Nanotechnologies in Radiochemical Technology and radioecology including technetium speciationand separations

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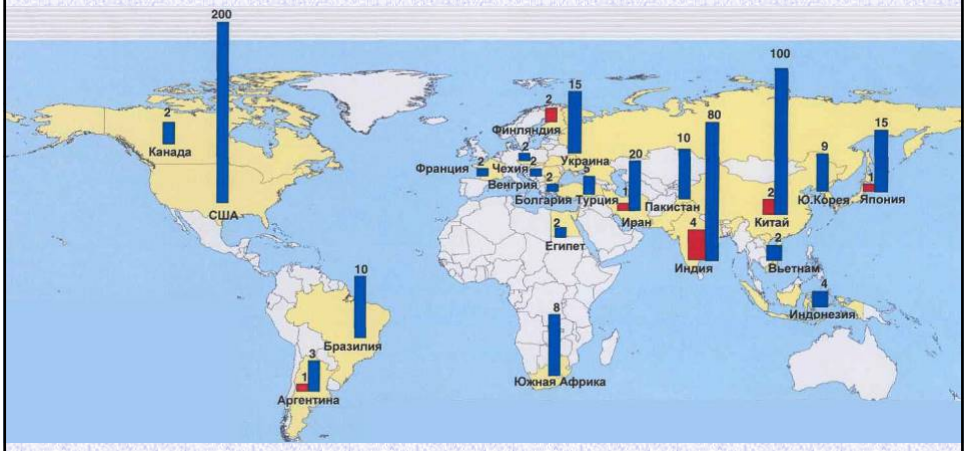
"Nuclear Renaissance"

- In view of the growth of "barrel price", the interest to the development of world nuclear energy is re-estimated and enlarged, called now as a "Nuclear Renaissance".
- Even Fukushima accident was not able to change this estimations globaly.
- Many countries that do not have a nuclear power plant are considering building one.
- Many nations that already have one are considering expanding their nuclear enterprises.

Plans of Development of Nuclear Power Stations in the World



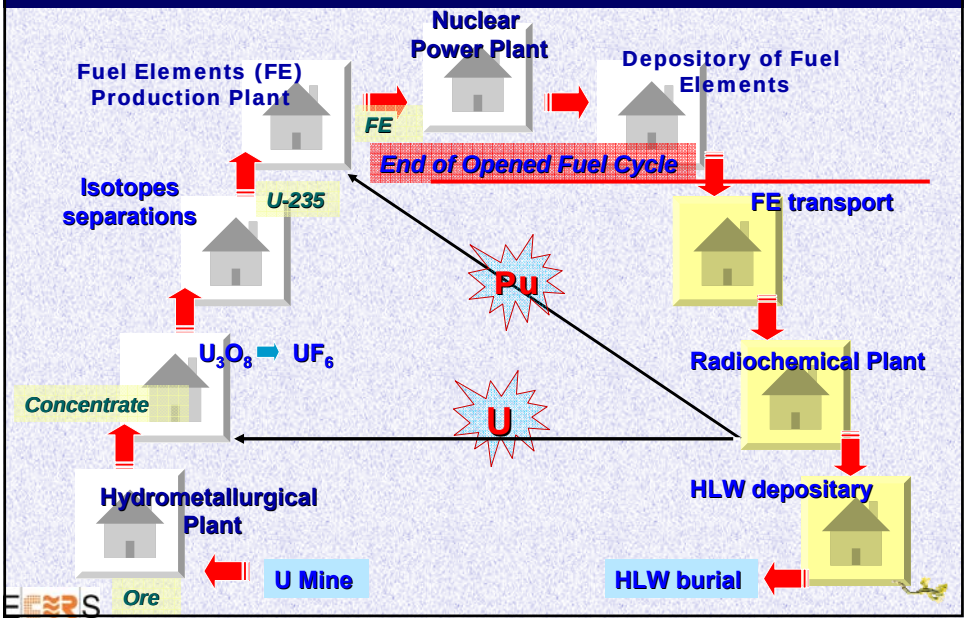
Program of putting into operation APP, GWatt:

