7th International Symposium on Technetium and Rhenium Science and Utilization

How to Manage Technetium (Nuclear Rare Metal) and Actinides, Toward Future Reprocessing System Providing Non-Proliferation

From Adv.-ORIENT Cycle to Après ORIENT

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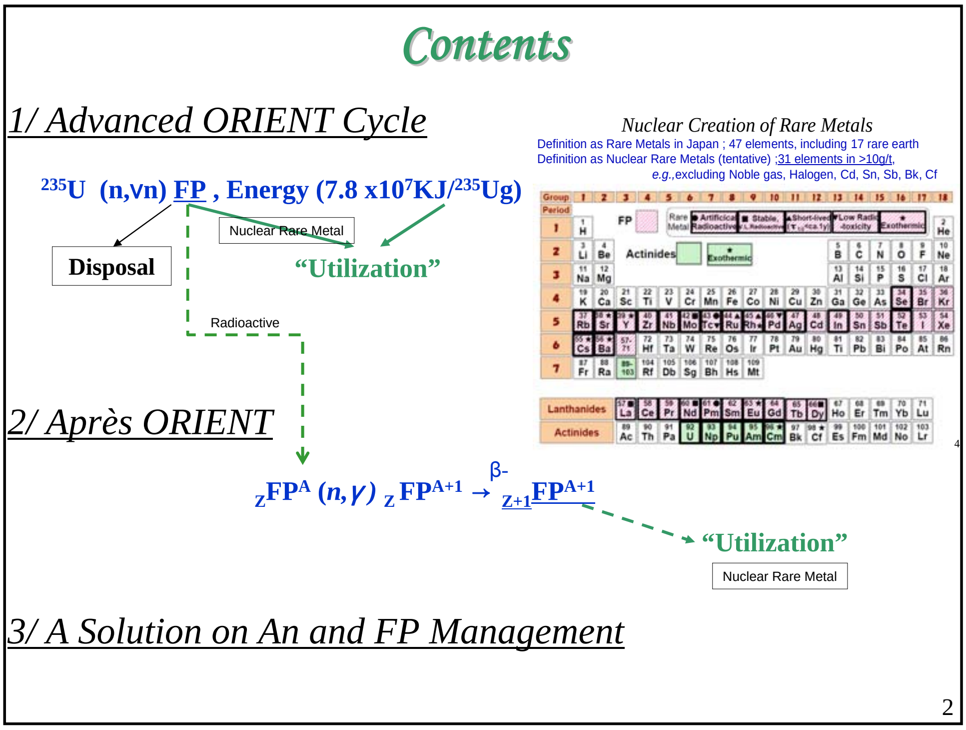


Contents

1/ Advanced ORIENT Cycle

^{235}U (n,νn) FP , Energy (7.8 x10^{7}KJ/^{235}Ug)

Nuclear Creation of Rare Metals

Definition as Rare Metals in Japan ; 47 elements, including 17 rare earth
Definition as Nuclear Rare Metals (tentative) ;31 elements in >10g/t,
e.g.,excluding Noble gas, Halogen, Cd, Sn, Sb, Bk, Cf

