Separation of Rare Metal Fission Products in Radioactive Wastes in New Directions of Their Utilization

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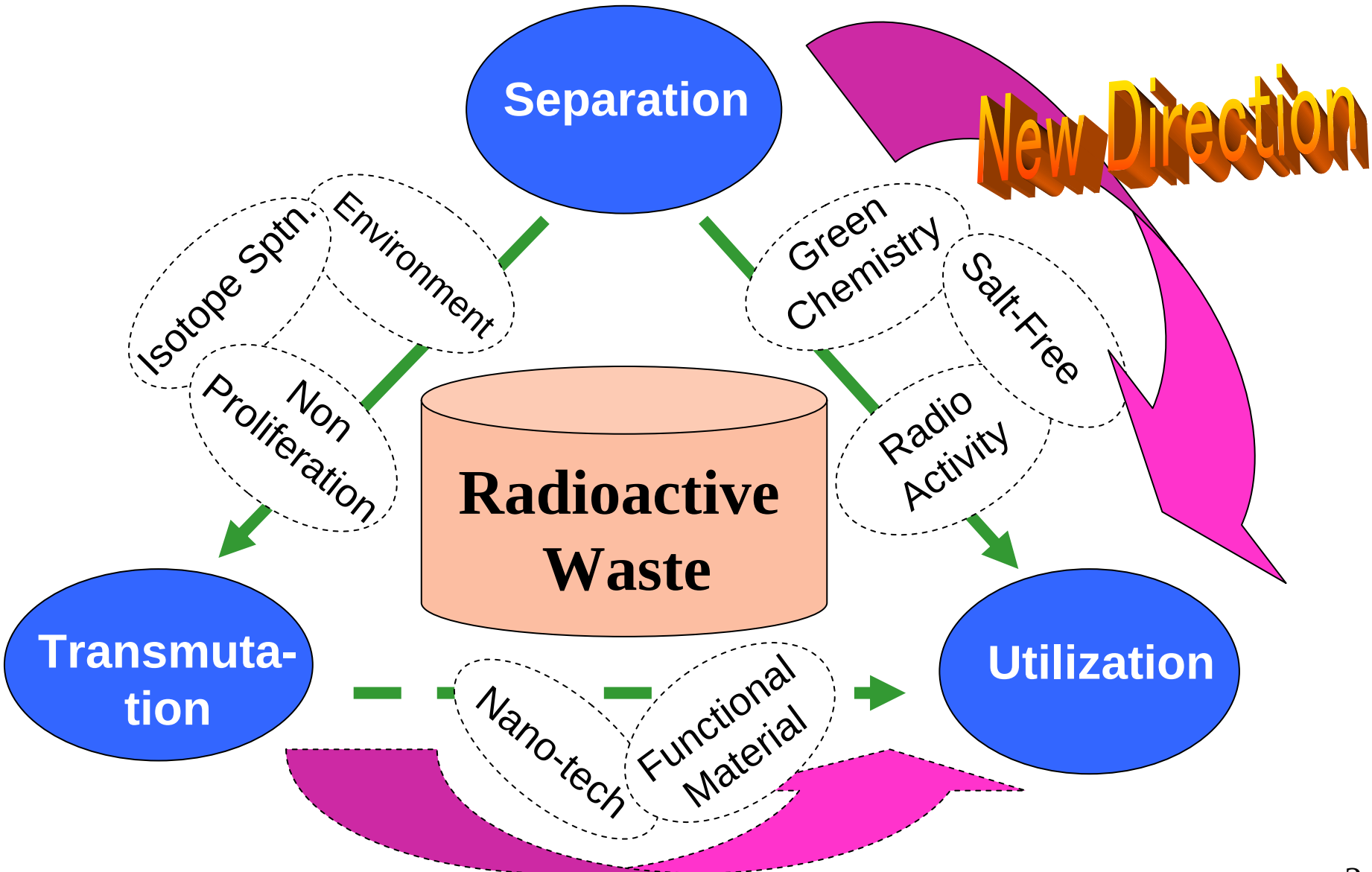
JAPAN

Separation, Transmutation and Utilization



Fuel Cell

One of the Essential Issues on the Practicability of Fuel Cell is Cost Minimization by Decreasing Consumption of Platinum Element Catalysts; News , 27 July., 2001.

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資エ庁の「燃料電池実用化戦略研究会」
来年度予算要求控え報告書の再吟味へ

資エ庁長官の私的研究会「燃料電池実用化戦略研究会」は来月八日に会合を開き、この場で一月にまとめた燃料電池実用化・普及への課題等に係わる報告書内容をさらに煮詰めることとした。来年度予算要求時期を控え燃料電池の普及促進を図るための具体的施策を整理することが目的。

燃料電池戦略研究会は燃料電池導入の意義を明確化するとともに、その実用化に向けた課題の抽出と課題解決の方向性を探るため昨年十二月に発足したもの。

同研究会が一月にまとめた報告書では▽燃料電池の実用化・普及に向けた課題は燃料電池本体（スタック）改質器、水素燃料貯蔵、全体システム等について、高効率化、耐久性等の向上に向けた技術開発が必要▽特に固体高分子電質膜製造の低コスト化、白金触媒の使用量低減による低スト化等が課題▽触媒に使用される希少な資源の制約、体高分子電解質膜に使用されるフッ素系化合物について廃棄・処分の問題、社会的受容性の醸成・向上、研究開に携わる人材不足への対応が必要▽燃料電池の燃料となる水素をどのように製造・供給するかが、その燃料供給インフラの整備と合わせて大きな課題ー等としている。

て試験に入る予定。

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択捉島に希少金属

火山ガスから抽出

【モスクワ＝五十嵐弘一】北方領土・択捉島北部のクドリャブイ火山で、ロシアの研究者グループが十日までに、火山ガスから希少金属レニウムの抽出に成功した。作業を指揮したロシア火山・地球力学研究所（サハリン島・ユジノサハリンスク）のゲンリフ・シティンベルク所長が同日、本紙の電話取材に対して明らかにしたもので、当面、同研究所が年間約五百キロのレニウム生産を開始する予定。

レニウムの世界全体の年間生産量は二十五トンから三十トンとされるが、シティンベルク所長は、「産業化に必要な技術はこれまでに開発済み。市場の需要次第だが、理論的には、年間二十トン程度の生産が可能」としている。同所長によると、ロシアではレニウムは産出されず、将来、北方領土の返還問題に影響する可能性もある。

シティンベルク所長によると、特定のガス噴出口にドーム型の火山ガス吸収装置を設置。新技術を用い、最終的に固形物として分離・抽出することができたという。レニウムの市場価格は一キロ当たり千二百―千四百ドル（約十四万四千円―十六万八千円）で、チリやカナダが主な生産国。

