# $^{137}$Cs and other radionuclides retention by geochemical and engineered barriers

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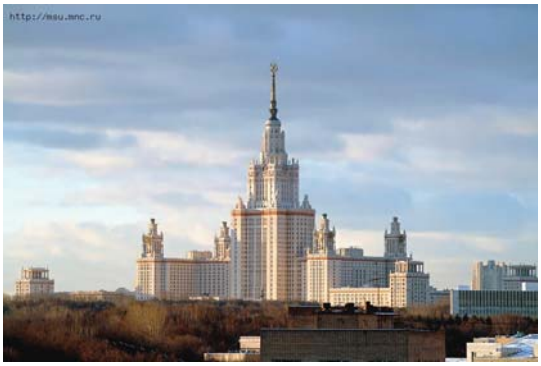
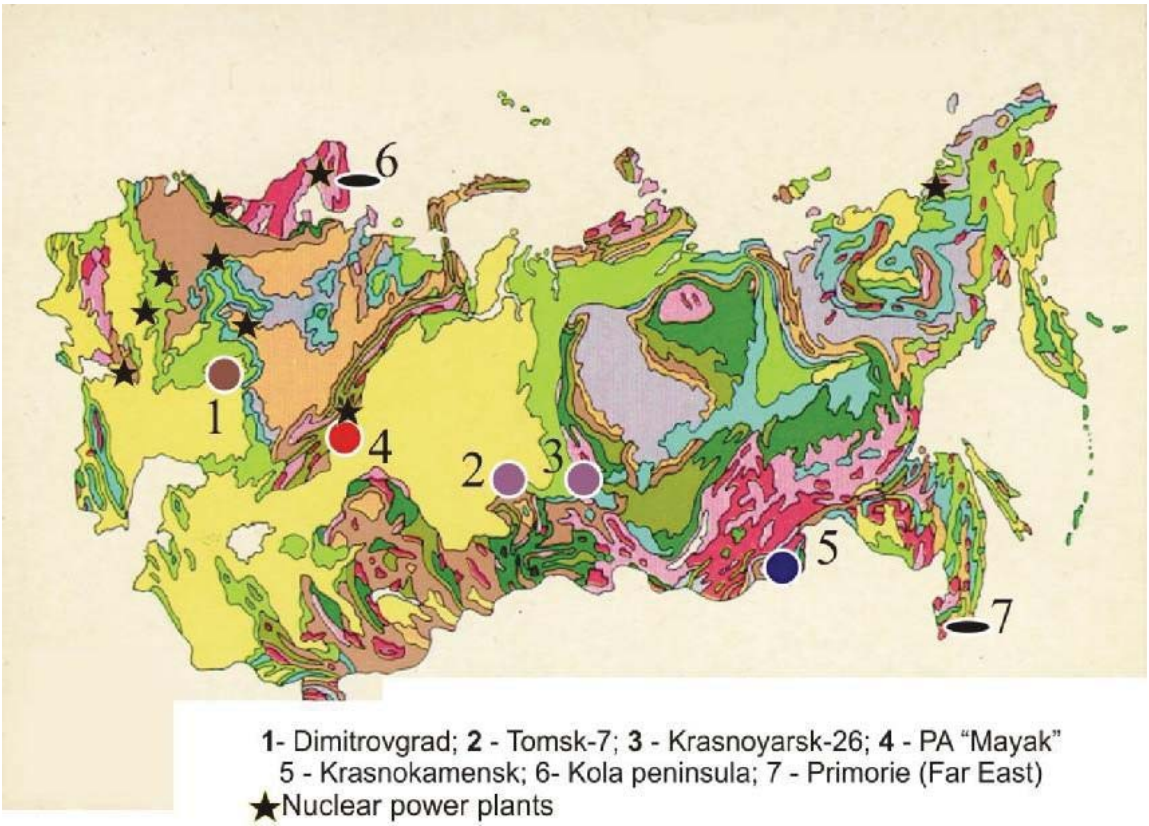


## Nuclear Russia

| Source | Volume ($m^3$) | Activity (Ci) |
|---|---|---|
| Uranium ore mining and treatment | $10^8$ | $1{,}8\times10^5$ |
| Isotope enrichment and fuel production | $1{,}6\times10^6$ | $4\times10^4$ |
| Nuclear power stations | $3\times10^5$ | $2{,}5\times10^3$ |
| Radiochemical enterprises activities | $5\times10^8$ | $9\times10^8$ |
| Submarine and ice-boat operation | $2{,}9\times10^4$ | $2{,}1\times10^4$ |
| Submarine utilization | $4\times10^3$ | $2\times10^2$ |
| Isotope sources | $2{,}0\times10^5$ | $6{,}0\times10^2$ |

**As a result more than 600 $Mm^3$ of nuclear wastes were accumulated with total activity of 2.5 billion Ci**

# Nuclear Russia




## Radionuclide speciation and local (nanoscale) distribution in samples collected at the contaminated sites

Techniques available in MSU:

UHR TEM (JEOL 2500),

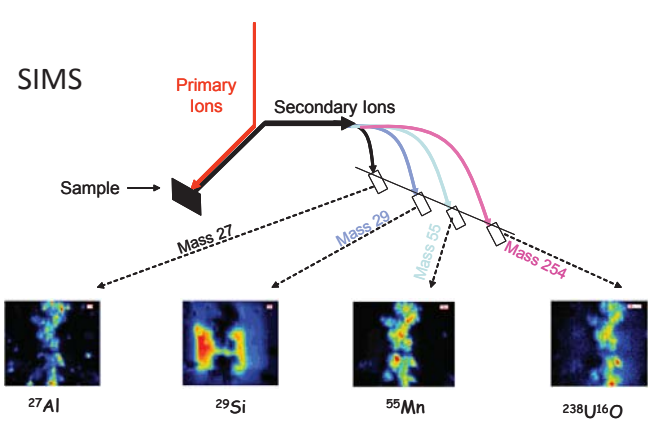
μ-XPS, Auger and SIMS (Kratos),

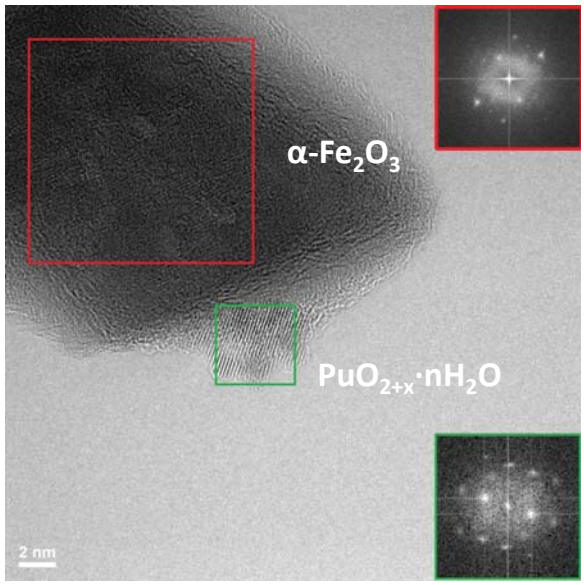
XAFS (2.5 GeV line at Kurchatov Institute in Moscow ),

TRLIF

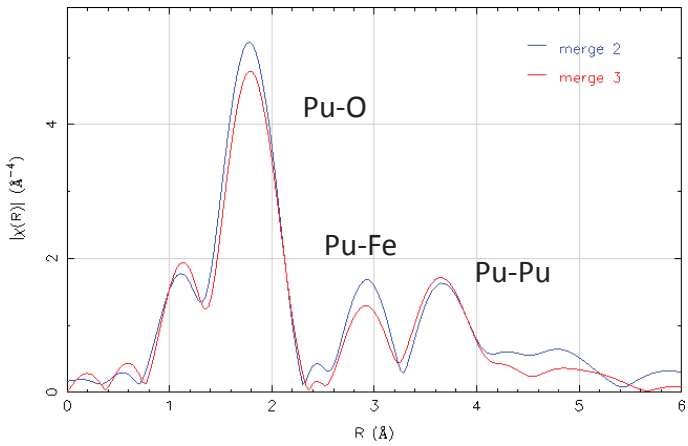
additionally:
Nanosizer Nano-ZS (Malvern),
SIMS,
SAXS, etc.

Alpha- track and fission track analysis



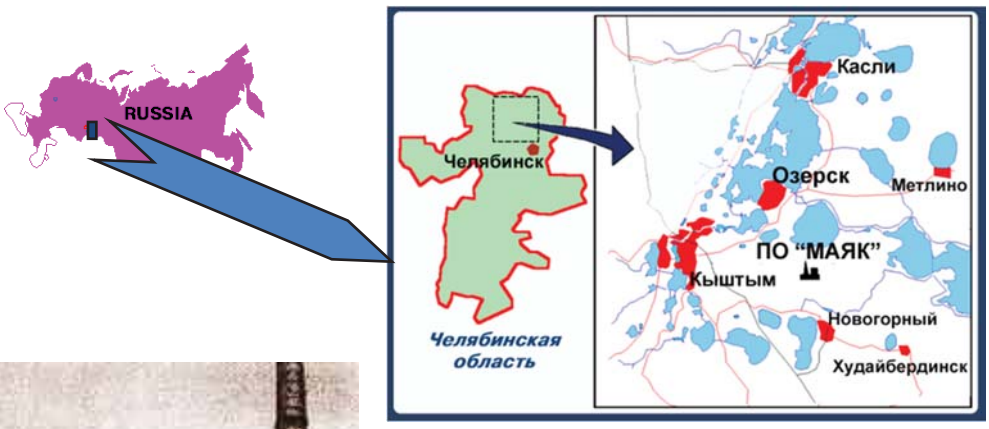




HR TEM




EXAFS

## Sources of radioactive contamination of South Ural




**Dec. 22, 1948 – the plant to separate weapon grade Pu from irradiated uranium was launched**

**Production capacity was around 1 ton of U blocks per day**

**about $10^5$ Ci of wastes**

Year before the plant was launched, complex “C” was constructed that is the assembly of tanks for HLW. The capacity was estimated around 15000 $m^3$ per year. However the real volume of wastes was 200 $m^3$ per day.