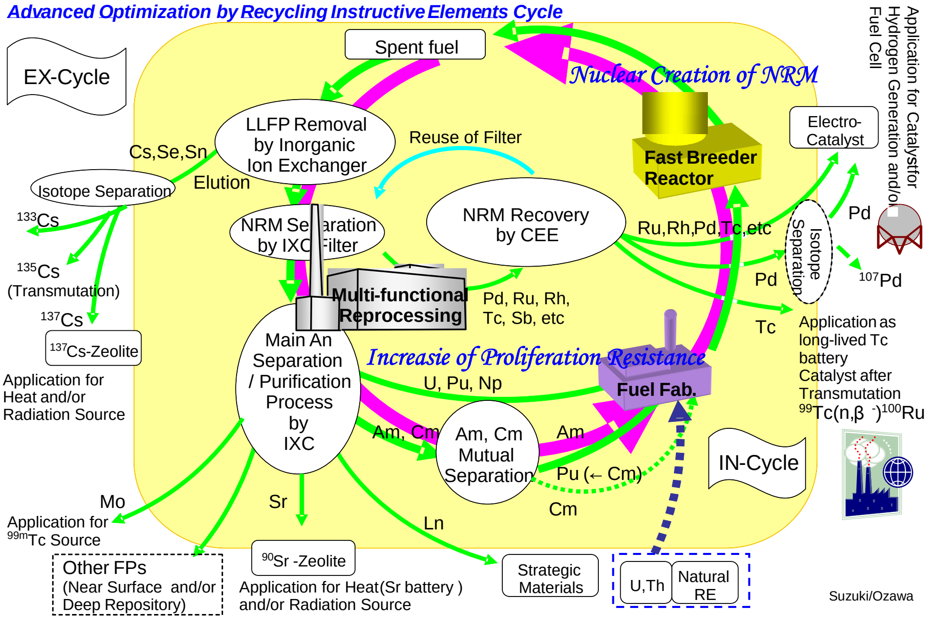
2/ Après ORIENT

$_{Z}FP^{A}\ (n,\gamma)\ _{Z}FP^{A+1} \xrightarrow{\beta-}\ _{Z+1}FP^{A+1}$

3/ A Solution on An and FP Management

Adv.-ORIENT Cycle *Since 2006*

Advanced Optimization by Recycling Instructive Elements Cycle



EX-Cycle

Spent fuel

Nuclear Creation of NRM

Application for Catalystfor Hydrogen Generation and/or Fuel Cell

LLFP Removal by Inorganic Ion Exchanger

Cs,Se,Sn

Elution

Reuse of Filter

Isotope Separation

^{133}Cs

^{135}Cs (Transmutation)

^{137}Cs

^{137}Cs-Zeolite

Application for Heat and/or Radiation Source

NRM Separation by IXC Filter

NRM Recovery by CEE

Fast Breeder Reactor

Electro-Catalyst

Ru,Rh,Pd,Tc,etc

Isotope Separation

Pd

^{107}Pd

Pd

Tc

Multi-functional Reprocessing

Pd, Ru, Rh, Tc, Sb, etc

Main An Separation / Purification Process by IXC

Increasie of Proliferation Resistance

U, Pu, Np

Fuel Fab.

Application as long-lived Tc battery Catalyst after Transmutation ^{99}Tc(n,β$^-$)^{100}Ru

Am, Cm

Am, Cm Mutual Separation

Am

Pu (← Cm)

Cm

IN-Cycle

Mo

Application for ^{99m}Tc Source

Sr

Ln

Other FPs (Near Surface and/or Deep Repository)