- under construction
- prospects

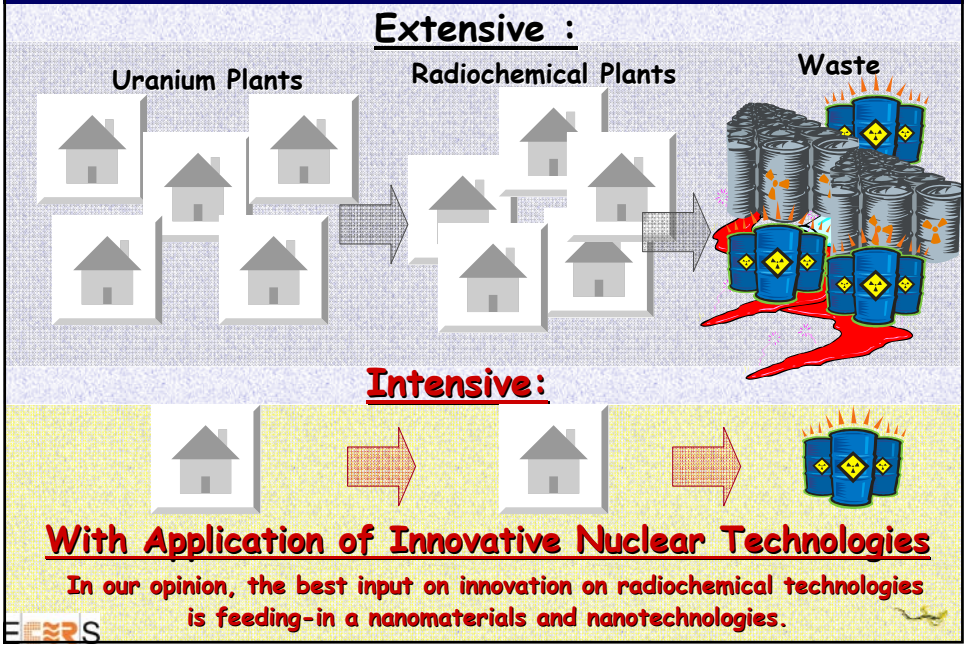
In Russia: at present 31 power units operate at 10 Nuclear Power Plants

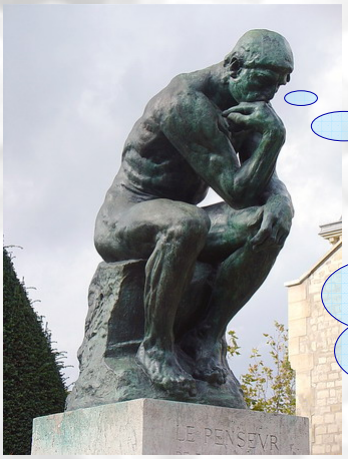
- From 2010, at least two nuclear power units with a total capacity of 2 GW are to be founded annually.
- As a result, by 2015, 10 new power units will be put into operation, total installed capacity of which will make up 9.8 GW.
- Implementation of a special-purpose program will increase total installed capacity of all NPPs up to 33 GW (at present, it makes up 23 GW).
- It will lead to the increase of Nuclear Power Plant share in the total volume of generated electric power up to 18%.

Scheme of typical Opened, and Closed Fuel Cycle for reactors on slow neutrons



Two ways of Production Magnification:





Arises the First Question:

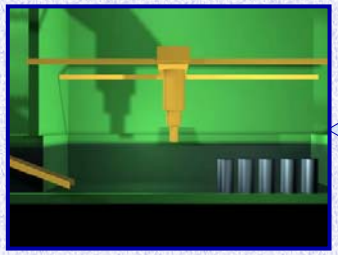
what is the best site for NanoTecnology implementation ?

Answer: Production Association Mayak !

See photo

Don`t be surprised ! PA Mayak achieved the main aim of ancient alchemists: Transmutation of an elements from one to another !

PA Mayak now :



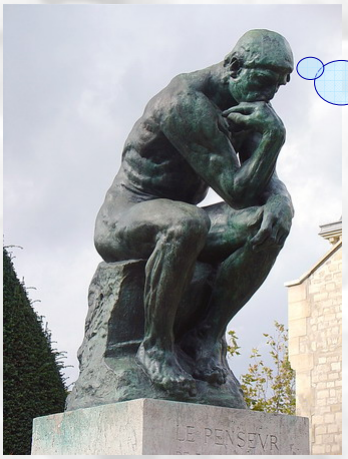
SNF reprocessing plant

Isotope production

and

Reactor enterprise

Arises the Second Question:



to find the main directions in development of NanoScience for Radiochemistry?

