of the platinum metals. The source of the combined recovery of rhenium and platinum group metals is copper-molybdenum deposit Almalyk's ore field. Their characteristic feature is the presence of radiogenic isotopes of osmium-187 - a product of the decay of rhenium-187, as well as appreciable amounts of palladium, platinum, iridium, ruthenium, rhodium.

In the process of smelting of copper concentrates from 6,7 up to 13,2 % of each of the platinum group goes from the gas phase in the dust, caught in a dust chamber and electrofilter [1]. Solutions formed during the preparation of sulfuric acid from metallurgical gases of copper and molybdenum production are the main source of rhenium. They contain up to 150 grams per liter of sulfuric acid, fluorine, arsenic, copper, zinc and rhenium [2].

The aim is to investigate the possibility of sorption and preconcentration of palladium from rhenium-containing sulfuric acid solutions. As sorbents were used: a low basic anion exchanger AN-105, ampholyte VP-14KR, ion exchange resins with different basicity of the company Purolite (A 170, MN 202 and D 4384), as well as the company Lanxess (Lewatit MP 62, MonoPlus TP 207 and MonoPlus TP 214), carbon sorbent, modified by polytetrafluoroethylene (CS-PTFE).

Sorption of palladium was carried out in batch conditions for 3 days from the solution of the following composition: palladium - 24 mg/l, sulfuric acid - 100 g/l. The phase ratio of the sorbent to the solution was 1:500. Desorption of palladium was carried out also in batch conditions at the ratio of 1:60 using ammonia (8%) and/or hydrochloric acid (4 mol/l).

The results show that the distribution coefficient of palladium in the sorption of the materials under study is located within $3{,}8 \cdot 10^1 \div 4{,}0 \cdot 10^4$ cm^3/g, decreasing in line: TP 214> D 4384 Aliquat 336> TP 207> AN-105> CS-PTFE> A170> MN 202 TAA> MP 62> VP-14KR.

The best results were observed for the elution of palladium from the ionite D 4384 Aliquat 336 by ammonium hydroxide solution (distribution coefficient - 31.7 g/cm^3) and TP 207 by hydrochloric acid (distribution coefficient - 38.9 g/cm^3).

Thus, for the combined recovery of palladium from rhenium containing solutions sorbents CS-PTFE, AN-105, MonoPlus TP 214, MonoPlus TP 207, Purolite D 4384 can be used.

REFERENCES

1. Rabicheva L.M., Morozov V.N., etc. Tsvetnye Metally, **12**: 54-55 (1981)

2. Popov I.F., Mekler L.I., etc. Scientific works of the Central Asia Research Institute of Nonferrous Metals, **11**: 59-98 (1975)

3.P9.

ULTRAFILTRATION SEPARATION OF RHENIUM AND URANIUM USING NITROGEN-CONTAINING POLYELECTROLYTES

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Uranium ores are one of the rhenium sources. Their hydrometallurgical processing produces solutions where rhenium concentration is 0.n mg/l. In case of large quantities productive solutions and due to high market value of rhenium its recovery becomes reasonable.

This work is connected with the rhenium recovery from uranium solutions by the method of complexing ultrafiltration. As a complexing agent water soluble polyelectrolytes of different types − Praestol (Germany) and Heng Floc (China) brands are used. The main element of the laboratory ultrafiltration device is tubular ultrafiltration module with polysulfone hollow fiber separating membranes. This hollow fiber module works under pressure of feed solution 0,2÷0,5 bar.

Separation is based on stability of polyelectrolyte-metal complex in water solutions and depends on salt composition and pH value.

Preliminarily the membrane selectivity for each metal was studied in presence of different polyelectrolytes. Influence of pH value and contents of different ions in initial solutions on the selectivity were studied in presence of each polyelectrolyte. The possibility of reagent regeneration of polyelectrolytes was investigated.

Under certain conditions it is possible to gain full complexing of polyelectrolyte and both metals, or just selective complexing of polyelectrolyte and one of them.

Concentrating of both metals using of polyelectrolyte Praestol 658 (0.1 %) are observed. Membrane selectivity reaches 91 % for rhenium and 92 % for uranium by pH value 7.4. In case of concentration of nitrate ions 0.1 mol/l and pH value 6.9 membrane selectivity of rhenium decreases to low values, but membrane selectivity of uranium increases to 92 %.

When pH value decreases to 4.1 membrane selectivity of uranium reduces to 11 %, but the membrane selectivity of rhenium increases to 96 %.

3.P10.

RECOVERY OF RHENIUM FROM AQUEOUS SOLUTIONS BY FIBROUS MATERIALS

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Nitrogen containing anionites and complexing ionites as well as amino containing impregnates are used for sorption of rhenium, one of the least distributed rare metals. The possibility of rhenium recovery from aqueous solutions by fibrous materials was investigated. The main advantage of them as compared with granular ionites is a high sorption rate.

Sorption characteristics of the following fibrous materials: carbon fiber (Busofite and Actylene), carbon fibers modified by electrochemical and chemical method (adsorption on the surface of natural polyelectrolyte – chitosan), acrylic fibers FIBAN are studied. FIBAN-sorbents contain following anion-exchange groups: $-N(CH_2COO^-)_2$ (FIBAN A-6); $=NH$, $-NH_2$, $-COOH$, $\equiv N$ (FIBAN AK-22).

The rhenium sorption by fibrous materials was carried out in batch conditions. The ammoniac solution was used for rhenium elution.

The equilibrium and kinetic characteristics of rhenium sorption by Busofit-based fibrous carbon materials treated electrochemically with recovery potentials varying from –900 to +600 mV from aqueous solutions in the presence of natural biopolymer chitosan. Materials obtained in the anodic potential region and at the open-circuit potential have the best capacity characteristics. The highest rhenium capacity is observed for the material prepared at the recovery potential +600 mV. The relevant sorption isotherm is described by the Langmuir equation with the constant 73 ± 8.1 mL/mg; the half-conversion time is 3 min.

The degree of rhenium sorption was 71 and 97 % for the ionites FIBAN A-6 and AK-22 accordingly. Elution characteristics for sorbent FIBAN AK-22 are better than for ionite FIBAN A-6.

3.P11.

RHENIUM RECYCLING FROM HEAT-RESISTANT RHENIUM-CONTAINING NICKEL-BASED SUPERALLOYS

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It is known that heat-resistant alloys (HRA) of the latest generations contain 4-9% rhenium, so both their treatment and operation wastes can be regarded as fairly rich rhenium sources. However, although the amount of such wastes, annually turned out in Russia, is ~25-35 t (according to FSUE “VIAM” data [1]), only a small part of them are being recycled.

At our Institute, two variants for a technology of nickel-based HRA wastes of the ZhS-32 type have been developed.

The advantage of the technology consists in the possibility of processing both fine and lump material. Grinding of the latter is achieved by high-temperature fusing with an embrittling agent, i.e. aluminium metal, followed by grinding of the fusion cake on standard equipment.

The fine product can be processed following either a hydrometallurgical or a hybrid scheme. The first pattern involves oxidizing sulphuric-acid leaching of HRA wastes with rhenium removing to an acid solution, and it’s selective recovery by solvent extraction [2]. By the second pattern, the alloy base is leached out by mineral acid solution with rhenium concentrating in the leaching residue, and high-temperature distilling of Re_2O_7 from the solid concentrate, followed by hydrometallurgical purification of the absorber solution from molybdenum. Both laboratory and pilot testing have demonstrated high performance of these schemes of rhenium recycling from nickel-based HRA wastes, yielding a NH_4ReO_4 salt utilizable in the production of rhenium metal powders.

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References

1. V.M. Paretskiy, A.D. Besser, E.I. Gedgagov, Tsvetnye Metally (Rus). 10: 17-21 (2008).
2. Kasikov A.G., Petrova A.M., Bagrova E.G., Serba N.V., Kalinnikov V.T. RF Pat. 2412267, 2011.

3.P12.

INSTALLATION FOR LIQUID-LIQUID EXTRACTION CONCENTRATING AND RECOVERY OF RHENIUM FROM AQUEOUS SULFATE SOLUTION

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Academinvestservise Ltd., JSC NPO Innovation and development

Liquid-liquid extraction is a powerful method for separation of rare metals in course of its hydrometallurgical reprocessing. It is widely used in course of technetium separations in the reprocessing of spent nuclear fuel. Its application for the separation of rhenium – a close neighbor of Tc in the Periodic Table – is considerably less abundant as the sorptive technologies are well developed [1].

Although less abundant, the extraction separations of Re are also known and used for example in the case of separation of Re from W in its nucleus generator [2].

Here we present an installation that could be applied to liquid-liquid extraction concentrating and recovery (LLEC-I) of Re from aqueous sulfate solution.

The principle blocks of the LLEC-I include the clarification blocks (CS 1, 3), LLE and stripping block (LLESB, 2), precipitation block (PB, 4). In a special installation modification LLEC-I-C the conversion block (CB, 5) is adopted.

The CS block is based on a know-how spiral principle. The LLESB is a conventional extractor, while PB is presented by two modifications (C – a conventional one, and M – equipped with a melter of special design with know-hows and a patent providing with the possibility of melted organic perrhenate separation.

References

1. Pallant A.A., Troshkina I.D., Chekmarev A.M. *Rhenium metallurgy*. M.: Nauka Publ.. 2007. 298 p.
2. M.P.Zykov, A.T.Filyanin, G.E.Kodina, A.Yu.Tsivadze, V.N. Romanovsky et.all., 2011, This issue.

3.P13.

RECOVERY OF RHENIUM FROM OIL SHALE

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Carbonaceous source which is represented by a large group of minerals, such as oil, bitumen, carbon, oil shale (OS) is a non-traditional potential raw material of rhenium. Since the deposits of these minerals run into milliards of tons, the rhenium resources in them are great, in spite of the relatively low rhenium concentration. Data on rhenium content in carbonaceous raw materials are relatively scarce and contradictory, although all of them considerably exceed its abundance ratio in the crust ($7\cdot10^{-4}$ g/t by A.P.Winogradov).

Rhenium is found in solid combustible minerals enriched with Mo, V, Cu and U. This complex of microelements is more characteristic of oil shale than of the coal. Comprehensive energy-technological processing of metalliferous oil shale with complete utilization of organic and mineral parts includes their thermal treatment for production of electric and heat energy, chemical products, metals, and building materials. Traditional methods for the thermal treatment of OS are pyrolysis, semicoking, heat dissolution.

Rhenium distribution at high temperature combined processing of oil shale (OS) - oxidizing pyrolysis and the semicoking was studied. The semicoking of OS (Uzbekistan) was performed at the pilot device with solid heat-transport medium at 750°C, the pyrolysis –in the reactor at universal device. The oxidizing pyrolysis of OS at 750-800 °C results in extensive decomposition of the organic substances, which presumable incorporate rhenium. Rhenium heptaoxide, which is a highly volatile compound, passes into the gaseous phase and concentrates in the coke (84.7%). During the semicoking, the main part of rhenium also concentrates in the solid product-semicoke (60.0 %).

Rhenium recovery from the coke was investigated. The rhenium leaching from the coke by water was carried out. Rhenium is successfully recovered from obtained solutions by sorption on active carbon, modified active carbon and anionite. The sorption degree of rhenium was reached 50 % (active carbon BAU), 94.6 % (modified active carbon) and 99.4 % (anionite).

Notes

Rezoscan, ^{99m}Tc (Zoledronic acid)

The novel third-generation bisphosphonate (zoledronate) radiopharmaceutical for bone scintigraphy with radionuclide ^{99m}Tc.

Rezoscan,^{99m}Tc indications:

- Detecting, staging, and follow-up of metastatic disease (osteoclastic, osteolytic metastasis);
- Primary and secondary bone neoplasms;
- Infections inflammatory disease (osteomyelitis, tuberculosis of bones & joints);
- Metabolic and endocrine diseases;
- Traumas and vascular bone diseases;
- Osteoarticular disease (arthritis & arthrosis of different etiology).

Octreotide, ^{111}In (Pentetreotide)

The drug is designed for radionuclear diagnosis of tumors having high density of somatostatin receptors, as well as for the establishment of receptoral status of the tumor for the clinic effects prognosis of treatment with Octreotid.

Octreotide, ^{111}In indications:

- Carcinoid Tumors;
- Islet Cell Tumors (Gastrinoma, Insulinoma, VIPoma, Glucagonoma);
- Small Cell Lung Carcinoma;
- CNS Tumors (Paraganglioma, Pituitary Adenoma, Meningioma);
- Miscellaneous Tumors (Pheochromocytoma, Undifferentiated APUDoma);
- Determination of tumor receptors status in patients receiving therapeutic doses of Octreotid for clinic effects treatment forecast.

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Session 4.

Tc and Re in Nuclear Medicine

Chairs : G.E. Kodina, H. Braband, F. Groppi

Sponsors : FMBC FMBA, CJSC “Pharm-Sintez”, Diamed Ltd., NTC Amplituda Ltd.

4.1.

Tc-99m AND Re-188 IN RUSSIAN NUCLEAR MEDICINE

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The main tendency of modern nuclear medicine is substantial growth of radiopharmaceuticals (RP) using for therapy, first of all in oncology, but at a proceeding expansion of diagnostic RP. Thus, despite of rapid development of PET quantity of diagnostic procedures with ^{99m}Tc SPECT and SPECT/CT also continue to grow.

New line for fission ^{99}Mo production started at the end of 2010 in RIAR (Dimitrovgrad). It has allowed to liquidate a problem of ^{99}Mo deficiency in Russia and a significant amount is already exported. There are 3 enterprises on ^{99m}Tc-generators (chromatographic type) production in our country – at IPPE and BPCI (Obninsk) and at PTI (Tomsk). New manufacture of the generators on GMP requirements is projected in Obninsk at the near future. Exstraction generators providing centralized deliveries of a Na^{99m}TcO$_4$-solution work in Moscow, St.-Petersburg and Tomsk. Capacities of operating manufactures are quite sufficient for full satisfaction of the Russian clinics and capable to increase release of generators significantly. Growth of volumes of release restrains with lack of the equipment in hospitals as well as unsatisfactory schemes and time of delivery to some Russian regions.

^{99m}Tc-kits are let out by DIAMED Ltd. (Moscow), certificated according to requirements GMP. The enterprise during 20 years completely satisfies needs of domestic and NM-departments and also is capable to increase volumes of release significantly. It is necessary to note, that to 2008 the volume of kits supplied to domestic clinics has returned on a level which has been reached up to a default (1998г.), but is not observed growth (for the reasons specified above) not looking at expansion of the nomenclature further. Nowadays the list includes 13 positions. Analysis of changes in ^{99m}Tc-kits usage for diagnostics of various diseases is resulted in the report.

Among last development of new ^{99m}Tc-RP, introduced in manufacture or clinical trials it is necessary to note « Resoscan, ^{99m}Tc» (for osteoscintigraphy, on the base of zoledronic acids) and «Nanotech,^{99m}Tc » (nanocolloid for sentynel lymph nodes visualization).

^{188}Re-Generators are let out by IPPE (Obninsk). R&D on ^{188}Re production in a centrifugal extractor are spent in KRI (St.-Petersburg) in collaboration with IPCE RAS (Moscow).

Preclinical trials of «Zoleren,^{188}Re» (^{188}Re-zoledronic acid for therapy of bone metastasises) are starting in June, 2011 and then clinical trials will be held in 2012. The RP was developed in FMBC under the order of JS-Company «Pharm-Sintez». The R&D program on creation of ^{188}Re-RP for radiosynovectomy is begun this year.

As a whole it is possible to conclude, that in Russia there are necessary and sufficient conditions for progress and development of new technologies for nuclear medicine with use both ^{99m}Tc, and ^{188}Re. Researchers and manufacturers of generators and RP on the basis of these radionuclides hope, that realization of the Federal program «Development of the pharmaceutical and medical industry of the Russian Federation for the period till 2020 and the further prospect» as well as the Project «Progress of nuclear medicine in the Russian Federation » will allow to expand significantly researches and to increase volumes of release of already existing and new radiopharmaceuticals.

4.2.

THE *fac*-$\{TcO_3\}^+$ CORE – A CHALLENGE FOR HIGH-VALENT TECHNETIUM CHEMISTRY

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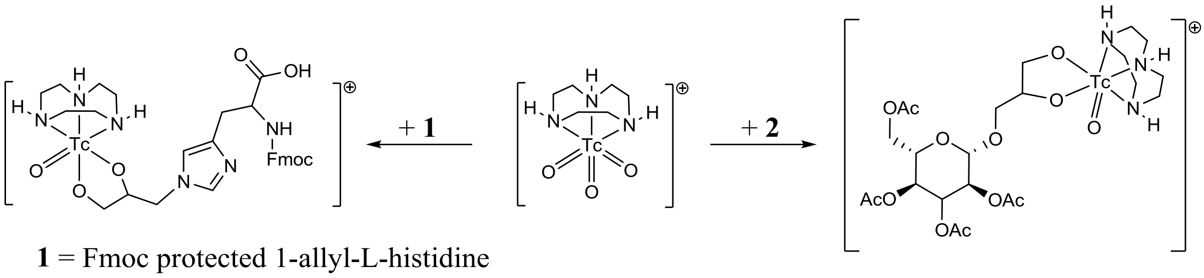
We are aiming at a general understanding of the reactivity of technetium at its highest oxidation state +VII. Our research foremost focuses on compounds containing the *fac*-$\{TcO_3\}^+$ core, due to its interesting chemical properties ([3+2] cycloaddition with alkenes).[1] To make the *fac*-$\{TcO_3\}^+$ core accessible for a broad range of investigations new methods for the synthesis of *fac*-$\{TcO_3\}^+$ complexes needed to be developed. Activation of $[^{99}TcO_4]^-$ by reaction with strong Lewis acids and the oxidation of stable Tc^{+V} complexes are new opportunities for the synthesis of $\{^{99}TcO_3\}^+$ complexes containing tripodal ligands. At the tracer level phosphates were used to develop the first synthesis for $\{^{99m}TcO_3\}^+$ complexes. With these new reactions at hand the high-valent technetium chemistry of *fac*-$\{TcO_3\}^+$ complexes containing ^{99}Tc can be investigated as well as at the tracer level by using the nuclear isomer ^{99m}Tc. A main aim of our research is the establishment of a new labeling strategy based on the reactivity of *fac*-$\{^{99m}TcO_3\}^+$ complexes with alkenes ([3+2]-cycloaddition) to enable new opportunities for nuclear medicine.[2] Water stable $[^{99m}TcO_3(tacn\text{-}R)]^+$ type complexes (tacn-R = 1,4,7-triazacyclononane and derivatives) are versatile precursors for this approach. First bio-distribution studies of the hydrophilic $[^{99m}TcO_3(tacn)]^+$ showed that the bio-profile of this compound differs fundamentally from the well known precursor $[^{99m}Tc(OH_2)_3(CO)_3]^+$ which unspecifically binds to blood pool proteins, thereby inhibiting a fast clearance from the body (essential for imaging). To demonstrate the potential and flexibility of the [3+2] cycloaddition labeling concept, a pharmacophore, the Fmoc-protected 1-allyl-L-histidine as a possible single amino acid chelate (SAAC) group and the monosaccharide allyl 2,3,4,6-tetra- O-acetyl-β-(D)-glucopyranoside were synthesized and labeled with $[^{99m}TcO_3(tacn)]^+$.