^{90}Sr -Zeolite

Application for Heat(Sr battery) and/or Radiation Source

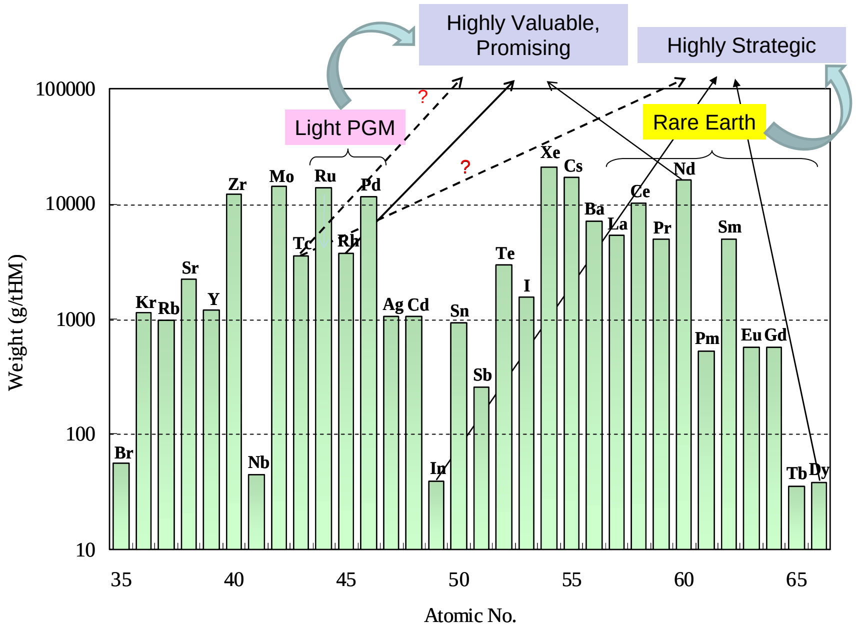
Strategic Materials

U,Th

Natural RE

Suzuki/Ozawa

NRM in FBR *(Adv.-ORIENT Cycle)*

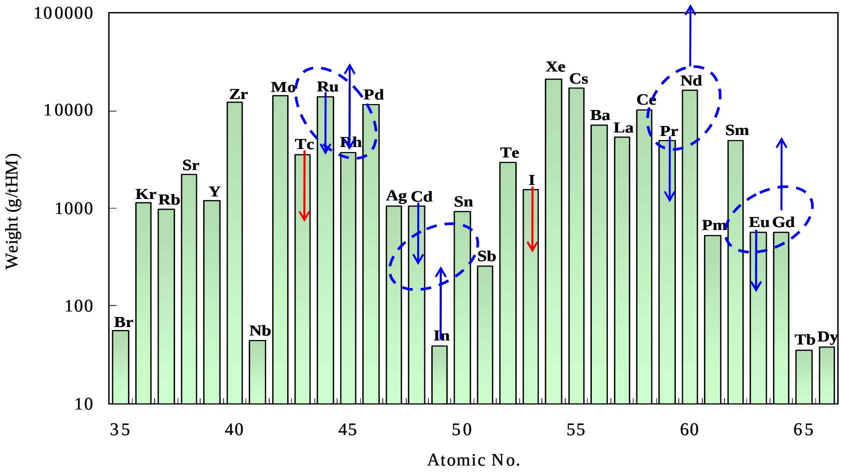


FBR MOX, Inner core, 150GWd/t, cooled 5 years

Nuclear Creation of Rare Metal (*Après ORIENT*)

①P&T：Transmutation of MA (^{241}Am,etc) , LLFP (^{99}Tc, etc) ⇔ Decrease of Environmental Burden, Increase of Proliferation Resistance

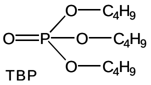
②Positive P&T：Transmutation of Radioactive FP to Highly Valuable Rare Metal FP⇔ Element Strategy, Decrease of Environmental Burden, Increase of Proliferation Resistance ⇒ Irradiation Experiments in Japan, Russia, etc in future?



From “Separation” to “Creation”(*Après ORIENT*)

Dissolver Solution of SF-FR
“JOYO” (JAEA, CPF)

Reprocess
-ing



TBP
tributylphosphate

HLLW of SF-LWR(JAEA, Tokai-Reprocessing Plant)

$$UO_2^{2+} + 2NO_3^- + 2\overline{TBP} \Leftrightarrow \overline{UO_2(NO_3)_2 \cdot 2TBP}$$

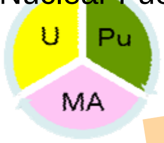
$$Pu^{4+} + 4NO_3^- + 2\overline{TBP} \Leftrightarrow \overline{Pu(NO_3)_4 \cdot 2TBP}$$

$$M^{3+} + 3NO_3^- + \overline{3CMPO \cdot (HNO_3)}$$

$$\Leftrightarrow \overline{M(NO_3)_3(CMPO)_3 \cdot (HNO_3)_m} + (3n-m)HNO_3$$

Nuclear Fuel

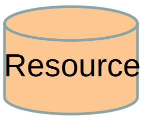
Fuel Fab.

