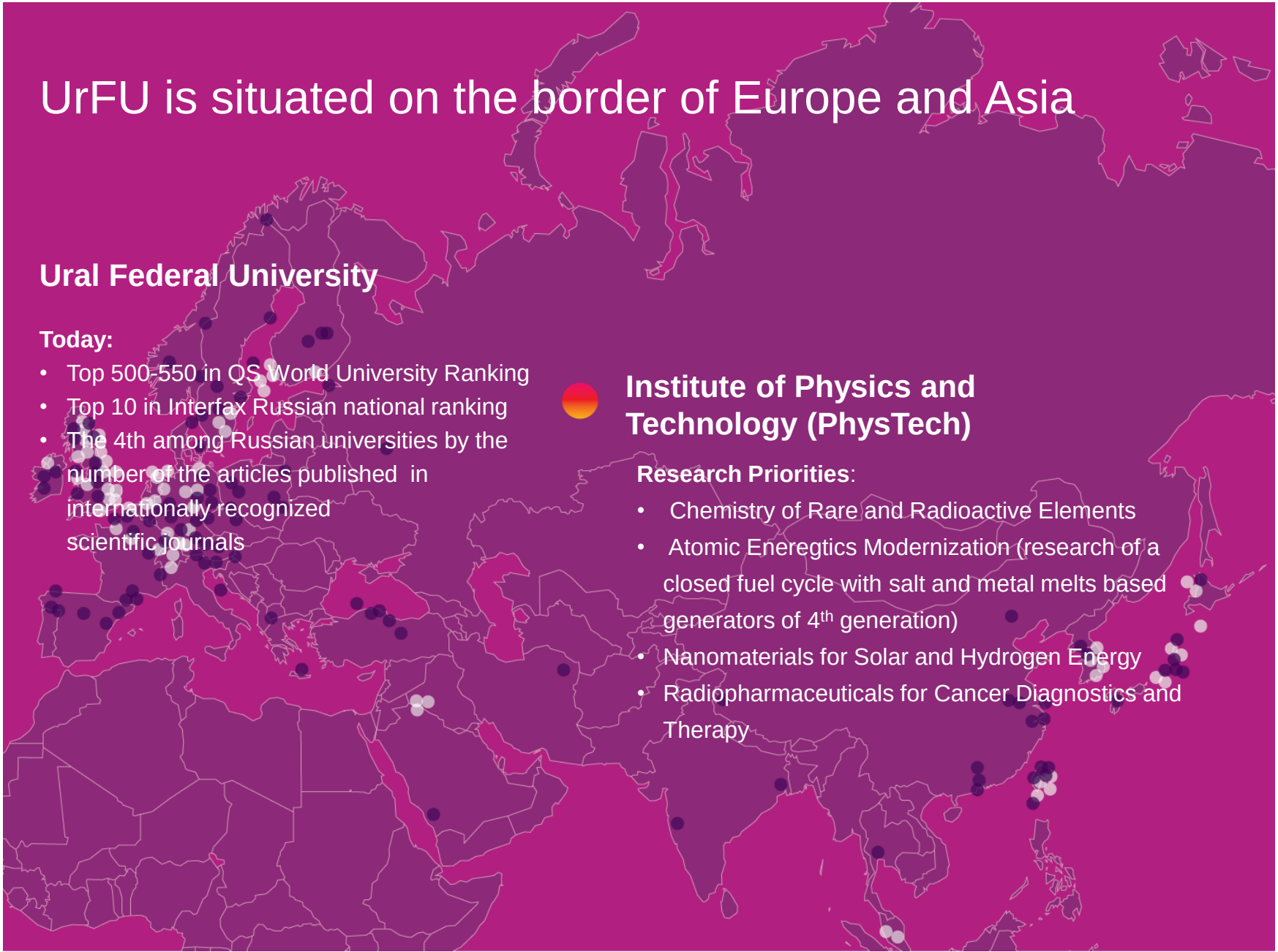
RECOVERY OF RARE EARTHS AND SCANDIUM FROM URANIUM LEACHATES

Ural Federal University
Physical Technology Institute
The Department of Rare Metals and Nanomaterials