1 = Fmoc protected 1-allyl-L-histidine
2 = Allyl 2,3,4,6-tetra-O-acetyl-β -(D)-glucopyranoside

[1] R. M. Pearlstein, A. Davison, Polyhedron, **1988**, 7, 1981.
[2] H. Braband, Y. Tooyama, T. Fox, R. Alberto, Chem. Eur. J., **2009**,15, 633.

4.3.

NEW RADIOPHARMACEUTICALS BASED ON TECHNETIUM-99m WITH BIFUNCTIONAL CHELATING AGENTS

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Currently, ^{99m}Tc is radionuclide of choice for the preparation of SPECT-radiopharmaceuticals (RP) in the whole world. ^{99m}Tc is eluted from the generator in the form of a solution $Na^{99m}TcO_4$, and then subjected to reduction and complexation with ligands. The complexity of technetium chemistry makes it necessary to search for new, improved and multifunctional complexing agents. Particular attention is paid to ligands that can not only bind technetium, but also can be linked to biomolecules such as peptides or monoclonal antibodies. Among these ligands, called bifunctional chelating agents (BCA), best results are showed by DTPA (Diethylene triamine pentaacetic acid), MAG_3 (Mercaptuacetyltriglycine), and HYNIC (6-Hydrazinopyridine-3-carboxylic acid).

Published data on the synthesis and application of some peptides labeled with ^{99m}Tc using HYNIC, and DTPA and MAG_3 are reviewed. There were found changes in the behavior of conjugates with the same peptide using different BCA. This suggests that the choice of BCA should be the first stage of planning the development of each new BCA RP with technetium-99m.

As a biological basis for the creation of conjugates with different radionuclides (^{111}In, ^{68}Ga) octreotide is often taken. Octreotide is an analogue of the somatostatin wich is accumulated in cancer cells of neuroendocrine nature. It was found that the conjugates with ^{99m}Tc-octreotide are not effective enough, and the peptide has been modified. The most successful results of such modifications are Vapreotid (RC-160) and tyrosine-Octreotide (TOC).

When comparing DTPA, MAG_3 and HYNIC most researchers coincide that preference over the other two BCA is given to HYNIC, which is caused, first of all, by its more suitable pharmacokinetic properties. Nevertheless, data on biodistribution of all three BCA conjugates still remain controversial.

The report also discusses published data on the choice soligand to HYNIC. The following soligands are considered: tricine (1,1-bis(hydroxymethyl)ethyl)glycine), EDDA (Ethylene diamine diacetic acid) and the mixture tricine with nicotinic acid. All these soligands provide obtaining of peptides labeled with ^{99m}Tc, in good yield and stability. According to some reports, the best pharmacokinetics (accumulation in tumors, the rapid excretion via the kidney) was detected in the RP with EDDA as soligand. With the data presented, it is clear that not only conjugates known soligands (mostly tricine and EDDA) should be further developed, but also new ones should be looked for. The peptide most advisable to use is TOC.

4.4.

“Rezoskan, ^{99m}Tc” IN THE DIAGNOSIS OF METASTATIC BONE LESIONS

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“Rezoscan, ^{99m}Tc” is the first kit used in the domestic and international practices for commercial radiopharmaceuticals (RP) based on zoledronic acid, being intended for the diagnostic of bone pathology by Single Photon Emission Computed Tomography (SPECT).

Our clinical studies provided with the data on the high diagnostic value of the drug enabling to identify metastatic bone cancer patients. The primarily observed pharmacokinetic characteristics of the drug, compared with those applied in the clinic counterparts, indicate that it is characterized with more rapid RP elimination from the body, low accumulation in organs and tissues at high tropism to sites of metastasis in the skeleton. It provide with higher sensitivity and resolution in detecting metastatic lesions of the skeleton of variable nature.

Due to favorable pharmacokinetics, the “Rezoscan, ^{99m}Tc” SPECT examination is possible 1 - 1.5 hours after administration of the radiopharmaceutical, whereas all the existing RP require at least 3 hours waiting period before the patient bone scan examination. This ensures high economic and technological efficiency and lower patient irradiation dose rates.

Using “Rezoscan, ^{99m}Tc” it was possible to identify both blastic, mixed, and, most important, the lytic metastases in primary bone scan, that were not detected by commonly used radiopharmaceuticals in clinics. It should be noted that in recent medical practice there were no other radioisotope diagnostic products providing with the possibility to detect lytic metastases in the skeleton.

The investigation conducted on a selected group of patients has shown that bone scanning with “Rezoscan, ^{99m}Tc” allows control of skeletal metastases by means of therapy with zoledronic acid combined with chemotherapy.

Based on the foregoing, we conclude that the drug “Rezoscan, ^{99m}Tc” significantly differs from the previous generation of diagnostic radiopharmaceuticals and it has prospects for wider use in clinical practice.

4.5.

OBTAINING TECHNETIUM-99M LABELED NANOCOLLOIDS BASED ON ALUMINUM OXIDE FOR MEDICAL DIAGNOSTICS

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In recent years, labeled with technetium-99m (^{99m}Tc) nanosized colloids of various compositions are widely used in medicine for the diagnosis of inflammatory processes, the identification of "sentinel" lymph nodes in cancer patients, for labeling autoleukocytes etc. Presupposition for using aluminum oxide as a "carrier ^{99m}Tc label is its relatively low toxicity, combined with good adsorption properties, availability and low cost. As the object of research, we used gamma-Al_2O_3 nanopowder with a particle size of 7 nm obtained from aluminum hydroxide by cyclic heating to 500°C.

In order to obtain stable compounds of ^{99m}Tc with Al_2O_3 oxide there was previously studied the effect of acid activation of oxides on the value of their sorption capacity in relation to ^{99m}Tc which has different degrees of oxidation in static conditions for adsorption. As a reducing agent tin (II) chloride dehydrate ($SnCl_2 \cdot 2H_2O$) was used. As a result, it was found that the maximum adsorption of ^{99m}Tc is observed on oxides Al_2O_3, treated with HCl solution on the basis of $2 \cdot 10^{-4}$ mole per 1 g of oxide, which corresponds to pH 5.6 colloid. In these conditions the adsorption of ^{99m}Tc (VII) ions is about 30%, and of reduced ions of ^{99m}Tc (IV) – more than 90%. The method of filtering the resulting product through a filter with a pore diameter of 100 nm revealed that in the latter case, the output of labeled nanocolloid exceeds 98%. In this case, adsorbed on oxide ^{99m}Tc (IV) is not washed off with saline (0.9% solution of NaCl), which indicates the stability of the compound. The investigation of the chromatograms showed in the resulting product apart to ^{99m}Tc (VII) the presence of two reduced forms of ^{99m}Tc. Perhaps one of them is ^{99m}Tc (V).

Medicobiological tests of ^{99m}Tc labeled oxide Al_2O_3 were conducted on “Vistar” line white male-rats with weight 300-350 g. Inguinal lymph node in all the animals clearly visualized in 15 minutes, when it accumulated from 1,2 to 2,1% of introduced amount of labeled colloid. This shows the principal possibility of using the obtained compound for conducting lymphoscintigraphy.

4.6.

RECEIVING OF NANOSIZED COLLOIDS BASED ON MODIFICATED DTPA MOLECULE LABELED WITH TECHNETIUM-99m

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Currently, the significantly intensification of interest to use of radioactivity colloid nonmaterial's in medicine is note all around the world. Radioactivity nanocolloid application in oncology is based on quick and effective ability of «sentinel» lymph nodes detection.

Optimal method of «sentinel» lymph node detection is consider in use of colloid nonmaterial's marked by technetium-99m for scintigraphic or radiometric detection of node localization. Rich coordination chemistry of technetium can obtain on its basis the various simple and complex, biologically active coordination compounds with desired properties.

As a result of the spent researches the methods of receipting of new nanocolloid based chemical systems on basis of modification of diethylene triamine pentaacetic acid (DTPA) molecule has been worked out. The main factor, which is affect on using DTPA as chelator of radioactive mark, was molecule or one's derivative ability to form enough stable complexes with different radioactive metals including combination of technetium-99. The DTPA molecule hydrophilic and that's why one can't form colloidal particles. Hydrophilic fragments addition gave the ability to receive insoluble's modified complex of DTPA.

Preliminary research of compound transmission density, show's that the middle radius of generated colloids is near 100 nanometers. But the middle radiochemical emission of nanocolloid, which have the diameter less than 100 nanometers, is about 80%, and this is closed to foreign analogs rate.

The result of dynamic scintigraphic research showed, that after being injected, the preparation goes to lymphatic system very active. Eventually one can say that modify nanocolloids are functionally suitable for lymphoscintigraphy and « sentinel» node visualization.

That work has been carried out in the network of federal program «Scientific and scientific-pedagogical manpower of innovated Russia for 2009-2013»

4.7.

SYNTHESIS AND COMPLEX ANALYSIS OF BIOLOGICALLY ACTIVE POLYMERS (POLY-N-VINYLPYRROLIDONE) WITH $Re(CO)_3$SPECIES

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Over the last 15 years chemistry of organometallic species, $M(CO)_3^+$ (M = Tc, Re) has been intensively studied. This interest grow up due to promising properties of these species: relatively small size and low metal charge of metal atom (+1). Potentially, these parameters should not disturb biological properties of organometallic biocojugates. However, worldwide practice of synthesis of low molecular compounds labeled with the $M(CO)_3^+$ fragment and biudistribution studies demonstrates significant decreasing of target site transport of conjugates and accumulation of radioactivity in non target organs. More successful was introducing of organometallic species into high molecular biomolecules (antibodies, proteins). However, despite promising diagnostic and therapeutic results, this approach has limitations due to complicated multistep synthetic and purification procedure and, moreover, is rather expensive.

In the this work we present approach for labeling of biologically active synthetic polymers (BASP) with the $M(CO)_3^+$ fragment. To the best of our knowledge there were no attempts for radiolabel grafted BASP.

We propose combination of macromolecular pharmaceutical chemistry and radiopharmaceutical chemistry for the development of novel, more efficient and less expensive targeted radio-polymers (BASP) useful for tumor diagnosis and therapy

As polymer-carriers poly-N-vinylpyrrolidone was chosen due to its known pharmacological properties. Polymer with attached chelation iminodiacetate groups were synthesized in a wide range of molecular masses (9 000 -30 000 Da). Metallo-polymeric conjugates with $Re(CO)_3^+$ fragment (as a model of “hot $^{99m}Tc(CO)_3^+$) were prepared in aqueous solutions in different pH value and were characterized by ^1H NMR, IR, chromatograpy, ESI MS, dynamic light scattering and thermogravimetry. Basing on comprechensive analysis of “cold” models we propose, that “hot” radiochemical synthesis will be available.

This work was supported with SCOPES Project No. **IZ73Z0_128443**

4.8.

DEVELOPMENT OF DOSIMETRIC SUPPORT AND PLANNING OF RADIONUCLIDE THERAPY WITH RADIOPHARMACEUTICAL LABELED ^{188}Re

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Now in MRRC of Ministry of Health of Russian Federation is realized the program of skilled-technological and preclinical tests perspective radiopharmaceutical labeled ^{188}Re. For some of them carrying out of a phase of clinical researches in the near future is planned. With a view of increase of efficiency of medical technologies by employees INPE together with MRRC the complex of development in the field of individual dosimetric support and planning radionuclide therapies of some diseases with radiopharmaceutical on the basis of ^{188}Re is carried out. They include: 1) development of techniques for dosimetry of critical organs (kidneys, bladder, blood, red bone marrow, etc.) and target organs (tumours or metastasises) which, in turn, lean on offered optimum, and sparing for patients, protocols for clinical researches of radiopharmaceutical pharmacokinetics (with light invasive and noninvasive techniques); the criterion of an optimality here means use minimally necessary number of time measurements and an opportunity of restoration of data about accumulation of radiopharmaceutical in those organs in which it is impossible direct to carry out radiometry; 2) a substantiation and development of techniques for mathematical (multichamber) modelling of radiopharmaceutical metabolism in an organism of patients, and realization of numerical identification of corresponding kinetic parameters - with the purpose of restoration continual dependences of radiopharmaceutical dynamics, carried out on the basis of the limited volumes of skilled data; 2) development of techniques of carrying out of single-photon emission images in a problem of identification of activity ^{188}Re, accumulated in amazed and healthy organs of patients; in particular, development of mathematical models for target organs - the bone structures allowing with certain accuracy to restore distribution of activity in view of factors of degradation single-photon emission images; 3) mathematical modelling of fields of absorbed doses by a method of Monte-Carlo in the volumes of tumors and critical organs; 4) development of Radiation Safety recommendations under scripts of patient's contact with relatives after their extract from hospital.

Results of numerical calculation of fields of absorbed doses in phantoms of tumours and also results of variational modelling of radiopharmaceutical pharmakokinetics with ^{188}Re in an organism of patients with bone metastasises are resulted.

4.9.

EDUCATION AND TRAINING IN NUCLEAR MEDICINE, RADIOPHARMACY, MEDICAL PHYSICS AND MOLECULAR IMAGING: THE INSTN EXPERIENCED APPROACH

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Nuclear medicine, radiopharmacy, molecular imaging or related fields combine advanced engineering in chemistry, nuclear science, molecular biology and physiology together with state-of-the-art technology for non invasive *in vivo* imaging. This field contributes immensely to biomedicine because it is the major technology that can explore and measure the chemistry of life in a non invasive manner. It is thus a key for the development of new diagnostics and therapeutics. Considering the rapid development of technologies, there is an urgent need of specific educational programs in these fields. Physicians, researchers and chemists must be well qualified and appropriately trained to adapt themselves to these new technologies. This must be achieved through suitable and updated trainings.

Since 1974, the National Institute for Nuclear Science and Technology (INSTN) within the French Atomic Energy Commission (CEA) has been responsible for organising the theoretical training of medical doctors, pharmacists, chemists and physicists in **nuclear medicine**, **radiopharmacy** and **medical physics**. This Institute is recognised by the European Association of Nuclear Medicine (EANM) as a training centre in radiopharmacy. The INSTN provides solutions to satisfy needs in nuclear medicine, radiopharmacy and molecular imaging training in the requirements from professionals. To do so, the institute is in charge of organising short trainings for professionals (Life-Long Learners). It also brings training solutions to special needs for national and/or international trainings. At last, the INSTN is deeply involved in the academic field.

Among the training courses provided by the INSTN, the new **European Master in Molecular Imaging** (EMMI) offers an international program entirely dedicated to **molecular imaging**. Supported by the European Commission under the SOCRATES programme, this two years interdisciplinary curriculum is brought together by prominent European molecular imaging research groups, with the objective to prepare students for both academic and industrial positions.

Courses are held in parallel at the partners Institutions: the INSTN (Saclay, France) –coordinating, and the Universities of Paris Sud 11 (France), Antwerp (Belgium), Crete (Greece) and Turin (Italy). The curriculum includes courses on the basics of physics, chemistry, biology and physiology for Molecular Imaging, advanced courses on each imaging technology (PET, SPECT, MRI, OI, and ultrasound) as well as a full time six months immersion in one of over forty industrial or academic partner laboratories around the world. In just two years, EMMI students acquire full theoretical and practical competences in all molecular imaging modalities. The master programme is entirely held in English, built for students with a bachelor degree in biology, biomedical sciences but also in physics, chemistry and computer science as optional bridging courses are offered in physiology and biology.

Those highly specialized theoretical and practical courses, which are recognized by professionals, are open to students and employees willing to improve their professional qualification in these fields. It would be clever to ask one or many Universities in order to face the setting up of a middle-term academic training allowing the training of the future radio pharmacists. Thus, Russia could be inspired by the trainings (INSTN) made for these professionals in France at the present time.

4.10.
HIGH SPECIFIC ACTIVITY RADIONUCLIDES IN NCA FORM: Re-186g PRODUCED BY CYCLOTRON

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The ^{186g}Re is a double purpose β and γ emitter, that, thanking to its suitable chemical and nuclear properties: $T_{1/2}$ = 90.64 h; E_{β}^{max} = 1069.5 keV (74.3%) and 932.3keV (18.8%); main γs at 137.155 (8.22%) and 122.58 (0.56%) keV, is presently used in metabolic radiotherapy with palliative pain elimination of bone metastases but it is a good candidate to be used in metabolic radioimmuno-therapy (RIT) combined with molecular imaging devices (i.e. theragnostics). Unfortunately this radionuclide cannot be used yet in RIT therapeutic procedures, because its present production route - by radiative neutron capture on moderately enriched ^{185}Re in thermal nuclear reactor - leads to a relatively low specific activity A_S, in carrier-added (CA) form. The possibility to improve the use of this radionuclide is strictly linked to the possibility of increasing the A_S, approaching the theoretical carrier-free (CF) value of 6.88 GBq μg^{-1}. A way is its production by proton or deuteron bombardment on tungsten-186 targets via either (p,n) or (d,2n) nuclear reactions.

In order to assess the effectiveness of the W(p,n)^{186g}Re and/or W(d,2n)^{186g}Re nuclear reactions to produce ^{186g}Re in no-carrier-added (NCA) form, new sets of thin target excitation functions and experimental thick-target yields for each RN were measured, at variable proton energies up to 22.0 ± 0.2 MeV and deuteron energies up to 19.0 ± 0.2 MeV [1-3]. The experiments were carried out at first by using W targets of natural isotopic composition. This leads to a production of a range of Re radioisotopes and to an effective ^{187}W "internal spike". A first conclusion is that natural W is not a suitable target due to the low A_S(NCA) and radioisotopic purity achievable, caused by the production of several other stable and radioactive nuclides of Re and secondly that the production by deuteron beam is envisaged, due to the substantially higher yield. Besides, a suitable radiochemical separation of Re isotopes from W and ^{186}W targets and from ^{183}Ta by-product was set up for both proton and deuteron bombardments. A single radiochromatography method based on activated acidic aluminum oxide (AAO) was adopted. The radiochemical recovery yield obtained in each separation is greater than 98 % within the first 12.5 mL and the values reach 100 % within 15 mL of solution for a 100 mg W metal target. For W target weights up to 500 mg, the solution and column volumes have been scaled-up. NAA and ET-AAS have been adopted for determination and quality control of chemical purity and A_S(NCA).