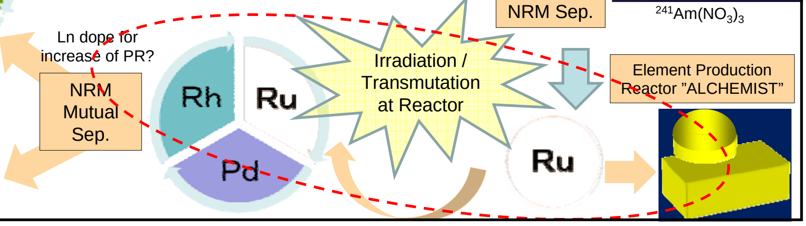


MA Sep.

^{241}Am(NO$_3$)$_3$

NRM Sep.





Composition of Actinides and Irradiation Conditions for Calculation

Economy tipe core (B.R. = 1.03)												
O/M ratio = 1.05												
Loaded fuel (kg/batch)												
Region	Pu content (%)	U235 (kg)	U238 (kg)	Pu238 (kg)	Pu239 (kg)	Pu240 (kg)	Pu241 (kg)	Pu242 (kg)	Np237 (kg)	Am241 (kg)	Am243 (kg)	Cm244 (kg)
Inner core	18.3	22.3	7407.5	19.4	955	566.5	75.9	68.9	8.8	35.3	17.6	17.7
Outer core	21.1	20.5	6802.5	21.3	1048	621.8	83.3	75.6	9.7	38.8	19.4	19.4
Axial Blanket	0	20.7	6885	0	0	0	0	0	0	0	0	0

Table Operation condition of Japanese fast reactor

	JOYO MK-II core	MONJU	Commercial Reactor
Thermal output (MWt)	100	714	3570
Power fraction	0.95	0.53	0.50
Number of subassembly	67	108	288
Lattice pitch (mm)	81.5	115.6	206.0
Stack length (mm)	550	930	1000
Active core volume (cc)	211974	1162393	10584188
Power density (W/cc)	448	326	168
Neutron flux ($n \cdot cm^{-2}s^{-1}$) (E ≧ 0.1 MeV)	3.05×10^{15}	4.09×10^{15}	2.27×10^{15}

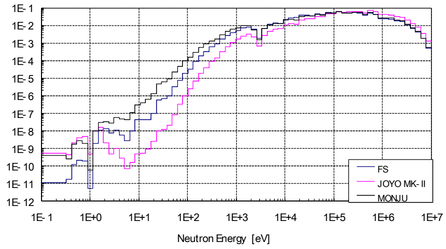


Fig. Neutron energy spectra at inner core

Irradiation result of single element by ORIGEN2.2

Composition before irradiation

	U235	U238	Pu238	Pu239	Pu240	Pu241	Pu242	Np237	Am241	Am243	Cm244
Mass(Kg)	22.3	7407.5	19.4	955	566.5	75.9	68.9	8.8	35.3	17.6	17.7

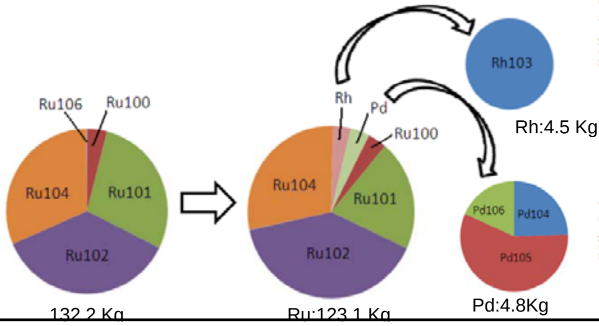
Irradiation: 800day/cycle * 4cycle
Regular checkup time between cycles: 45.5days

Analysis condition
Reactor type: FBR
Nuclear data: JENDL3.2
ENDF/B-VI
Flux: 2.27×10^{15}[n/cm^2/s]
Burn and decay chain:
ORIGEN-2/82

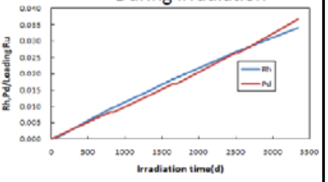
Composition of Ru after element partitioning (Cooling time: 5years)