SCALE Scandium-Inventory Workshop – 27/11/2018

Уральский федеральный университет

UrFU is situated on the border of Europe and Asia



Ural Federal University

Today:

- Top 500-550 in QS World University Ranking
- Top 10 in Interfax Russian national ranking
- The 4th among Russian universities by the number of the articles published in internationally recognized scientific journals

Institute of Physics and Technology (PhysTech)

Research Priorities:

- Chemistry of Rare and Radioactive Elements
- Atomic Eneregtics Modernization (research of a closed fuel cycle with salt and metal melts based generators of 4th generation)
- Nanomaterials for Solar and Hydrogen Energy
- Radiopharmaceuticals for Cancer Diagnostics and Therapy

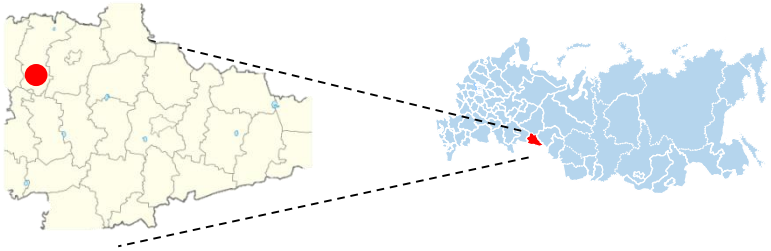
The border between Europe and Asia

Main recent achievements

The technology of recovery REE and scandium as by-products to uranium ISL

The technology of extraction REE from apatite and phosphogypsum

JSC Dalur is located in the Dalmatovsky District of Russia's Kurgan Region. The company conducts commercial development of deposits in the Trans-Ural Uranium-Ore Area (Dalmatovskoye and Khokhlovskoye). JSC Dalur produces uranium by downhole in-situ leaching method.
The company's finished product is concentrate of natural uranium (yellow cake).



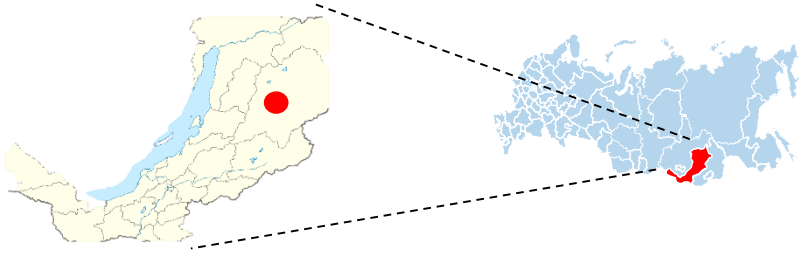
Concentrations:

- **REE– 30 mg/l**
- **Sc – 0.8 mg/l**

The distribution of lanthanides in solution ISL uranium

LREE	HREE
70	30

JSC Khiagda is located in the Bauntovsky District of the Republic of Buryatia. The company develops the deposits of the Khiagdinskoye ore field.
Test uranium mining with the use of in-situ leaching method began in 1999.
Productive solutions are processed into the end product — concentrate of natural uranium (yellow cake).



Concentrations:

- **REE – 60 mg/l**
- **Sc – 0.5 mg/l**

The distribution of lanthanides in solution ISL uranium

LREE	HREE
70	30

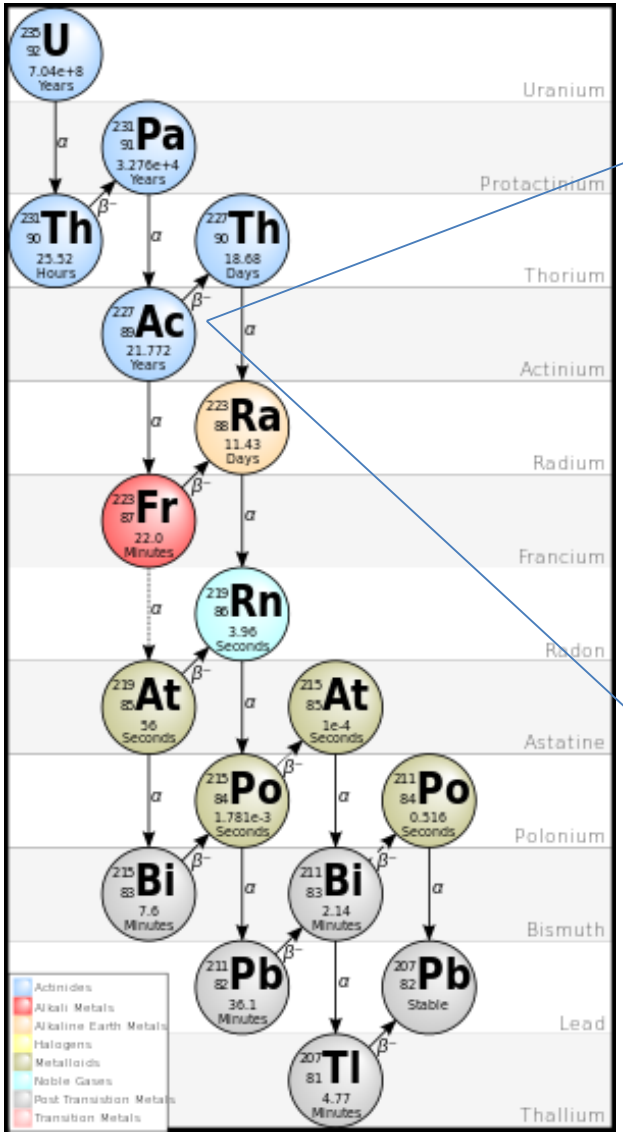
10-15% scandium oxide concentrate and 85-90% REE concentrate

Carbonate REE concentrate and its activity rate

№	Element	, %	№	Element	, %
1	Li	0,0007	26	Zr	0,0083
2	Be	0,0029	27	La	7,7836
3	B	0,0203	28	Ce	22,3859
4	Na	0,2442	29	Pr	3,3187
5	Mg	0,0536	30	Nd	11,6157
6	Al	0,6719	31	Sm	1,9142
7	P	0,1306	32	Eu	0,4196
8	K	0,0583	33	Gd	2,4324
9	Ca	0,2452	34	Tb	0,2170
10	Sc	0,0202	35	Dy	2,7096
11	Ti	0,0022	36	Ho	0,0713
12	V	0,0005	37	Er	0,1224
13	Cr	0,0084	38	Tm	0,0060
14	Mn	0,0086	39	Yb	0,0476
15	Fe	0,0885	40	Lu	0,0059
16	Co	0,0003	41	Th	0,0004
17	Ni	0,0044	42	U	0,0084
18	Cu	0,0051	43	**Σ REE**	**54,2757**
19	Zn	0,0436	activity concentration		$5,8 \pm 0,9 \cdot 10^6$ Bq kg^{-1}
20	Ga	0,0207			
21	Ge	0,0331			
22	Se	0,4656			
23	Rb	0,0002			
24	Sr	0,0012			
25	Y	1,2257			

REE concentrate activity is basically caused by Ac-227 and its decay products.

Uranium-235 decay chain



- It occurs in uranium and thorium ores
- One tone of natural uranium contains only $6*10^{-5}$ gram of actinium
- To produce 1 gram of actinium you need to recycle 16,000 tons of uranium, (or 1000 wagons)

Methods of REE and Ac separation

Actinium has a similar chemical behavior as REE (La, Ce and others)

Chromatographic actinium separation from REE:

It is based on the ionic radius difference

For this aim complexation ionic exchange chromatography is used with organic acid or salts solutions (citrates, lactates, etc) as eluents

In this case Actinium is eluted last

Extraction method of actinium separation from REE :

It is based on the extraction coefficients difference

Tributyl phosphate (TBP, phosphoric acid ester) $(C_4H_9O)_3P=O$ is used to remove Actinium from low pH solutions in a significant amounts of salting-out agents presence (ammonium nitrate, aluminum and others)

Also TTA (tetradecylthioacetic acid) is used to separate actinium from radium and its decay products as TBP

REE recovery mini-pilot test

Developed deactivation technology was tested under industrial conditions at the uranium mining plant. Approximately 100 g of the REE's concentrate with high activity was treated; after deactivating it was about 90 g of REE's concentrate with activity concentration of

$(1\text{-}5) \times 10^3$ Bq kg^{-1}.