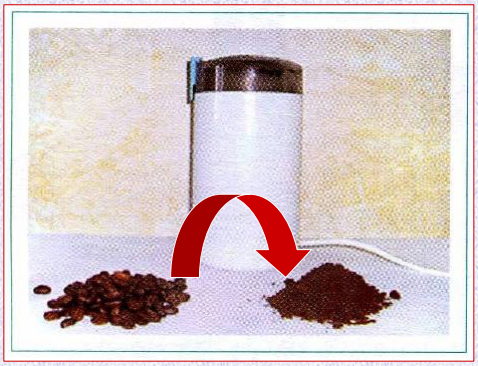
The 1st Symposium «NanoIndustry and NanoMaterials in Radiochemical Technology» PA Mayak, Ozyorsk, 1-3 June 2009 elaborated the main directions of nanoscience implementation :

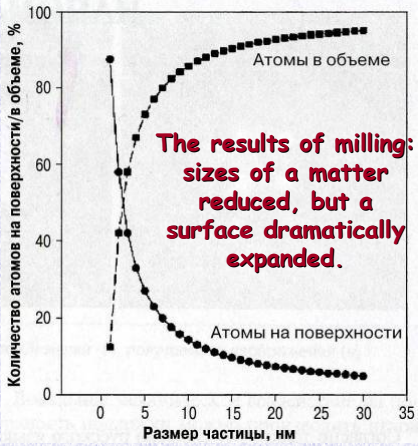
General Modern Directions in Development of NanoScience on Radiochemistry:

1. Nuclear Fuel Fabrication;
2. Development of modern Technologies for Spent Nuclear Fuel Reprocessing;
3. Radioactive Waste Handling;
4. Radioecology and Remediation

Some examples of application of NanoMaterials and NanoTechnologies in a radiochemical practice.

NanoPowders



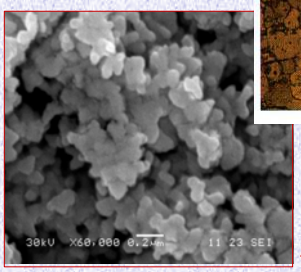


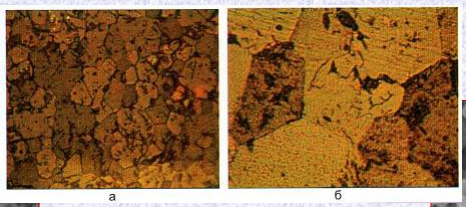
The results of milling: sizes of a matter reduced, but a surface dramatically expanded.

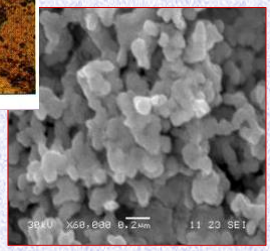
This leads to unusual reactivity of milled materials.
This process realize not only for preparation coffee, but for nuclear fuel fabrication !

New nuclear fuel compositions based on nanofractions of UO_2 was fabricated at the PA Mayak facilities.

The physical-chemical properties and reactivity of nanoscale UO_2 were studied. It was found that incorporation of nanoscale UO_2 fractions (1-5%) results in important improvement of fuel pill ceramic quality, homogeneity of solid solutions for dioxide mixture. This procedure improved the quality of MOX-fuel for fast reactors.





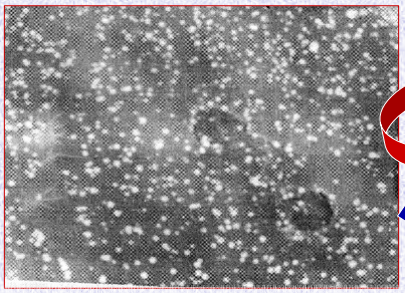


Standard microstructure (а) and microstructure of nuclear fuel, produced by incorporation of nano-additions (б)

S_{BET} = 10 m^2/g; Ø 100-120 nm

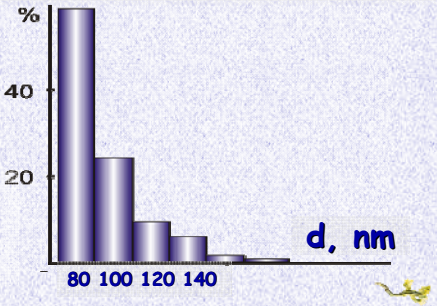
NanoCatalysts

The NanoParticles of Pt, Pd, Rh, Ru coating the porous supports are used as heterogeneous catalysts in radiochemical technology increasing efficiency of chemical processes used, helping to reduce the volumes of radioactive waste.