レニウム 領土問題に影響も

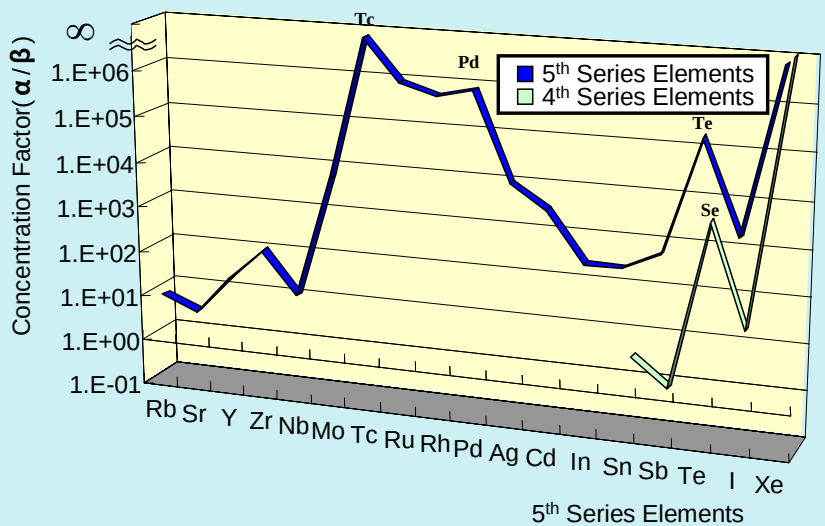
レニウム 原子番号75の希少金属。融点が3180度と、タングステンに次いで高く、これを混ぜた合金は耐熱性に優れる。ロシアでは、石油精製の触媒や、ロケット、航空機のエンジン素材として用途が注目されている。

Re Resource

Russia extracted Re (ReS_2?) from Volcano gas of Kudryavy at Etorohu Island. Annually 500 kg (possible max.20 ton) of Re will be produced; News , 11 Sep., 2003.

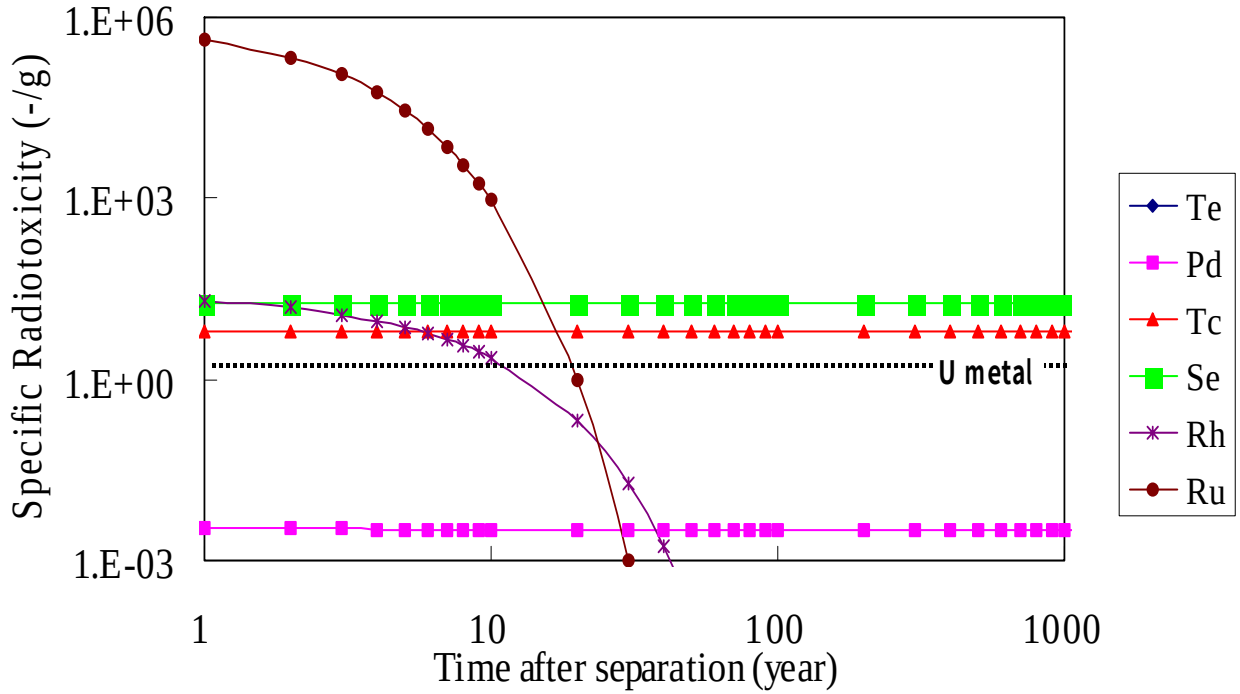
Rare metal	Ru	Rh	Pd	Tc	Te	Se	Note
Amount (kg/HMt)	12.5	3.6	11.1	3.3	2.7	0.2	FBR-SF;150,000MWd/t, Cooled 4 years.

Spent Nuclear Fuel, As an Artificial Ore



α: Elements in the FBR-S.F. (g/t), β: Elements in the Earth Crust (g/t)

Fig. Specific Radio Toxicity（Hazard Index）of RMFP in FR Spent Fuel after 4 years cooling.



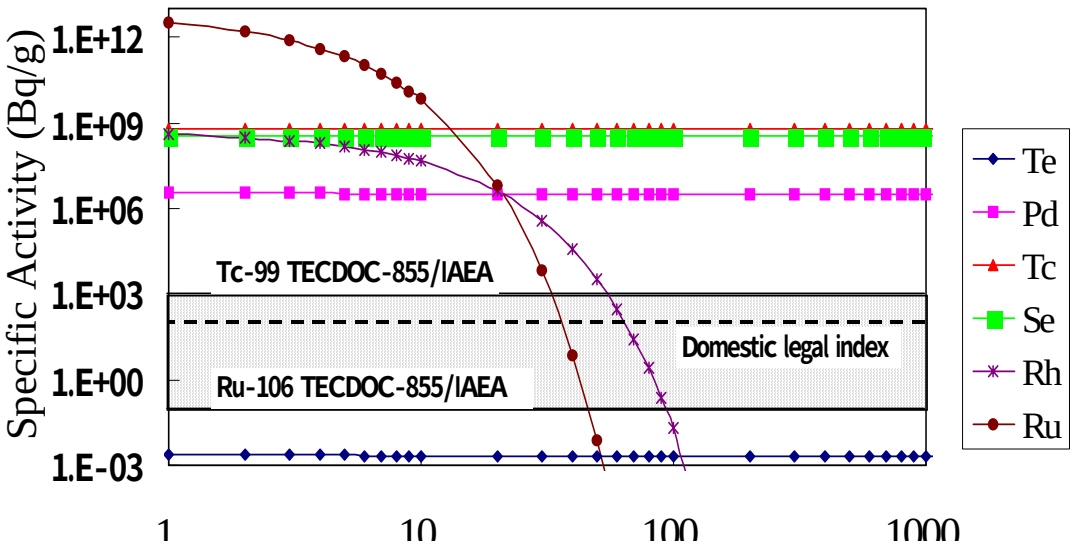


Fig. Time Dependency of Specific Activities of RMFP Separated from the FBR Spent Fuels cooled for 4 years

"Clearance levels" are proposed by IAEA"TECDOC-855" from 10^{-1} to 10^{3} Bq/g, for instance,
0.1≦Ru-106 <10、100≦Tc-99<1000 (as for reference, 74 Bq/g , Japan domestic legal index).