Uranium sorption column 50 m^3

REE deactivation column 15 dm^3

Prospective industrial sources of scandium in Russia

Source	Sc content
Uranium leach liquors (ULL)	<1 mg/l
Hydrolytic waste acid after production of TiO_2	~20 mg/l
Red mud (bauxite treatment waste)	0.007–0.011%
Coal ash	0.006-0.012 %
Uranium ores	Up to 0.002%
Tungsten ores	0.01–0.1%

Ion exchange resins for preliminary scandium separation

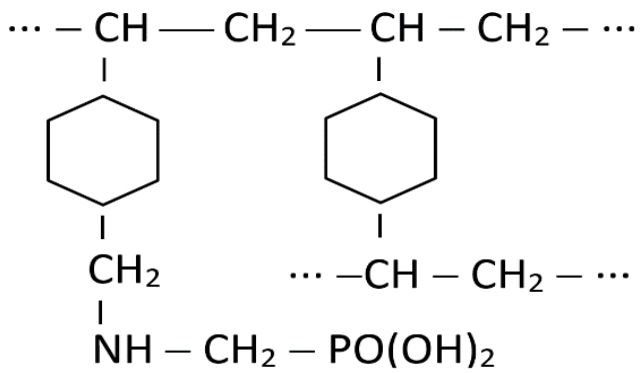
Aminomethyl phosphonic ampholytes

Purolite S-950

Lewatit TP-260

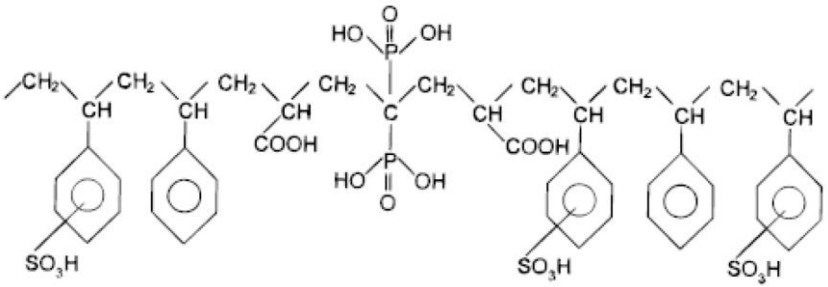
Tulsion CH-93

ЭКО-10