The morphology of a surface of catalysts (scan electronic microscope in a beams of secondary electrons of Pt granule)

Distribution of Pt particles sizes for 1% Pt/SiO_2 catalysts.
The middle Ø of a clusters is ~80 nm.



Effective methods of stabilization of actinides ions in given oxidation states were developed. The kinetic parameters of more 100 catalytic redox-reactions were calculated.

- Reduction of Uranium(VI) to (IV)
  - Reducing agents: H_2, N_2H_4, HCOOH, H_2CO, C_2H_5OH
- Reduction of Plutonium(IV) to (III), Neptunium(VI,V) to (IV)
  - Reducing agents: H_2, N_2H_4 , HCOOH
- Oxidation of Neptunium(IV)
  - Oxidizer: HNO_3

The main advantages of catalytic redox-processes: application of «not saline» reagents in technology.

The perspective methods of decomposition of organic radioactive waste were developed :

- Decomposition of oxalic acid, EDTA at so on;
- Decomposition of $N_2H_5NO_3$, HNO_3, NH_4NO_3, carbamide.

Example of developed catalytic processe in radiochemical technology:

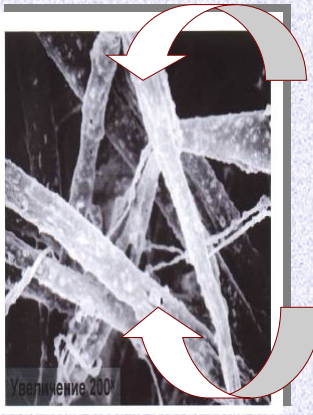
Decomposition of oxalic acid on the stage of Np and Pu purification

$1\%\ Pt/SiO_2$ 50^oC, 60 min in $1M HNO_3$	Without a catalysts, 90^oC, 48 hours in $8M\ HNO_3$
100% Decomposition	80% Decomposition

Results: the pilot device for dynamic decomposition of oxalic acid – a mother solutions of Np, Pu – was created at PA Mayak.

NanoFibers

"Filled" Fibrous Complexing Sorbents

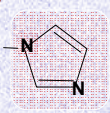


Basis:

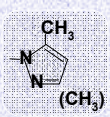
Polyacrylonitrile porous fiber (300-400 nm)

Filler:

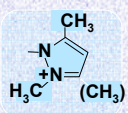
Complexing Sorbents (Ø ~100 nm)