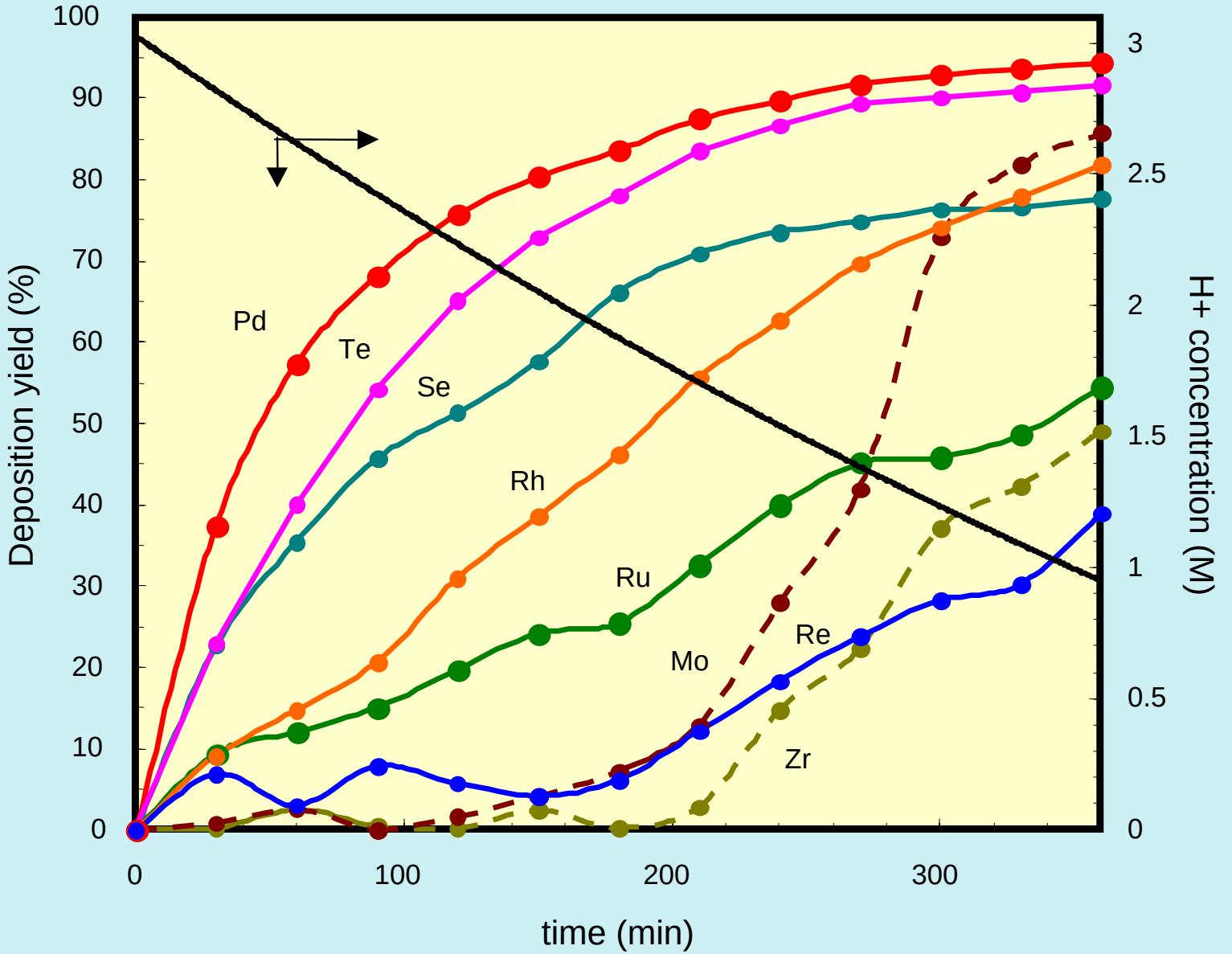
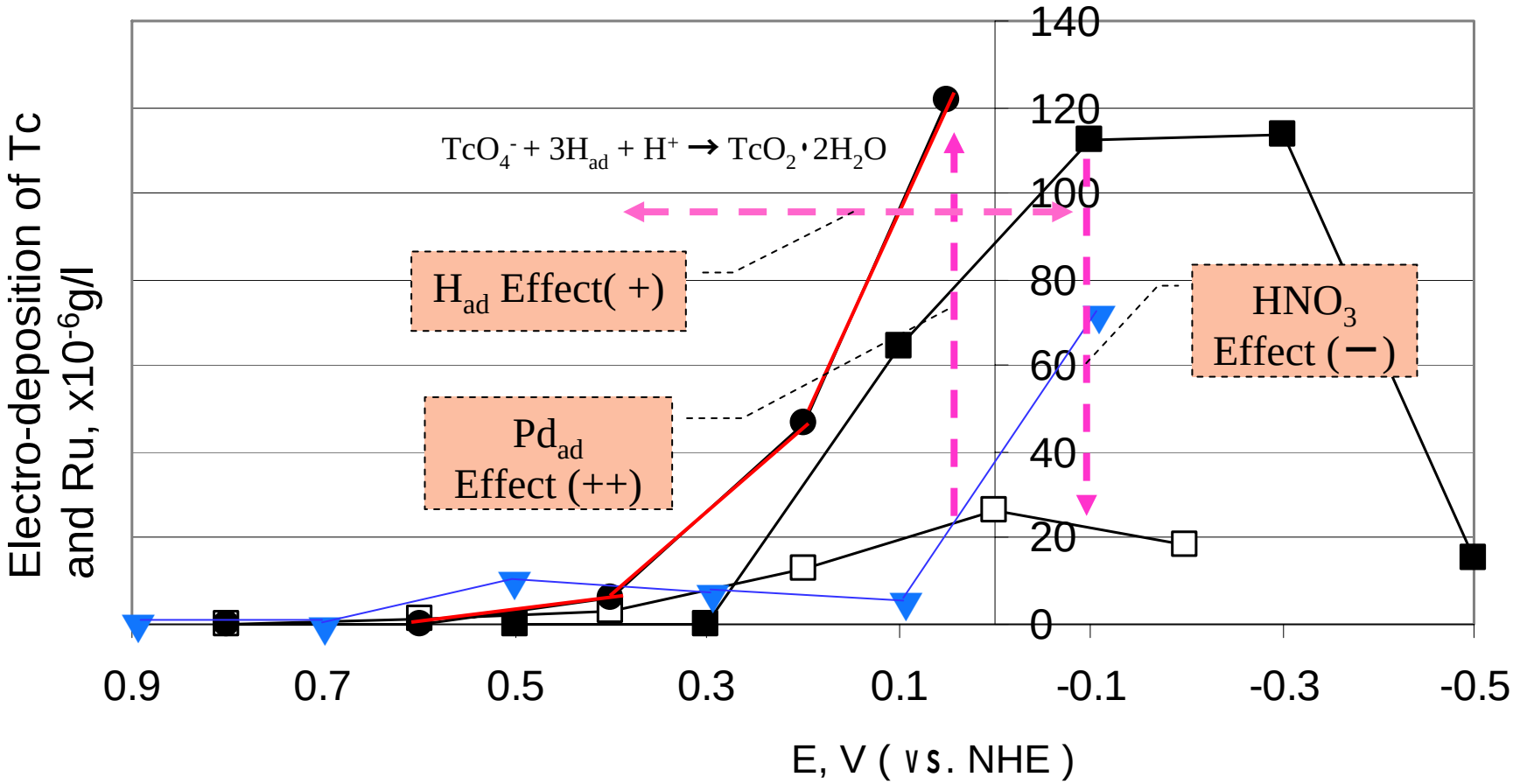