	Ru99	Ru100	Ru101	Ru102	Ru103	Ru104	Ru106	Total
Mass(Kg)	0.0	5.3	37.5	47.7	0.0	41.5	0.2	132.2

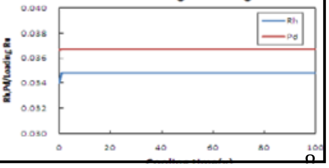
Loading: Inner core
Irradiation: 800day/cycle * 4cycle
Regular checkup time between cycles: 45.5days



During irradiation

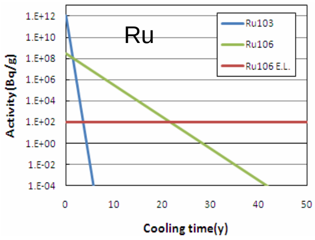


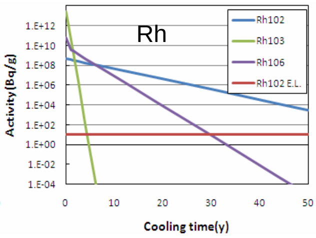
During cooling

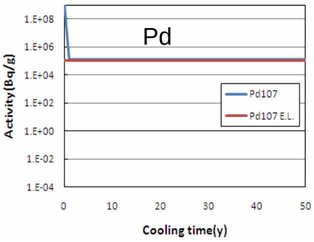


Time Dependence of Specific activity (Bq/g) by Abundance

Irradiation of FP Ru (→ Ru, Rh, Pd)



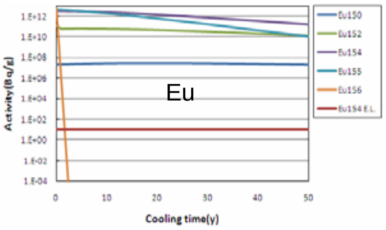


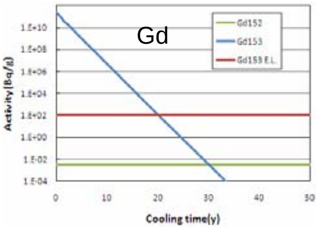


Transmutation ratio: 3.5%(shutdown)
*Very short-lived ^{102}Rh and ^{106}Rh were generated
ca. 48mg and ca.0.38μg, respectively

Transmutation ratio:3 .7%(shutdown)

Irradiation of FP Eu (→ Eu, Gd)

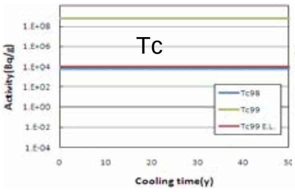


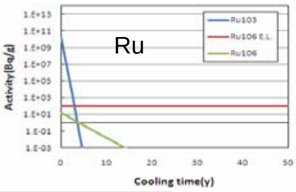


Transmutation ratio:
54.0%(Shutdown)

Time Dependence of Specific activity (Bq/g) by Abundance

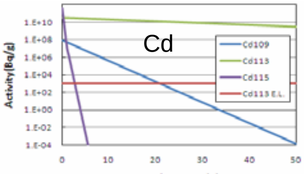
Irradiation of FP Tc (→ Tc, Ru)

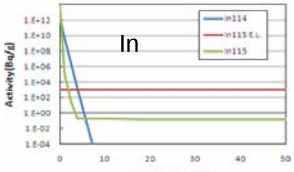




Loading Tc: 34.4kg
Shutdown: Tc 25.5kg, Ru 8.98kg
Transmutation ratio: 26.1%

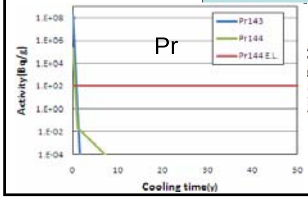
Irradiation of FP Cd (→ Cd, In)