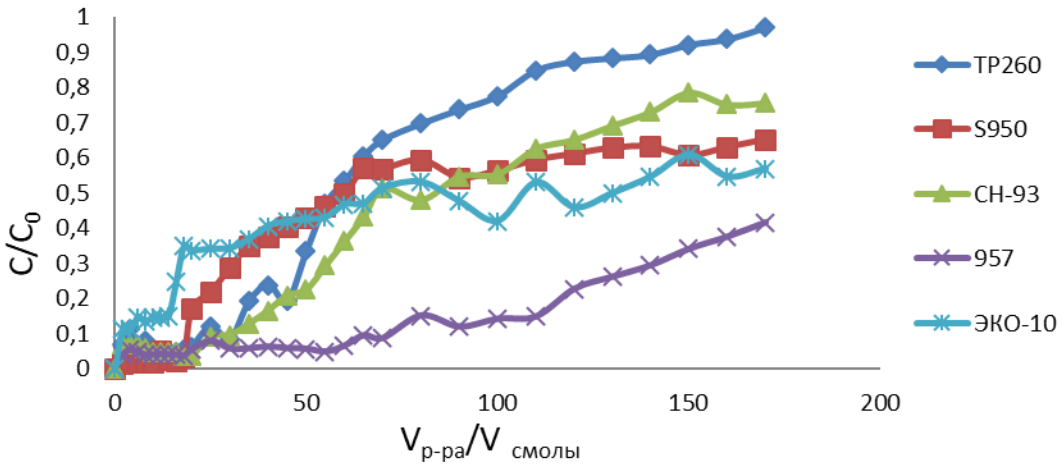
Polyfunctional ion exchange resin

Purolite S-957



Characteristics of Sc sorption from ULL by various IEX Resins

The dynamics of Sc sorption



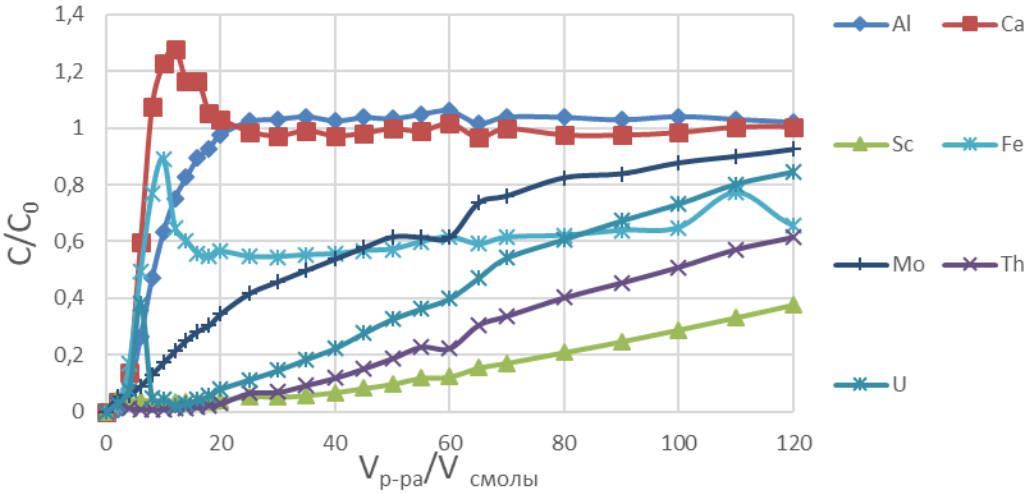
Full dynamic exchange capacity

Tulsion CH 93

Element	Sc	Th	Al	Fe	Ti	U
Capacity, mg per g of resin	0.28	0.58	7.41	3.21	1.38	0.38

$K_{d\ Sc/Th}$=1.14

Dynamics of elements sorption by Purolite S-957



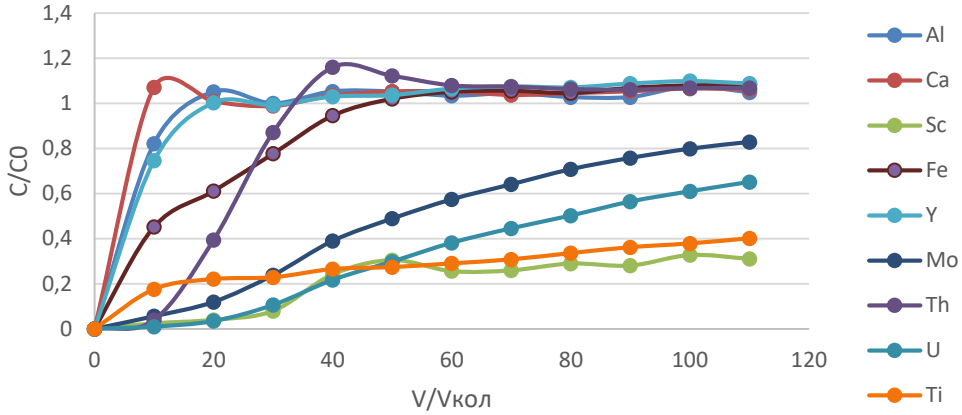
Purolite S-957

Element	Al	Ca	Sc	Fe	Th	U
Capacity, mg per g of resin	26.43	4.5	0.65	60.67	1.09	0.43