Fig. Catalytic Electrolytic Extraction of RMFP from Simulated HLLW

Galvanostatic Electrolysis ; 500mA/cm^2 (Cathode), Room temp. Cathode; Pt-Ti, 20cm^2, 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

Effect of CEE (II) ; Tc



■ - 0.1 g/l Tc, pH=4 (1st run)
□ - 0.1 g/l Tc, 0.5 M HNO_3 (2nd run)
● - 0.1 g/l Tc, 2.0 M HNO_3, 0,5 g/l Pd (3rd run)
▼-0.25g/lRu, 2.5MHNO_3

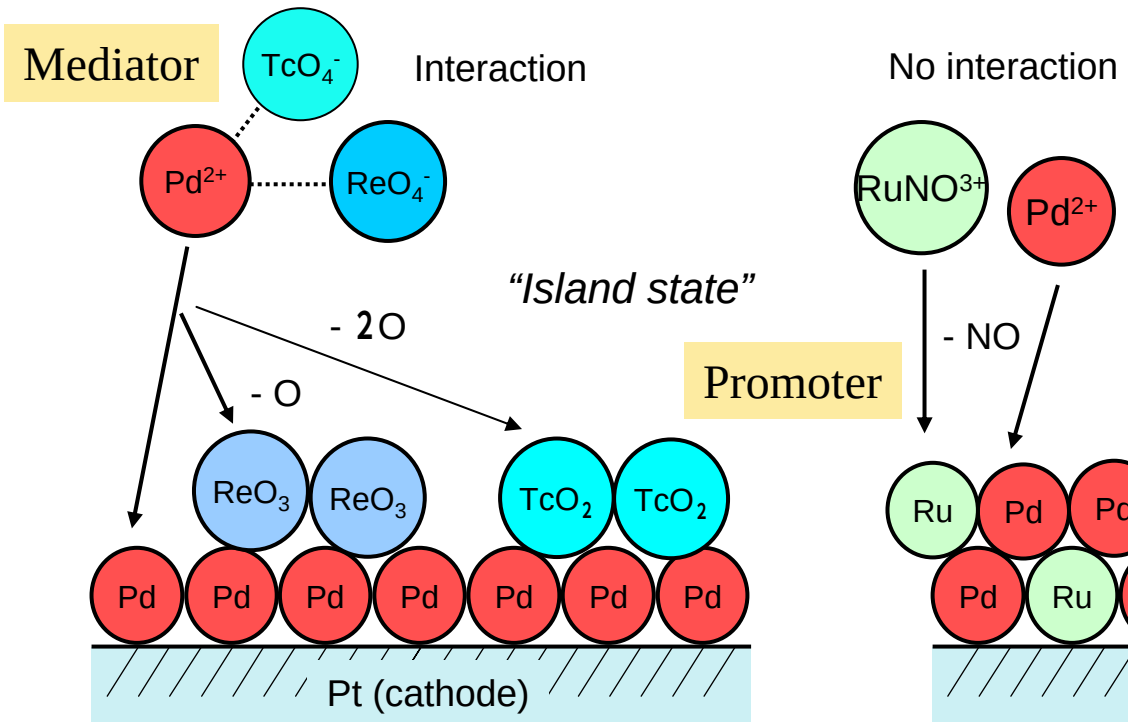
Fig. Acceleration of Electro-deposition of TcO_4^- by Addition of Pd^{2+}
Data obtained by KRI through JNC-KRI Collaboration 2003

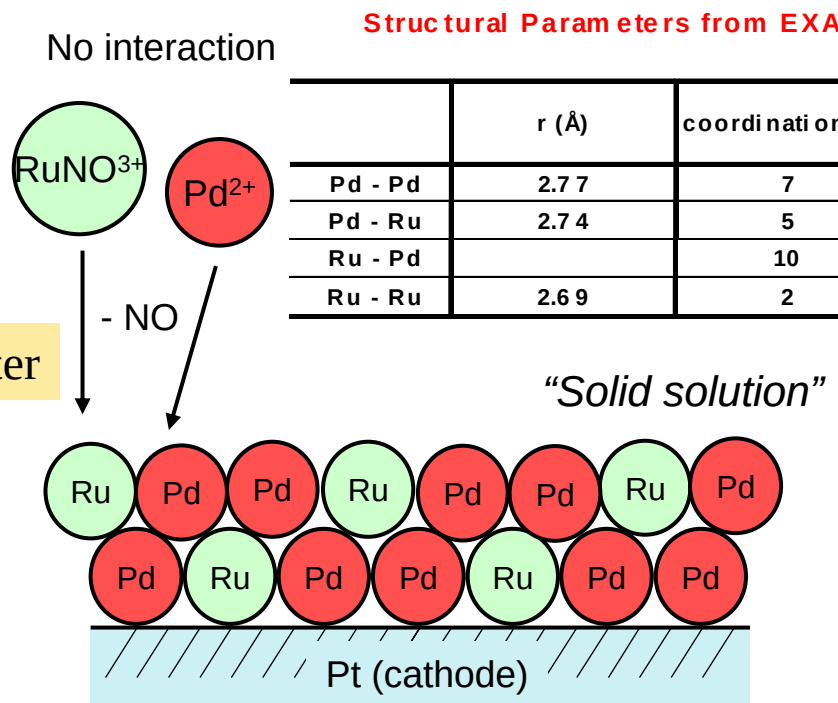
Deposition of Tc or Re with Pd

- Interaction between TcO_4^- or ReO_4^- and Pd^{2+} in the bulk solution
- Deposition of ReO_3 and Pd on the cathode
- No change of the deposition potential for Re from the mono ionic solution of Re

Deposition of Ru with Pd

- No interaction between $RuNO^{3+}$ and Pd^{2+} in the bulk solution
- Deposition of Ru-Pd alloy on the cathode
- Decrease of the deposition potential for Ru comparing to that in the mono ionic solution of Ru





Structural Parameters from EXAFS Curve Fitting

	r (Å)	coordination no.	Calculation with metallic bonding radius (Å)
Pd - Pd	2.77	7	2.76
Pd - Ru	2.74	5	2.71
Ru - Pd		10	
Ru - Ru	2.69	2	2.66