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References

1. Z.B. Alfassi, E. Persico, F. Groppi, M.L. Bonardi, *Appl. Radiat. Isot.*, **67:**240–242 (2009).
2. M.L. Bonardi, F. Groppi, S. Manenti, E. Persico, L. Gini, *Appl. Radiat. Isot.*, **68:**1595-1601 (2010).
3. M. Bonardi, F. Groppi, E. Persico, S. Manenti, K. Abbas, U. Holzwart, F. Simonelli, Z.B. Alfassi, *Radiochim. Acta*, **99:**1-11 (2011).

4.11.

OPTIMIZATION OF PARAMETERS OF THE ^{188}RE OBTAINING PROCESS IN A CENTRIFUGAL EXTRACTOR

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One of the most promising radionuclide for nuclear medicine is ^{188}Re, a daughter of ^{188}W. A main feature that distinguishes ^{188}Re from most other therapeutic β-emitters (for example, ^{90}Sr) is the emission of a soft gamma-ray (15%, 155 keV). This makes it possible to monitor the distribution in tissues and organs and, correspondingly, to calculate very accurately the therapeutic irradiation dose. Research on the RP based on ^{188}Re, which are already used or under development for therapy of several diseases, is being performed in many leading countries.

The goals of this work were to study the use of the centrifugal extractor to isolate medical-grade ^{188}Re from ^{188}W. The work included the manufacturing of the two-stage centrifugal extractor, the extraction of Re from W by MEK from alkaline solutions, a determination of chemical impurities in the ^{188}Re solutions, the construction in a hot cell of equipment for testing the process using actual solutions, a check of the selected extraction conditions, and a determination of the optimal extraction conditions for preparing medical-grade ^{188}Re.

Reagents. The following reagents were used for studying the extraction of Re and W and for analyzing solutions: KOH, WO_3, and K_2CO_3 (ultra-high purity); acetone, $CHCl_3$, and MEK (chem. pure). MEK was distilled before use as an extractant. ^{188}W was produced by irradiation of WO_3 in the WWR-M reactor of PNPI (Gatchina). The neutron flux $1\cdot10^{14}$ $n\cdot cm^{-2}\cdot sec^{-1}$) is sufficient to prepare 1-2 Ci of ^{188}W after irradiation of the target during 2-3 months.

Apparatus and process for preparing ^{188}Re. The use of centrifugal extractors is advisable for high-activity solutions because they guarantee the minimal contact time of the high-activity aqueous and organic phases. The apparatus for preparing medical-grade ^{188}Re with these features was assembled. The shielded box was constructed of steel 100 mm thick. The inner surfaces were lined with stainless steel. Work in the box could be observed through a lead-glass window 150 mm thick. The irradiated WO_3 is dissolved in an alkaline solution containing KOH (2.5 M) and K_2CO_3 (2.5 M) and fed by pressure into the first stage of the centrifugal contactor. MEK is fed into the first stage of the contactor using a peristaltic pump at 4 ml/min. After passing through the first stage, MEK is scrubbed in the second stage and then is fed into the evaporating apparatus, equipped with a jacket through which hot water (85-95°C) is circulated. After MEK is evaporated the evaporating apparatus is flushed with air for 15-20 min to remove traces of MEK. At this point the evaporating apparatus contains ^{188}Re. The appropriate aqueous solution is added from an intermediate tank to the evaporating apparatus to dissolve the ^{188}Re. The solution is bubbled in the apparatus for 3-5 min and fed through a filter into the vial-connector.

Results and conclusion. Tests of the equipment using model and actual solutions showed that the Re yield is >85%, the radiochemical purity is >99%, the pH value of the aqueous ^{188}Re solution is in the range 6.5 to 7.5, the content of radionuclidic impurities is $<1\cdot10^{-7}$, and the content of stable elements is determined practically by the quality of the aqueous solutions used to dissolve the ^{188}Re. Such equipment can be a prototype of a regional centralized generator of medical-grade

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4.12.

SUBSTANTIATION OF TECHNOLOGICAL PARAMETERS OF A STATIONARY RHENIUM-188 GENERATOR FOR RADIONUCLIDE THERAPY

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World current nuclear medicine applies Re-188 generators producing eluates of about 100mCi/ml concentration activity. Based on medical and technical requirements to Re-188 generators of new generation their concentration activity should reach 500mCi/ml.

One of the way solve this problem is the development of Re-188 stationary generator. The basis of this development is the technology of ^{188}W/^{188}Re generator GREN-1 of 1Ci activity based on W-188 sorption on aluminum oxide in acid form in chromatographic column.

Research results of determination of sorbent optimal graded size composition, sorbent sorption capacity and rate of the initial solution passage through the corption column are presented. Influence of specific activity of the mother radionuclide W-188 on the eluate concentration activity have been studied. Calculated substantiation of shielding material and dimension providing radiation safety during generator operation is presented.

Advantage of Re-188 stationary generator of 5Ci activity under development is the possibility to obtain different volumes of sodium perrenate solution with regulated concentration activity up to 500mCi/ml during its fractional elution. This will allow enlarge the number of radiopharmaceuticals being synthesized according to the demand of medical institutions.

4.13.

^{188}W/^{188}RE GENERATOR PRODUCTION TECHNOLOGY FOR NUCLEAR MEDICINE

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The aim of this research is the innovative technology optimization of high active chromatographic ^{188}W/^{188}Re generator production in the mode of sodium tungstate (^{188}W) dynamic adsorption. Synthesis of radiopharmaceuticals based on the generator eluate are carried out in hospitals for beta-radiation therapy of malignant tumors, bone metastases, rheumatoid arthritis and other diseases.

Optimal parameters for generator loading (sorbent mass, loading solution passage rate through sorption column, eluent volume) have been established. 100-1500 mCi activity Re-188 generator production technology has been developed and mastered.

Generator quality during their elution within 1 year is at the level of the best international analogs. Generator eluate is sterile and pyrogen free; ^{188}W concentration in the eluate is not more than $1 \cdot 10^{-2}$ %; the other radionuclide impurities concentration is not more than $1 \cdot 10^{-3}$ % of ^{188}Re activity on the date and time of production; chemical impurity concentration (Al, Fe) is not more than 5μg/ml. Rhenium-188 yield in eluate is not less than 80 %.

Pre-clinical investigations of radiopharmaceuticals based on eluate from these generators have been carried out as well as of cold kits for radionuclide therapy based on biphosphonic acids (for example, 1-hydroxyethylidene-diphosphonic acid - HEDP).

Since 2006 and up today SSC RF – IPPE produces Re-188 generators according to the orders of hospitals as a medical article (TS 9452-031-08624390-2006, registration certificate #ФС 02032006/5395-06).

Stationary ^{188}W/^{188}Re generator of 5Ci activity is a prospective development. It allows obtain eluate of (100–400)mCi of ^{188}Re/ml concentration activity. Generator can be located at large medical centers or nuclear pharmacies. Partial elution can be used to obtain a definite eluate volume of needed concentration activity allowing synthesis of any type of medicine in accordance with the requirement of medical institutions and efficiently apply the eluate from stationary generator.

4.14.

MATHEMATICAL MODELS FOR PHARMACOKINETICS AND DOSIMETRY IN EXPERIMENTAL RADIOBIOLOGICAL RESEARCHES OF BONE-SEEKING RADIOPHARMACEUTICAL ^{188}Re-KOEDF

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The purpose of work are modeling for pharmacokinetics radiopharmaceutical ^{188}Re-KOEDF and calculation of the absorbed doses (AD) in critical organs of laboratory animals according to experimental radiobiological researches. The received results are intended for the subsequent substantiation of application of data radiopharmaceutical in a clinical practice.

Materials and methods. The qualitative and quantitative analysis of results of radiobiological researches of accumulation ^{188}Re-KOEDF in an organism of laboratory rats (MRRC MH) is lead. With the purpose of definition of the adequate scheme of radiopharmaceutical pharmacokinetics various variants compartment models were involved. As a result restoration of continual-time dependences for radiopharmaceutical accumulation-deducing has been realized on the basis of model with 40 chambers. Transport of metabolites ^{188}Re-KOEDF in extracellular space of organs of a rat was considered. As a whole the model includes 62 kinetic parameters (constants of an interchamber exchange) which were defined by a method of numerical identification. Calculation of the absorbed doses was made following the MIRD methodology. Dose factors for organs of rats, including critical bone structures, have been taken from recent development Xie T., etc. (2010), Peixoto P.H.R., etc. (2008).

Results: 1) the good coordination of the simulated and experimental dependences of kinetic of radiopharmaceutical in a number of soft organs (a muscle, heart, a stomach, intestines, kidneys, etc.), and in bone structures, where dominate cancellous structures, is received; 2) with a view of correct dosimetry, and, accordingly, the correct description of radiometric data in chambers of "joint", "liver", "thyroid gland" and "blood" it is required to consider functional activity of radiopharmaceutical metabolites , in particular - to consider possible dissociation of radiopharmaceutical and occurrence a protein-connected ^{188}Re; 3) with use of settlement dependences of accumulation of radiopharmaceutical for all presented critical bodies of animals are calculated normalizied AD; in particular, for a red bone marrow variation AD on group of bones makes $D^{(REM)} = \left[7{,}9 \div 182{,}8\right] \cdot 10^{-9}\ Gy/Bq$.

Poster session 4.

Chairs: M.L. Bonardi, F. Groppi

Notes

4.P1.

THE GENERATOR ^{99m}Tc BASED ON INORGANIC SORBENT “TERMOKSID-5”

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The eluted activity from a technetium generator will contain small amounts of a variety of impurities. The nature of these impurities and their concentration is important. The following should be considered when preparing ^{99m}Tc radiopharmaceuticals. This end use places a stringent requirement on the various types of purity of the product. Product purity may be considered to consist of radionuclide impurity, radiochemical purity, chemical purity and biological purity. There are however contaminants that are inherent in the ^{99}Mo on to the generator column and that may be released from the alumina column during elution. Since these components are frequently present, their allowable concentrations may be defined and quality control tests for their presence and concentration may be applied. The following components contribute to the suitability of the eluted ^{99m}Tc: Al^{+3} ion end activity^{99}Mo.

It is impossible to completely eliminate all aluminum ions. Recommended limits for Al^{+3} (United Stated Pharmacopoeia [USP] for example) are 10 µg / mL when the column is prepared from fission molybdenum and 20 µg / mL when thermal neutron activation is used to prepare the ^{99}Mo.

There are varying regulations concerning the allowable levels of ^{99}Mo in the eluted product or in the radiopharmaceuticals prepared for human administration. A generally accepted requirement (United States Pharmacopoeia) is that the final radiopharmaceutical will not contain more than 0,15 KBq of ^{99}Mo per MBq of ^{99m}Tc at the time of administration.

The chemical composition of thermostable inorganic sorbent “Termoksid-5” (T-5) is a mixture of oxides titanium and zirconium. It has high molybdenum selectivity, radiation resistant and chemically stable.

The generator ^{99m}Tc (based on the brand sorbent T-5) can be produced for bigger activity at smaller sizes of the sorption column. Model experiments of the separation ^{99}Mo and ^{99m}Tc showed satisfactory results: 0,90 ± 0,05 technetium and less than 10^{-5} of molybdenum transfer to isotonic solution after multiple elution (more accurate results can be obtained at higher specific activity of the molybdenum).

4.P2.

INVESTIGATION OF THE SORBENTS ON THE BASIS OF THE NEW PHOSPHORYL-CONTAINING LIGANDS FOR ALLOCATION, CONCENTRATION AND PURIFICATION OF THE MOLYBDENIUM FROM THE IRRADIATED URANIUM TARGETS

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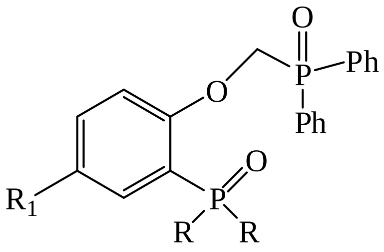
The ^{99}Mo is a precursor of ^{99m}Tc applied for diagnostics in the nuclear medicine. One of the main methods for ^{99}Mo-^{99m}Tc production is the U irradiation in the reactor, ^{99}Mo being produced due to ^{235}U fission with the yield of approximately 6%. Preparative chromatography with use of highly effective sorbents (PZC or Thermoxid) is promising separation method of allocation, concentration and purification of ^{99}Mo from accompanying collateral elements. A new kind of chelating polymeric adsorption materials were developed and synthesized by non-covalent fastening of the new ligands (I) into the pores (40-250 μm) of polymeric (styrene-divinylbenzene) particles to separate effectively_of_Mo from solutions, obtained by dissolution of the irradiated uranium targets in HNO_3. The adsorption of some typically simulated elements Mo, Tc, U, Th, Np, Pu towards adsorbent was investigated by examining__the influence of the structure of phosphoryl-containing ligands, their percentage contents in an adsorbent, contact time, concentration of HNO_3 and presence of the stripping agents in the solutions. It was found that a number of the investigated materials exhibited excellent selectivity for ^{99}Mo overall of the tested elements. The optimum conditions for effective adsorption and stripping of these elements have been determined. The dynamic distribution factors were high resulting in quantitative purification of ^{99}Mo from accompanying collateral elements in demi-industrial pilot scale. The technique for ^{99}Mo determination in the irradiated uranium targets was proposed. The obtained data testify the new adsorbents potential for radiochemical manufacturing of ^{99}Mo-^{99m}Tc generators.



I

R=Ph, p-Tol, OEt, OH, R_1=H, n-Alk

The work was supported by RFBR (grant № 11-03-00509-a)

4.P3.

NOVEL TECHNETIUM AND RHENIUM COMPLEXES WITH THE N-HETEROCYCLIC ALDEHYDE THIOSEMICARBAZONES - POTENTIAL RADIOPHARMACEUTICALS

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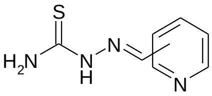
Technetium and rhenium, similarly to their congener - manganium, form cations/anions in one from a group of eight valence states. It is of interest to compare the physico-chemical and biological properties of the mono-, tri- and pentavalent technetium containing complexes (the most popular technetium/rhenium cations in the radiopharmaceutical since) with the same ligand.

This work presents our studies of the selected N-heterocyclic aldehyde thiosemicarbazones (TSC) labeled with the technetium/rhenium radionuclides.



TSC ligands are chosen because of their well-known pharmacological properties. It has been found that TSCs alone, as well as numerous of their transition metal complexes, bear the antimicrobial, antiviral, antineoplasm, antimalarial and/or anticancer properties [e.g. 1-4]. In spite of the fact that numerous transition metal complexes have been tested as potential diagnostic/therapeutic agents, data for the technetium/rhenium compounds are more than poor. Modification of the existing TSC molecules may lead to better binding different biomolecules, followed by proper targeting human organs of interest.

Biologically important physico-chemical properties of the mono-, tri- and pentavalent technetium/rhenium complexes are presented.

Studies are continued.

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References.

1. P. Singh, J. Jain, R. Sinha, A. Samad, R. Kumar, M. Malhotra, *Synthesis and Screening of Substituted Thiosemicarbazone Derivatives: An Approach Towards Novel Anticonvulsant Search*, Cent. Nerv. Syst. Agents Med. Chem. **2011**, Feb 7. [Epub ahead of print].
2. M.Z. Hernandes, M.M. Rabello, A.C. Leite, (and others), *Studies toward the structural optimization of novel thiazolylhydrazone-based potent antitrypanosomal agents*, Bioorg. Med. Chem. **18**(22), 7826-35 (2010)
3. Z. Debebe, T. Ammosova, D. Breuer, et all, *Iron chelators of the di-2-pyridylketone thiosemicarbazone and 2-benzoylpyridine thiosemicarbazone series inhibit HIV-1 transcription: identification of novel cellular targets-iron, cyclin-dependent kinase (CDK) 2, and CDK9,* Mol. Pharmacol., **79**(1), 185-96 (2011)
4. G. Pelosi, F. Bisceglie, F. Bignami, P. Ronzi, P. Schiavone, M.C. Re, C. Casoli, E. Pilotti, *Antiretroviral activity of thiosemicarbazone metal complexes*, J. Med. Chem. **53**(24), 8765-9 (2010)

4.P4.

^{99m}Tc-LABELLED VASOPRESSIN ANALOG d(CH_2)$_5$[D-Tyr(Et^2),Ile^4,Eda^9]AVP AS A POTENTIAL RADIOFARMACEUTICAL FOR SMALL-CELL LUNG CANCER (SCLC) IMAGING

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The aim of the work was to synthesise and investigate the conjugate of the vasopressin peptide analog d(CH_2)$_5$[D-Tyr(Et^2),Ile^4,Eda^9]AVP with the “4+1” mixed-ligands technetium(III) complex.

In recent years interest increased in the role of vasopressin in such diseases as schizophrenia and autism [1]. The overexpression of vasopressin receptor V2 has been found on small-cell lung cancer (SCLC) [2]. The analog d(CH_2)$_5$[D-Tyr(Et^2)-Ile^4-Eda^9]AVP (**AVP(an)**), is one of the several effective antagonists (Fig. 1A) of the antidiuretic (V2-receptor) responses to arginine vasopressin.

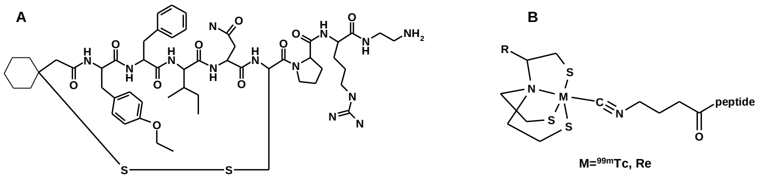

Figure 1. (A) - d(CH_2)$_5$[D-Tyr(Et^2)-Ile^4-Eda^9]AVP, (**AVP(an)**), (B) - ^{99m}Tc labelled peptides using the “4+1” approach

The *log D* value of the ^{99m}Tc-labelled AVP(an) (Fig. 1B) is equal to -0.44±0.03.

The conjugate ^{99m}Tc(NS_3)(CN-AVP(an)) exhibited to be very stable [3]. After 24 h of the isolated coniugate incubation at 37°C with an excess of histidine or cysteine the obtained HPLC chromatograms have shown only one radioactive species of the retention time characteristic for the complex studied.

The studied conjugate, on the contrary to the ^{99m}Tc-labelled arginine vasopressin peptide, is also stable in human and rat serum. The biomolecule AVP(an), being the antagonist of the V2 vasopressin receptor, does not undergo the enzymatic biodegradation *in vivo*, even in rat serum.

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References.

1. E**.** Frank, R**.** Landgraf**,** *Best Pracice & Research Clinical Anaesthesiology* **22**: 265-273 (2008).
2. C. Pequeux, B. P. Keegan, M.-T. Hagelstein, V. Geenen, J.-J. Legros, W. G. North, *Endocrine-Related Cancer,* **11**: 871–885 (2004).
3. S. Seifert, J.-U. Kuenstler , E. Schiller, H.-J. Pietzsch, B. Pawelke, R. Bergmann, H. Spies, *Bioconjugate Chem*. **15**: 856-863 (2004).