$K_{d\ Sc/Th}$=1.41

Characteristics of Sc sorption from ULL by various IEX Resins

Dynamics of elements sorption by Purolite AA-03

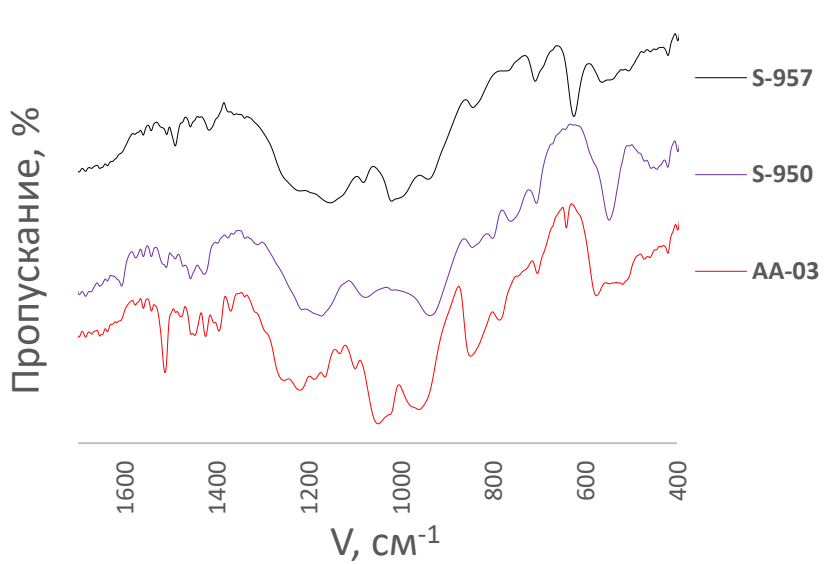


Purolite AA-03

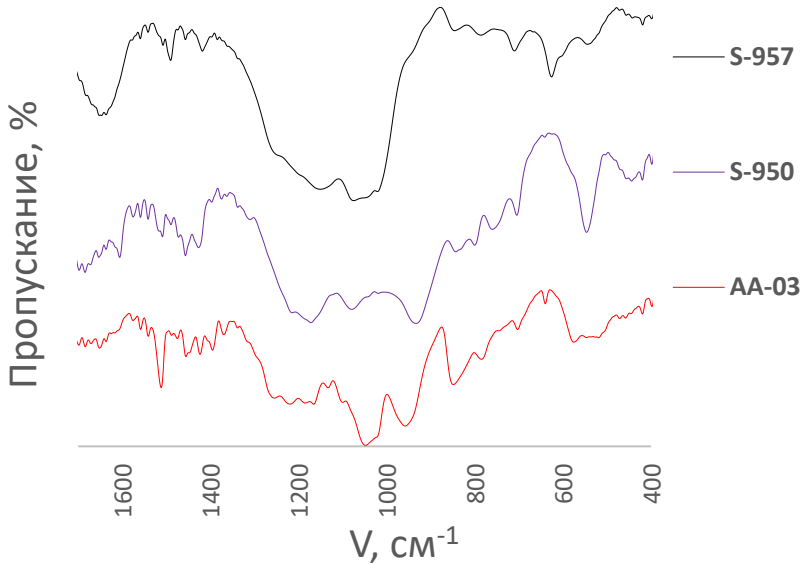
Element	Al	Ca	Sc	Fe	Th	U
Capacity, mg per g of resin	10.14	0.27	0.37	15.47	0.14	0.44

$K_{d\ Sc/Th}$=6.28

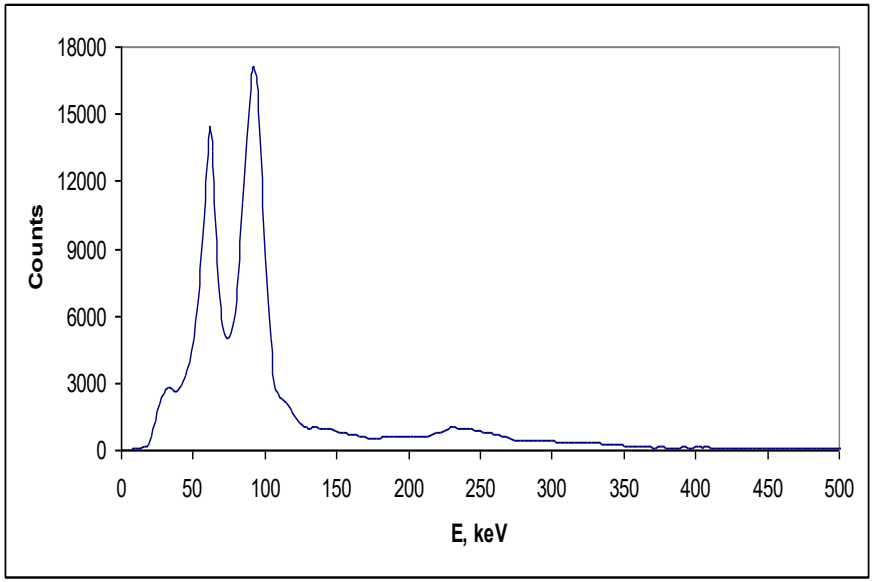
IR spectra of Purolite S-957, S-950 and AA-03 in H^+ form