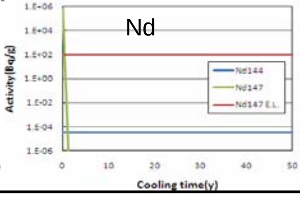




Loading Cd: 10.3kg
Shutdown: Cd 10.0kg, In $8.1*10^{-2}$kg
Transmutation ratio:0.8%

Irradiation of FP Pr (→ Pr, Nd)

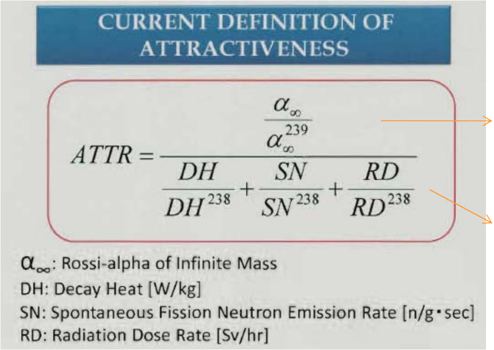




Loading Pr: 48.4kg
Shutdown: Pr 43.6kg, Nd 4.84kg
Transmutation ratio:10.0%

Index of Proliferation Resistance of ^{239}Pu

Saito's ATTR



CURRENT DEFINITION OF ATTRACTIVENESS

$$ATTR = \frac{\dfrac{\alpha_\infty}{\alpha_\infty^{239}}}{\dfrac{DH}{DH^{238}} + \dfrac{SN}{SN^{238}} + \dfrac{RD}{RD^{238}}}$$

α_∞: Rossi-alpha of Infinite Mass

DH: Decay Heat [W/kg]

SN: Spontaneous Fission Neutron Emission Rate [n/g・sec]

RD: Radiation Dose Rate [Sv/hr]

Peculiarity of Explosive Energy Release

Technical Difficulty

Rossi-α　The Rapidness of Neutron Population Change

Explosive Yield* ;　$Y(t_i) \sim \alpha^3$, $\alpha = (k\text{-}1) / l$

[k-1: super-criticality

l: prompt neutron life time]

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^{239}Pu Proliferation Resistance by Recycling of FP (Ln, etc)

- Technical Difficulty
- Detection Probability
- Material Type
- Proliferation Cost
- Proliferation Time
- Safeguards Cost

Index of Material Type(MT)
is estimated for
predominant pathway

- MA (^{237}Np, ^{241}Am)
- Rad. Ln (^{144}Ce, ^{147}Pm, ^{151}Sm, ^{154}Eu)
- ^{99}Tc (as a reference), etc

Doping

How increase of PR of ^{239}Pu ?

Estimation; Increase of interatomic distance of ^{239}Pu and decrease of atomic density (ρ) of ^{239}Pu. Might increase of critical mass of ^{239}Pu

⇒ Decrease of infinite multiplication factor (K_∞) and maximum burn-up

⇒ Decrease of Rossi-α, increase of RD and DH?, decrease of SN

Question;
- Which Ln nuclide is the most effective to affect PR?
- Are there any threhold numbers like ^{238}Pu or ^{240}Pu for doped Lns between WG- and RG-Pu?
- Is there any rational necessity to separate Lns from MA for those recycling in those point of

Conclusions

- Rare metals are inevitable in the leading industries, and thus hold the national GDP. Nuclear fission reaction will create 31 rare metals as well as energy. Now, SF and HLLW should be considered as not a waste but a new artificial ore.
- *Adv.-ORIENT Cycle has been* dealt with , chemical separation and utilization of nuclear rare metals (NRM) as the second resources.

- *Après ORIENT* will deal with **positive transmutation** to produce highly valuable & strategic elements.

  $${}_{Z}\mathbf{FP}^{A}\ (n,\gamma)\overset{\beta-}{)}\ {}_{Z}\mathbf{FP}^{A+1} \rightarrow {}_{Z+1}\mathbf{NRM}^{A+1} \Rightarrow \textbf{Strategic Utilization}$$

  where, ${}_{Z+1}\mathbf{FP}^{A+1}$ are （Ru→） Ru, Rh, Pd, （Tc→）Ru, （Cd→）In, （Pr→）Pr, Nd, etc・・・
- Proposed distribution of An and FP will be,

  Category 1; All actinide and some radioactive FP (“raw elements”, ${}_{Z}\mathbf{FP}^{A}$) for incineration / transmutation / creation in the reactor.