4.P5.

COMPLEXES OF TECHNETIUM-99m AND RHENIUM-188 WITH ZOLEDRONIC ACID IN NUCLEAR MEDICINE

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Skeletal metastases are clinically significant because of associated symptoms, complications such as pathological fracture and their profound significance for staging, treatment and prognosis. Detection of bone metastases is, thus, an important part of treatment planning. Zoledronic acid, a novel bis-phosphonate, has demonstrated more potent inhibition of osteoclast-mediated bone resorption than all other bisphosphonates in both in vitro and in vivo preclinical models.

^{99m}Tc and ^{188}Re represent an attractive pair of radionuclides for biomedical use because of their favorable decay properties for diagnosis (^{99m}Tc: 6 h half-life, 140-keV γ-radiation) and therapy (^{188}Re: 17 h half-life, 2.12-MeV β^- max-radiation) and because of their onsite availability, thanks to corresponding ^{99}Mo/^{99m}Tc- and ^{188}W/^{188}Re generator systems.

The aim of this study was to investigate the influence of reaction conditions such as pH, concentration of $SnCl_2$, concentration of the ligand (ZA), adding of carrier (in the case of ^{188}Re), time and temperature of reduction and etc. for the synthesis of ^{99m}Tc-ZA and ^{188}Re-ZA complexes, to prepare corresponding lyophilized forms and investigate their biodistribution in experimental animals.

It was found that radiopharmaceutical composition of ^{99m}Tc-ZA with radiochemical purity > 95 % can be prepared using ligand:$SnCl_2$ molar ration from 2.5 to 3.5 at pH 5.0 – 6.5 after incubation for 20 min at room temperature.

The described composition of ^{188}Re-ZA can be prepared with radiochemical yield > 90 %. The composition was stable during 3 h from the moment of it preparation.

From our preliminary experiments it was found that pH of the solution on the first step of preparation ^{188}Re-ZA (during rhenium reduction) should be quite acidic (pH < 1.5). The yield of ^{188}Re-ZA was decreased to 80 % at pH 2.5 - 3.5.

We also observed the influence of adding the carrier on the yield of ^{188}Re-ZA. Without the carrier the radiochemical yield was also more than 90 %, but the composition was unstable.

The skeletal uptake of ^{99m}Tc-ZA was about 50 %, the uptake ratios of bone-to-blood were more than 20 at 1 h and up to 100 at 5 h after injection respectively. Differential coefficient of uptake (CDU) femur-to-femur with pathology was between 1.7 to 2.1.

^{188}Re-ZA rapidly accumulates and securely fixed in both normal femur bone and in bone pathology.

Nowadays the preclinical trials with ^{188}Re-ZA are in progress.

4.P6.

PRODUCTION OF ^{188}W AND EXTRACTION OF ^{188}RE AT IRT-T

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Every year about 480 thousand cases of malignant neoplasmas are diagnosed in Russia. The morbidity has increased by 16% for the past 10 years. Nowadays more than 2.5million patients are registered on the books in oncological medical facilities, it's 1.8% of the country population.

From the view point of effective medical care ^{188}Re radioisotope is considered the most perspective radionuclide for application of its compounds in beta-rays therapy of malignant neoplasmas, bony metastasis, rheumatoid arthritis and other diseases by open radionuclide sources.

Radioisotope of ^{188}Re ($T_{1/2}$=16,98 h) is received as a daughter product at beta decay of ^{188}W ($T_{1/2}$= 69,4 days), which in its turn is produced in the reaction (n;γ) of the second order in nuclear reactors by irradiating tungsten oxide of the natural isotopic composition (28,64 % ^{186}W), or by concentrating ^{186}W isotope more than by 90%. The use of the cheap raw material as a starting target results in further application of concentrating technologies for extraction of daughter radioisotope of ^{188}Re, the sublimation and extraction technologies are primary ones.

At nuclear reactor IRT-T of Physical-technical Institute of Tomsk Polytechnic University (the maximum flux of thermal neutrons is up to $1{,}5\cdot10^{14}$ н·с$^{-1}$·см$^{-2)}$ research works on production of parent ^{188}W and sublimation extraction of ^{188}Re from the target of natural isotope compound were carried out. Sublimation extraction of ^{188}Re from irradiated targets of tungsten oxide (VI) was carried out in the apparatus supplied with a refrigerated condenser, onto which Re precipitated during gaseous phase in the form of Re_2O_7. The research of ^{188}Re extraction rate was studied in the temperature mode of 600-700^{0}C depending on the target mass and heating time. It is shown that the content of ^{188}W in the fallout does not exceed 0,005% of the daughter isotope activity. The percentage of molybdenum and antimony radio nuclides that are present in initial tungsten oxide (VI) as admixtures is less than the limits of detection. Radiochemical purity of the desired preparation is more than 99%.

Thus, the experiments mentioned above create the preconditions for the development of the regional ^{188}Re sublimation generator for providing medical facilities with ^{188}Re based radiopharmaceuticals.

4.P7.

TECHNETIUM-99m GENERATOR PRODUCTION AND APPLICATION EXPERIENCE

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Improvement of SSC RF – IPPE activity in the field of medical radioisotope production is a strategic plan for stimulation of Russian nuclear medicine development.

SSC RF – IPPE is one of developers and Russian producer of Technetium-99m generators since 1989. Within the 21-years manufacturing experience the quality parameters of the generator eluate have reached the level of the best Russian and foreign samples: daughter radionuclide yield is not less than 80%; radiochemical purity is not less than 99.8%; radionuclide impurity concentration is not more than 10^{-3}% of Tc-99m activity; stable impurity total concentration is not more than 5μg/ml.

Tc-99m generator production technology is improved on the base of experimental research and has been patented in Russia (Patent of the Russian Federation #2153357). The invention consists in the application of multilayer sorbent as adsorbing material consisting of silica gel modified by manganese dioxide, aluminum oxide in alkaline, acidic and neutral forms.

At all stages of the certified process of Tc-99m generator production a system of quality control has been developed and operates including the input control of initial materials and reagents, the auxiliary product production control, the end product batch control within its service life, and utilization review of Tc-99m generators delivered to medical institutions as well.

Currently a set of work for modernization of production and quality control of medical products produced is carried out at SSC RF – IPPE in accordance with State Standard R 42 249-2009 “Regulations of production arrangement and quality control of medical products” (GMP). Reorganization of production and quality control system will allow provide competitiveness of Tc-99m generators at a world level and promote them to foreign market.

4.P8.

DETERMINATION OF ASCORBIC ACID IN KIT BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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Technetium-99m hydroxyethylidene diphosphonate (HEDP) and rhenium-188 hydroxyethylidene diphosphonate were developed at the MRRC for diagnose and treatment of bone metastases, accordingly. The main quality control tests of radiopharmaceuticals are: concentrations of HEDP, Sn(II), ascorbic acid, the percentage of ^{99m}Tc or ^{188}Re unbound with preparation (radiochemical impurity or RCI). In the present work, an HPLC method for identification and quantification of AA in non-radioactive kit was developed.

Numerous analytical techniques have been proposed for its determination in different matrices and at different levels. There is no information about AA determination in radiopharmaceutical kits. There are some difficulties in quantifying ascorbic acid in kits due to simultaneous stannous ions presence and AA instability in aqueous solution. AA has limited stability and may be lost from kits during preparation and storage. AA is readily oxidized primarily to dehydroascorbic acid (DHA), which is a reversible reaction. Generally, the total AA is defined as the sum of both AA and its oxidized form DHA. The quantification of DHA is usually performed after its conversion into AA in the presence of reducing agents.

The HPLC system (Shimadzu, SCL-10A), was equipped with UV detector system. The LC-analyses were performed under isocratic mode at a flow rate 1 ml/min with detection at 265 nm. Sample and standard injections of 20 µl were made on a Supelcosil LC-18 column; 5 µm; 4.6∗250 mm; at 25 °C. The separation was performed with a sodium acetate eluent (pH 5.4) containing decylamine as ion pairing agent. Standard solutions (AA and DHA) and samples were prepared daily in volumetric amber glass flasks. Chromatographic peaks were identified by comparing its retention times with external standards. The experimental data were analysed statistically to validate the proposed method.

AA was quantified in standard by means of an external calibration curve in the concentration range 0.005 to 0.5 mg/ml. The HPLC method offers good accuracy and reproducibility, relative shot analysis time, unambiguous identification of AA in presence of DHA. To prevent the loss of AA in the standard and the samples solutions, it was necessary to prepare their with deaerated water and protect from light by using amber flasks. The DHA was not quantified in AA standard and in samples. The presence of HEDP and Sn(II) in kit vial had no influence on the results of AA determination by HPLC.

4.P9.

SYNTHESIS AND CHARACTERISATION COMPLEX OF THE $\{ReO\}^{3+}$CORE WITH SN AND N DONOR LIGANDS

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A novel ``2 + 1" mixed ligand ^{99m}Tc complex with mercaptobenzothiazole as ligand and Aminothiazole as coligand was prepared and evaluated as potential brain radiopharmaceutical. Preparation at tracer level was accomplished by substitution, using ^{99m}Tc-gluconate as precursor and a coligand/ ligand ratio of 5. Under these conditions the labeling yield was over 87% and a major product with radiochemical purity >87% was isolated by HPLC methods and used for biological evaluation.

The reaction of $[ReO(Citrate)_2]^-$ with mercaptobenzothiazole and Aminothiazole in hot MeOH yields $[ReO(mer)(amino)OH\ (H_2O)_2]$. The structure and DFT study demonstrated that the complex consists of distorted octahedral ReO(V). The coordination geometry at the rhenium is defined by a terminal oxo-group, the nitrogen and sulfur donors of the chelating mercaptobenzothiazole, the nitrogen of Aminothazole ligand, is present as a deprotonated amido nitrogen.

Biodistribution in mice demonstrated early brain uptake, fast blood clearance and excretion through hepatobiliary system. Although brain/blood ratio increased significantly with time, this novel ^{99m}Tc complex did not exhibit ideal properties as brain perfusion radiopharmaceutical since brain uptake was too low.

Keywords: $[ReO]^{3+}$, DFT, mercaptobenzothiazole ligand, ligand, ^{99m}Tc-gluconate, B3LYP.

References:

1. S. S. Jurisson, S.Z. Lever, J.D. Lydon, C.S. Cutler.; *Radioactive Metal in Imaging and Therapy Comprehensive Coordination Chemistry II*, WILEY, New York, 2004, pp. 883-911.
2. K. Schwochau.; *Techenetuim Chemistry and Radiopharmaceutical Applications*, Wiley-VCH, 2000.
3. D. Papagiannopoulou, I.C. Pirmettis, M. Pelecanou, C.Tsoukalas, C.P. Raptopoulou, A. Terzis, E. Chiotellis, M. Papadopoulos, *Inorg. Chim. Acta*. **320**:174-177 (2001).
4. Dhara. B., Chattopadhyay. P, *Appl.Radiat.Isot*, **62**, 729-735 (2005).

4.P10.

STABLE SOLS OF RHENIUM SULFIDE FOR RADIOISOTOPE DIAGNOSIS OF CANCER

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Colloidal solutions of nanoparticles geptasulfide measurements are increasingly used for medicinal purposes - both for cancer therapy and for diagnosis. In the first case, these solutions introduce isotope ^{188}Re, the second of labeled ^{99m}Tc.

The authors have worked out ways to obtain stable sols rhenium sulphide with particle sizes of 80 - 100 nm with the use of thiosulphates.

The size of the nanoparticles geptapsulfides was evaluated by atomic - force microscopy.

The ability sols retention of technetium - 99m under various conditions were determined using electrodialysis.

4.P11.

PREPARATION AND BIOLOGICAL STUDY OF «Nanotech, ^{99m}Tc»

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The concept of sentinel lymph node imaging is one of the most interesting recent developments in clinical oncology that holds the promise of a major breakthrough in the detection and treatment of early lymphatic metastasis from solid tumors, mainly melanoma and breast cancer. The sentinel node is the first lymph node to receive lymphatic drainage from a tumor site and therefore, it is the most suitable tissue for histological examination. The new procedure of intra-operative lymphatic mapping demands corresponding radiopharmaceuticals with particle size 10 – 100 nm, which now are absent in Russia.

The aim of this study was to found simpler method of sol Re_2S_7 preparation, to develop a radiopharmaceutical on it base and investigate it biodistribution in experimental animals. In this work we compared two methods of sol preparation, using so called “dry” and “wet” technology.

It was found that sol of Re_2S_7 with yield of about 30 % can be prepared using $Na_2S_2O_3$: $NaReO_4$ molar ratio from 1.75 to 3.5. Time of synthesis was not more than 10 min. The yield of sol was determined using ^{188}Re. Particle size of this sol was 20 – 80 nm.

The radiopharmaceutical «Nanotech,^{99m}Tc» was prepared from the kit, which include two vials – one vial with synthesized sol and the second vial contain tin dichloride and sodium pyrophosphate. The radiopharmaceutical with radiochemical purity more than 90 % was obtained.

From our preliminary experiments in rats it was found that maximal uptake of «Nanotech,^{99m}Tc» in the inguinal lymph node was observed using $Na_2S_2O_3$: $NaReO_4$ molar ration 2.2 during sol preparation.

4.P12.

SORPTION RENOVAL OF $Na^{99m}TcO_4$ FROM EXTRACTS OF EXTRACTION GENERATOR $^{99}Mo/^{99m}Tc$

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Extraction technology of ^{99m}Tc from irradiated natural Mo or enriched with ^{98}Mo is well known during more than 30 years [1]. Nevertheless, in the conditions of the ongoing "^{99}Mo -crisis", as well as environmental reasons, an alternative in relation to fission ^{99}Mo and ^{99m}Tc production methods have received in recent years a new development.

In such method ^{99m}Tc is extracted from the alkaline solution of irradiated Mo by methyl ethyl ketone (MEK) with the subsequent evaporation to dryness and dissolution of the residue in the saline [2]. This technology more than 20 years is successfully used in Russia as well [3,4]. However, the evaporation of organic solution is the most long-term and insecure operation, in addition, the full automation of process in such performance is difficult to implement.

In the present work we studied ^{99m}Tc sorption behavior when removing it from MEK without stage of extract evaporation

As a result of experiments it was established that ^{99m}Tc can be sorbed on alumina (Merck, 0,06-0.20 mm) in both acidic and alkaline forms from MEK solutions pre-cleared out of cations abundance on ion exchange resin (Dowex, 50W-X8, 100-200 mesh). After washing of alumina with water ^{99m}Tc in the $^{99m}TcO_4^-$ form can easily be desorbed with saline. The table presents the results of determining the ^{99m}Tc output in sorption stages and process in general.

№	**Column 1(Dowex)**		**Column 2** (alumina)			**Yield**
	Sorbtion, %	Eluate, %	Sorbtion, % (% from initial)	Washing , % from initial	Eluate, %	**%**
1	4,3	95,7	99,9 (95,6)	2,1	93,0	86,9
2	7,7	92,3	95,8 (88,4)	0,5	85,3	75,0
3	6,2	93,8	90,0 (84,4)	1,5	89,1	73,8
4	3,2	96,8	89,5 (86,6)	1,5	79,9	74,6
5	2,0	98,0	91,3 (89,4)	2,5	91,7	79,4

The MEK content in the final solution << 0.5 mg/ml (range, regulated domestic and foreign pharmacopoeias). Radiochemical purity (RCP) ≥ 99%. The pH values are 6.5 - 7.4. Thus, we can conclude that the final solution $Na^{99m}TcO_4$ is suitable for medical use.

Other ^{99m}Tc-radiopharmaceuticals, prepared with the use of the final solution $Na^{99m}TcO_4$ and the domestic ^{99m}Tc-kits also comply with pharmacopoeia requirements.

1. Boyd R.E. Radiochem. Acta, 1982, 30 N 3, p. 123 - 145.
2. Melichar F., Svoboda K., Prokop J., Budsky F. IAEA-SM-131-50, Vienna, 1986, p.81.
3. Skuridin V., Glukchov G., Chygriaev M. Extraction generator of technetium-99m. USSR Priority1426019; C01G 57//00, 14.04.86, reg. 22.05.88.
4. Zykov M.P., Romanovsky V.N., Kodina G.E. et al. J. Radioanalyt. Nucl. Chem., 1997, 221 N 1 - 2, p. 227 – 230.

4.P13.

SEMI-AUTOMATIC ^{99m}Tc SOLVENT EXTRACTION SYSTEM

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The majority of the needs of medical centers in the sodium pertechnetate, ^{99m}Tc met by the supply of generators ^{99}Mo/^{99m}Tc chromatographic type that are used for 1-2 weeks, depending on the nominal of the generator and the schedule of diagnostic studies of each laboratory.

Pertechnetate, ^{99m}Tc as may be obtained on extraction technology, which provides preparation of a large quantity of the radionuclide in one technological cycle of selection. At the same time as a feedstock to produce ^{99m}Tc can be used ^{99}Mo any activity. This creates the possibility of centralized supply RP in ready to use form («isotope pharmacy»).

The experimental results revealed that:

- pH of the solutions Na^{99m}TcO$_4$ extraction of ≈6-7,5, which satisfies the existing requirements;
- quantity of MEK in solutions Na^{99m}TcO$_4$ extraction does not exceed the allowable values (<0,5 mg/ml);
- RP produced by the extraction Na^{99m}TcO$_4$ have an adequate quality;
- when using semi-automatic ^{99}Mo/^{99m}Tc extraction system obtained pharmaceutically pure Na^{99m}TcO$_4$ with the release about of 80 %;
- on the basis of this system is possible to organize a network of pharmacies isotope with a centralized supply of radiopharmaceutical in the ready to use form.

Notes

Session 5. Applications of Tc and Re in technology, including their alloys in Modern Constructing Materials

Chairs: B.Bryskin, F. Morito, K.German

5.1.

THE FABRICATION DEVELOPMENT OF RHENIUM USED IN HIGH TEMPERATURE ROCKETS AND HIGH TEMPERATURE SPACE POWER REACTOR

Boris D. Bryskin, Edwin D. Sayre

The use of tungsten as the thin liner of high temperature rocket nozzles in solid fuel rockets tended to produce very brittle tungsten carbide with the graphite nozzle structure underneath. It was found that rhenium provided a good bond and it did not react with the graphite and provided a good bond of the tungsten during the entire length of the rocket flow.

Rhenium has been found to improve the high temperature jet engine blade service by alloying slight amounts in nickel and cobalt high temperature alloys. In the development of the SP100 Nuclear Space Power System it was found that uranium nitride was the ideal fuel and Nb1%Zr alloy tubing was the best fuel cladding.