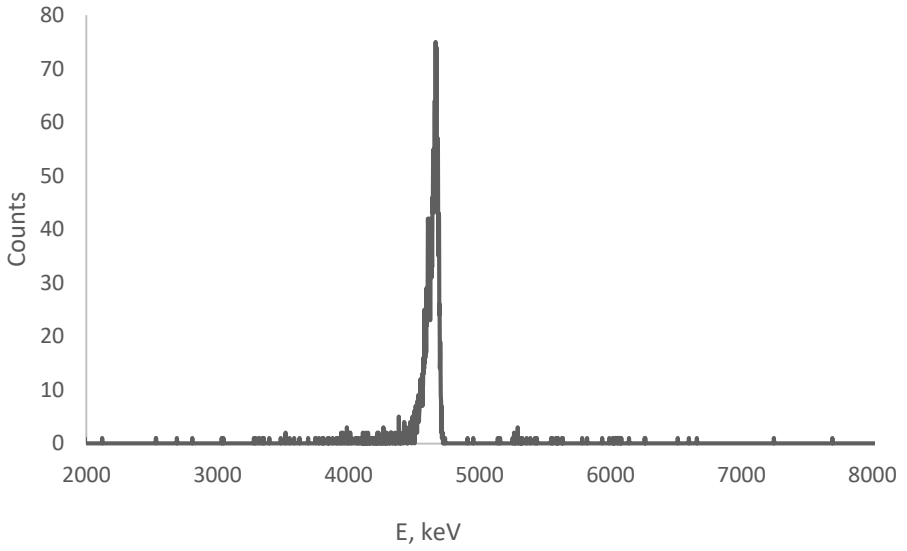
IR spectra of Purolite S-957, S-950 and AA-03 in Sc^{3+} form



Radioactive contaminants in the primary scandium concentrate



Gamma spectrum of the Sc concentrate



Alpha spectrum of the Sc concentrate

Radioactivity of the Sc concentrate is conditioned by presence thorium-234 (half-life is 24 days, beta and gamma emitter) and thorium-230 (half-life is 80,000 years, pure alpha emitter). Activity was up to 10^8 - 10^{11} Bq/kg depending on the resin type being used for scandium separation.

Sc/Th separation is necessary

Scandium recovery mini-pilot test

The results of work of the mini-pilot test

Composition of the scandium concentrate obtained at the mini-pilot test

Compound	% wt.	Compound	% wt.
Sc	30.09	Cl	0.063
Na	9.61	K	0.049
Al	3.29	Sr	0.007
Mg	0.78	P	0.005
Ca	0.65	Y	0.004
Fe	0.12	Zr	0.003
Si	0.08	Th	0.003
S	0.070	Ni	0.001

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Scandium recovery pilot scale plant (200 m^3 of ULL per hour)

The results of work of the pilot scale plant

Composition of the scandium concentrate obtained at the pilot scale plant

Compound	% wt.	Compound	% wt.
ScF_3	98.040	Y_2O_3	0.037
FeF_2	0.395	CeO_2	0.009
SO_3	0.355	Pr_6O_{11}	0.006
NaF	0.340	Nd_2O_3	0.004
AlF_3	0.298	V_2O_5	0.003
Si	0.131	ThO_2	0.002
C	0.085	ZrO_2	0.002
MgF_2	0.080	SrO	0.002
CaF_2	0.058		

Vielen Dank für Ihre Aufmerksamkeit!

Thanks for Attention!