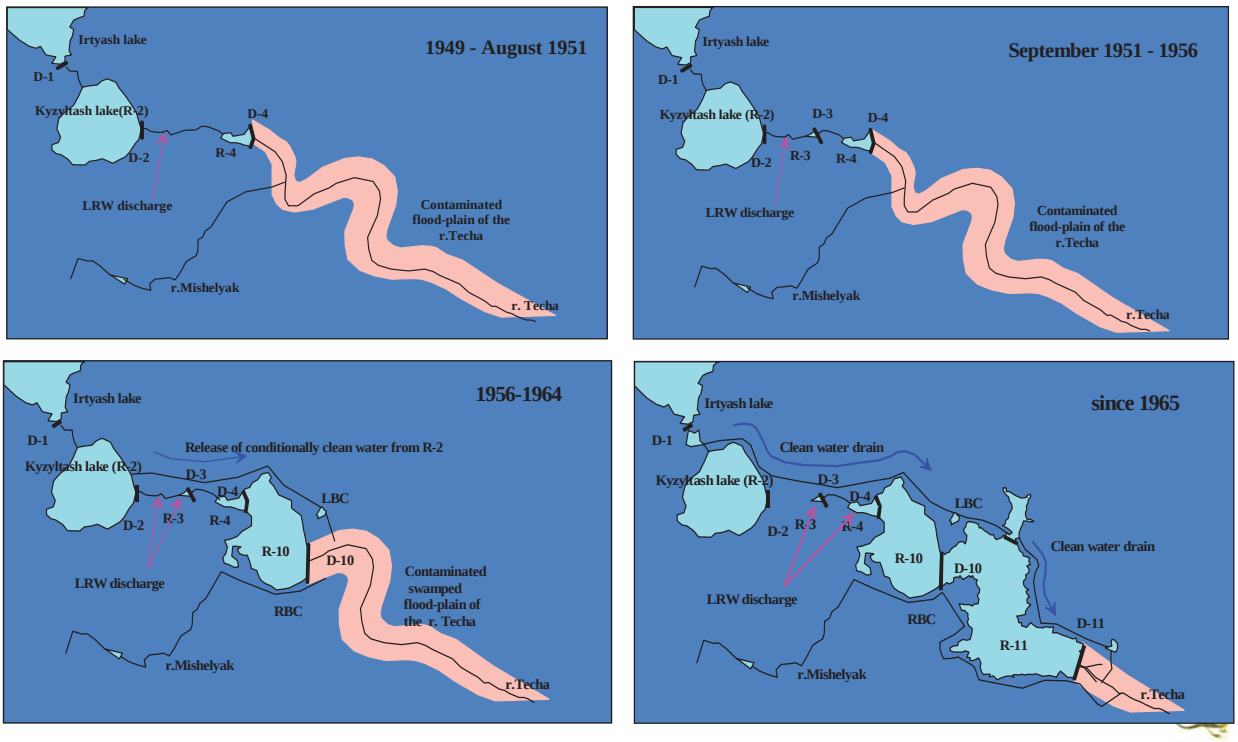
All tanks were filled with HLW before 1950 (about a year after the plant was launched).
The construction of new tanks for HLW was too expensive.

From 1949 till 1951 wastes were disposed to Techa river. During this period c.a. 76 $Mm^3$ of waste solutions were disposed equal to 2.8 MCi.

## Volume of waste disposed to Techa river

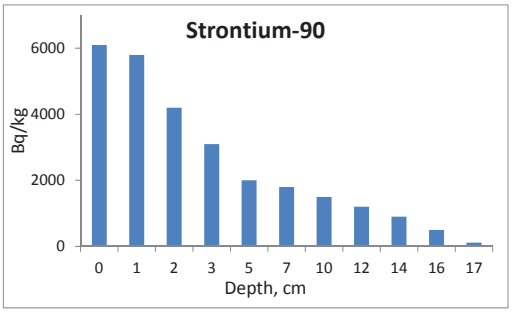
| | I-XI.1949 | XII.1949 -II.1950 | III.1950 -XI.1951 |
|---|---|---|---|
| Total β-activity, Ci/day | 70 | 860 | 4300 |
| $^{89}Sr$ + $^{140}Ba$, % | 1.8 | 6.9 | 8.8 |
| $^{90}Sr$, % | 4.1 | 15.3 | 11.6 |
| $^{95}Zr$ + $^{95}Nb$, % | 30 | 9.0 | 13.6 |
| $^{103,106}Ru$, % | 55.6 | 45.3 | 25.9 |
| $^{137}Cs$, % | 11 | 21.2 | 12.2 |
| REE, % | - | 5.7 | 26.8 |

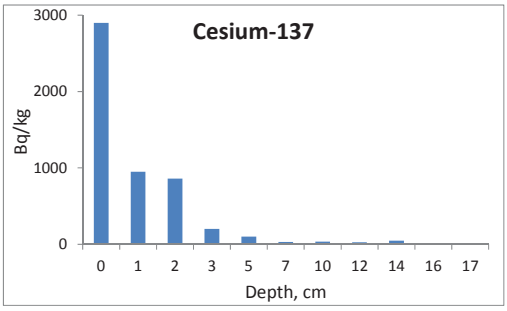
# Creation of Techa cascade of reservoirs

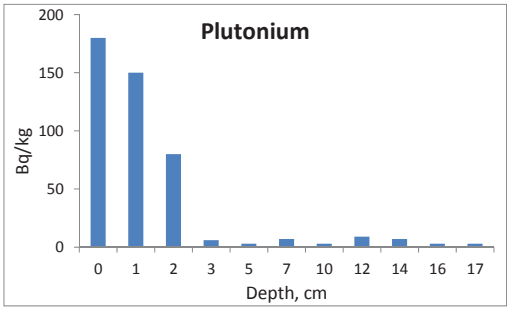



## Contamination of flood plain soils, kBq/m$^2$.

| Location | $^{90}$Sr | $^{137}$Cs | $^{239,240}$Pu |
|---|---|---|---|
| Right bank | 61-750 | 18-1200 | 0,2-16,4 |
| Left bank | 20-220 | 15-270 | 0,3-2,0 |