However it was found that the Nb1%Zr alloy tube reacted with the fuel and fission products at such high operating temperature, (1077^0C). It was found that rhenium tubing on the inside protected it for the life of the system.

No rhenium tubing to meet the requirements had been produced and none was available on the market that could be used for the SP100 Nuclear Space Power System. We in the program had to work with the rhenium sources and develop the rhenium strips needed and develop the tube production process.

Rhenium-Molybdenum alloy large tubing was developed for nuclear reactor control. This paper is devoted mainly to the development of the two processes for making the very high quality rhenium tubing. One process produces welded and drawn tubing and the other process produces cold formed seamless tubing drawn to finish.

Acknowledgment. The presentation of the work was in part supported by the grant No 01-05-2011 from “ACADEMINVESTSERVICE” Ltd.

5.2.

MAKING AND SHAPING OF RHENIUM AND RHENIUM CONTAINING ALLOYS

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The focus of this paper is to discuss the advancements in the production of rhenium and rhenium containing alloys along with science and understanding of the impact of powder morphology, powder compaction, sintering, and the consolidation methods of hot isostatic pressing and extrusion.

Rhenium is extremely sensitive to processing conditions because of its high work-hardening coefficient. This intrinsic property dominates the processing options available for production. A comparison will be made of the different densification/compaction processes on the microstructures and mechanical properties of powder metallurgy rhenium and rhenium containing alloys of molybdenum and tungsten.

The addition of rhenium in the concentration of 47.5 weight percent rhenium in molybdenum and 25 weight percent rhenium in tungsten has a significant impact on the microstructures and mechanical properties of these alloys.

Several processing methods will be compared and contrasted and the resulting microstructures, morphologies of the fracture surfaces, and mechanical properties obtained from tensile testing at room temperature and up to 1927°C will be discussed.

5.3.

HETEROMETALLIC Re, Ni, Co-ALKOXIDES AS PRECURSORS FOR FUNCTIONAL MATERIALS SYNTHESIS

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Nickel-based superalloys, containing rhenium (6-10 %) and cobalt (5-18 %) exhibit excellent mechanical strength and creep resistance at high temperatures, good surface stability, corrosion and oxidation resistance. Its typical applications are: aerospace, industrial gas turbine and marine turbine industry, e.g. for turbine blades in hot sections of jet engines. We have applied alkoxide route to their preparation using trimetallic nickel-rhenium-cobalt metoxocomplexes as a precursors.

At the first stage of investigation individual $\mathbf{Re_4O_6(OCH_3)_{12}}$ **[I]** $\mathbf{Ni(OCH_3)_2}$ [**II**] and $\mathbf{Co(OCH_3)_2}$ [**III**] complexes were obtained using anodic dissolution of rhenium, nickel and cobalt in absolute methanol correspondingly. Said methoxo-derivatives were characterized by XRD, SEM, IR and DTG. It was shown, that thermal or hydrolytic decomposition of these complexes yields: $\mathbf{ReO_3}$ (**[I],** air, 200°C**); Re** (**[I],** hydrogen, 350°C**);** $\mathbf{Ni(OH)_2}$ (**[II],** hydrolysis**); NiO** (**[II],** air, 270°C**);** $\mathbf{Co_3O_4}$ (**[III],** air, 200°C**); CoO** (**[III],** argon, 225°C**)**.

Consequent anodic dissolution of rhenium and nickel in absolute methanol provides bimetallic $\mathbf{Ni_xRe_y(OCH_3)_z}$ [**IV**] complexes with **Ni : Re** ratios range: from **9.8:1** to **1:2.7**; we certainly can control metals ratio during synthesis. It is of common knowledge that chemical uniformity of precursor compound leads to homogeneous distribution of doping elements in alloys and chemical composition stability at all. IR-spectra shows, that derivative [**IV**] is definitely not a mechanical mixture of **[I]** and [**II**]. Thermal decomposition of [**IV**] at as low as 400 ^{o}C in the air leads to formation of $\mathbf{NiReO_4}$; and in hydrogen gas provides solid solutions according to Re-Ni phase diagram in dependence of metals ratio.

Consequent anodic dissolution of rhenium, nickel and cobalt in absolute methanol provides trimetallic $\mathbf{Ni_xRe_yCo_z(OCH_3)_n}$ [**V**] complexes with adjustable metals ratio. According to IR-spectra this is another chemically mixed precursor compound. Thermal decomposition of [**V**] in hydrogen atmosphere at as low as 400 ^{o}C leads to formation of ultrafine powder of trimetallic nickel-rhenium-cobalt alloy. XRD pattern and chemical analysis data shows, that metals ratio in precursor compound and in resulting alloy powder are almost identical.

Therefore, methoxo-derivatives can be effectively applied as a precursors to obtain metals, alloys and ceramic powders and, potentially, coatings by means of CVD technique.

Work granted by RFBR (projects 06-03-32444 and 09-03-00328).

5.4.

METALLOTHERMIC METHOD FOR PRODUCING RHENIUM-BASED ALLOYS

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The aim of this work was to design a technology for producing rhenium alloys with low carbon content (<0,05 % of the mass) by metallothermal method.

The initial mixture components such as ReO_2; $CaMoO_4$; NiO and PA – 4 (Aluminium powder) as a reducing agent were used to obtain the master-alloy based on rhenium.

ReO_2 was produced on automated plant VME-8-10,5 by thermal decomposition of ammonium perrhenate in argon atmosphere. Direct metal yield achieve 95,3 %.

Calcium molybdate (technical standards 48-3812-28-87), nickel oxide (GOST (state standard) 609-4125-75), AP – 4 (Aluminium powder) aluminium powder (GOST (state standard) 6058-73) were used in this research. Inert additive of calcium oxide was applied to reduce thermal effect of the reaction.

To study metallothermic processes of obtaining rhenium alloys a variation content of initial mixture components $m(ReO_2) : m(CaMoO_4) : m(NiO)$ in the range from 1 : 0,298 : 0,125 to 0,457:0,197: was conducted, and also the effect of reducing agent excess from 0% to 20% was studied.

The results of the experiments have shown that the optimal compounds mixture was of 1 : 0,38 : 0,155, and percentage of aluminum excess varies from 7 to 10 % of the mass. In this case ingot extraction amounts to 95,3%.

Due to slag processing and extraction of supplementary metallic phase ingot extraction can be increase to 98%.

There was produced an enlarged batch of master-alloy that fully met the requirements of technical standards 1-92-202-2001.

5.5.

RHENIUM EFFECT IN Mo-Re WELDS

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Rhenium is widely used to alloys VIA group refractory metals. In particular, the strength and plasticity, creep resistance, and low temperature ductility of Mo are all improved with increasing the rhenium content due to the so-called “rhenium effect”. In addition to traditional applications, such as heating elements, electron tube components, etc, Mo-Re alloys are considered as candidate materials for structural applications for chemicals and energy facilities, including elements of fusion or fast breeder reactors. Welds are obligatory elements of practically any complex construction while working conditions are characterized by high temperatures (>1000 K), aggressive medium (liquid metals) and high neutron fluence ($>10^{21}$ n/cm^2).

Therefore, good weldability, high radiation performance, thermal stability and corrosion resistance are the key issues for these application fields. Tendency of Mo alloys to embrittle at low temperatures assumes probable degradation of the mechanical properties either during welding or under irradiation. In spite of the fact that significant progress has been achieved in studying the mechanism of rhenium effect, many details of Mo-Re alloy behaviour under extreme operating conditions are not studied yet.

This work analyses several Mo-Re alloys and welds with the Re content 0-50% in as-received state and after electron beam welding and/or radiation treatment. The mechanical properties and microstructure of Mo-Re welds are examined focusing on the effect of Re concentration. Phase stability, microstructural changes and impurity redistribution are studied for better understanding and predicting the long-term performance of Mo-Re alloys at high temperatures and/or high neutron fluences.

In particular, a strategy of welding of Mo-Re alloys is discussed with emphasis on the sensitivity of alloys to pre-weld heatings and on the development of post-weld treatments, such as warm rolling and annealing, to provide optimal phase composition. Grain refinement during directional solidification after welding, ductility improvement and fracture mode change from intergranular to transgranular one are clearly observed with an increase of Re content.

Effect of neutron irradiation on the strength of Mo-Re welds is studied for a wide temperature range. Mo-Re welds exhibit a large radiation-induced strengthening. At room temperature, the strengthening effect is rather limited and unstable because of lack of ductility. The strengthening becomes strongly pronounced at high temperatures. Damaging effect of neutrons at high temperatures is shown to be smaller than that at low temperatures. Intensification of homogeneous nucleation of Re-rich sigma phases in all studied Mo-Re alloys is observed after high temperature neutron irradiation. As a result, all parts of as-irradiated welds display approximately same level of strength.

High-temperature annealings with different heating/cooling rates have been used to simulate thermal conditions in different welding zones. Impurity redistribution in Mo-Re alloys has been studied by surface analysis methods. The role of carbon and oxygen segregation as well as formation of carbides and Re-base phases is discussed to minimise intergranular embrittlement of welds.

5.6.

USE OF TUNGSTEN AND RHENIUM ALLOYS FOR MANUFACTURING OF HIGH-TEMPERATURE THERMOCOUPLES W5%Re/W20%Re

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Features of development in Russia and application of thermocouples with thermoelements made of tungsten-rhenium alloys are briefly characterized in the paper. The choice of alloys with the rhenium contents 5 and 20 % is proved. Thermoelement materials are produced by a method of powder metallurgy. Powders of tungsten and ammonium perrhenate (NH_4ReO_4) are preliminary mixed, and then the mixture is pressed into cylindrical columns and melted. The columns are forged and drawn into a wire of diameters varied from 0,5 to 0,1 mm. Finished wire is subjected to stabilizing annealing in hydrogen.

According to the national verification scheme (GOST 8.558-93) standard thermoelectric thermometers based on W-Re thermocouples had been developed to transfer temperature unit in the range 900…2500 ºC to industrial thermoelectric thermometers. To certificate W-Re wires the Ural's Institute of Metrology (Ekaterinburg, Russia) had developed and introduced into metrological practice standard specimens of thermoelectric materials (wires) of W-Re5 and W-Re20 alloys. They were calibrated with expanded uncertainty about 11 ºC at 2500 ºC by a "wire bridge" method.

W-Re thermocouples of types A (W5%Re/W20%Re) and C (W5%Re/W26%Re) recently were included into the new draft of IEC standard 60584-1 and 2. Due to this fact, there was the necessity of reproducibility check for thermoelectric characteristics of W5%Re/W20%Re thermocouples, manufactured now in Russia. The calibration program and comparison of calibrations results were performed by Russian metrologists (in ROSTEST-MOSKVA; VNIIM, OTC, SIA"LUCH") and experts of foreign research laboratories (PTB, Berlin, Germany; NIST, Gaithersburg, USA; NIMJ, Tsukuba, Japan; NRC, Ottawa, Canada). All participants investigated the thermocouple specimens made of the same pairs of wire coils having diameters 0.5 and 0.35 mm.

The Russian researchers realized calibration of W5%Re/W20%Re thermocouples in the range of temperatures 600 … 2500ºC by various methods. There were performed "wire-to-wire" comparison of the tested specimens with standard W-Re wires and comparison of W-Re thermocouples with a reference type B thermocouple or a reference pyrometer. In all range of temperatures calibrations data were within the 0,7 % limit of permissible deviations from reference table of the Russian standard GOSTR 8.585-2001. New draft of IEC standard has the limit of permissible deviations ±1 %. The results of researches well agreed with results of foreign participants of the project in the investigated temperature range (600 …

1850 ºC). New draft of IEC 60584 standard has been fully agreed and in the nearest future it will be transferred for voting to National Committees of the countries- IEC participants.

At present time systematic researches of W-Re thermocouples in the range of temperatures 2000 … 2500 ºC are necessary. In this range the following factors are very essential: EMF drift of thermocouples, signal shunting through insulating armature, compatibility of materials at high temperatures. Commonly approved calibration procedure of thermocouples also needs to be developed for this range of temperatures. To manufacture more stable thermoelectric materials nano-technologies of disperse hardening of alloys may be used. The first investigation results in this direction give positive effect.

These researches will be extremely important for such areas as manufacture of rocket engines, nuclear power and technologies, space programs, manufacture of carbon composite materials. Interest to these fields increases recently every year. Reliable temperature control is very essential for these industries to manage the process in totally.

5.7.

MODERN STRUCTURAL MATERIALS BASED ON THE W-Mo-Re SYSTEM

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The high-rhenium alloys, based on the bcc Group VI metals of the periodic table (W and Mo) are known. These alloys exhibiting the “Re effect-1” (a simultaneous increase in low-temperature ductility and strength of Group VI metals after the addition of 25-35 at. % Re connected with an additional deformation mechanism by twinning) are lied near the α(W,Mo)/$\alpha+\sigma$ interphase boundary.

These high-rhenium alloys are as good as W and Mo alloys in high-temperature strength, but, unlike them, are not cold-brittle and do not become embrittled after high-temperature service and thermal cycling.

The binary W-Re, Mo-Re and ternary W-Mo-Re alloys have satisfactory formability and can be produced both as bulk articles and structures and as micron-scale semiproducts (foil, wire), which cannot be produced from Re because Re is expensive metal and demonstrates poor deformability caused by intense strain hardening.

The manufacture of the alloys by vacuum melting (VM) provides a high purity relative to interstitial impurities and a homogeneous Re distribution. This prevents the σ phase formation (deteriorating the plasticity), promotes the deformability, and allows the realization of “Re effect-2” (an abrupt increase in the strain hardening rate of W and Mo alloys due to the Re addition, up to σ_B = 4500-6000 MPa for micron-scale wire).

Such micron-scale wire from alloys of the MRe-47VM type retain the ability to deformation by flattening and to spiral coiling. In the case where high-rhenium alloys are manufactured by the cheaper PM method, none technique of the Re introduction into the initial powder provides a uniform distribution of Re, whose segregates provoke the formation of grain-boundary σ-phase precipitates. Therefore, the Re content in the PM alloys is smaller than in the VM alloys (WRe20PM//WRe27VM and MRe40PM//MRe47VM).

The investigation of the effect of Re on the electronic structure, physical and mechanical properties of W and Mo have revealed the “Re effect-3” (a substantial increase in low-temperature ductility of W and Mo alloys at 2-7 at. % Re).

This allowed the development of low-rhenium high-temperature W-Re alloys for bulk products, including those reinforced by refractory MeC-type carbides and Y_2O_3-type oxides for massive parts of the structures operating at temperatures above 2000ºC.

5.8.

TECHNETIUM - A RARE METAL PRODUCED BY MAN FOR STRUCTURAL AND MEDICAL USE

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Technetium-99 is a manmade element made for medical and high temperature structural use. Technetium is too rare in nature for any use so it is made as Tc^{99m} with short half life for medical use and Tc^{99} with long half life and low beta radiation for structural use is provided by the fission products in spent nuclear fuel. The needed Tc^{99m} for medical use is produced by radiation of molybdenum with nuclear reactors. The Tc^{99} metal with very much longer half life and less radiation is separated from the spent nuclear fuel, reduced and purified to pure metal powder and melted to ingots. Technetium has physical properties very similar to Rhenium. Technetium-99 was taken from the waste tanks in Hanford, Washington, purified, reduced to metal powder and melted into an ingot programmed by the author in 1964.(1) The Tc^{99} was then used to alloy with tungsten to improve its ductility similar to rhenium. The tungsten alloy with 25% technetium could be cold forged indicating the improved ductility. The current nuclear power plants produce about 800 grams of technetium per metric ton of used nuclear fuel. The commercial value of the technetium produced by a 1000 megawatt reactor in one year is about $240,000 assuming the value of Tc^{99} equal to that of rhenium. Almost all of the literature on technetium is about the medical Tc^{99m} since there has been very little removed from used nuclear fuel fission products. The author also had Tc^{99} inserted to locate cancer cells to be irradiated for destruction. It was successful ten years ago. The value of technetium will help pay for the reprocessing of used nuclear fuel around the world.

Poster session 5

Chair : G.S.Burkhanov

Notes

5.P1.

COMPLEXATION IN THE SYSTEM Re (V) ÷ 1-methyl-2-MERKAPTOIMIDAZOLE ÷ 8 mol/l HCl

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By potentiometric titration the process of chelation of rhenium (V) with 1-methyl-2-mercaptoimidazole was investigated in 8 mol/l HCl at 308 K. A comparison of the pKi for oxochloro-1-methyl-2-mercaptoimidazole complexes of rhenium (V) in the medium 8 mol/l at 308 K with similar values obtained in the medium 7 mol/l HCl shows that increasing the concentration of hydrochloric acid leads to a decrease in the value of all stepwise formation constants.

Reducing the formation constants increase HCl concentration can be explained by an increase in competition between chloride ions and molecules of 1-methyl-2-mercaptoimidazole for a place in the coordination sphere. Formation constants oxochloro-1-methyl-2-mercaptoimidazole complexes of rhenium (V) defined by the curves of education (Table 1) were used to estimate the thermodynamic characteristics of complexation by the temperature coefficient (table 2).

Table 1

Formation constants of oxochloro-1-methyl-2-mercaptoimidazole complexes of rhenium(V) in 8 mol/l HCl at 273-338K

T,K	K_1	K_2	K_3	K_4	K_5
273K	$1,1\cdot10^6$	$7,4\cdot10^4$	$9,3\cdot10^3$	$1,9\cdot10^3$	$3,1\cdot10^2$
288K	$5,6\cdot10^5$	$4,4\cdot10^4$	$6,4\cdot10^3$	$1,3\cdot10^3$	$2,6\cdot10^2$
298K	$3,5\cdot10^5$	$3,6\cdot10^4$	$4,6\cdot10^3$	$1,0\cdot10^3$	$1,6\cdot10^2$
308K	$2,1\cdot10^5$	$2,5\cdot10^4$	$3,2\cdot10^3$	$7,5\cdot10^2$	$1,4\cdot10^2$
318K	$1,1\cdot10^5$	$1,4\cdot10^4$	$2,3\cdot10^3$	$3,5\cdot10^2$	$9\cdot10^1$
328K	$9,1\cdot10^4$	$9,3\cdot10^3$	$1,9\cdot10^3$	$1,1\cdot10^2$	$6\cdot10^1$
338K	$3,3\cdot10^4$	$6,9\cdot10^3$	$8,5\cdot10^2$	$8\cdot10^1$	$3\cdot10^1$

Table 2

The values of thermodynamic functions of the educational process oxochloro-1-methyl-2-mercaptoimidazolnyh complexes of rhenium(V) in the medium 8 mol/l HCl

The compound	ΔH, kJ/mol	ΔG, kJ/mol	**ΔS,** J/mol·K
$[ReOLCl_4]^-$	-39,37	-31,36	-26,89
$[ReOL_2Cl_3]$	-28,79	-25,55	-10,84
$[ReOL_3Cl_2]^+$	-26,82	-20,74	-20,41
$[ReOL_4Cl]^{2+}$	-36,48	-16,45	-67,20
$[ReOL_5]^{3+}$	-26,39	-12,53	-46,55

Using the estimated values of the formation constants were calculated distribution curves of all complex forms, resulting in a system $[ReOCl_5]^{2-}$ - 1-methyl-2-mercaptoimidazol-8mol/l HCl at a temperature of 308K.