Fig. Model of Catalytic Electrolytic Extraction

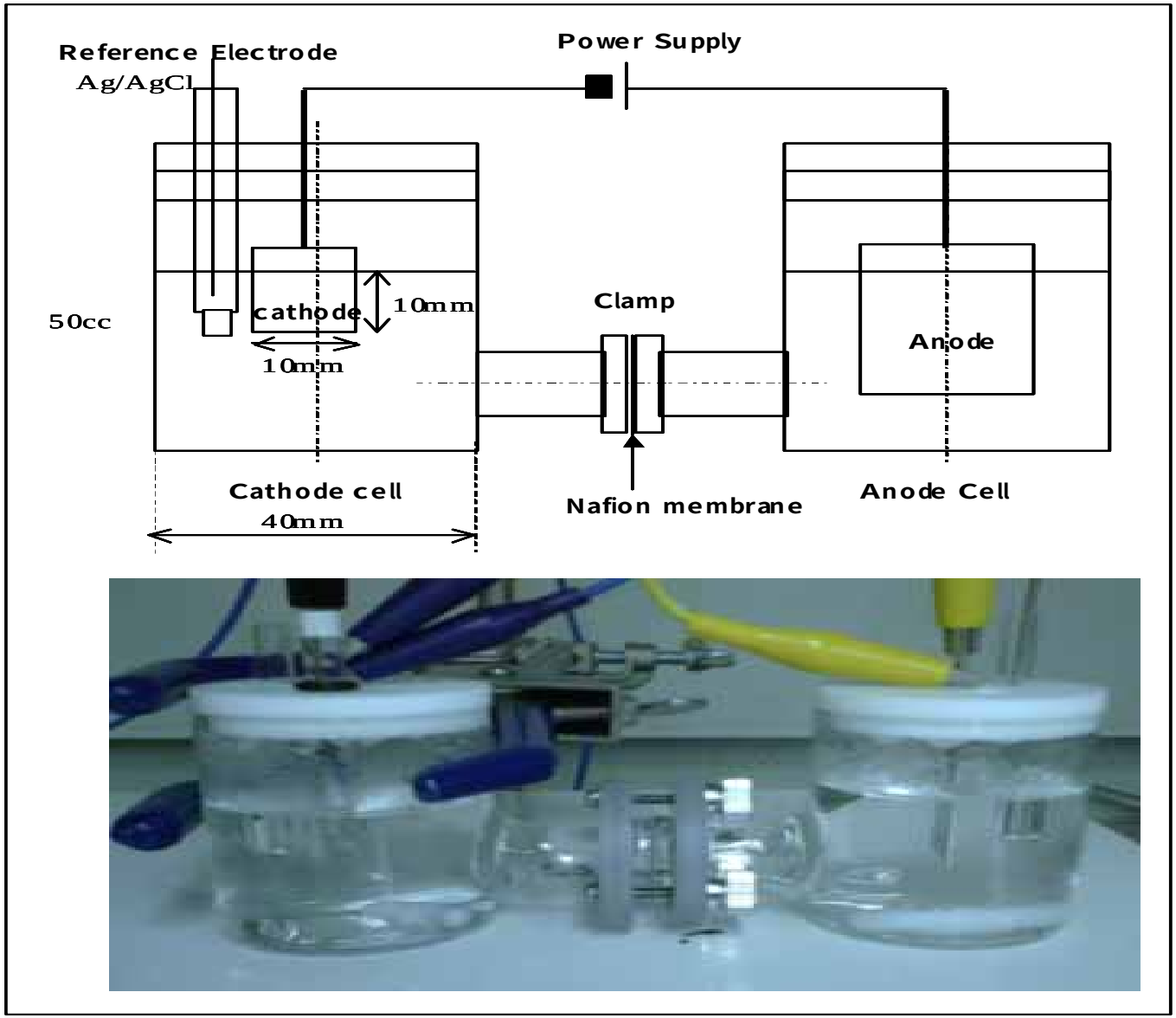


Fig. Experimental Cell

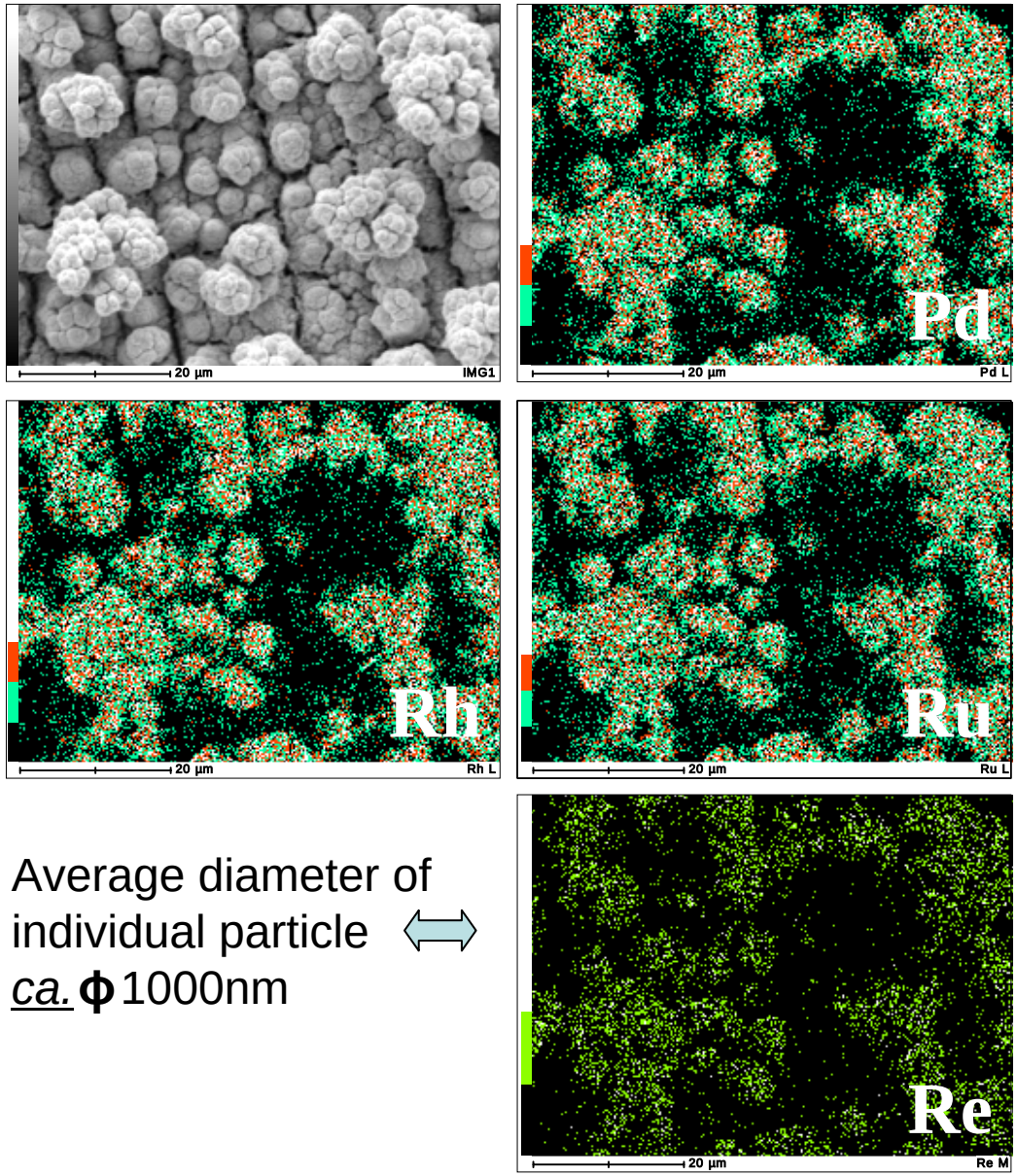
Table Reduction Ratios by Catalytic Electrolytic Extraction