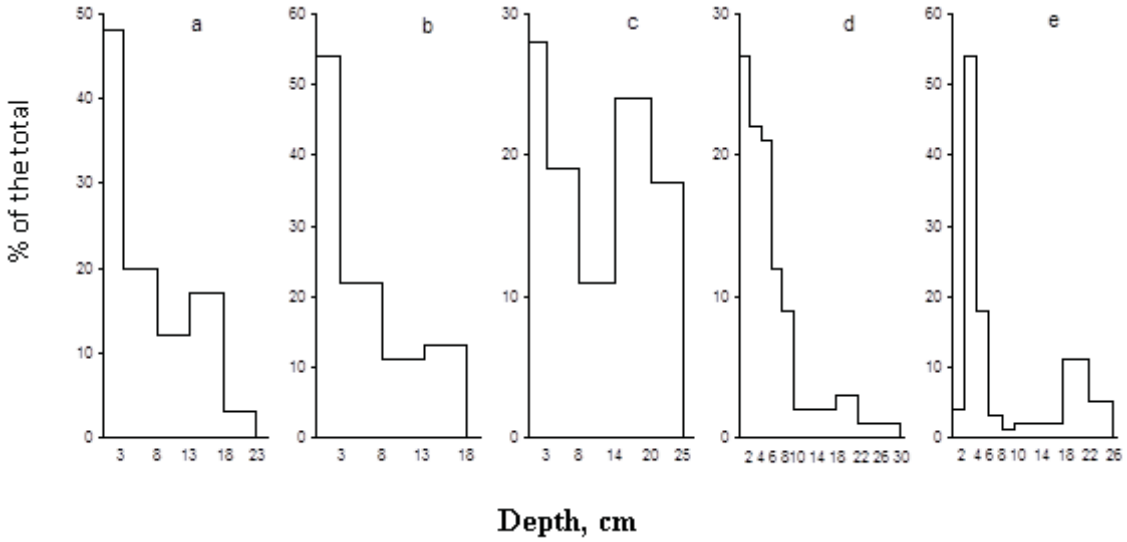




**Cs binding:**
**Competition between clays and organic matter**

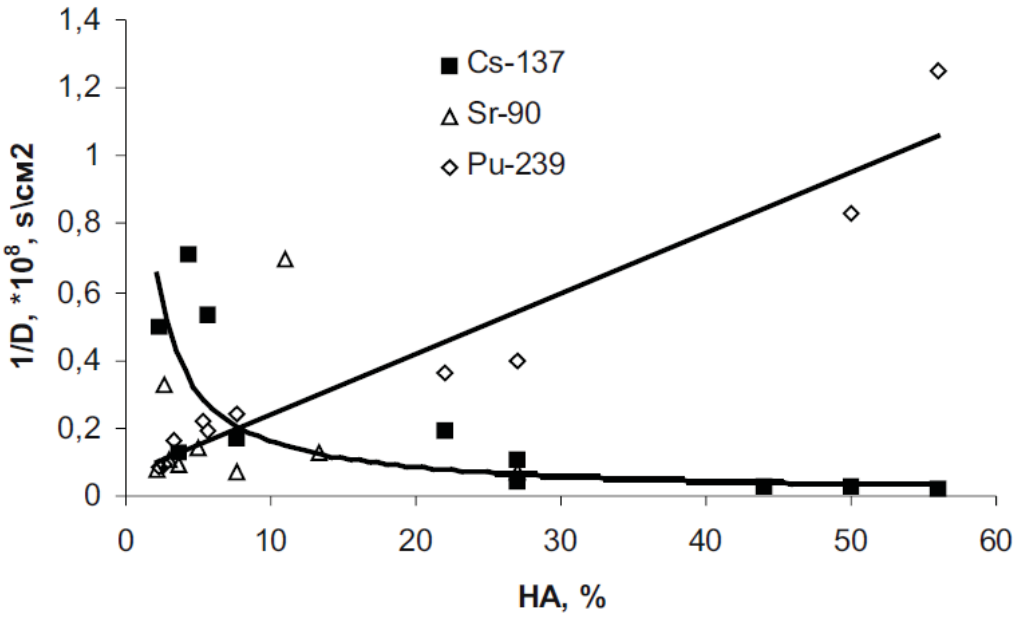
# Cs-137 distribution with soil types

Increase of clay content

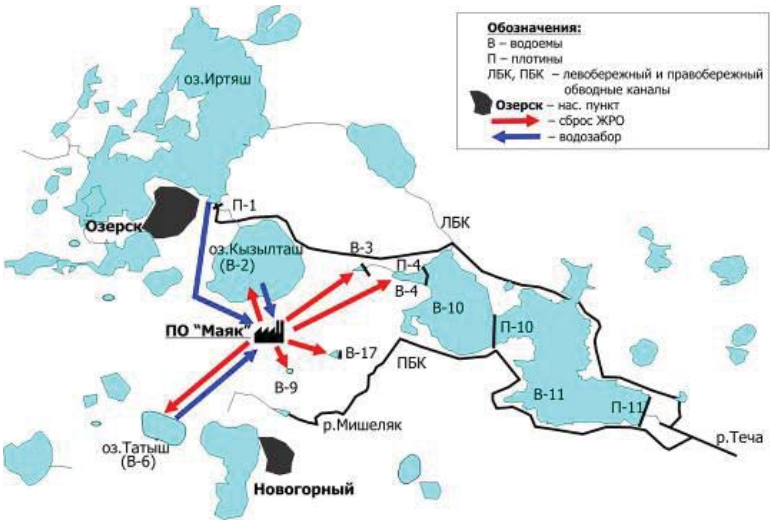
Increase of humic content




## The dependence of diffusion resistance of various soils to $^{137}Cs$, $^{90}Sr$ and $^{239}Pu$ vertical migration upon HAs concentration

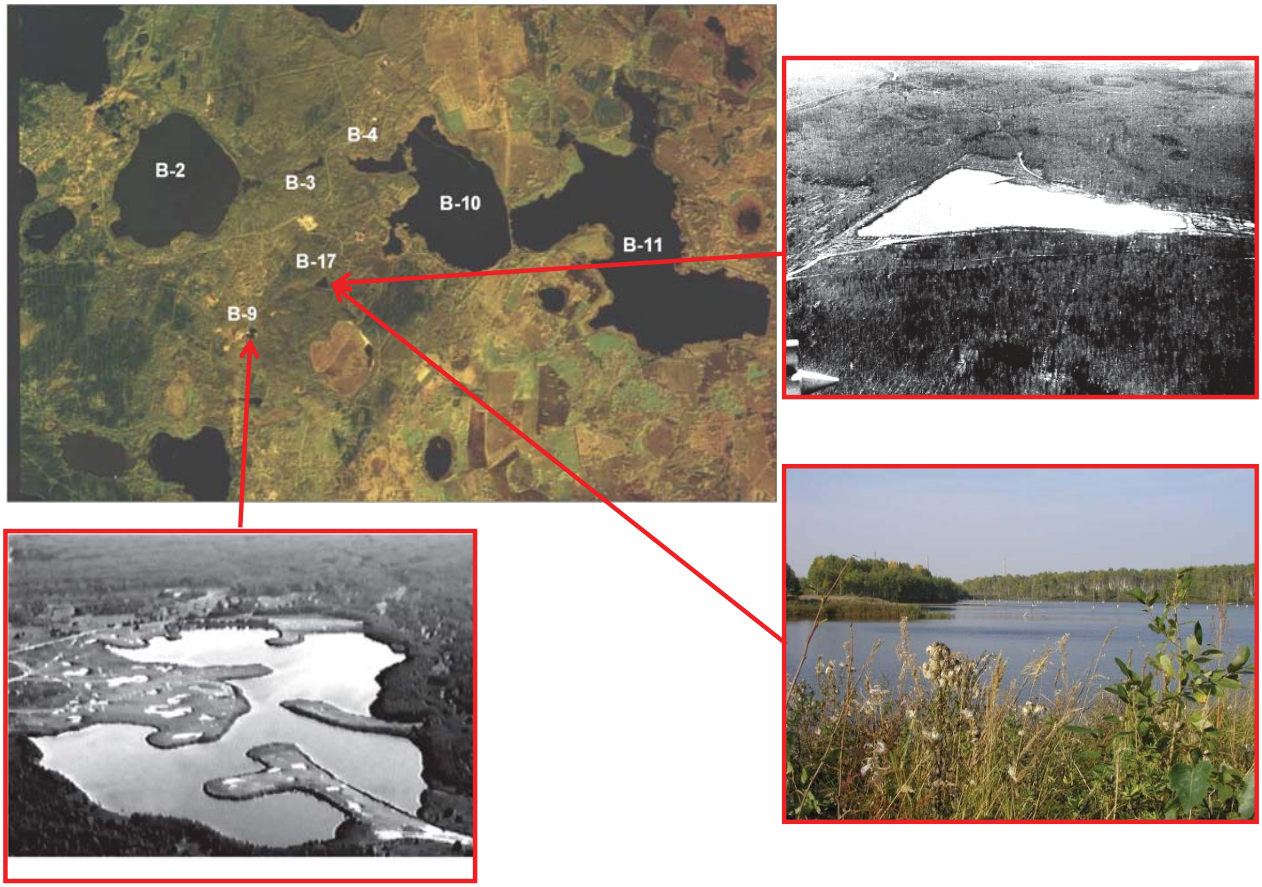


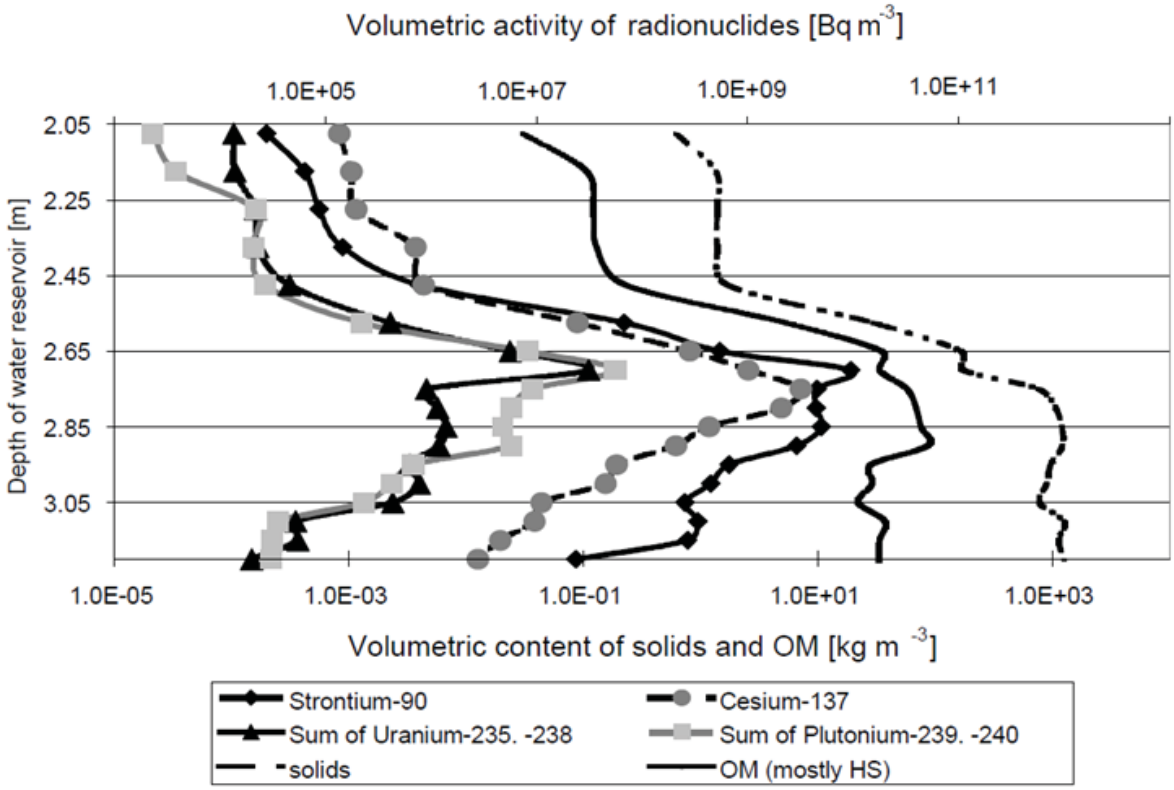
# Industrial reservoirs at “Mayak” site

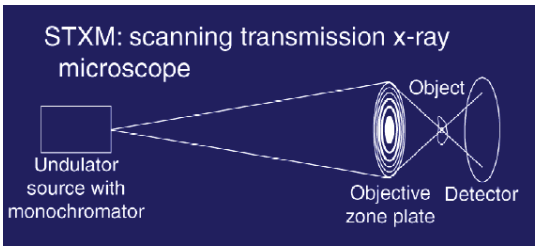


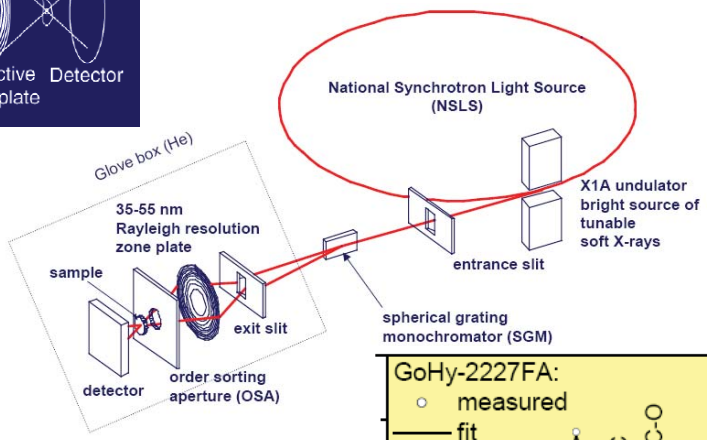

In 1951 the disposal of wastes to Techa was stopped and changed to lake Karachay that don’t have connection with open hydrological system. LLW and ILW were also disposed to 8 artificial reservoirs: B-2 (lake Kiziltash), B-3, B-4, B-10, B-11, B-6, B-17 (called also Old Swamp) and B-9 (lake Karachay). About 120 MCi ($4.4 \cdot 10^{18}$ Bq) of beta-emitters and 1 MCi ($3.7 \cdot 10^{10}$ Bq) of alpha-emitters were disposed.