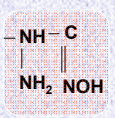
imidazole groups



3(5)-methylpyrazole groups

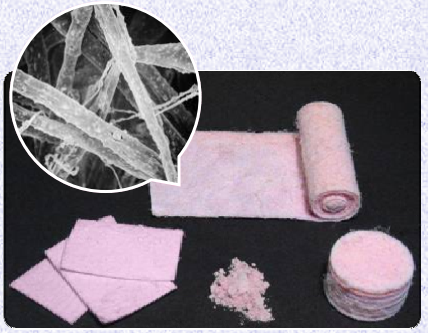


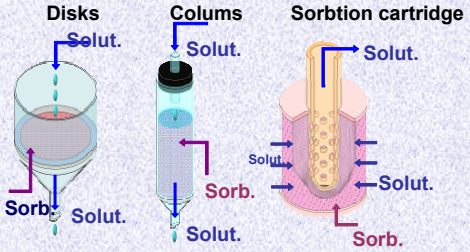
1,3(5)-dimethyl-pyrazole groups



amidoxime and hydrazidine groups

Fibrous "Filled" Sorbents Application

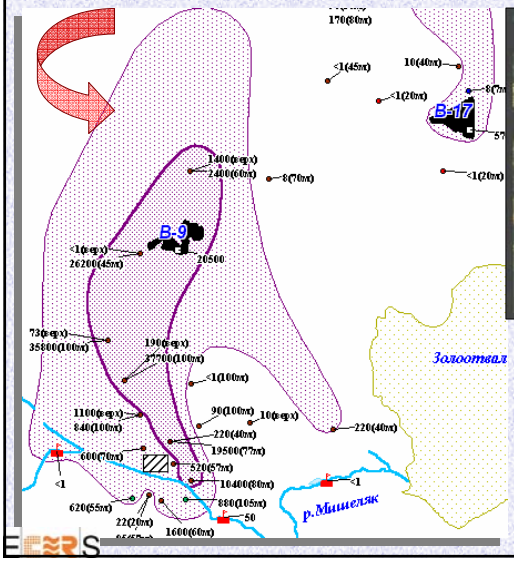




Tc(VII) sorption by fibrous sorbents from underground waters (20°C; time contact 2 h; V : m = 100 cm³/g)

Sorbent	K_d (cm³/g)
Poliorgs 17-n	$2{,}8 \cdot 10^5$
АВ-17-Н	$1{,}0 \cdot 10^4$

The radiometric map of Tc-99 contamination around the technical depositories B-9 and B-17 in the PA Mayak were determined first time.



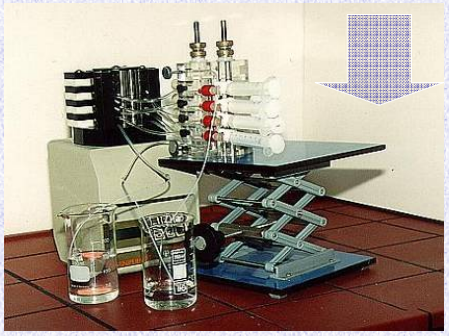
^{99}Tc contamination around B-9:
220 Bk/L - 11,7 км²,
2200 Bk/L - 2,9 км²;

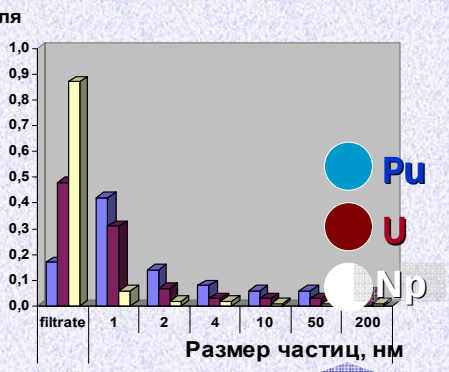
around B-17:
220 Bk/L - 1,2 км².

NanoMembranes

for discovery of radionuclide species migration

Device of multistage membrane filtration

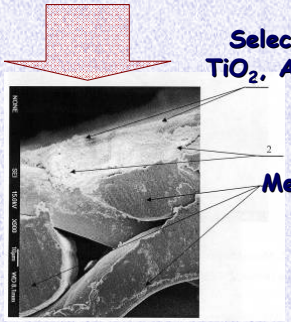




Distribution of actinides forms founded by membrane partitioning

Pilot Installation of Membrane Cleaning of a Natural Waters (PA Mayak)

Membrane «Trumem», Size from 2 to 250 nm.



