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Combined separation of Pd and Tc from the raffinates of spent nuclear fuel reprocessing.

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Recently the hydrogen energetic has been rapidly developed all over the world. One of the ways to increase the role of hydrogen energetic is using of the nuclear power plants area for placing of water electrolysis units. Such approach allows using energy generated on nuclear power plants for electrolysis units and provides good conditions for safe work with materials which contain radionuclides without getting them outside the plant.

It is wise to use “reactor” Pd, Ru, Rh and Tc to product electrodes used in the sea-water electrolysis units.

One of the evident sources of these metals is highly active raffinates generated in the first extraction cycle during the spent nuclear fuel reprocessing.

PUREX-process

SNF APP (Pd, Rh, Ru, Tc, etc.) → Dissolving in HNO_3 → First extraction cycle (recovery of U, Pu –by TBP) → U, Pu – separation and affinage

Dissolving in HNO_3 → «Insoluble residue»- composite of Mo, Ru, Rh, Pd, Tc

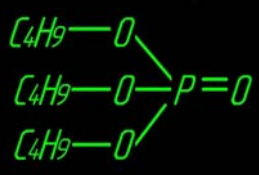
First extraction cycle (recovery of U, Pu –by TBP) → Raffinate (Pd, Rh, Ru, Tc)

For further recovery of Pd, Ru, Rh and Tc from first extraction cycle raffinates of Purex-process different methods can be used such as extraction, sorption, electrochemistry.

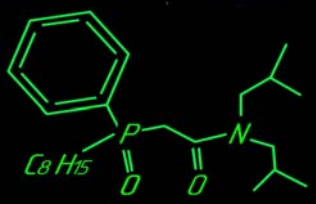
Extractants for recovering of platinum-group metals from raffinates of the first extraction cycle are:

amines and quaternary ammonium bases,

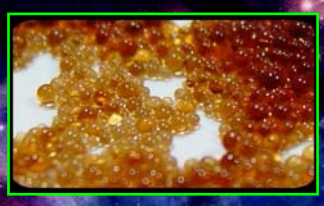
Tributyl Phosphate



Carbamoyl phosphine oxides



Strongly basic anionites and solid extractants on the base of silica gel impregnated with CMPO or formazan derivatives are usually used in sorption.

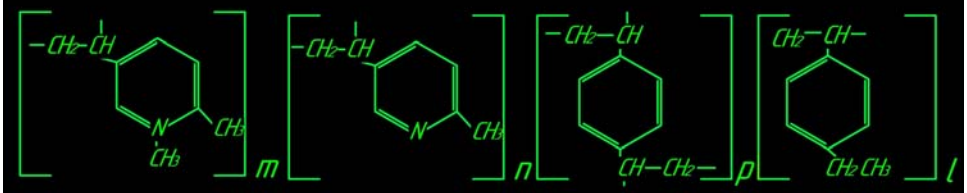


The examples of individual Pd and Tc sorption by anion exchange resin from nitric acid solutions are well-known. However, there are no data in literature on simultaneous recovering of Pd and Tc.

The goal of the present work was to study Tc and Pd sorption behavior, to find the reagents for their stripping and conditions for effective simultaneous recovery of metals from raffinates of spent nuclear fuel reprocessing.

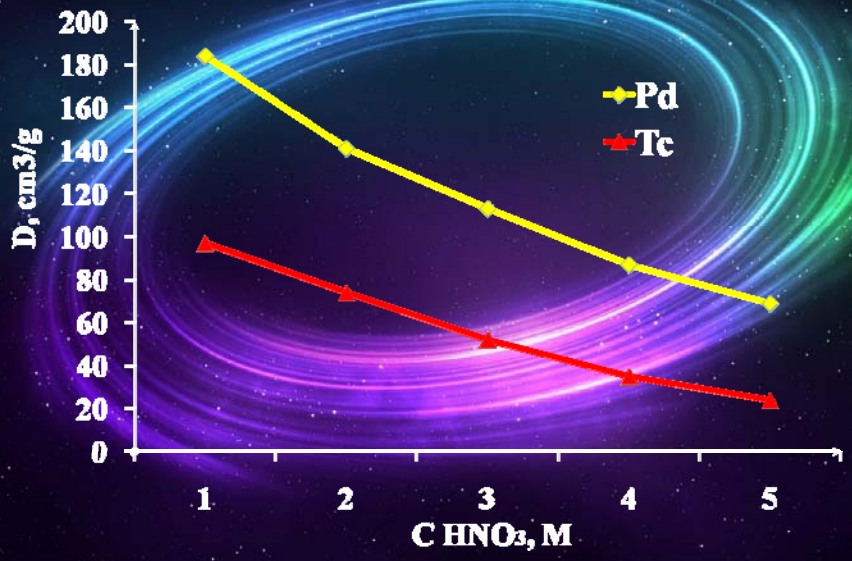
***VP-1AP*- strongly basic anionite which contains two types of ionogenic groups: N-methyl-pyridine nitrogen and pyridine nitrogen.**

Assumed structure of elementary link of VP-1AP anionite.