## Industrial reservoirs at PA “Mayak”



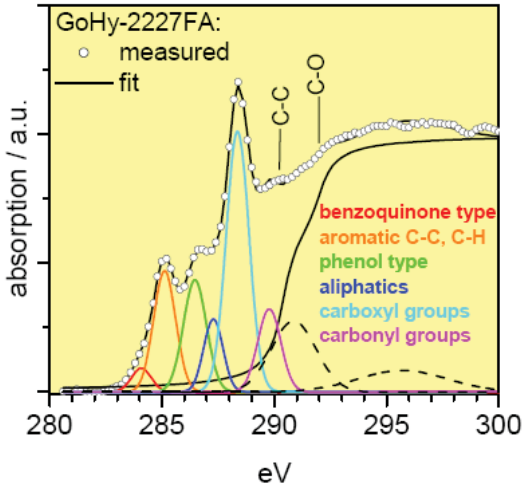


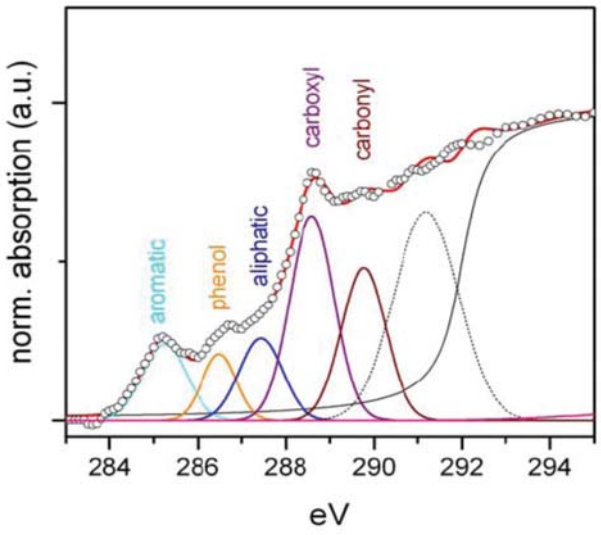

X1A1 (outboard): **C, K, Ca**
X1A2 (inboard): **(N), O, (Mn), Fe**

- ***High spatial resolution:*** 30-60 nm
- ***Energy resolution***: 0.1-1.0 eV
- ***Analysis without sample pretreatment***



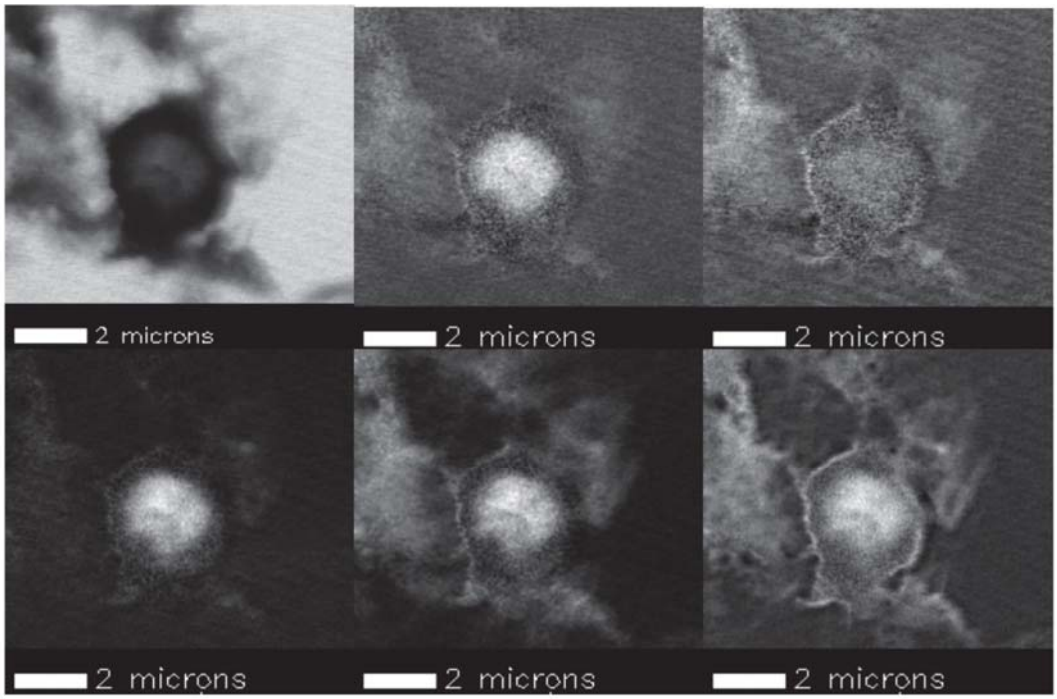
## Deconvolution of the average C1S spectra of humic-mineral aggregates

| Functional group | Content, % |
|---|---|
| C=C, C-H | 14 |
| Phenol | 9 |
| Aliphatic | 15 |
| Carboxyl | 37 |
| Carbonyl | 25 |



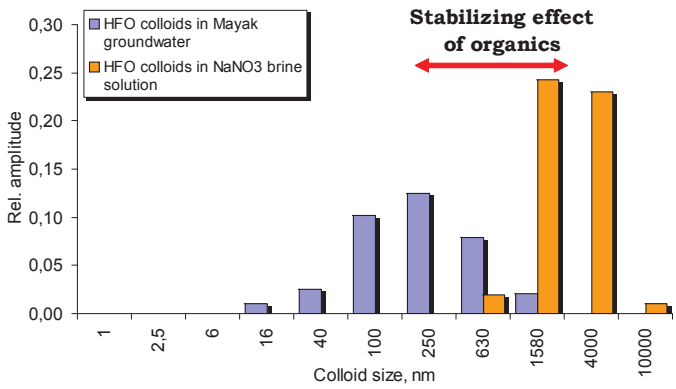

**Deconvolution fit of sample with different carbon functionalities as indicated by the labels. The open dots represent the smoothed measured spectra obtained by cluster analysis and the red line indicated the fitted spectra**

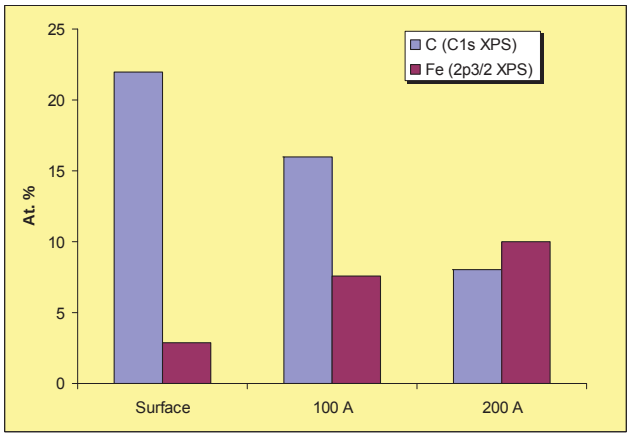
## STXM



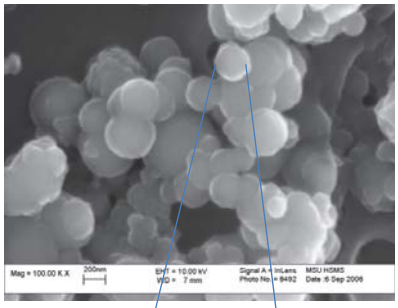

**From left to right, upper row; absorption image at 280eV below the C1s edge; ratio images showing the distribution of aromatics, phenol-type groups and lower row aliphatics, carboxyl-type groups and total organics. Bright grey values indicate high concentrations of organic functionality**

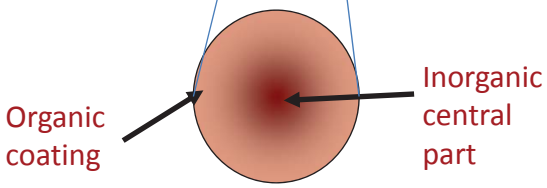
# Effect of organics on colloid particle stability