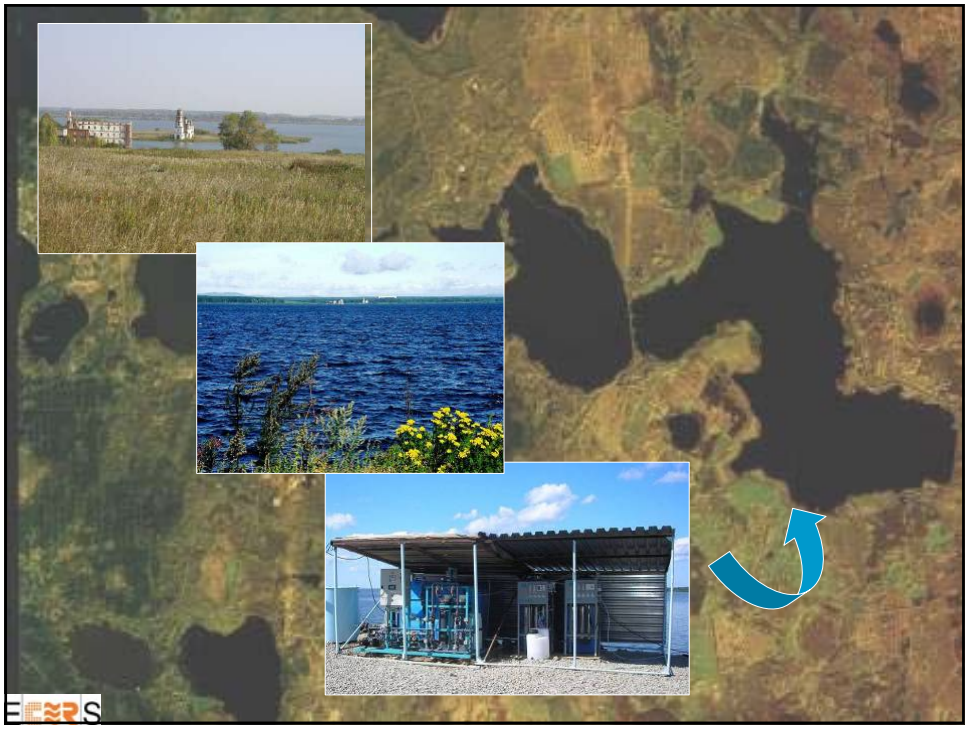
Selective layer TiO_2, Al_2O_3, Cr_2O_3

Gel layer

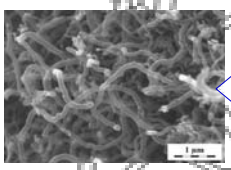
Metal Grid

Decontamination factor for:

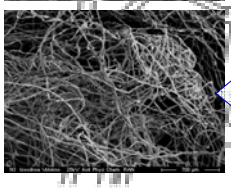
$\Sigma\alpha = 2 \cdot 10^3$; $\Sigma\beta = 10^3$; $^{90}Sr = 10^4$; $^{137}Cs = 90$



Carbonic NanoMaterials:



Taunit: 1D - NanoScale filous formations with inert Ø 5-8 nm as a powder



NanoPorous coals as a powder

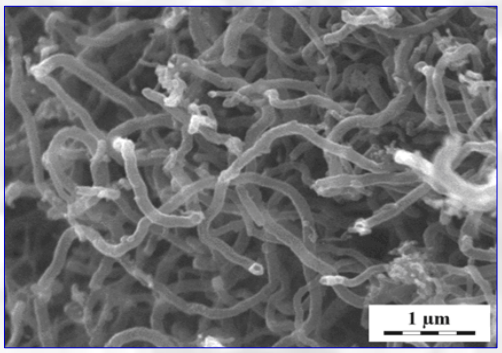
- as a perspective sorbents for radwaste treatment;

-as an additive for hardening of solid matrixes;

-as a NanoFuel elements;

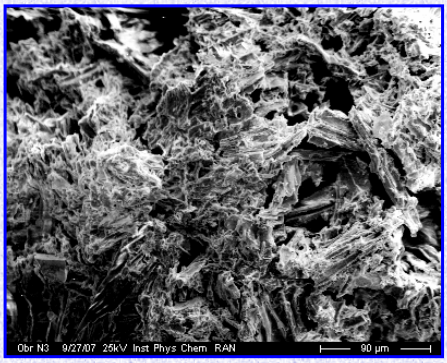
- as a matrixes for immobilization of organic waste.

- Taunit – 1D nanoscale filous formations with inert Ø from 5 to 8 nm as a powder

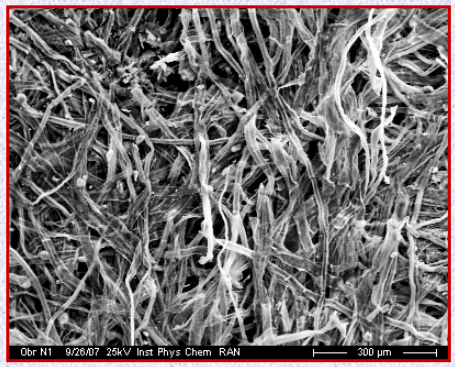


The Installation for Taunite fabrication in the Tambov State University

Charcoal structures



Conventional heating



Electron beam heating

Atomic composition

C – 82.6 %
O – 16.0 %

C – 89.5 %
O – 9.6 %

Such processing conserves structure of feed stock fibrils.