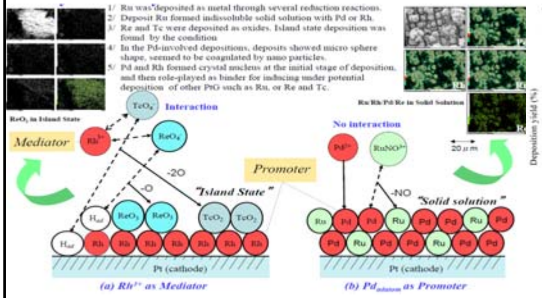
  Category 2; Valuable and stable, or acceptably less radiotoxic FP for industry .

  Category 3; Other radioactive, less valuable FPs for disposal.

  where, proliferation resistance is the key issue for Category1.
- Mo/Tc/Ru, 5th period transition metals , are considered as “raw elements” to produce highly valuable & strategic elements from the nuclear fuel cycle.

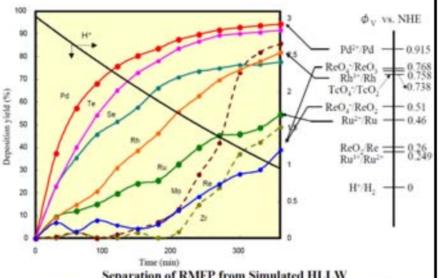
Pd_{adatom}-induced CEE, as a Separation tool for PGM/Tc/Re

- ***CEE*** **(Catalytic Electrolytic Extraction) based on UPD (Under Potential Deposition)**



1/ Ru was deposited as metal through several reduction reactions.
2/ Deposit Ru formed indissoluble solid solution with Pd or Rh.
3/ Re and Tc were deposited as oxides. Island state deposition was found by the condition
4/ In the Pd-involved depositions, deposits showed micro sphere shape, seemed to be coagulated by nano particles.
5/ Pd and Rh formed crystal nucleus at the initial stage of deposition, and then role-played as binder for inducing under potential deposition of other PtG such as Ru, or Re and Tc.

(a) Rh^{3+} as Mediator (b) Pd_{adatom} as Promoter

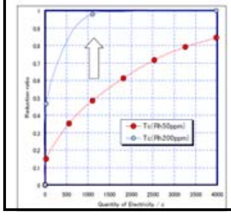


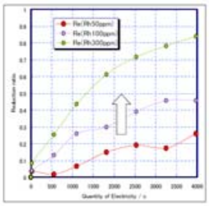
Separation of RMFP from Simulated HLLW

Galvanostatic Electrolysis ; 2.5M HNO_3, 500mA/cm² (Cathode), Room temp.
Cathode; Pt-Ti, 20cm², S/V: 1/15cm⁻¹, Pd^{2+} Addition; Continuously (2.53gPd^{2+}/hr),
Pd_{added}/Ru=3.6, Pd_{added}/Rh=16.0, Pd_{added}/Re=9.1

- **Extension of *CEE* in HCl Media**

CEE Conditions
- Electrodes; Smooth Pt , Cathode (2cm²) , Anode (8cm²) , Ag/AgCl
- Catholyte; 0.5MHCl
- 50 ℃
- Ic: 2.5mA/cm² (1hr) → 75mA/cm² (2hr) → 100 mA/cm² (4hr)