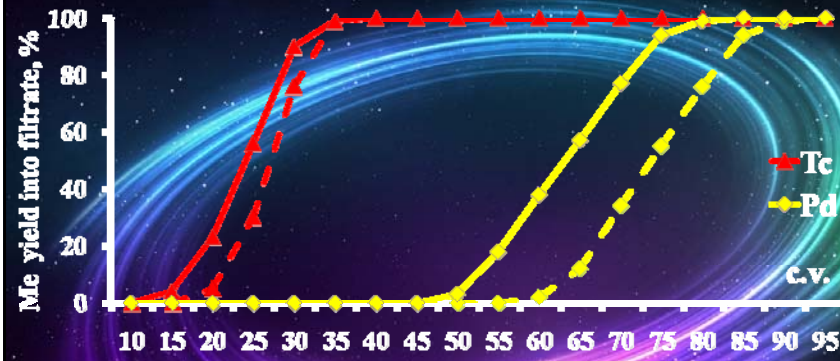
An analogue of anionite VP-1AP is a sorbent A-560 produced by Purolite.

Dependence of metal distribution ratios on HNO_3 concentration. C_{Pd} 115 mg/l, C_{Tc} 100 mg/l.



Individual and combined sorption of Pd and Tc

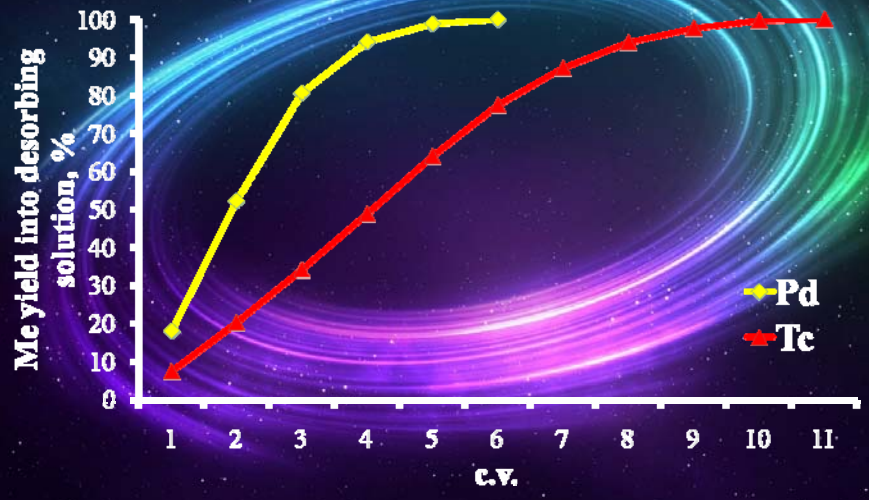
Heavy lines– simultaneous sorption, dashed lines – individual sorption.



Sorption characteristics of resin for individual and combined sorption of Pd and Tc

Characteristic	Individual sorption		Combined sorption	
	Tc	Pd	Tc	Pd
D, cm^3/g	70	195	62	172
DEC, mg/g	6.9	19.2	6.2	17.7

Palladium and Technetium desorption.
T=60 ^{0}C



Stripping solution: 30 g/l DTPA in 7 M HNO_3

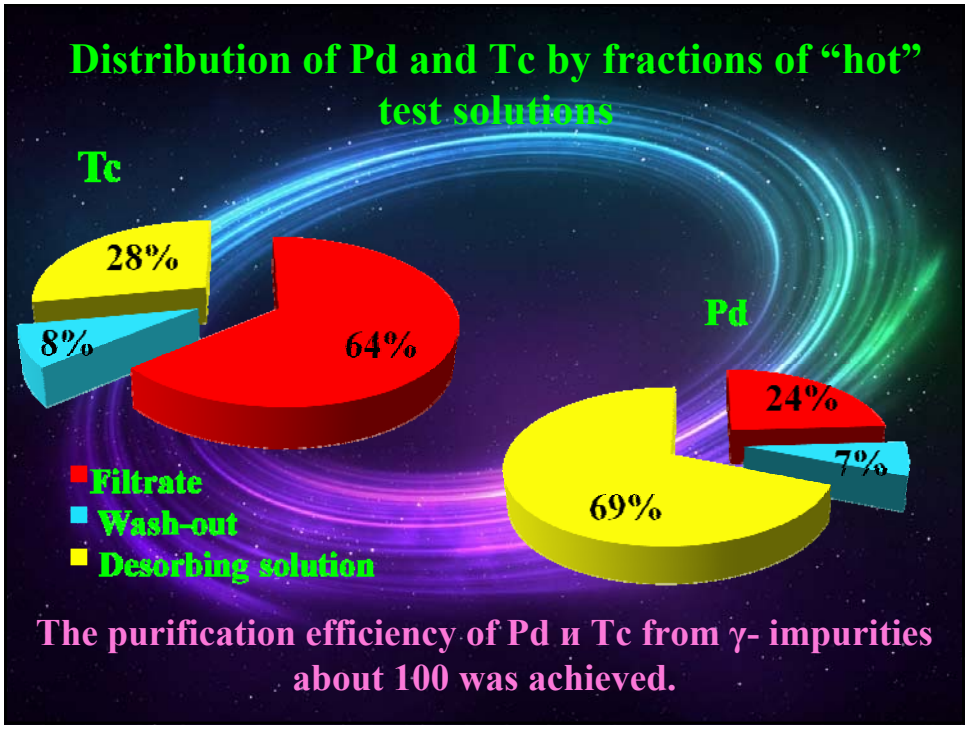
Characteristics of real raffinates:

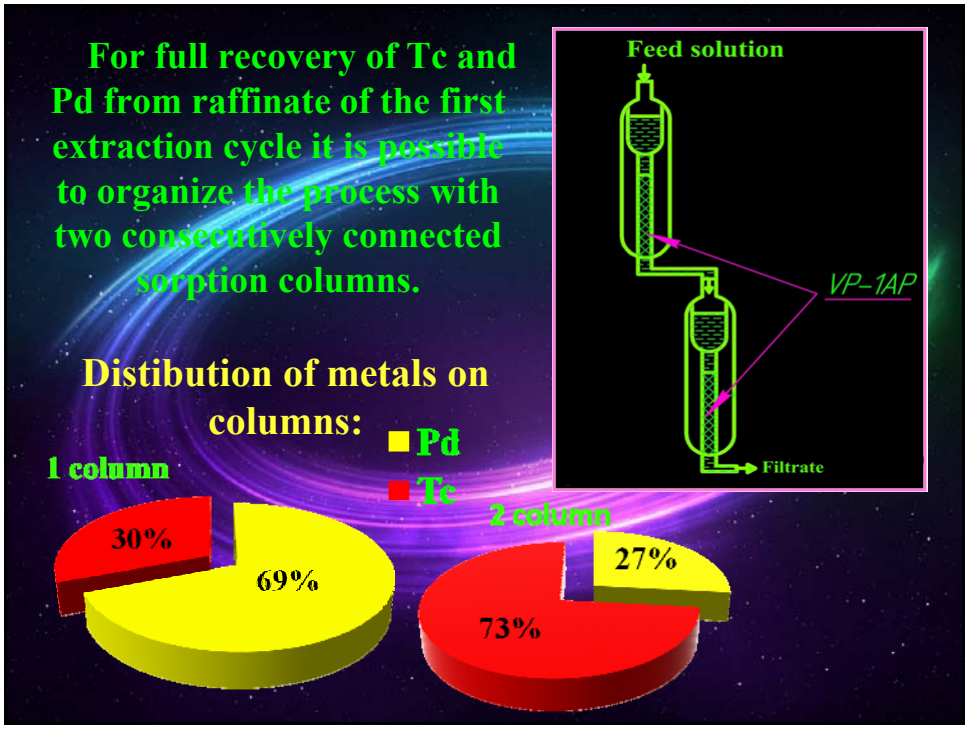
Volume of feed solution – 2 L
Pd and Tc - 213 mg/l and 137 mg/l, 2 M HNO3

Isotope	Activity, Bq/cm^3
^{137}Cs	$2.4\cdot10^8$
^{134}Cs	$5.2\cdot10^6$
^{154}Eu	$6.9\cdot10^6$
^{155}Eu	$2.1\cdot10^6$
^{241}Am	$5.9\cdot10^6$
Total	$2.6\cdot10^8$

γ – activity of feed solution

The column was filled with 50 cm^3 (18.7 g) of VP-1AP.
Fraction of resin is 0.25-0.5 mm. Column diameter- 2 cm.


Distribution of Pd and Tc by fractions of “hot” test solutions
Tc
28%
8%
64%
Pd
24%
7%
69%
Filtrate
Wash-out
Desorbing solution
The purification efficiency of Pd и Tc from γ- impurities about 100 was achieved.


For full recovery of Tc and Pd from raffinate of the first extraction cycle it is possible to organize the process with two consecutively connected sorption columns.
Feed solution
VP–1AP
Filtrate
Distibution of metals on columns:
Pd
Tc
1 column
30%
69%
2 column
27%
73%

Conclusions:

- The conditions of simultaneous Pd and Tc separation from the solution of SNF reprocessing by strongly basic anionite VP-1AP were studied.
- It was shown, that about 70% of Pd and 30% of Tc were sorbed on the resin from 2M HNO_3 solutions with following desorption.
- It was shown, that 11 column volumes are enough for 100% yield of Pd and Tc at their simultaneous stripping by solution of 30 g/L DTPA in 7 M HNO_3 at 60°C.
- In hot test on real spent nuclear fuel reprocessing raffinate Tc and Pd purification efficiency from gamma-impurities about 100 was achieved.
- It was shown, that using of two consecutively connected columns provides quantitative sorption and stripping of Tc and Pd.
- It was confirmed, that Pd and Tc could be simultaneously recovered by sorption from solutions of SNF reprocessing.