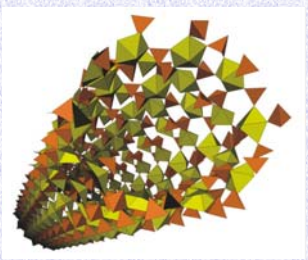
The high absorption ability of carbon nanomaterials with respect of technical oils or another organic compounds (TBP, diluents) was found.

For "Taunite" – 4 g/g;
For coals – 19 g/g.

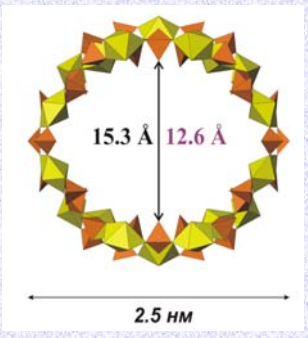
Effective method of fixation of technical oils on a carbon NanoMaterials with following solidification by epoxy-resin or cement was developed.

- Oil inclusion up to 25%;
- Compressing strength 570 kg/cm^2;
- Oil secession was not found;
- Oil Leaching Degree <0,01 %;
- Rate Oil Leaching $<1\cdot10^{-5}$ g/cm^2·day;
- Diffusion Coefficient of ^{3}T is 10^{-12} m^2/s

Highly porous uranyl selenate nanotubules: nanostructures in actinide chemistry



$[C_4H_{12}N]_{14}[(UO_2)_{11}(SeO_4)_{17}(H_2O)]$

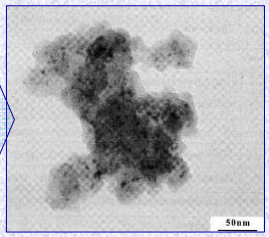


Krivovichev S.V., Kahlenberg V., Tananaev I.G., Kaindl R., Mersdorf E., Myasoedov B.F. *J. Am. Chem. Soc.* **2005**, *127*, 1072-1073.

One ton of a spent nuclear fuel contains about 300 gram of radioactive nuclides of Iodine-127, 129 and 131.

A volatile aerosols of HJ, J_2, CH_3J according a IAEA declarations should fixed and localized.

A granulated sorbent «Физхимин» containing a nanosize particles of Silver and Nickel is synthesized in Frumkin Institute



- Sorbent produced by contact of a silica gel КСКГ and aqueous solutions of Ag^+ and Ni^{2+} with following treatment of this matrix by NH_4OH and heating at 250-300°C;
- Sorbent isolate a different forms of a radioactive Iodine from gas phase with the decontamination factor more than $K_{оч}$ >10^4.
- 720 kg of the "Физхимин" was installed in the modules of a passive filtration of an average filters in the NPP "Kudankulam" (India).

The main method of immobilization of high level waste at the PA Mayak is incorporation on the alumo-phosphate glass matrix.

Year	Weight, tons	Activity, MCi
1987-1990	162	3.96
1991	178	28.2
1992	563	77.7
1993	448	46.8
1994	407	57.4
1995	216	31.7
1996	270	38.2
1997-2000	>600	>100
2001-2006	1793	175,2
2007	584	35,7
Total	>5221	>594

NanoGlass ?

We hope that incorporation of a NanoParticles of a furnace leads to increase of a thermo conductivity, and decrease an amorphization of a glass matrix. These effect extend a time storage of a matrix.

Chemically Bonded Phosphate Ceramics

Example: potassium-magnesium ceramic

$MgO + KH_2PO_4 + 5H_2O = KMgPO_4 \cdot 6H_2O$

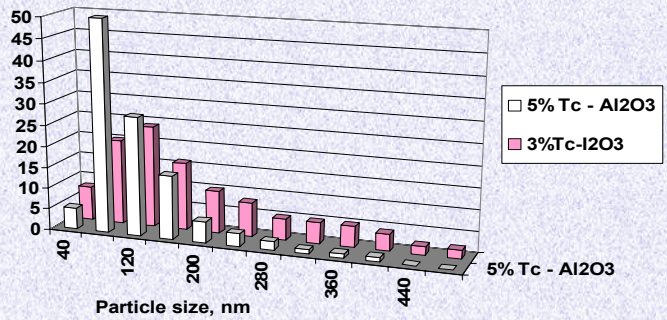
- Formed at room temperature;
- Made by acid-base reactions;
- Hard, durable, dense, and hence
- the Ideal for macro-incorporation.