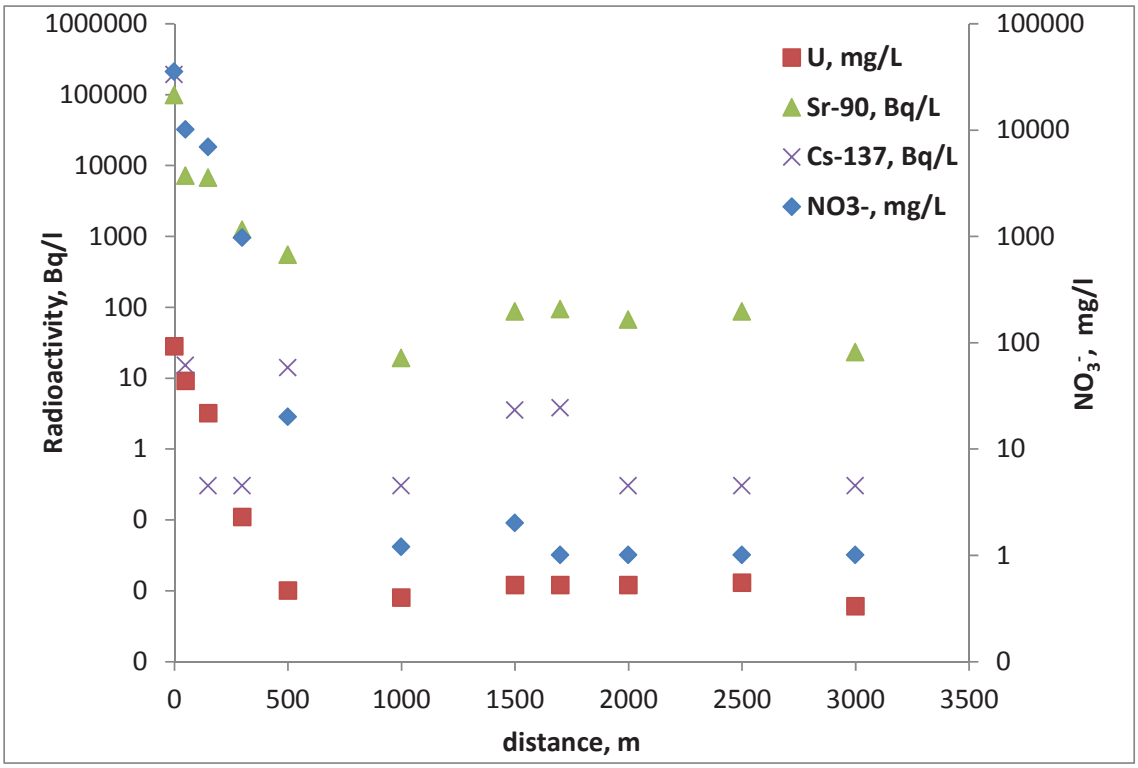




**XPS, Auger microscopy with ion etching**






# Penetration of various radionuclides and $NO_3^-$ by geological media



# Approaches for barriers design

## Bentonite clays

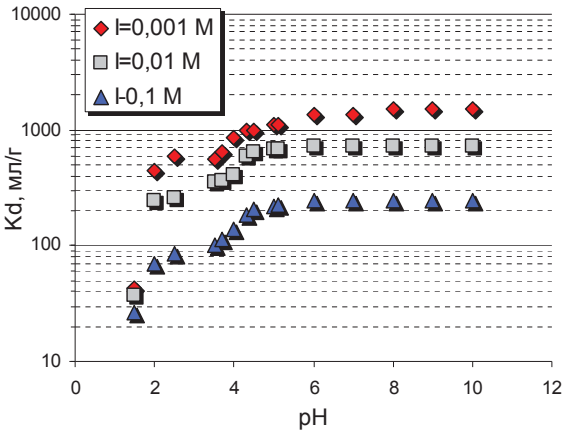
## Immobilized humic derivatives

## Carbon nanomaterials

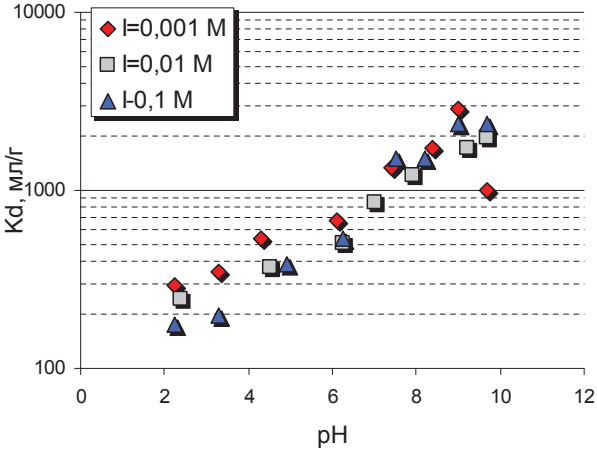
### Khakassiya bentonite

| Mineral | Weight concentration, % |
|---|---|
| Montmorillonite | 70–80 |
| Quartz and kristobalite | 10–12 |
| Albite | 4–6 |
| Calcite | 2–3 |
| Hematite and magemite | <2 |
| Pirofilite | 1–2 |

Cs(I) sorption onto bentonite




Np(V) sorption onto bentonite



## Khakassiya bentonite

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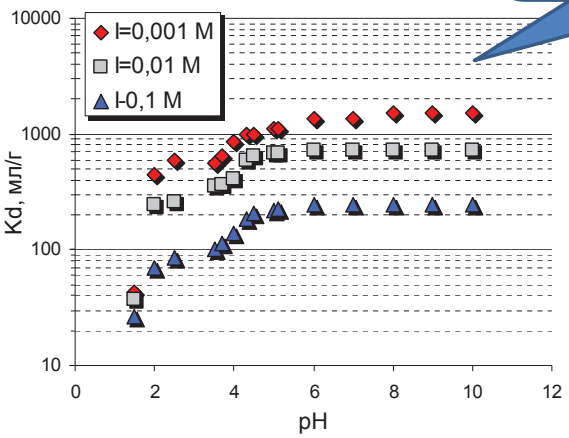
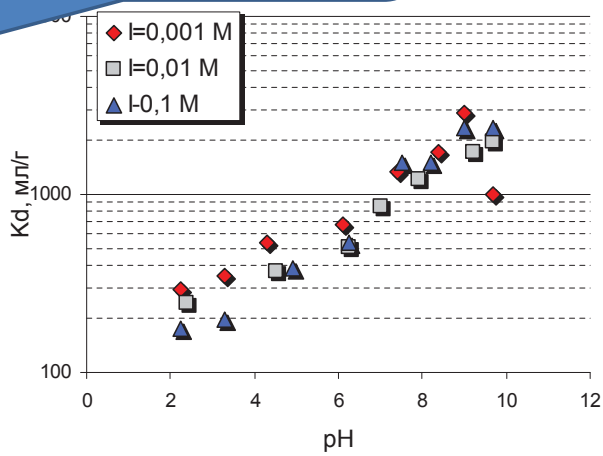
| Calcite | |
| Hematite and magemi | |
| Pirofilite | |