System	Reduction ratio / %					Composion on electrode Surface
	Pd	Ru	Rh	Re	Tc	
Pd	>99	-	-	-	-	-
Ru	-	14	-	-	-	-
Rh	-	-	>99	-	-	-
Re	-	-	-	16	-	-
Tc	-	-	-	-	1.7	-
Pd-Ru	99.3	60.9	-	-	-	Pd Ru
Pd-Rh	99.0	-	84.7	-	-	Pd Rh
Pd-Re	99.4	-	-	10.0	-	Pd>Re
Ru-Rh	-	58.2	32.5	-	-	Ru Rh
Ru-Re	-	14.5	-	13.5	-	Ru>Re
Rh-Re	-	-	10.0	43.0	-	Rh>Re
Pd-Ru-Rh-Re(1:1:1:1)	95.7	46.0	14.5	19.0	-	Pd Ru Rh>Re
Pd-Ru-Rh-Re(3.5:4:1:1)*	99.0	11.8	2.10	33.4	-	Pd Ru Rh>Re
Pd-Ru-Rh-Re(3.5:4:1:1)*	94.7	16.5	26.6	55.3	-	Pd Ru Rh>Re

*1：Pd block addition

*2：Pd 5 divided additon

(×2000)



Average diameter of individual particle *ca.* Φ1000nm

Fig. EDS(EPMA) of the deposits on the Pt Electrode from Nitric Acid Solution ; Soln. Composition : Pd-Ru-Rh-Re(3.5:4:1:1), Divided Addition of Pd^{2+}

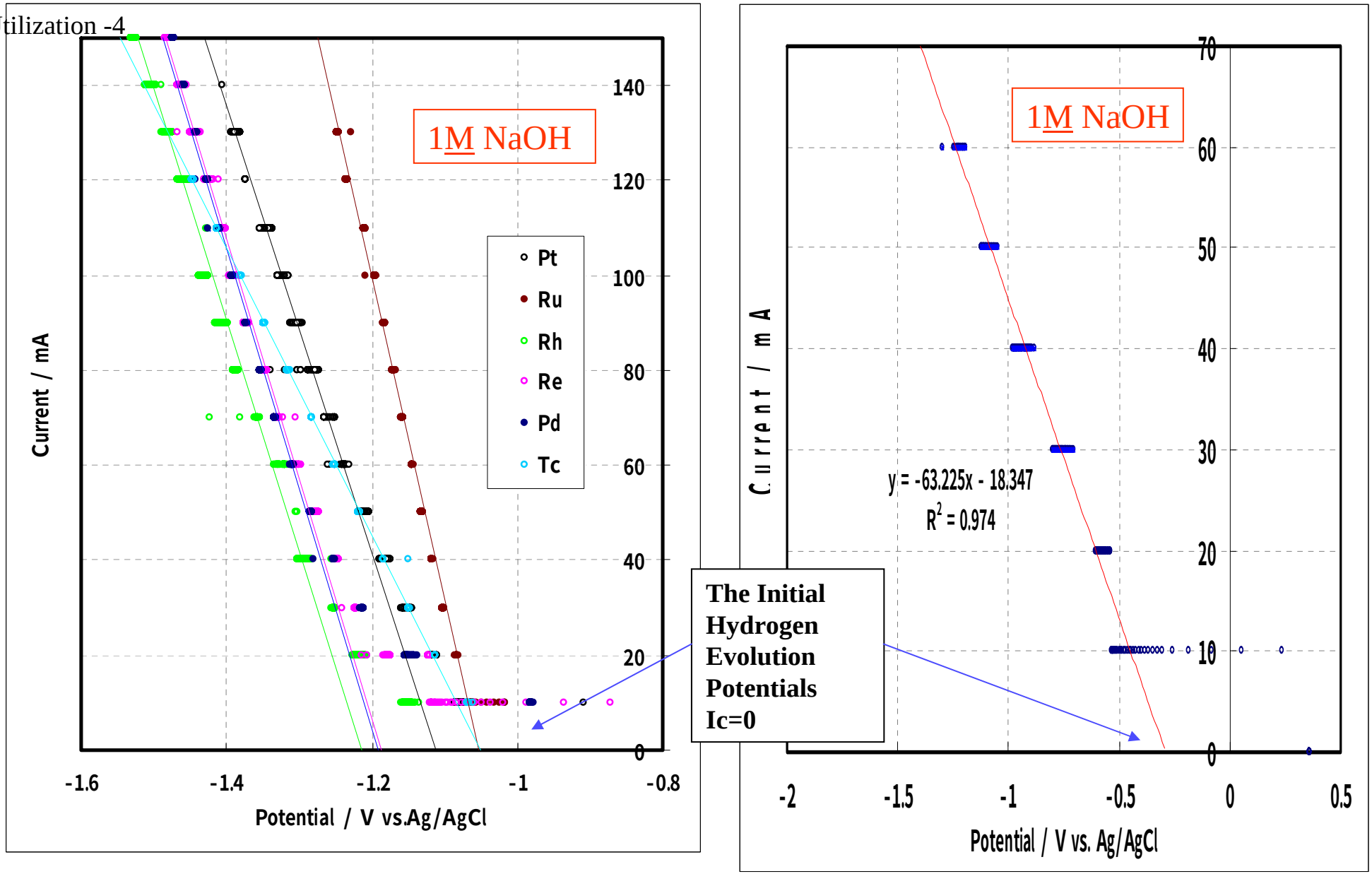


Fig. The Cathodic Polarization Curves of Pd, Ru, Rh, Re and Tc deposit Pt Electrodes and Pt Electrode *(left)*, and Pd-Ru-Rh-Re deposit Pt Electrode* *(right)* *Soln. Composition : 3.5:4:1:1, Pd^{2+} Divided Addition