5.P2.

INFLUENCE OF OXOCHLORO-THIOPYRINE RHENIUM(V) COMPLEX ON RADIATION FIRMNESS OF CELLULOSE DIACETATE

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Inversigation of the influence of γ – radiation onto explosive durability of cellulose diacetate films modified with thiopyrin complex of oxo-rhenium(V) has shown the established anti irradiations properties. On inclusion of coordinated thiopyrin into the structure of cellulose diacetate (DIC) its explosive durability under the influence of γ-radiation decreases considerably compared to the initial DIC. So, the resistence of DIC samples containing 0,1 % thiopyrin to γ radiation with a dose 95 X-ray/hour have the mechanical durability that is 1,4 times higher compared to the samples not containing this additive. With increasing concentration of DIC thiopyrin in cellulose diacetate its resistance to radiation increase, due to the screening mechanism of this additive action. On the curve of the tensile γ- radiation maxima do not occur. Another radiation dose rate effect is observed with the introduction of chlorides complex of oxo-rhenium (V) with thiopyrin. Even on the introduction of low chlorides oxo-rhenium (V) complex concentrations (0,001% by weight) resistence to γ-radiation increases in the values of tensile polymer under the action of strength. At this concentration, additive process of hardening films for DIC occures up to the γ-radiation dose of $19 \cdot 10^4$ Roentgen per hour. This effects of the film has strengthened by 1,3 times. This increase of the dose leads to a slow decrease in the tensile strength. At $190 \cdot 10^{10}$ X-ray/hour of film not modified DIC become fragile and to define their durability to become very difficult. Samples DIC films containing 0,001 % of a complex of oxo-rhenium (V) at the specified dose of an irradiation keep the appearance and plasticity, and their explosive durability on comparisons by the not irradiated modified film decreases from 8,3 kg/mm^2 to 6,8 kg/mm^2 that is in 1,2 times. It is necessary to note that explosive durability of polymer of a complex not containing an additive at influence γ-radiation with the specified dose of an irradiation decreases from 8,1 kg/mm^2 to 1,8 kg/mm^2, that is in 4,5 times. With increase of concentration of a complex its anti radiating effect amplifies. By results of experimental researches shown the interval of concentration of a complex in which is defined its maximum effect in quality anti radiating additives for cellulose diacetate. Even at introduction of insignificant concentration chlorides a complex of oxo-rhenium (V) under the influence of γ-radiation to occur increase of value of explosive durability. Increase the irradiation dose lead to slow reduction of value explosive durability. On the basis of the analysis of dependences of explosive durability from a dose of an irradiation influence-γ- makes the conclusion from volume that, maxima of these dependences can be used for reception cellulose diacetate materials possessing the improved physical properties.

5.P3.

PLASTIC DEFORMATION OF RHENIUM AND PLATINUM-GROUP METALS

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Plasticity, as well as strength is a complicated function of several terms i.e. the nature of the interatomic bond, macro-and microstructure, various kinds of defects, external factors (temperature, pressure, composition), test conditions (stress state, strain rate, surface condition, scale factor), etc. Plasticity is not only the property but also the state of matter.

Rhenium and technetium,by their physical and mechanical properties,are close to platinum-group metals. They are distinguished by high degree of strain hardening, which makes the process of obtaining rhenium semi-products very labor-intensive. Rhenium isthe only of alloying elements, which increases both ductility and strength of tungsten and molybdenum (rhenium effect), neutralizing the harmful carbon and oxygen effects on physical and mechanical properties.

Of platinum-group metals, only palladium and platinum have high ductility. Rhodium and iridium of technical purity, having the same crystalline structure, are fragile. In the state of technical purity, ruthenium and osmium are practicallyno deformable.

Deep cleaning of rhenium and platinum-group metals sharply increases their ductility. Investigation of structure and properties of rhenium and platinum-groupmetals in the pure poly-and single-crystal stateshas enabled to determine the contribution of impurities to changing their plasticity, the cause of brittleness and deformation mechanisms.

Developed on the base of studies, the regimes of plastic deformation have enabled to obtain thin foils of iridium, rhodium and rhenium. For the first time, by plastic deformation, it is obtained ruthenium foil by thickness of less than 1 mm.

Session 6. Tc and Re nanotechnology and applications in the field of nanomaterials

CHARMEN : B. G. Ershov, K.E. German,
I.D. Troshkina, A.I. Kostylev

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6.1.

SYNCHROTRON DIAGNOSTICS OF FUNCTIONAL NANOMATERIALS

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Synchrotron radiation (SR) offers unique capabilities in structural characterization of complex functional materials. Nowadays, there are about 70 operating SR centers all over the world. Russia hosts two of them located at the Budker Institute of Nuclear Physics (Novosibirsk) and Kurchatov Institute (Moscow).

This lecture surveys current status and future plans of experimental stations installed at the Kurchatov Synchrotron Radiation Source.

The emphasis is placed on the design and recent results obtained with the "Structural Materials Science" end-station. This station is dedicated to structural investigations of non-crystalline and nanostructured materials by a set of mutually complementary methods, viz. small-angle X-ray scattering (SAXS), X-ray powder diffraction (XRD) and X-ray absorption spectroscopy (EXAFS/XANES).

These techniques yield structural information at different distance scales over the range of 0.1-100 nm (interatomic distances, unit cell parameters, size of crystallites/particles/pores, etc.) thus enabling more comprehensive characterization of a material.

The station is equipped with a special sample environment chamber to study samples under non-ambient conditions (high/low temperature and a specific gas atmosphere, including vacuum, inert gases, oxidative/reductive gases, etc.). This is especially important for functional materials since a structural study can be performed under conditions similar to those required for their target exploitation.

Over the last few years, diverse classes of functional materials have been elucidated, including supported catalysts for petrochemical processes, metal alloys, polymers, functional metal oxides and complexes.

The logic of application of different synchrotron X-ray techniques to solve specific structural problems is discussed. Possibilities and advantages of combined utilization of several techniques are illustrated with a number of examples.

6.2.

MANUFACTURE OF NANO - AND ULTRADISPERSE POWDERS OF RHENIUM AND REFRACTORY METALS FROM TECHNOGENIC RAW MATERIALS.

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Results of the researches executed in MUCTR and Radium Institute within the framework of the project ("Rosnanotech") on the organization of manufacture of nano powders of rhenium and some refractory metals from technogenic raw materials are presented.

The purpose of the work was elaboration of optimal technological methods and working off of the key stages of a manufacture in a pilot industrial scale: preparation of initial raw materials, separation of a multicomponent mix of metal compounds and obtaining of rhenium, tungsten and molybdenum high clean powder, with exact phase and granulometric composition. The manufacture is focused on the obtaining a final product: nano - and ultradisperse powders or microgranules in a form which would be suitable for the application in powder metallurgy of superalloys and special refractory alloys.

In the first part of the report the manufacture and consumption structure of rhenium superalloys is analyzed and mechanical engineering sectors, defining a demand of recycling metals from superalloys are allocated. The presented data is compared with long-term (till 2027) forecasts of the rhenium consumption market by the main manufacturers of superalloys for power and gas turbines.

In the second part of the report the basic technological methods worked off in a pilot industrial scale and taken as a principle of manufacture are stated. These methods concern a stage of preparation of raw materials, a stage of obtaining rhenium, tungsten and molybdenum and a stage of synthesis of nano - and ultradisperse powders of these metals.

For raw material preparation an electrochemical processing is used. It makes possible to destruct the pieces of an alloy on intergranular borders with formation of fine-dispersed powder with the crystallite size which is corresponding to the size of crystalline particles in the γ - phase in an initial alloy (1-5 micron). In practice, a power consumption needed to destroy 1 kg of the alloy is around 1.3 kWh. Separation of rhenium, tungsten and molybdenum is based on plasmochemical oxidation of the obtained ultradisperse material in a combination with high-temperature sublimation and cleaning of oxides of these metals.The subsequent gas-core reduction of oxides according to technology of chemical sedimentation from a gas phase (CVD) provides obtaining of nano - and ultradisperse powders of these metals. The firm cinder formed at plasmochemical oxidation of raw materials, and containing mainly nickel, aluminum, cobalt, tantalum oxides and impurity of other metals, is retreated in the modified hydrometallurgical mode.

In a final part of the report data on experience of processing domestic and foreign rhenium-containing technogenic raw materials (more than 30 tons, a waste of superalloys ЖС-32ВИ, МК4 and RENE5) are presented. Characteristics of obtained production (nano - and ultradisperse powders) are compared with requirements of MMTA (Minor Metals Trade Association) to materials for powder metallurgy of superalloys.

6.3.

NON-STOICHIOMETRIC SYNTHESIS OF RHENIUM HEPTASULFIDE HYDROSOL

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Nanoparticles of rhenium heptasulfide (Re_2S_7) are promising as effective and extremely selective catalyst of hydrogenation with high specific surface. Stability of the substance to its poisoning does these particles even more attractive.

Synthesis of hydrosol possessing thermal, aggregative and sedimentation stability during its storage for a long-time as well as after addition of electrolytes and in wide range of pH became the purpose of the present work.

In this work the Re_2S_7 nanoparticles were synthesized in the exchange reaction of perrhenate and hyposulfite. The influences of synthesis time, acidity, ratio of reactants, and quantity of the stabilizer on the disperse phase yield were investigated. Kinetic characteristics of the reaction are obtained. A method of complex removal of ionic and mechanical impurities is offered.

It is found that formation of particles at a temperature of 100 ^{o}C finishes after 2 minutes. Attempts to prolong the synthesis time do not result in a growth of the disperse phase yield but increase a risk of its coagulation. Reduction of the synthesis time has allowed lowering the stabilizer concentration in 3-4 times. It is shown that fast coagulation is provoked by acids (> 0,4 *N*) when heating reaction mixture up to 100 ^{o}C.

The product was purified from mechanical impurities (sulfur, *etc*.) by centrifugation. By-products of the reactions and residual quantities of the reactants were removed by ion exchange on a mixed resin bed. Non-ionic water-soluble impurities are offered to be removed by dialysis (in this case the deionization procedure is not necessary).As a result of the work, visually transparent non-opalescent deionized product, stable within a wide range of pH (1-9), not coagulating in saturated solutions of salts (including polyvalent cations) even at long heating up to 100 ^{o}C has been synthesized. Effective hydrodynamic diameter of the nanoparticles (photon correlation spectroscopy) is at least 2-3 times more than diameter of the dense core (transmission electron microscopy). Particles have a wrong form. Polydispersity is low: 75% (mas.) of the particles have hydrodynamic diameter between 35 to 75 nm. Particles with a size of more than 90 nm are not found in the hydrosol. Deionized hydrosols can be stored in an inert atmosphere for indefinitely long time (years).

6.4.

CONTROLLED SYNTHESIS OF ULTRA DISPERSED (NANO SISED) RHENIUM OXIDES (IV) AND (VI): SYNTHESIS OF PRECUSORS AND PROPERTIES OF THE MATERIALS

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Recently the interest to chemistry of rhenium compounds and a problem of synthesis of new materials on its basis has considerably increased. The interest is caused by unique and important properties of rhenium compounds. In particular, alloys of rhenium with other refractory metals are characterized by a combination of useful mechanical properties (durability, hardness, plasticity).

A significant amount of rhenium compounds are used in catalyst manufacture, possessing high activity and selectivity in various organic and inorganic reactions. It is known that the application of nano sized particles in catalysis allows to reduce the expense of active components. Therefore ultra and nano size rhenium oxides cause the practical interest due to its special physical and chemical properties.

The aim of work is development of methods of functional ultra disperse (nano sized) materials on the basis of rhenium with application as precursors homo - and heteroligand rhenium alkoxocomplexes. Electrochemical synthesis was improved to obtain $ReO_3(OBu^n)\cdot mBu^nOH$ **(I)** and $Re_4O_x(OEt)_y(OPr^i)_z$ **(II)**.

Synthesis products have been characterized by chemical analysis, X-ray and infrared spectroscopy methods. Measurement of the particles sizes was performed on the Delsa™Nano Submicron Particle Size and Zeta Potential Particle Analyzer PN A54412AA.

Electrochemical synthesis of Re complex with n-butanol **(I)** was carried out. It was established that complex **(I)** decomposes with formation of oxide mixture ReO_3 and ReO_2 at T = 412°C. Electrochemical synthesis of Re complex with ethanol and isopropyl alcohol (molar ratio 1:1) **(II)** was carried out and it was shown that it decomposes with formation of oxide ReO_3 (cub) at 470 °C. Methods of obtaining ultra disperse (nano sized) Re oxide (VI) with d=24±5 nm and mixtures of Re oxides (IV) and Re (VI) with d=59±5 nm were developed.

The authors express thanks to the Russian Foundation for Basic Research (the project 09-03-00328) for financial support.

6.5.

VOLATILE TECHNETIUM CARBONYL COMPOUNDS AND PROSPECTS FOR THEIR APPLICATION

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The results obtained in synthesis and studies of volatile technetium carbonyl compounds (mainly by the authors) are summarized. The main chemical forms of these complexes are considered: $Tc_2(CO)_{10}$ and its analogs, Tc(I) carbonyl halides, products of replacement of CO groups and halide ions by other ligands, and technetium carbonyl hydrides. The results of studies of technetium carbonyl complexes in the gas phase by IR spectroscopy and mass spectrometry are analyzed. Vaporization of volatile technetium compounds is characterized by the preparative sublimation conditions and temperature dependences of the saturated vapor pressure. Factors affecting the capability of technetium carbonyl compounds for vaporization are discussed. The thermal stability of technetium carbonyl complexes is analyzed in the aspects of resistance to decarbonylation (for higher carbonyls), loss of σ-donor ligands (for heteroligand complexes containing σ-donor ligands), and deep degradation. Unique properties of β-diketonates as ligands for designing volatile compounds are demonstrated.

The possibility of using technetium carbonyl compounds for chemical vapor deposition of corrosion-resistant technetium coatings is examined. Such coatings can be of interest for protection of certain units operating in seawater from biofouling. Samples of technetium coatings on model supports were prepared from a large series of volatile carbonyl precursors. The chemical and physical compositions of the coatings were determined, and their corrosion resistance in seawater was evaluated. Some samples are not inferior to dense Tc foil in the corrosion resistance.

The volatility of technetium carbonyl compounds opens new prospects for their use in nuclear medicine. First, transfer of the complexes through the gas phase allows preparation of radiopharmaceuticals free of any foreign reagents and of finely dispersed carriers which may exert a side effect on the patient. Second, it becomes possible to perform chemical transformations in nonaqueous media starting from higher technetium carbonyls, i.e., routes to compounds synthetically inaccessible from the standard precursor, tricarbonyl triaqua complex $[Tc(CO)_3(H_2O)_3]^+$, are opened. Third, the volatility allows technetium compounds to be directly used for diagnostics of respiratory organs with inhalation administration.

Technetium-99*m* pentacarbonyl iodide prepared by carbonylation of the eluate from a technetium generator at a high CO pressure in the presence of HI and released into the gas phase in the course of relieving CO pressure demonstrated selective and persistent accumulation in lungs of laboratory animals at intravenous administration. This property, in combination with the volatility of the complex and possibility of its inhalation administration, opens a unique possibility of using the same agent for investigation of both ling perfusion and lung ventilation. The images of lungs of laboratory animals, obtained with intravenous and inhalation administration of $[^{99m}TcI(CO)_5]$, are presented. However, additional studies are required to evaluate the selectivity of this agent in revealing possible pathologies.

6.6.

SYNTHESIS AND CHARACTERIZATION OF Ni-M (M = Pd, Pt) NANOPARTICLE PAIR STRUCTURES

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The process of interaction of nickel nanoparticles (Ni NPs) with ions of Pd(II) and Pt(II) was studied. Bimetallic nanoparticle pair structures were synthesized.

The process was performed in two steps. The Ni NPs were synthesized through the chemical reduction 2×10^{-4} M Ni^{2+} in water in the presence of the 1×10^{-4} M sodium polyacrylate (M. w. = 2100 g/mol) by sodium borohydride.

Nickel ions reduction occurred instantly after adding of $NaBH_4$, solution color changed to yellow. In ultraviolet range formation of the specific for Ni NPs absorption band at 215 nm was observed [1]. According to TEM, nickel nanoparticles were of spherical shape and narrow size distribution with mean diameter 5 nm.

Interaction of Ni NPs with Pd(II) и Pt(II) led to formation of palladium and platinum nanoparticles. Reduction of the metal ions took place at surface of the nickel nanoparticles. According to the spectrophotometric data, reduced noble metal layers did not cover the entire surface of Ni NPs. Gradual addition of Pt(II) was accompanied by significant increase of optical density in the whole range of UV-VIS wavelengths. At concentration ratio Ni/Pt $\leq$ 2:1, formation of shoulder at 220 nm in solution spectrum was observed.

Addition of Pd(II) resulted in progressive decrease of light absorption and scattering by the solution. TEM and electron diffraction studies proved that synthesized bimetallic nanoparticles Ni-M (M = Pd, Pt) were of contact pair type.

Acknowledgments: The work was supported by Russian Fundation for Basic Research grant 09-03-00432-a.

References:

1. B.G. Ershov, Izv. Akad. Nauk, Ser. Khim., №10: p. 1733 (2000).

6.7.

Pd NANOPARTICLES IN AQUEOUS SOLUTIONS: SYNTHESIS AND PROPERTIES

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Studies on two techniques of palladium nanoparticles (PdNPs) synthesis in aqueous solutions were performed. PdNPs were synthesized through chemical reduction of dissolved of Pd^{2+} ions by gaseous hydrogen or photochemical reduction of dearated Pd^{2+} solutions by UV-VIS radiation of xenon high-energy pulsed lamp. Process of photo-induced reduction was enhanced by using of sodium formate as a source of reducing $^{\bullet}COOH$ radicals in irradiated samples. Stabilizing agents used were sodium polyphosphate (NaPP) and sodium polyacrylate (NaPA); both polymers were of molecular weight ~2100 g/mol.