$$XNa + Cs^+ \leftrightarrow XCs + Na^+$$

$$\log K_{ie} = 1.7$$

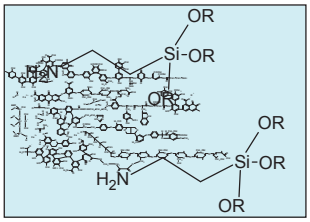
Cs(I) sorption onto bentonite

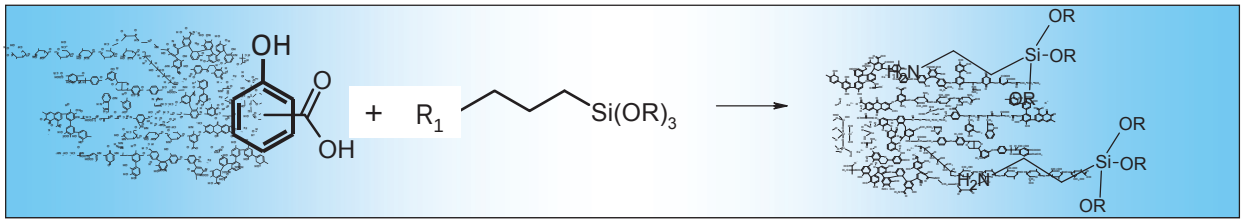


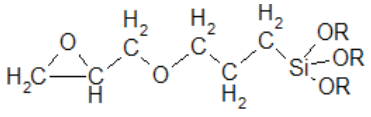



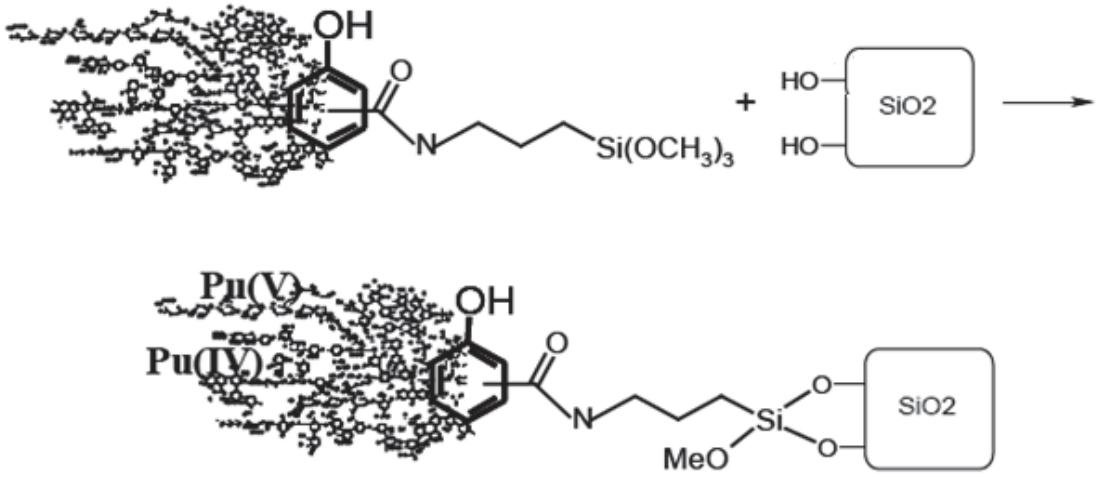

In collaboration with Irina Perminova, MSU

## Preparation of alkoxylenated derivatives of humic acids with various organosilans

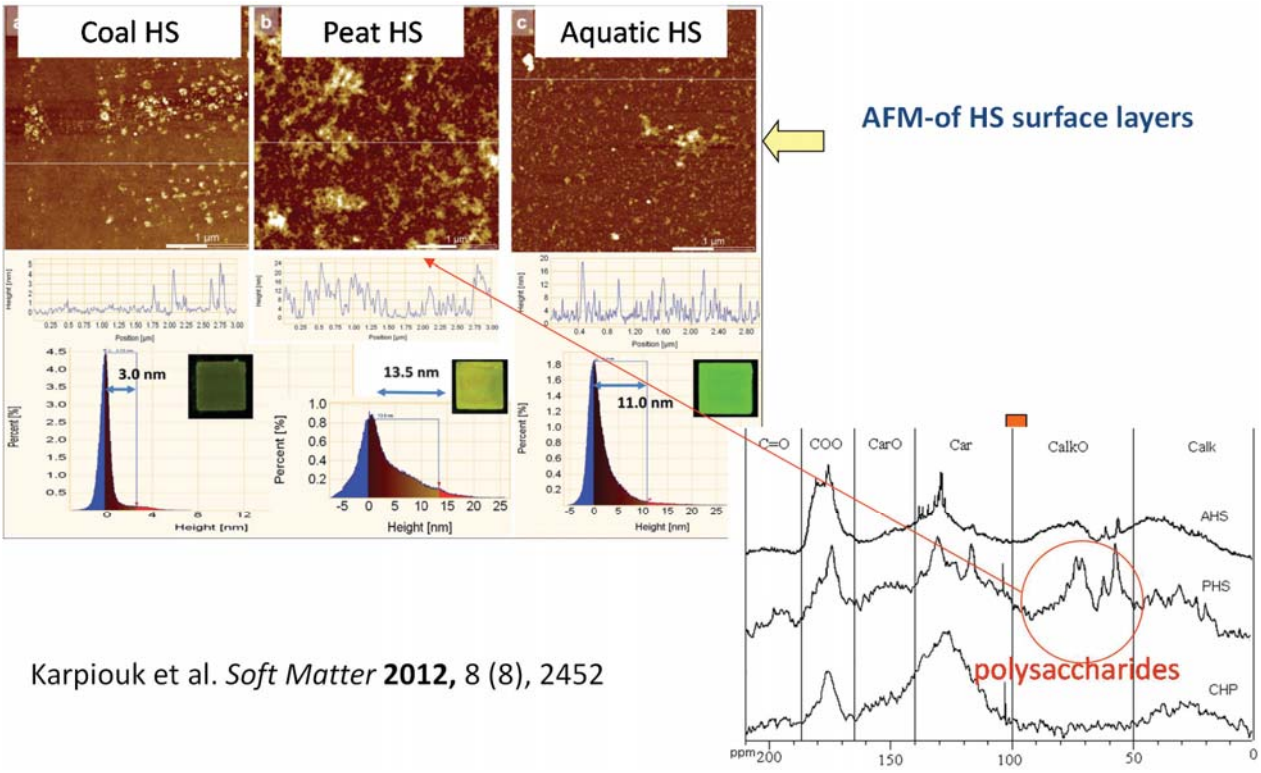



| $R_1$ | Organosilan | Structure |
|---|---|---|
| **Amino** | 3-aminopropyl-trialkoxysilane (**APTS**) | $H_2N(CH_2)_3Si(OR)_3$ |
| **Epoxy** | 3-glycidoxypropyl-trialkoxysilane (**GPTS**) |  |
| **Isocyanate** | 3-isocyanatopropyl-trialkoxysilane (**IPTS**) | $OCN(CH_2)_3Si(OR)_3$ |

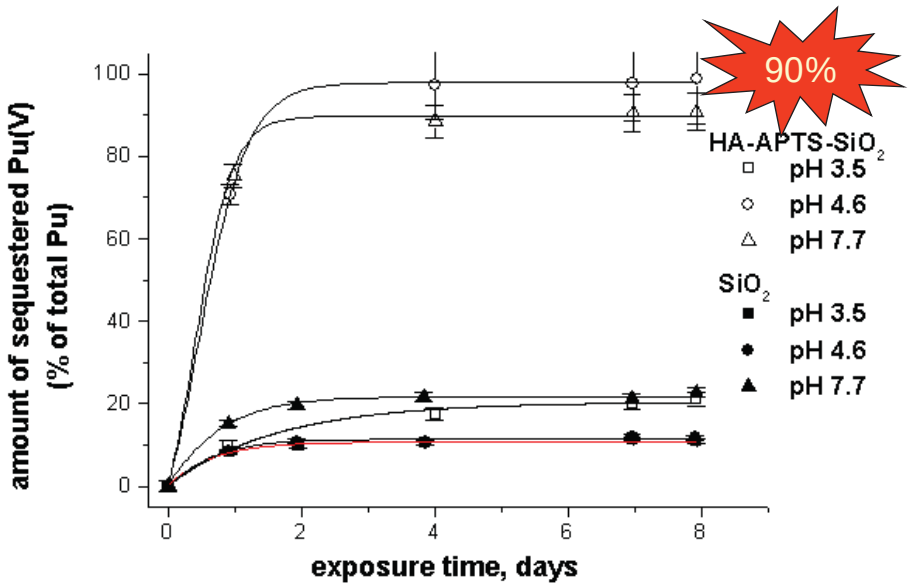



# Humic sorbents on $SiO_2$ support



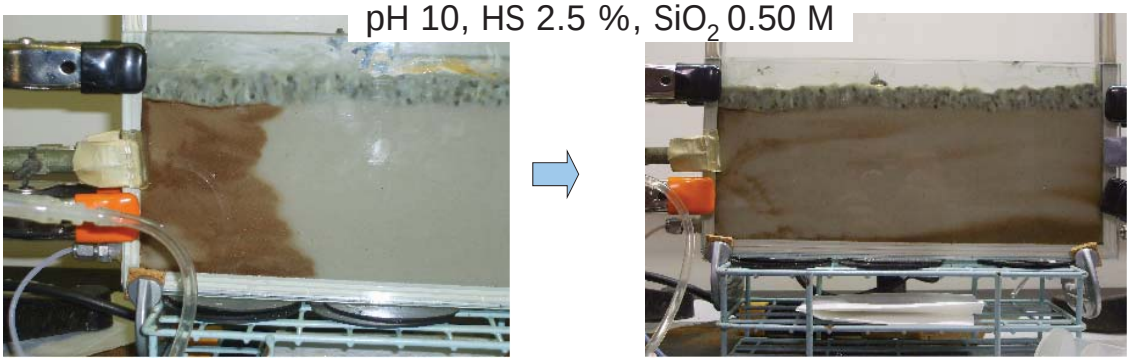

Karpiouk et al. *Soft Matter* **2012,** 8 (8), 2452

# Example: Pu sorption

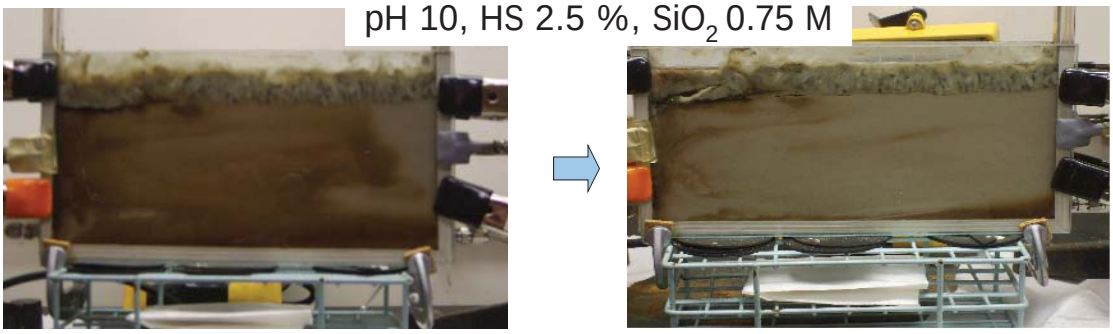



# Simulation of permeable reaction barrier

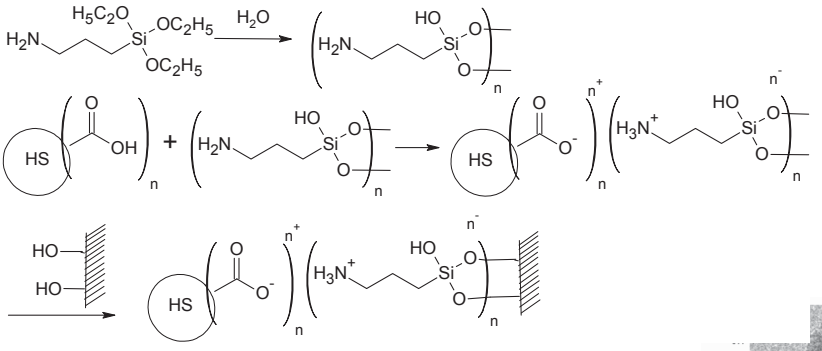
pH 10, HS 2.5 %, $SiO_2$ 0.50 M

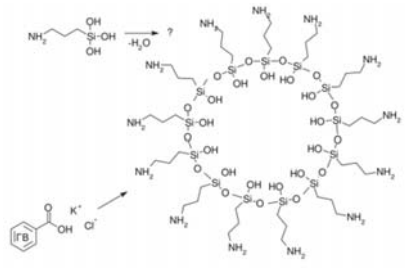


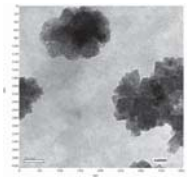
pH 10, HS 2.5 %, $SiO_2$ 0.75 M

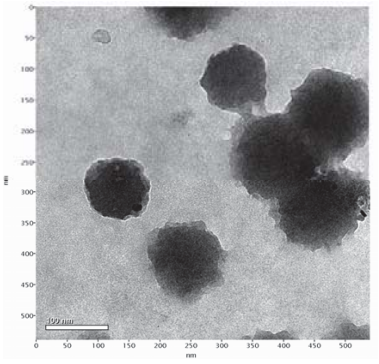


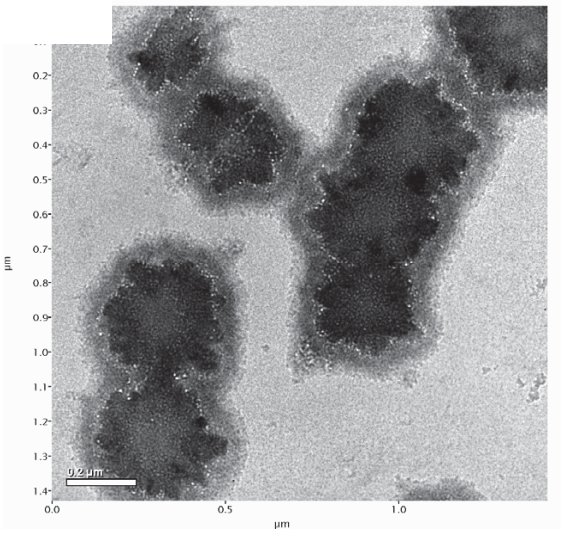
# Aminoorganosilane – formation of micelles