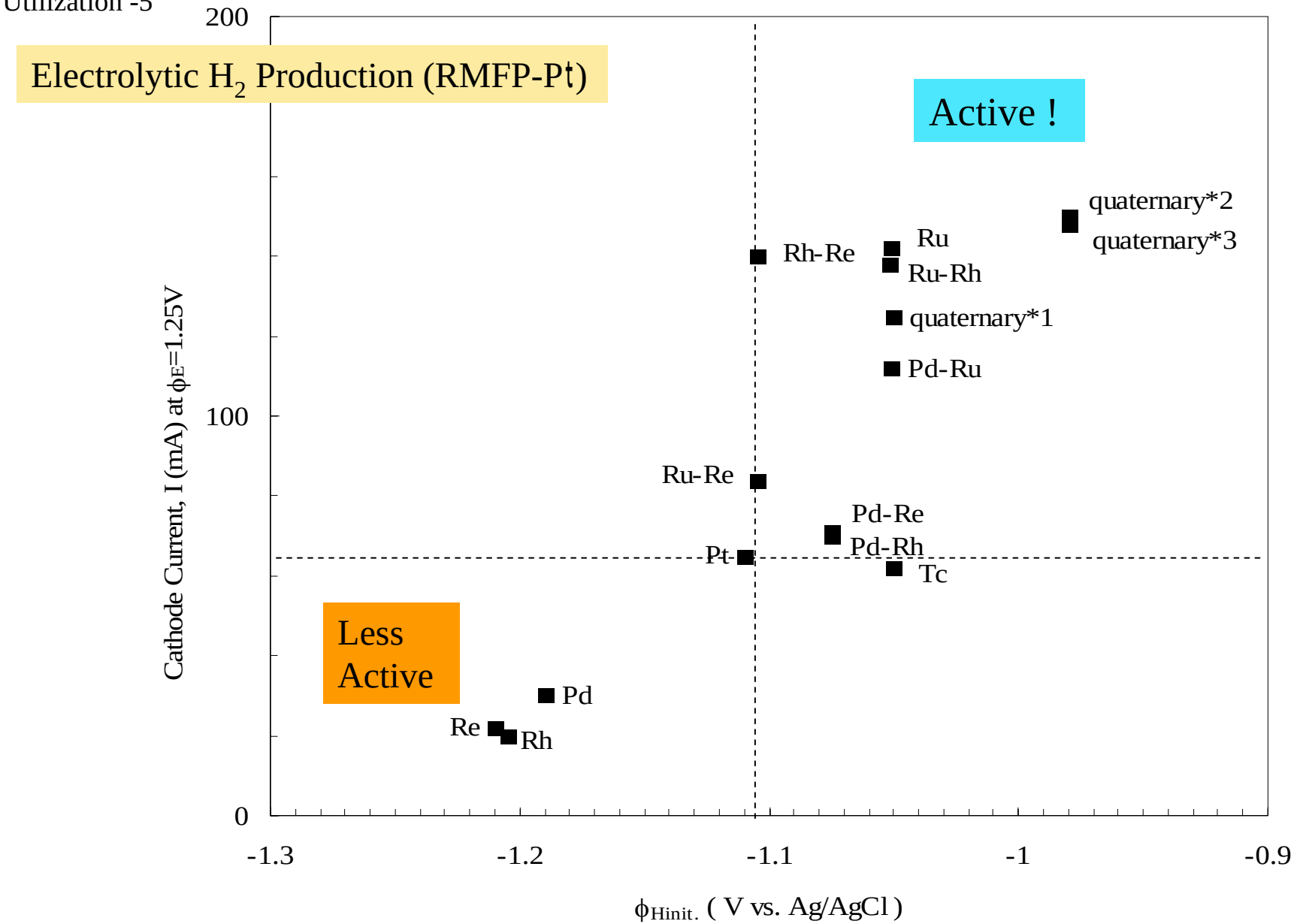


Fig. Relation between Cathodic Current Corresponds to Hydrogen Evolution at -1.25V and Initial Hydrogen Evolution Potential ($f_{Hinit.}$) on each Deposit Electrode in 1M NaOH.

Deposits from the quaternary ionic solution; *1, Pd:Ru:Rh: Re=1:1:1:1, *2, Pd:Ru:Rh:Re=3.5:4:1:1(Pd^{2+} bloc addition), *3, Pd:Ru:Rh:Re= 3.5:4:1:1(Pd^{2+} divided addition)

Electrolytic H_2 Production (RMFP-Ti)