H_2-Process. Investigation of the effect of stabilizing agent concentration on PdNPs stability proved that sodium polyacrylate was more preferred surfactant: the lowest concentration ratios providing long-term stability of nanoparticles for $[Pd^{2+}]/[NaPP]$ and $[Pd^{2+}]/[NaPA]$ were 1:20 and 1:2.5 respectively. Studies of chemical reduction of Pd^{2+} with concentration up to 0.75 mM showed that the initial concentrations of Pd^{2+} allowing to produce sedimentation stable nanoparticles were as high as 0.5 mM; using of higher $[Pd^{2+}]_0$ values led to rapid precipitation of palladium black. Furthermore, the sedimentation of PdNPs stabilized with NaPP was accompanied by particles flocculation, what had not been observed in the similar experiments with NaPA solutions. The atypically significant effect of $[Pd^{2+}]_0$ on sizes of hydrogen-reduced particles was revealed: at $[Pd^{2+}]_0=0.35$ mM mean diameter of Pd-NPs was 30 nm and at $[Pd^{2+}]_0=0.50$ mM it was 45 nm. Size distributions and dispersity of PdNPs with both surfactants were found to be quite similar; however polyacrylate-stabilized particles were 2 to 5 times more sedimentation-stable.

Photochemical process. The optimal concentration of sodium formate used in irradiation-induced reduction was found to be 10 times as high as Pd^{2+} concentration. Obtained PdNPs exhibited narrow size distribution, Pd-NaPP and Pd-NaPA particles diameters were 2–7 nm and 1.5–4 nm respectively (at $[Pd^{2+}]_0=0.2$ mM). The fact that Pd-NP synthesized photochemically were of lesser size is explained by the difference of nanoparticles formation mechanisms – intensive irradiation of solution results in instant formation of Pd seeds over the entire volume of sample, while the interaction of H_2 with Pd^{2+} takes place on the surfaces of a limited number of the most active nucleating centers.

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6.8.

WAVELET ANALYSIS OF EXAFS SPECTRA AS APPLIED TO POLYNUCLEAR AND CLUSTER TRANSITION METAL COMPLEXES

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The most convenient way for processing of extended X-ray absorption fine structure (EXAFS) spectra is based on the Fourier transformation (FT) [1]. FT extracts information about contributions corresponding to a specific shell of neighbors around the central atom. However, in those cases when two groups of different atoms are located at similar distances, their contributions in R-space overlap and become indistinguishable.

The wavelet transform (WT) [2-4] represents an alternative and potentially more powerful approach to retrieve useful information from EXAFS spectra. The WT has been widely used in different fields and applications such as sound and image processing, data compression and digital signal de-noising [5]. When applied to EXAFS data analysis, the WT is capable of providing not only radial distance information, but it resolves data in k space as well giving a quick-glance estimate of the atomic number Z of an element in a specific coordination sphere.

In this work, the wavelet-based approach is systematically applied to analyze EXAFS spectra for a series of Pd, Re, and Tc polynuclear and cluster compounds. A possibility of straightforward differentiation between M-N(O)/M-Cl/M-M (M=Pd, Re, or Tc) contributions in EXAFS spectra of complex species is demonstrated.

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References:

1. F.W. Lytle, D.E. Sayers, E.A. Stern. *Phys. Rev.* B **11** (1975), 4825–4835.
2. H. Funke, A.C. Scheinost, M. Chukalina. *Phys. Rev.* B **71** (2005) 094110.
3. H. Funke, M. Chukalina, A.C. Scheinost. *J. Synchr. Rad.* **14** (2007) 426.
4. J. Timoshenko, A. Kuzmin. *Comp. Phys. Com.* **180** (2009) 920–925.
5. Q. Tao, V.I. Mang, X. Yuesheng (Eds.) Birkhäuser-Verlag, Basel, 2007.

6.9.

NANODIAMONDS FOR BIOMEDICAL AND SORPTION APPLICATIONS: STRUCTURE AND DEFECTS

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Nanodiamond (ND) particles belong to a broad family of nanocarbon-based materials with a structural diversity that is based on specific synthesis conditions, post-synthesis processes, and modifications. ND particles with sizes up to several tens of nanometers currently find broad application in polishing, structural materials, and lubricants, as well as prospective applications in biotechnology and medicine.

Recently, several important new application areas have been proposed based on the potential of incorporating impurity atoms and point defects into the nanoparticle lattice. Major breakthrough areas where controlled doping of NDs and on-demand production of the nitrogen-vacancy (N-V) centers. The spin state of the negatively charged N-V center can be polarized by optical pumping and can be manipulated using microwaves, permitting implementation of an efficient single photon emitters for quantum information processing or a magnetic sensor with a nanoscale resolution. Optical transitions in the N-V centers in diamond provide bright and stable photoluminescence.

We have recently shown that very small nanodiamond particles (1-2 nm) may also possess bright luminescence from another defect - Silicon –Vacancy complex (Si-V) [1]. Thus, on-demand production of the N-V and Si-V centers in nanodiamond is of paramount importance for quantum information processing and quantum computing, nano-scale imaging magnetometry and photoluminescent probes for bio-research. We will discuss recent advances in understanding defects and structural peculiarities of nanodiamonds, important for various applications.

Another important and yet not fully explored niche for nanodiamonds is their application as sorbents. Various ways of surface modification are invented, thus allowing creation of efficient, durable and reusable nanodiamond-based sorbents. Recent results on radionuclides sorption will be reported.

References:

1. Shiryaev et al., *Geochim. Cosmochim. Acta.* **75**, 3155-3166 (2011)

2. Vlasov et al., *Small* **6,** 687-694 (2010)

6.10.

NANOTECHNOLOGIES IN RADIOCHEMICAL TECHNOLOGY AND RADIOECOLOGY INCLUDING TECHNETIUM SPECIATION AND SEPARATIONS

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Modern approaches to sustainable development of Atomic Energy, development and improvement of nuclear fuel cycle in Russia are directly linked to the development of nanoindustry. The following items will be elucidated and discussed herein: major scientific advances in the production of nuclear fuel compositions, search of new technologies for the reprocessing of spent nuclear fuel (SNF) and optimization of existing ones, the solutions of the problem of radioactive waste of different activity levels management, development of radioecology. Information about search results in getting of oxide fuel modified compositions will be presented in the report also. The results on the synthesis and use of heterogeneous catalysts based on noble metal nanoparticles drawn on the carrier surface to improve processing of SNF also will be presented. The advanced technologies of water low-acid and fluid (in liquid CO_2) dissolution of uranium and plutonium oxides resulting in significant decrease of radioactive waste volume will be also considered.

With respect to nuclear waste treatment we shall discuss the major results for processing both liquid (water/organic) and gaseous wastes using nanocollectors for cleaning of industrial drain productions, pieces of carbon materials (activated and modified coals, nanotubulens), as well as sorbents for fixing of various forms of radioactive iodine based on Ag nanoparticles, respectively key results in producing the above mentioned carbon materials, including development of method of electron-beam conversion of ligno-cellulosic material to obtain nanoporous coals with unique physical and chemical properties will be presented. Also the data on processing of alkali radioactive material handling, methods of improvements of various solid matrixes (cement compounds, glass composition, ceramics materials) by method of nano-additives for immobilization of high-level waste will be proposed.

In the end of the report data on development of methods of radionuclides and espessially technetium-99 determination and concentration in environmental media objects using nanostructured high-performance agents – extractans and sorbents will be given. On the basis of the information submitted will provide key conclusions on advisability and development of researches in the field of nanoindustry in radiochemical technology and radioecology.

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Poster session 6

Chairmen : E.V. Abkhalimov, P.A. Morozov, B.G. Ershov

Notes

6.P1.

HIGH TEMPERATURE INTERACTION OF RHENIUM, MOLYBDENUM AND TUNGSTEN METALS WITH URANIUM MONONITRIDE

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The study was aimed to research the new materials for the utilization in high temperature nuclear devices and to increase their efficiency and safety.
The interaction of nitride nuclear fuel $U(N_{0.90}\,C_{0.05}\,O_{0.07})_{1.02}$ with rhenium, molybdenum and tungsten metals acting as cladding materials at T=1773 K was investigated. Uranium in the fuel was enriched in ^{235}U to 90 %.

Uranium nitride and metal samples in a form of the disks, possessing 2 - 3 mm thickness and 8 - 9 mm diameter were placed in turn into the rhenium, molybdenum and tungsten metal ampoules. The ampoules were welded in vacuum and annealed in the vacuum furnace at 1773 K for 1000 hours.

The diffusion coefficients of uranium from UN to Re, Mo and W phase were determined using layer by layer radiometric analysis, measuring the integral α-activity of metal samples. The diffusion coefficients values were calculated in terms of diffusion model for the instant source to the semi-infinite body using the equation:

$$I_i / I_o = \mathrm{erfc}\,[x_i / 2(Dt)^{1/2}]$$

The interaction of uranium mononitride with these metals at 1773 K was accounted for the diffusion of the fuel components to the metal phase.

Using autoradiography technique the difference in the diffusion mechanism for single crystals and polycrystalline samples was established.

The acceleration of uranium diffusion into the depth of the polycrystalline metals was associated with the diffusion at the grain boundaries. The corresponding diffusion coefficients values for uranium into polycrystalline (D_1) and single crystal samples (D_2) were determined as:

$D_1\,(U\rightarrow Re) = 1.2 \times 10^{-14}\ cm^2\times s^{-1}$, $D_2\,(U\rightarrow Re) = 4.0 \times 10^{-15}\ cm^2\times s^{-1}$
$D_1\,(U\rightarrow Mo) = 3.7 \times 10^{-12}\ cm^2\times s^{-1}$, $D_2\,(U\rightarrow Mo) = 4.9 \times 10^{-13}\ cm^2\times s^{-1}$
$D_1\,(U\rightarrow W) = 9.8 \times 10^{-16}\ cm^2\times s^{-1}$, $D_2\,(U\rightarrow W) = 3.3 \times 10^{-17}\ cm^2\times s^{-1}$

The presented results may be taken into account in the development of the fuel elements based on uranium mononitride for their utilization in the high temperature reactors for ground and space installation.

6.P2.

THERMAL BEHAVIOR OF PERRHENATE COMPLEXES OF NEODYMIUM AND PREPARATION OF NANODIMENSIAL RHENIUM CERMETES

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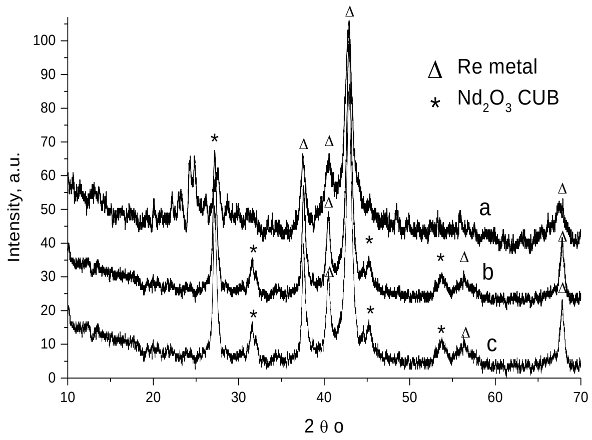
Trivalent f-elements perrhenate are proposed as promising precursor agents for cermet composites preparations. Regarding the targets for minor actinides and technetium incineration, the cermet composites are noted as the materials with the best thermal conductivity that can help to reduce the operating temperature. In this work efforts were focused in finding an original approach for their easy production. We propose a method of molecular Re(Tc)-Nd_2O_3 cermet preparation, where the rare earth element may serve as an analogue for americium and rhenium as an analogue for technetium, which transmutation should also be considered. For a complete understanding of the degradation process of the perrhenates under reductive conditions, thermoanalytical diagrams of $Nd(ReO_4)_3 \cdot 4H_2O$ and $Eu(ReO_4)_3 \cdot 4H_2O$ have been recorded in this work. These compounds originally contain four water molecules and the dehydration mechanism proceeds via similar schemes. Rhenium reduction with 6%H_2/Ar occurs at least in three stages distinctly observed in the TG profile of europium compound. The first reduction step starting at 430°C, is followed by a step at 590°C and a last one around 620°C. This thermodiagram profile leads to the conclusion that perrhenate reduction occurs via ReO_3 and ReO_2 intermediates to finally reach the metallic Re. Based on the thermogravimetric data, the temperature for Nd_2O_3-Re cermet preparation may be established at 590-600°C.



X-ray diffraction patterns of Nd_2O_3-Re cermet prepared at 600 °C: a: 1 hour, b: 4 hours, c: 10 hours

X-ray powder diffraction patterns of samples obtained at this temperature show line broadening, obviously due to the low metal crystallinity in the nanodimensional cermet material. Nevertheless, the lines corresponding to rhenium metal as well as to cubic Nd_2O_3 may be unambiguously identified. Increasing of the heating time at this temperature leads to very slow nanocrystalline cermet particles recristallization. SEM, EDX and EDS spectra confirm clearly the high degree of distribution of the primary components in the cermet product.

6.P3.

TECHNETIUM(VII) SORPTION BY MODIFIED NANODIAMONDS FROM AQUEOUS AND NITRIC ACID SOLUTIONS

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Nanodiamonds (ND) produced by detonation of high-energy explosives in oxygen-deficient environment present considerable interest for studies of nanoparticles and are also important for numerous applications in diverse fields ranging from tribology and photonics to biomedicine [1]. Many chemical properties of NDs are determined by surface radicals and currently various types of surface functionalisation are considered [2].

Technetium is a nuclear fission product and its reprocessing is often performed in intense radiation fields, precluding long-term use of many conventional ion-exchangers. High radiation stability of NDs may open new exciting possibilities for their applications in radiochemistry [3]. In our work we have studied Tc sorption on detonation nanodiamonds treated in different ways to modify surface radicals. The sample #1 represents NDs sintered at High Pressures – High Temperature conditions. The sample #3 is commercially available ND powder subjected to primary acid cleaning procedure after detonation. Such samples usually consist of very stable aggregates of ND grains. Whereas the size of the individual ND grains is 4-5 nm, the size of the aggregates lies between several tens to hundreds nanometers. Destruction of these aggregates is notoriously difficult. The sample #7 represents the disaggregated ND sample [4], i.e. it consists of individual 4-5 nm diamond particles. Its surface chemistry was not specially studied, though it is clear that it is dominated by various H- and O- containing radicals. The surfaces of the samples #2, 4-6 was modified by chemical and physical oxidation, see Table 1. The nanodiamond powders were ultrasonicated at ambient conditions. 10^{-4}M Tc in H_2O and HNO_3 solutions were prepared for sorption tests, the sorption efficiency was determined by β-LSC activity measurements of the solutions.Two samples (#2 – with surface aminogroups and #4 – heated in H_2 atmosphere at 800 C) showed high efficiency towards Tc(VII) sorption. Their sorption efficiency is comparable to the best anionites. The ionic state of Tc in these solutions is anion pertechnetate TcO_4^- and the most probable sorption mechanism should be anion exchange at the surficial cationic positions.

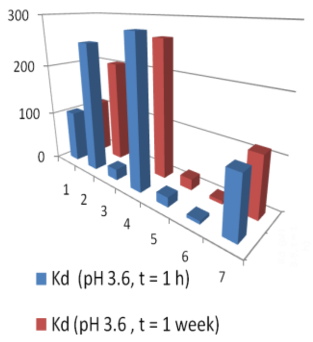

Fig. Distribution coefficients for sorption of Tc(VII) by modified nanodiamonds.

Table 1. Description of samples of detonation nanodiamonds

Sample No	Diamond treatment
1	Sintering at HPHT
2	HPHT sintered and aminated (NH-$C_{18}H_{37}$)
3	Standard industrial cleaning by HNO_3
4	Heated in H_2, 800 °C, 5 h
5	Oxidized by air at 450 °C
6	Oxidized by HNO_3+H_2SO_4
7	Disaggregated

References.

1. V.Yu. Dolmatov, *Russ. Chem. Rev.* **76**: 375-397.
2. I.I. Kulakova, *Solid State Physics* **46**: 621-629 (2004).
3. S.I. Chukhaeva, L.A. Cheburina, *Superhard materials (Russ.)* **2**: 43-48 (2000).
4. A. Kruger et al., *Carbon* **43**: 1722-1730 (2005)

6.P4.

STABILIZATION OF NANO-RHENIUM AND NANO-TECHNETIUM IN AMORPHOUS CARBON MATRIX.

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** - RRC “Kurchatov Institute” (Kurchatov sq.1, Moscow, Russian Federation)*

The noble metals and also Re were considered till recently to have no or very small affinity to carbon [1]. As for Tc, the formation of a carbide TcC_{1-x} with low content of carbon (x = 0.83) was proved [2,3] also indicating low affinity of Tc to carbon. Small amounts of carbon were shown to react readily with Tc metal causing its crystallographic distortion from *HCP* to orthorhombic structure and important enlargement of the specific unit cell volume [3]. This was confirmed by findings of distorted Tc metal and Tc carbide in Tc carbonyls thermal decomposition product [4]. In this work we consider in situ carbonization in course of thermal decomposition of several organic pertechnetates and perrhenates for the preparation of technetium and rhenium carbides. We studied the thermal decomposition of Tc and Re compounds taken as initial salts or supported at the γ-Al_2O_3 as an inert ceramic carrier. In the first case the metals were micro-particulated and when the initial compounds underwent the fusion before the decomposition the macro-agregates of metal or carbide phases were observed. In the second case the nano phase Tc and Re metals or carbides were prepared depending on the nature of the cation and the macroparameters of thermolyses. Hexametyleniminium pertechnetate and Triphenylguanidinium pertechnetate at 600 K in Ar gas undergo conversion to X-ray amorphous technetium carbide that could be stabilized in amorphous carbon matrx. Annealing of this product at 1073-1673 K leads to recrystallization and fine FCC structure with a = 3.98 Å forms. Hexametyleniminium perrhenate and Morfolinium perrhenate at 700 K in Ar gas undergo conversion to X-ray amorphous rhenium metal that is recrystallized under the following annealing at 1073-1673 K to form fine HCP structure. XRD patterns of nano dimension phases supported at the γ-Al_2O_3 were X-ray amorphous.

In the thermal decomposition of $TPGHReO_4$ just a mixture of Re metal, Re carbide and free carbon is formed. The product was solid-foam shaped. The principle product was new phase of rhenium carbide that was not described earlier. This was evidently due to higher concentration of carbon in the organic cation thermal distruction products. The deduction of XRD data is proposed for Re carbide formed from triphenylguanidinium perrhenate (Tab.1).

Table 1. X-ray diffraction pattern of new Re carbide phase (a = 5.095 A) formed in thermal decomposition of $TPGHReO_4$ at 623 K followed with annealing at 1273-1373 K in argon [5].

No	H K L	2Theta (exp.)	2Theta (calc.)	Differ.
1	2 0 2	50.70	50.604	0.096
2	3 1 1	60.30	60.153	0.147
3	4 0 0	74.26	74.374	- 0.114
4	2 3 3	90.20	90.266	- 0.66
5	4 0 4	117.60	117.542	0.070

The determined parameter **a** = 5,095 Å and the sp.gr. *Pm3m* indicates the Re carbide phase to be isostructural with a number of Ln carbides (Ho_3C, Yb_3C, Sm_3C) [6].