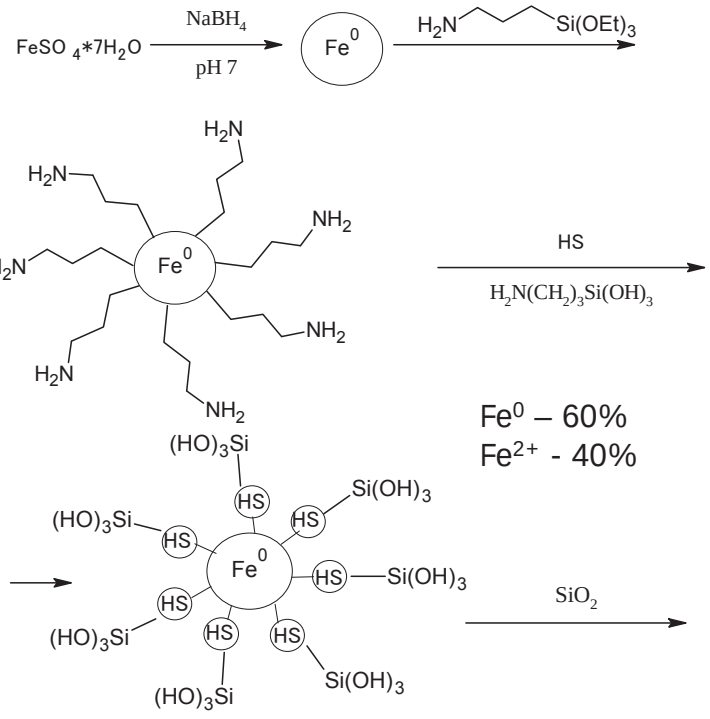




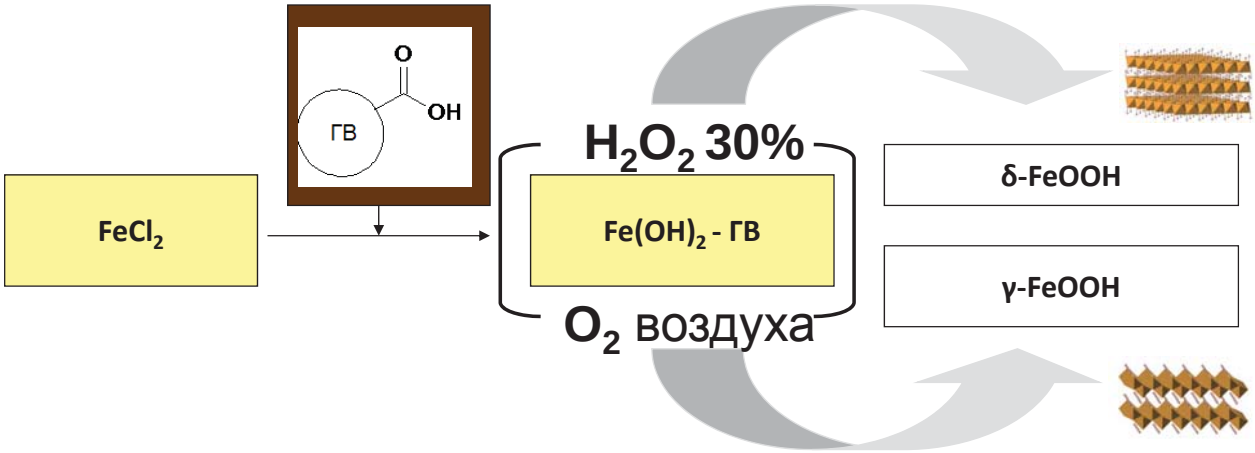


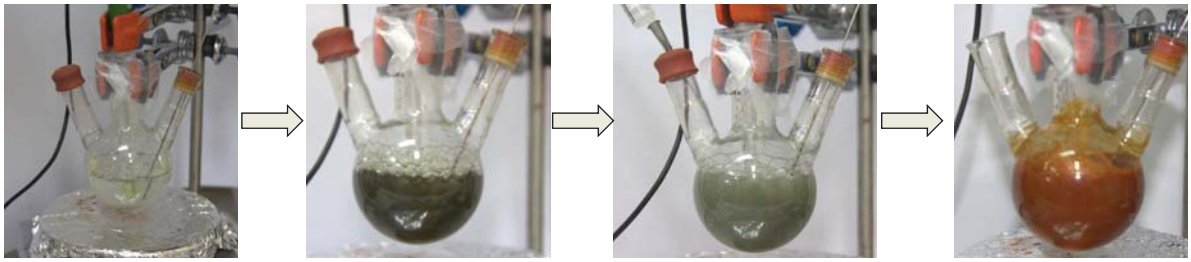


# Stabilization of zero valent Fe nanoparticles by HS

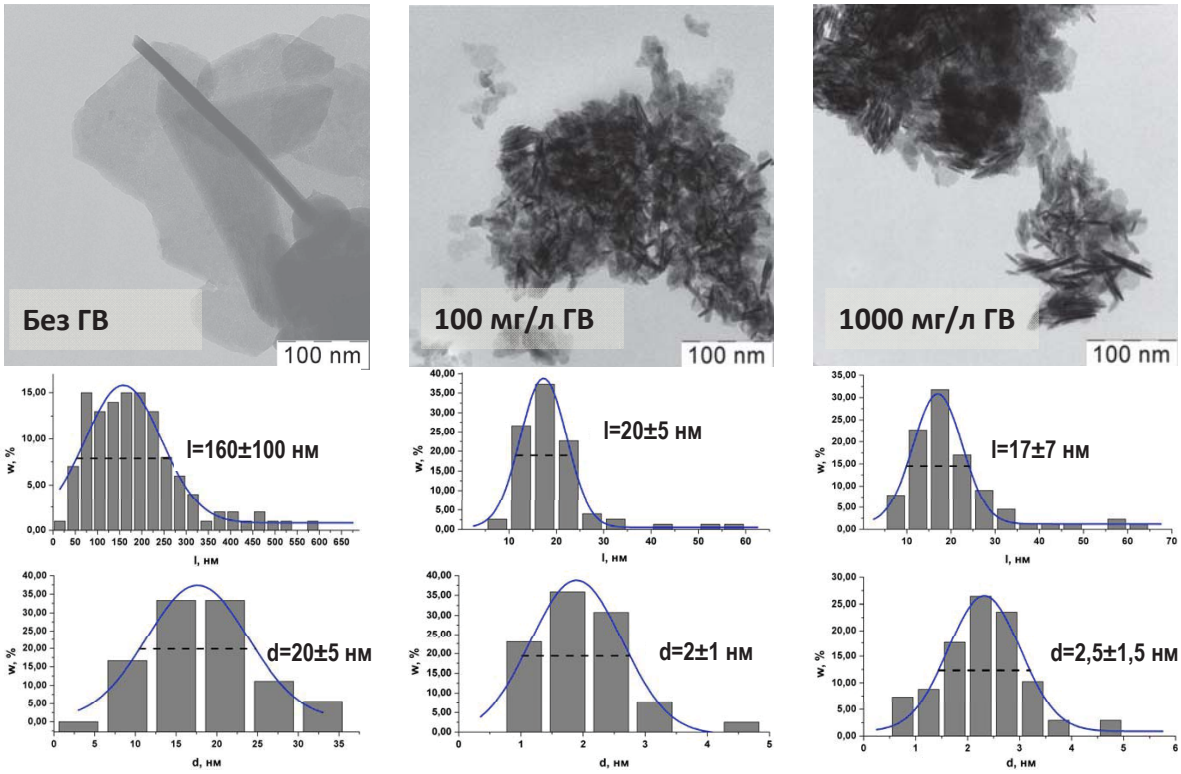



# Iron oxides nanoparticles stabilized by HS



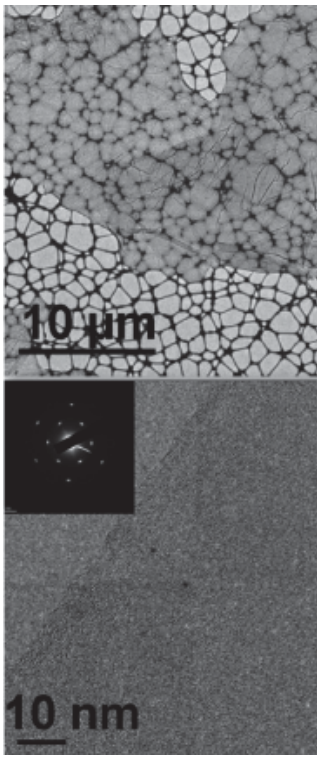



# Formation of δ-FeOOH in the presence of HS



In collaboration with James Tour, Rice University

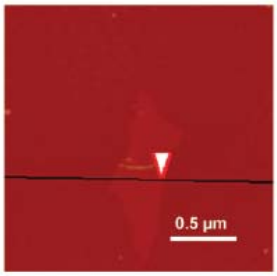
# Carbon nanomaterials as effective scavengers for radionuclides