Addition of NanoSize of a nature minerals to the stock mix during solidification of a radioactive waste leads to increasing of compressive strength of a ceramic matrix :

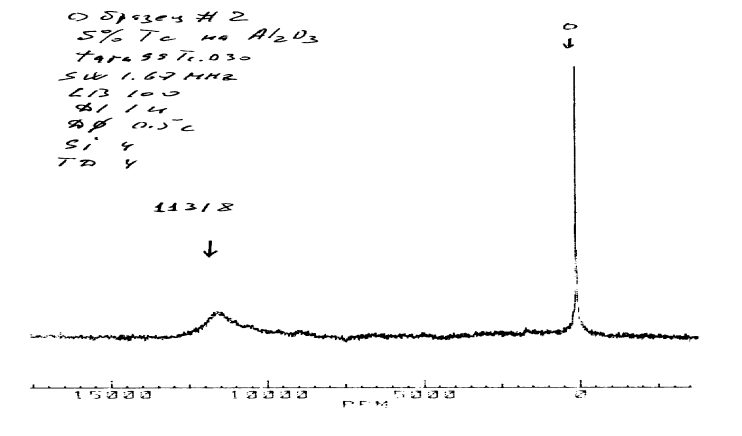
Content composition, %					Compressive Strength, Kg/cm^2
MgO	KH_2PO_4	HLW	Wollastonite $CaSiO_3$	Asbestos	
14	43	43	0	0	41,7
12	40	43	0	5	364,1
12	40	43	5	0	321,1

Particle size distribution in supported Tc metal

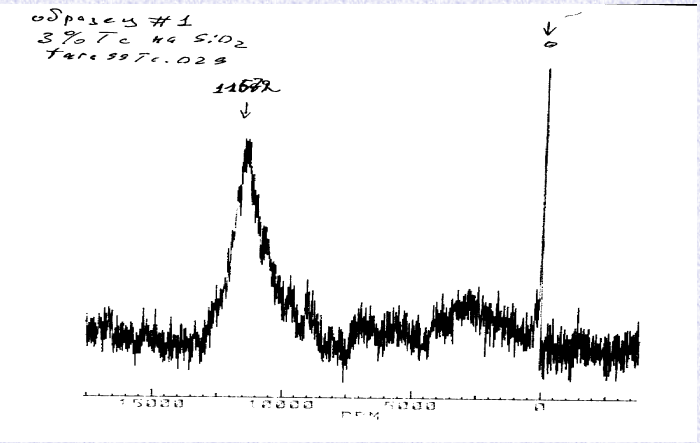
(based on the analyses presented by Dr. Panich)



^{99}Tc-NMR spectrum of 5%Tc on Al_2O_3

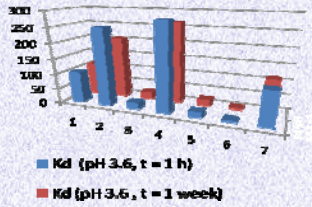


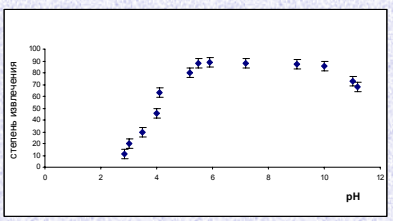
^{99}Tc-NMR spectrum of 3%Tc metal on SiO_2



Nanodiamonds as sorbents of radionuclides (*A. Shiryaev, Ya. Obruchnikova – this session*)

- **Sorption of Cs** *(Chukhaeva and Cheburina, 2000)*: **up to 0.5 mmol/g**
- **Sorption of Technetium** ***(see poster 6P.3 by Obruchnikova et al. today).***
  Partition coefficients are comparable to the best anionites
- **Sorption of Uranium.**
  Degree of U extraction from solution exceeds 90% in broad pH range.





Conclusion:

NanoMaterials and NanoTechnologies could be used in the field of radiochemical practice.

The Foreseeable Results are:

1. **Nuclear Fuel Fabrication;**
2. **Development of modern Technologies for Spent Nuclear Fuel Reprocessing;**
3. **Radioactive Waste Handling;**
4. **Radioecology Development.**