This observation suppose that usual inactivity of Re to C is due to very high fusion temperature of rhenium and not the absence of affinity. By contrast, when the Re metal phase (nano-phase) is generated *in situ* simultaneously with active carbon formed by organic cations thermolyses, both components are highly reactive and thus able to form Re carbide phase.

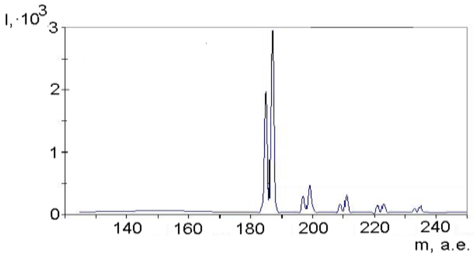

Fig.1. Laser microanalises mass spectrum registered with the LAMMA-1000 instrument from the product of thermal decomposition of TPGHReO$_4$ at 623 K followed with isothermal annealing at 1273-1373 K in Ar gas atmosphere [5].

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Gas products of the thermolyses indicate the oxidative mechanism of the destruction (CO$_2$, H$_2$O and different organic fragments of cations).

The laser evaporation of the Re-Re$_x$C-C composite formed by triphenylguanidinium perrhenate thermolyses in LAMMA-1000 instrument has given evidence for ReC$^+$, ReC$_2^+$ and ReC$_3^+$ ions formation (Fig.3) while the same analyses of non-thermolysed compound indicated just the first two satellites (185 1nd 187) presence. This is indicative of considerable affinity of Re to C not only in solid but also in gas phase under such conditions.

To sum up - Metallic rhenium or technetium nano phase could be generated by thermal decomposition of perrhenates/pertechnetates of organic cations under argon, the parallel carbonization of the cation provides the conditions favorable for Re and Tc carbide nano and micro particle formation. For hexametileniminium and thriphenylguanidinium pertechnetates the conversion provide with Tc$_6$C formation. In the thermal decomposition of triphenylguanidinium perrhenate just a mixture of Re metal, Re carbide and free carbon is formed. XRD patterns of nano dimension phases were X-ray amorphous, while for micro dimension Tc$_6$C phase the cubic lattice with a = 3.98 Å was deduced. For annealed sample the determined parameter **a** = 5,095 Å and the sp.gr. *Pm3m* indicates that new Re carbide carbide phase is isostructural with a number of Ln carbides.

Acknowledgments: The work was supported by RFBR grant 09-03-00017.

References.

1. T. Oyama (Ed.), *The Chemistry of Transition Metal Carbides and Nitrides*, Blackie Academic and Professional, London, 1996.
2. H. R. Heines, P. C. Mardok, and P. E. Potter, *Plutonium 1975 and other Actinides, Proc.: 5th Int. Conf. (Baden Baden, 1975)*. Amsterdam, 233-244 (1976).
3. K. E. German, V. F. Peretrukhin, K. N. Gedgovd, etc**.,** *Journal of Nuclear and Radiochemical Sciences*, **6:** 211-214 (2005).
4. G.V. Sidorenko, A.E. Miroslavov, D.N. Suglobov. *Radiochemistry*. **51**: 583-584 (2009).
5. K.E. German. In: Mazzi U.et all (Eds.). Proceedings of the International Symposium on Technetium and Other Radiometals in Chemistry and Medicine – Forum Brixen – Bressanone Congress Center (Italy) September 8-11, 2010, pp.125 -128.
6. K. A. Gschneidner and F. W. Calderwood. *Journ. Phase Equilibria*, **7:** 445-446 (1986).

6.P5.

ION SELECTIVE ELECTRODES BASED ON MONOCRYSTALLINE $KTiOPO_4$ WITH NANOCAPILLAR CONDUCTIVITY FOR DETERMINATION OF K^+-IONS.

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New improved $\mathbf{K^+}$–selective electrode based completely on solid single crystal KTP with nano-capillary conductivity is developed. The crystal KTP grown by two different methods had an ordinary orthorhombic structure ($Pna2_1$) with the chain structure of shared TiO_6 octahedrons, where the vacantly mobilized $\mathbf{K^+}$ ions provide the ionic conductivity through nano-dimension capillary. The membranes of 0.8 mm thickness and 6 mm diameter were hermetically sealed without glue materials into a IONIKS 111.080 solid membrane electrode body together with an inner standard Ag/AgCl reference electrode. The electrode presents linear response in the range of $pK^+=1 – 5$, the electrode function slope S=58.8±0.4 at 25° C and high selectivity coefficients for ions of alkali and earth-alkali elements that permits to use it for practical application in medicine. The electrode had a convenient response time, DL_K of $pK^+ = 5.2 \pm 0.1$ and the reproducibility of electrode potential ±0.2 mV in KNO_3 solutions during at least 28 months.

Extension of the design of potassium - selective electrodes for clinical chemistry, agriculture and industry is an actual and important task. The main problem of the ISE's is the short function time due to membrane degradation. Among the possible improvement approaches: the improvement of ion-selective electrode construction, the improvement of separate units quality, the optimum selection of membrane composition (with already known components), the search of the new membrane components, and the new sensitive elements – membranes – only the latter provide with important increase in durability of the device if made completely of inorganic materials. We reported the preliminary results of the investigation of a unique properties a single crystal $\mathbf{KTiOPO_4}$ (KTP) [1]. Here we present the design of new improved $\mathbf{K^+}$–selective electrodes based completely on KTP. The most known K^+-valinomicin electrode was used for comparison. The studied single crystal KTP were grown by using of two methods: hydrothermal and melting from a solution . They had ordinary orthorhombic structure (Pna21) with lattice parameters: a=12.814, b=6.404 and c=10.616 Å, and the chain structure made of TiO_6 octahedrons, where the potassium ions were able to move by vacancy mechanism, providing ionic conductivity. All measurements were carried out with using of a ionometer Orion Research Model-901 (USA). The external reference electrode was a IONIKS-112.024 (Russia) (double-junction Ag/AgCl electrode with 1M potassium chloride and 1M lithium sulfate electrolyte bridge). The selectivity coefficients were measured by the method of mixed solutions. The membranes of 0.8 mm thickness and 6 mm diameter were hermetically sealed in a IONIKS 111.080 solid membrane electrode body without glue materials. The 0.01 M KCl solution and a standard Ag/AgCl electrode were placed inside of reservoir. The electrode response was linear in the range of $pK^+=1 – 5$, with the electrode function slope equal to S=58.8±0.4 at 25° C. The high selectivity coefficients for ions of alkali and earth-alkali elements were found. We find the difference in selectivity proposed electrode, glass electrode ESL-47-07 (Belarussia) and valinomycin electrode Potential (Russia). Thus, the selectivity of proposed electrode permits to use it for practical application in a medicine. The electrode had a convenient response time, DL_K of $pK^+ = 5.2 \pm 0.1$ and the reproducibility of electrode potential ± 0.2 mV in KNO_3 solutions during at least 28 months.

[1] Buslaev Yu.A., Il'in E.G., Kopytin A.V., Politov Yu.A. Patent of Russia No 2017146, 30 July 1994.

6.P6.

QUANTUM CHEMICAL STUDY OF SUBNANODIMENTIONAL MIXED CLUSTERS OF TECHNETIUM AND RUTHENIUM

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Previous [1] quantum chemical DV-X_α [2] calculations based on the density functional theory proved adequacy and reliability of cluster models for the metallic technetium electronic structure analysis. We extended these models for mixed Tc_xRu_y phase appearing due to transmutation of radioactive Tc^{99} into stable Ru^{100} [3]. As a bulk phase our simple model clusters used the same electronic density for volume and surface sites. Interatomic distances for mixed models were linear interpolated by content between pure Tc and Ru metal ones as it’s shown in [4]. We took into account all low concentration models of Tc or Ru, but in the middle concentration area we used only statistically averaged data for rather small (~10) random sets of atom positions. Because it is similar character of results for both fragments, only the most informative electronic structure characteristics of 21-atomic model graphic data will be given further.The electronic configurations of pure metallic models Tc $4d^{5.66}5s^{0.73}5p^{0.60}$ and Ru $4d^{6.67}5s^{0.71}5p^{0.60}$ for mixed models vary slightly. It is about 10% for 5s5p-states and up to 3% for 4d-states. The most modification of 4d-Tc population is 0.15e for 13-atomic model. 4d-Tc population is monotone weakly logarithmically decreasing while Ru part enlarges. At the same time for effective charges we found approximately linear dependence from Ru content . For all atomic positions and some Ru concentration it was occured electronic density displacement toward Ru and very similar tendencies.

Fermi level position in our models approximately corresponds to the high occupied cluster orbital. Relative location of this level also linearly drop. Density of states (DOS) at Fermi level dependence has a rather intricate shape. At the low concentration of some metal DOS is relatively less then the same one for the pure metals or for the central part of the graphic. DOS absolute maximum position corresponds to ~70% output of transmutation products. Commonly this parameter has arising tendency during the transmutation process (dashed line). Finally, we estimated models stability by sum of Mulliken bond overlap population indexes over all bonds per one atom of model. It is excellent linear tendency for the bond weakening during transmutation. All this facts also well corresponds with general qualitative theory [5]: new more electronegative atom sublattice results to more strength bonding, correlates with the shift of occupied states in the lower energy area; descends Fermi level from the middle to the end of transition metal row and decreases density of states at Fermi level.

Therefore the same behaviour of electronic structure characteristics for both models arises the probability of these conclusions for the real samples. We can sum up that transmutation causes serious changes in electronic structure of initial metallic Tc, which influences on its chemical activity, physical-chemical and mechanical properties.

Acknowledgments: The work was supported by RFBR grant 09-03-00017.

REFERENCES

[1] *Yu.V.Plekhanov, K.E.German, R.Sekine* // Radiochemistry (Russ.), 45(2003) 217.
[2] *H.Adachi, M.Tsukada, C.Satoko* // J.Phys.Soc.Jpn. 45(1978) 875
[3] *V.F.Peretrukhin, S.I.Rovnyi, V.V.Ershov et al //* Zh. Neorg. Khim.(Russ.), 47(2002), no. 5, 722.
[4] *Y.Shirasu, K. Minato* // *J. Alloys Com*p., 335(2002), nos.1-2, 224.
[5] *R.Hoffmann* Solids and Surfaces: A Chemist’s View of Bonding, VCH Publisher Inc., 1988.

6.P7.

DEPOSITION OF TECHNETIUM COATINGS BY THERMOLYSIS OF VOLATILE CARBONYL COMPOUNDS

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Technetium carbonyl compounds [$TcBr(CO)_5$], [$TcI(CO)_5$], [$TcX(CO)_3]_4$ (X = Cl, Br, I), [$TcBr(CO)_3$en] (en = ethylenediamine), [Tc(RCOCHCOR')$(CO)_3(Et_2NH)$] [R = CH_3 or $C(CH_3)_3$, R' = CF_3], $Tc_2(CO)_{10}$ and [$Tc(C_5H_5)(CO)_3$] were tested as precursors for chemical vapor deposition of technetium coatings on model supports (external surface of titanium tubes) with the aim to evaluate the possibility of using technetium coatings for biofouling protection of critical units of installations operating in seawater. The deposition conditions and yields were determined. The necessary conditions for ensuring high deposition yield are occurrence of the decomposition in one effective step and, in the case of carbonyl halides, presence of a reductant, internal (ethylenediamine) or specially introduced into the gas phase.

The microstructure of the coatings obtained was examined by electron microscopy. The chemical composition of the coatings (carbon content) was determined. The coatings were studied by X-ray diffraction analysis, and phases of metallic technetium, solid solution of carbon in technetium, technetium carbide, and intermetallic compounds of technetium with titanium (support material) were revealed. Along with the well-known hexagonal phase, a new phase of technetium metal, body-centered cubic with $a = 0.325$ nm, was revealed; it is usually formed in thin (less than 1 μm) films. The corrosion resistance of the films in simulated seawater was studied by monitoring the accumulation of technetium in seawater contacting with the coated specimen. The correlation between the precursor composition, conditions of heat treatment of the coatings, chemical and phase composition of the coatings, and their corrosion resistance is discussed. High-temperature vacuum annealing (at no less than 900°C) is the necessary condition for preparing corrosion-resistant coatings. The highest corrosion resistance is attained at low (<2%) and high (>15%) carbon content in the coating. The best samples are not inferior in the corrosion resistance to dense technetium foil.

The most reliable results with respect to the whole set of parameters (deposition yield, adhesion of the coating to the support, corrosion resistance) were obtained with the system [$TcBr(CO)_3]_4$/ethylene glycol. Ways to further improve the deposition process are outlined. The most important of them is more efficient pumping-off of gaseous reaction products.

7. ROUND TABLE: Tc and Re as buiseness projects

Sponsors : Pharm-Sintez, CJSC, RUSNANO, NTC Amplituda,

Companies presentations:

1. Timofei Petrov (Pharm-Sintez, CJSC. General Director: Introduction of innovative Russian radionuclide pharmaceuticals into the local and global markets)
2. I.D. Troshkina Nano particles and nanotechnologies (technetium and rhenium)
3. G.S.Burkhanov - IMET RAS . Rhenium and PGM - PLASTIC DEFORMATION OF RHENIUM AND PLATINUM-GROUP METALS.
4. G.E. Kodina Nano Tc-99m
5. B. F. Myasoedov, K.E. German.Mo-99-Tc99m alternative production
6. I.S. Konovalov (NTC Amplituda)

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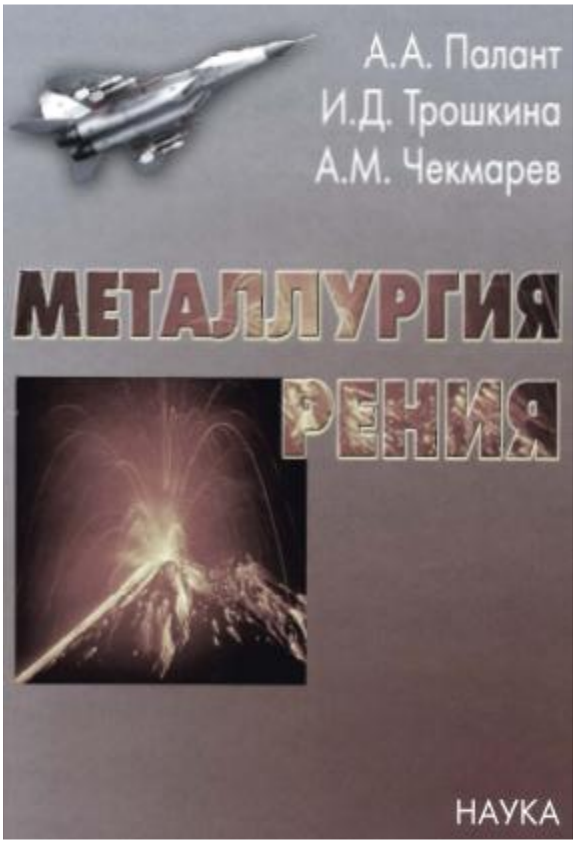

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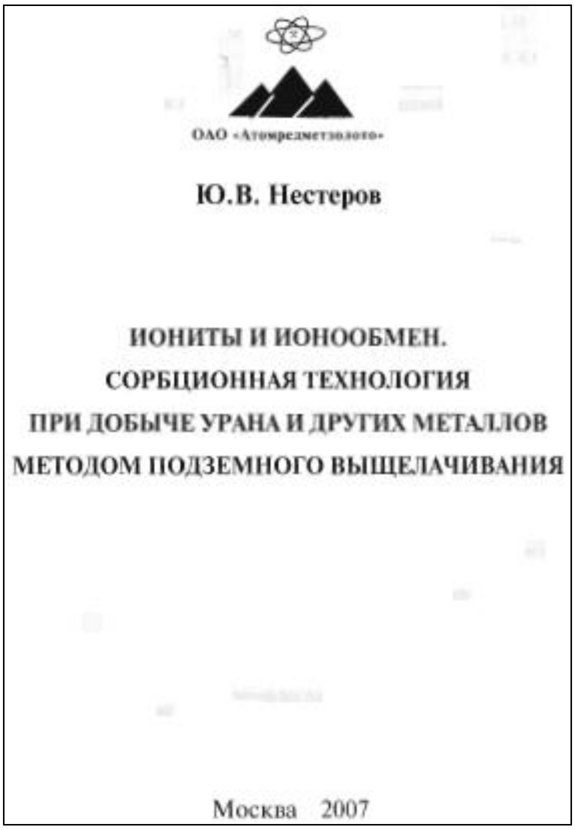

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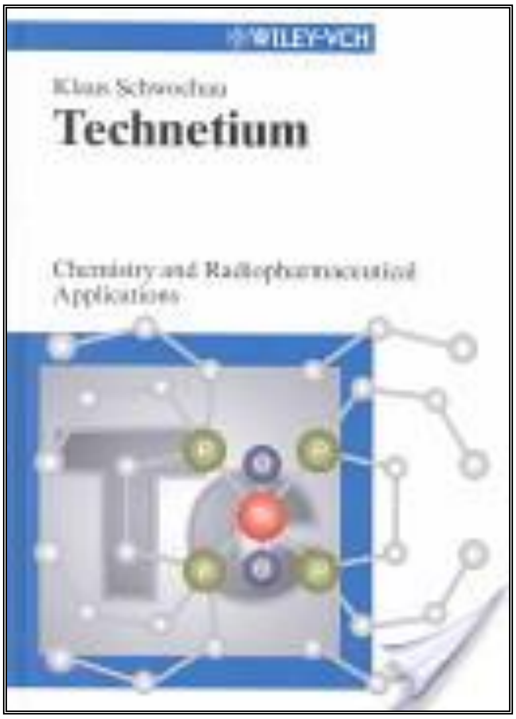

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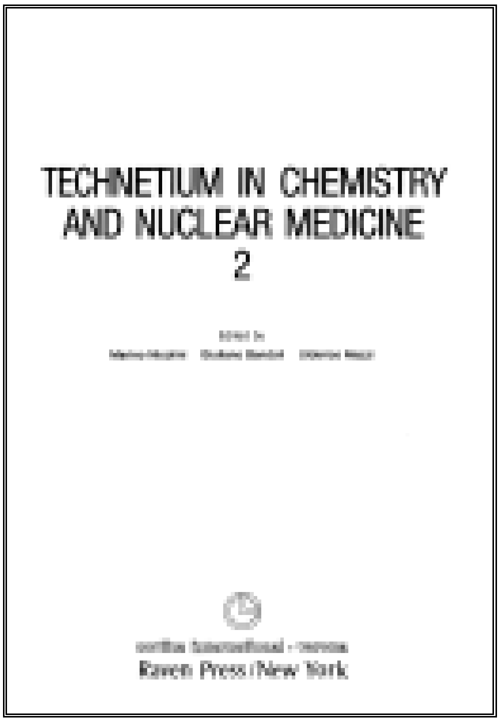

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2

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