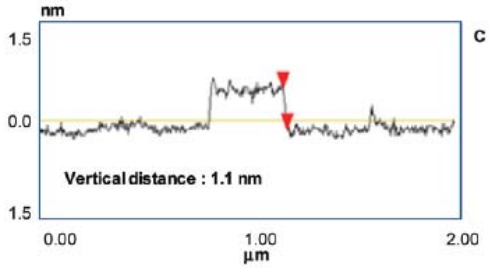



## Graphene oxide

Hummer modified method

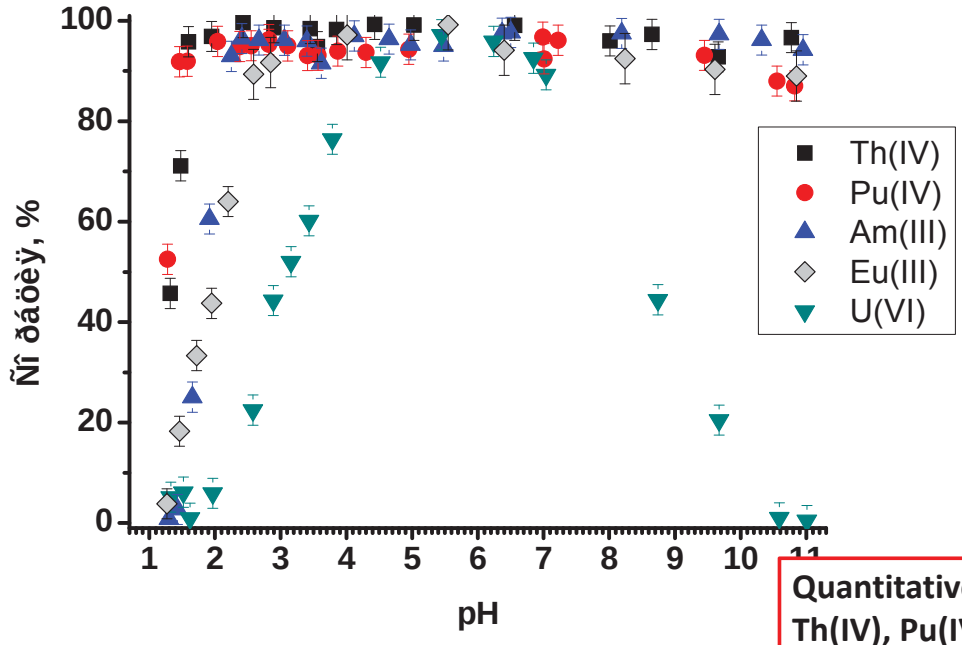
Graphite + $KMnO_4$ 9:1 $H_2SO_4$ и $H_3PO_3$




Marcano et al., ACS Nano, 2010

# Earlier the effective scavenging of actinides and lanthanides was shown

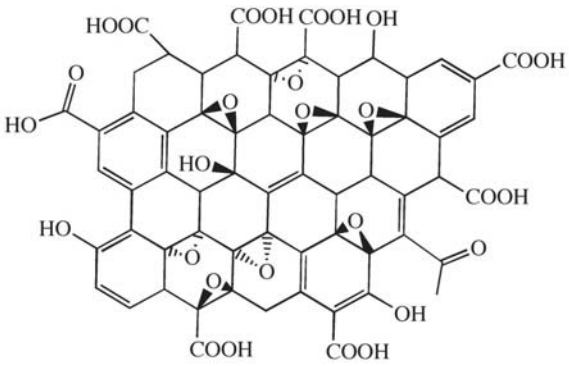



**Quantitative sorption:**
**Th(IV), Pu(IV) – pH> 1,5**
**Am(III), Eu(III) – pH> 2,3**

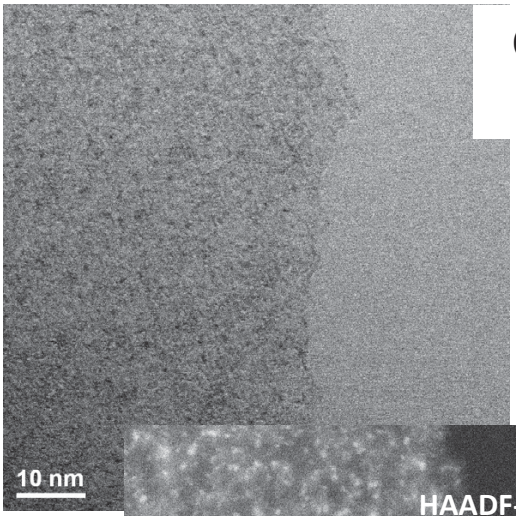
| | $Q_{max}$, мкмоль/г |
|---|---|
| U(VI), pH = 3,5 | 97 ± 19 |
| U(VI), pH = 5,0 | 116 ± 5 |
| Sr(II), pH = 6,5 | 272 ± 35 |
| Cs(I), pH = 7,0 | 160 ± 75 |

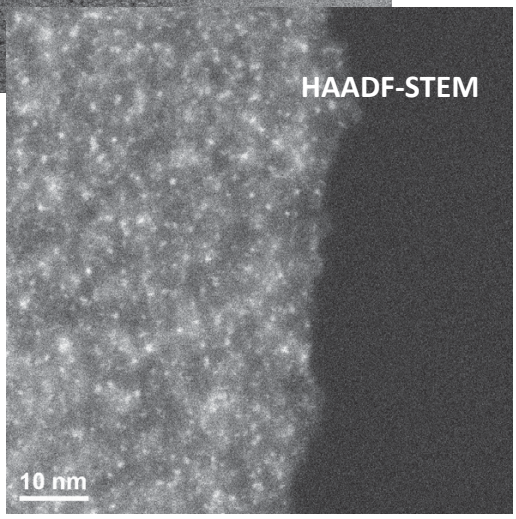
## GO + Cs(I)

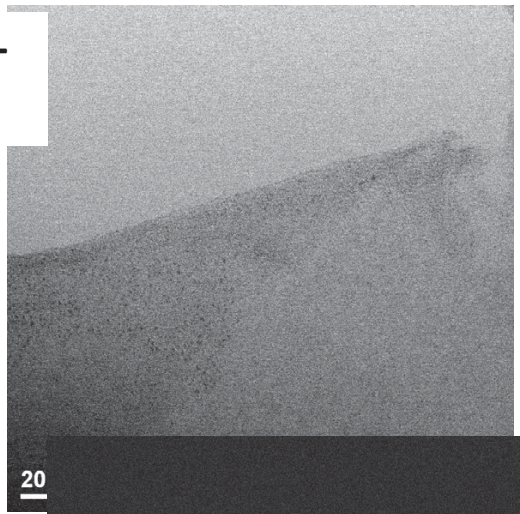
Distribution of Cs(I) on the surface

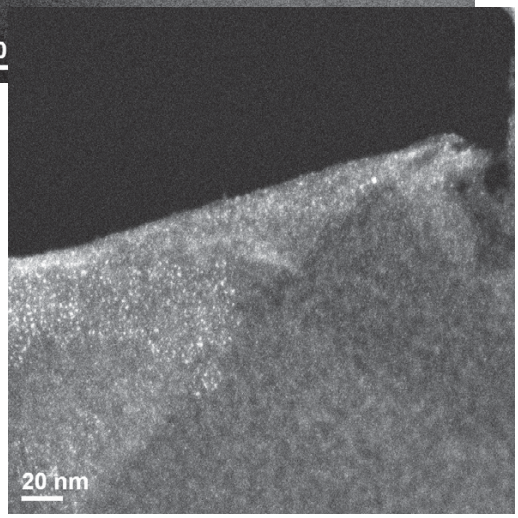




## Cations + GO

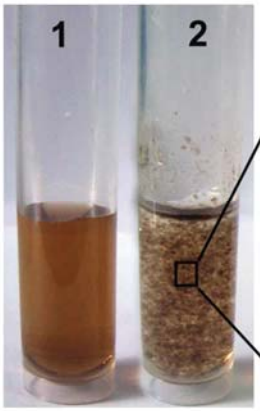


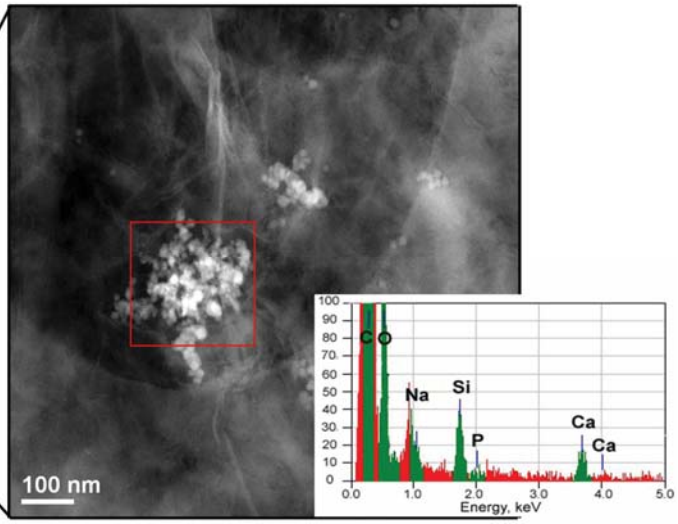



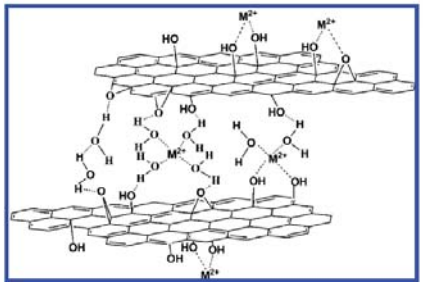



# Coagulation of GO



| | pH = 3 | pH = 7 |
|---|---|---|
| $Na^{+}$ | - | 0,4 M |
| $Ca^{2+}$ | 0,007 M | 0,001M |
| $Eu^{3+}$ | $< 1 \cdot 10^{-5}$ M | $< 1 \cdot 10^{-5}$ M |

## Conclusions:

1. As expected, clays effectively sorb $Cs^{+}$, but the presence of humic could change the mobility of $Cs^{+}$,
2. Humics form stable surface coatings on mineral particles that change their sorption and coagulation properties,
3. Humics could be easily modified and immobilized onto silica surfaces, as a result permeable barrier could be formed,
4. Graphene oxide could be considered as an effective scavenger for cationic forms of radionuclides.