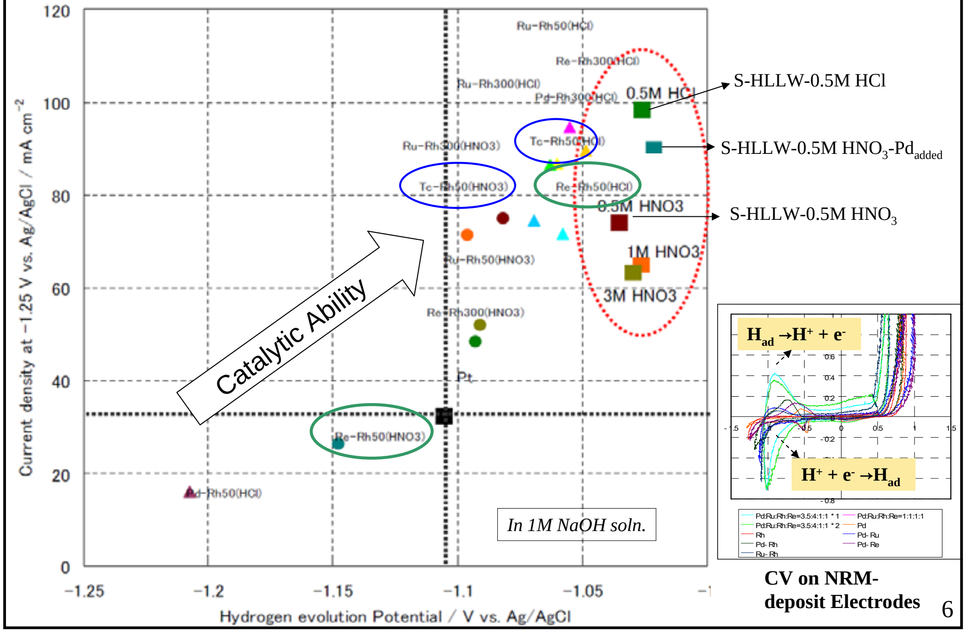




- **Recovery of *PGM/Tc* in HCl Media**

Run	RMFP	Reduction Ratio (%) Pd	Ru	Rh	Re	Tc
1	Pd	97.8	—	—	—	—
2	Ru	—	17.6	—	—	—
3	Rh	—	—	90.2	—	—
4	Re	—	—	—	13.2	—
5	Tc	—	—	—	—	57.5
6	Pd-Ru	>99	>99	—	—	—
7	Pd-Rh	99.1	—	98.9	—	—
8	Pd-Re	99.1	—	—	17.6	—
9	Ru-Rh	—	99.2	93.5	—	—
10	Ru-Re	—	6.8	—	11.3	—
11	Rh-Re	—	—	92.2	41.6	—
12	Rh-Tc	—	—	>99	—	99.7
13	Pd-Ru-Rh-Re(3.5:4:1:0.5)	>99	83.3	>99	91.4	—
14	Pd-Ru-Rh-Tc(3.5:4:1:0.5)	>99	86.9	>99	—	68.9

PGM, Tc, Re Deposits as Catalysts for Electrolytic H_2 Production



CV on NRM-deposit Electrodes

Lessons learned in the Past Research (Adv.-ORIENT Cycle) on Utilization of NRM-deposit Electrodes

1) Highest catalytic reactivity has been assigned to the quaternary deposit (Pd-Ru-Rh-Re (3.5:4:1:1)) electrode, in electrolysis either in NaOH or artificial sea water (Global2007).
2) Noblest $\varphi H_{init.}$ (>-1.05V) was observed on NRM deposit electrodes from S-HLLW (HCl, HNO_3)
3) Energy consumption of such electrodes on H_2 production was about half of smooth Pt electrode, specifically in artificial sea water (*ibid*.).
4) Those (including the deposit from S-HLLW) reactivity surpassed that of Pt-black electrode as well as smooth Pt (*ibid*.).
5) A high reactivity would attribute to higher numbers of Ru and Rh atoms at the surface (Global2007, 2009). Higher adsorption sites for H^+ by them was responsible.
6) Pd was independent of such a reactivity, but caused UPD by Pd_{adatom}.
7) Tc showed the same or higher reactivity than that of Re, in/off the combination with Rh (*ibid*.).