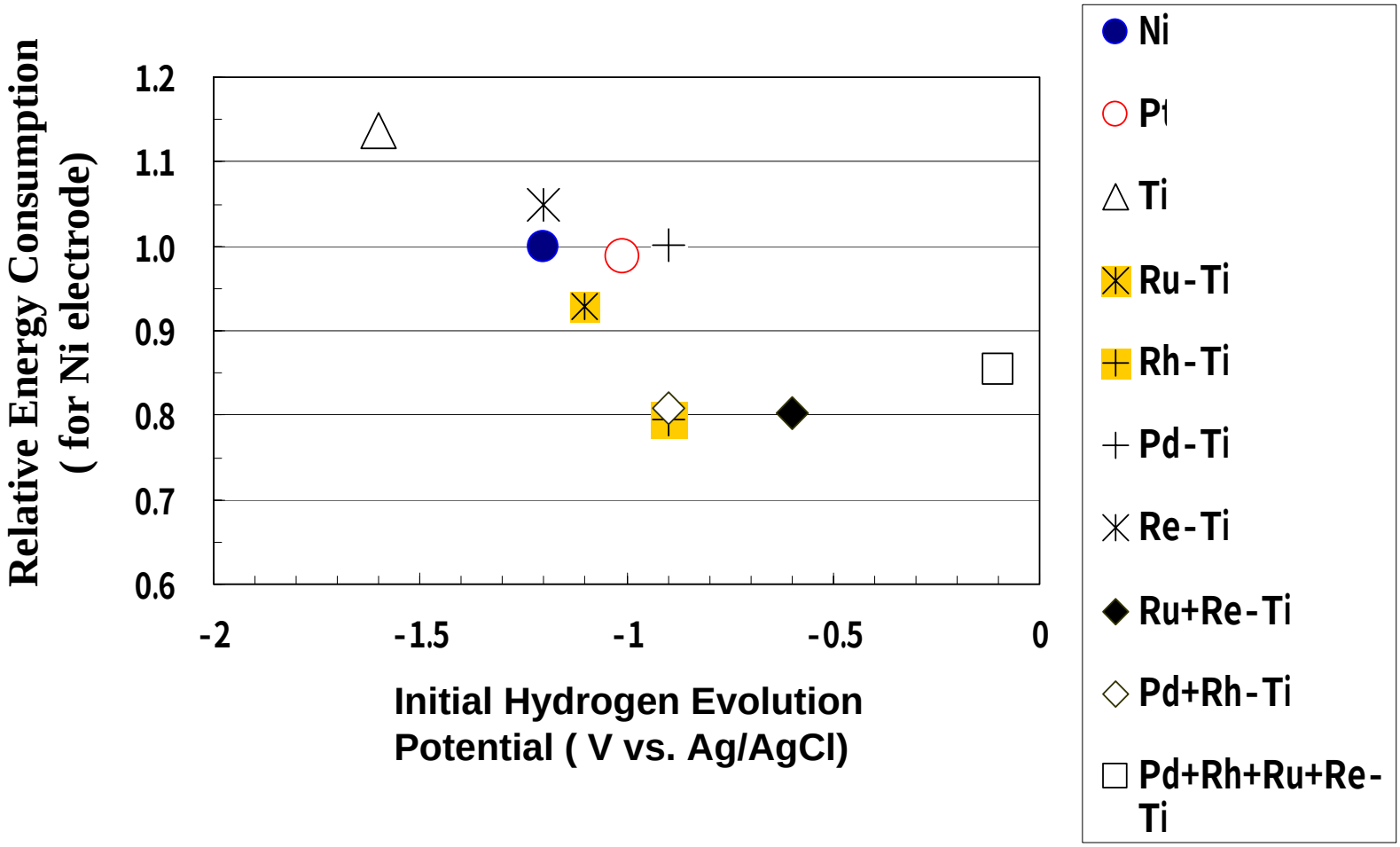
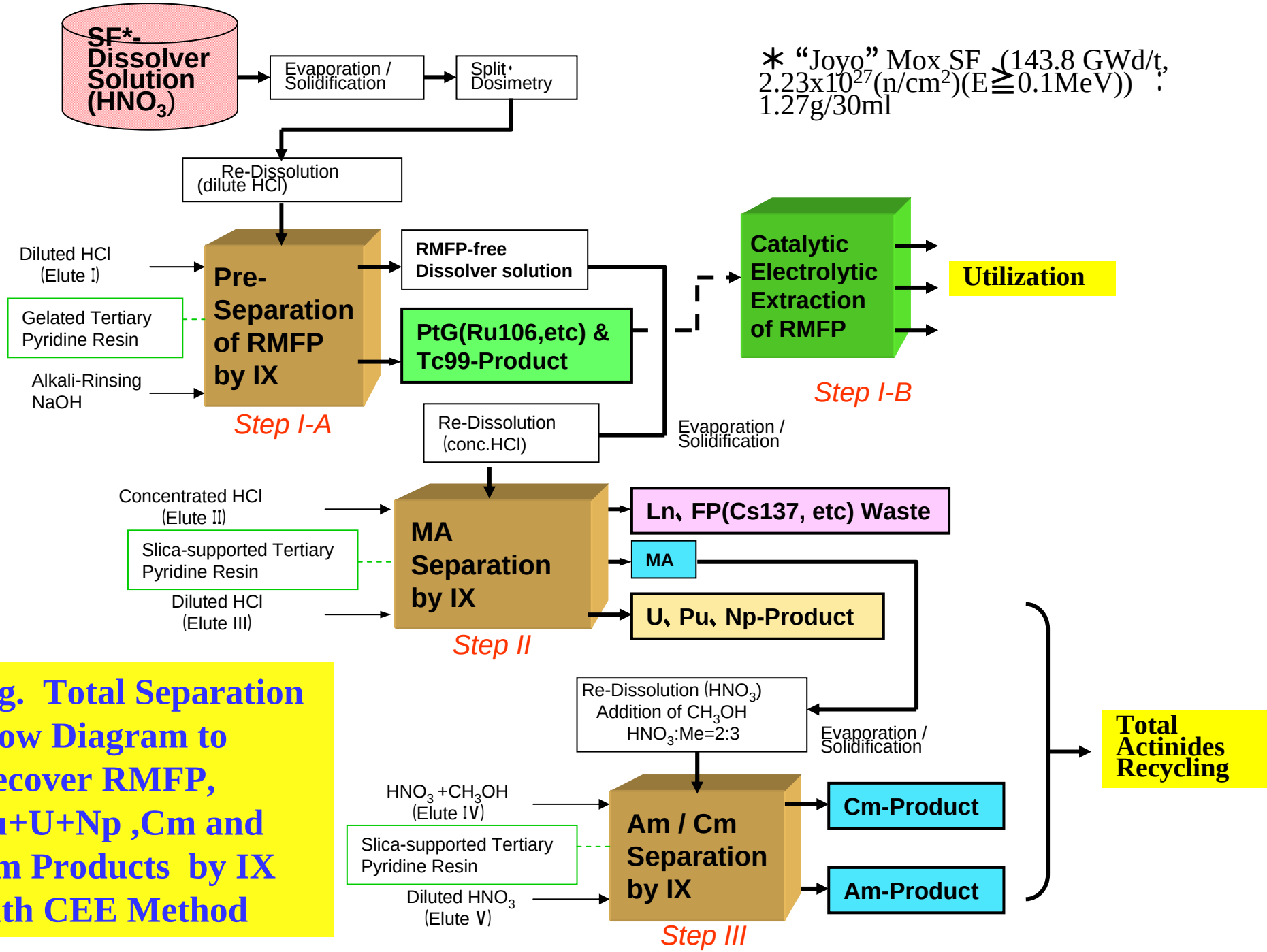


Fig. Energy Consumption for Electrolysis of 1M NaOH, in the case of RMFP deposit Ti Electrodes



＊ "Joyo" Mox SF (143.8 GWd/t, 2.23×10^{27}(n/cm^2)(E≧0.1MeV)) : 1.27g/30ml

Fig. Total Separation Flow Diagram to Recover RMFP, Pu+U+Np ,Cm and Am Products by IX with CEE Method

Direction -2

	(Bq)	(%)
Am 241	9.88E+4	100
Eu 155	6.10E+4	100
Ce 144	1.24E+5	100
Sb 125	1.07E+4	100
Ru 106	**2.76E+4**	**100**
Cs 137	7.18E+5	100

SF Dissolver Solution 0.5M HCl

＊"Joyo" Mox SF (143.8 GWd/t, 2.23×10^{27}(n/cm^2)(E ≧0.1MeV)) : 1.27g/30ml

Pre-Filtration

Gelated Tertiary Pyridine Resin

H_2O Rinsing

1M NaOH Rinsing

(Water-rinsed Resin)

Am 241	4.77E+1	0.05
Eu 155	2.59E-1	0.00
Ce 144	-	0.00
Sb 125	4.26E-2	0.00
Ru 106	**-**	**0.00**
Cs 137	3.27E+2	0.05

Am 241	7.16E+0	0.01
Eu 155	3.28E+0	0.01
Ce 144	1.70E+1	0.01
Sb 125	1.17E+3	10.9
Ru 106	**5.51E+2**	**2.00**
Cs 137	1.19E+1	0.00

Am 241	-	-
Eu 155	-	-
Ce 144	-	-
Sb 125	9.86E-5	0.00
Ru 106	**-**	**-**
Cs 137	-	-

(Alkaline soln.- rinsed Resin)

Am 241	2.76E+0	0.00
Eu 155	-	0.00
Ce 144	-	0.00
Sb 125	1.45E-1	0.00
Ru 106	**-**	**0.00**
Cs 137	-	0.00

Ru106- free Feed D.S.＊

Am 241	7.28E+2	≫0.74
Eu 155	3.16E+4	>51.8
Ce 144	5.36E+4	>43.2
Sb 125	3.57E+2	>3.34
Ru 106	**-**	**0.00**
Cs 137	5.01E+5	>69.8

＊Σγ (FP,Pu fractions, excluding MA fraction)

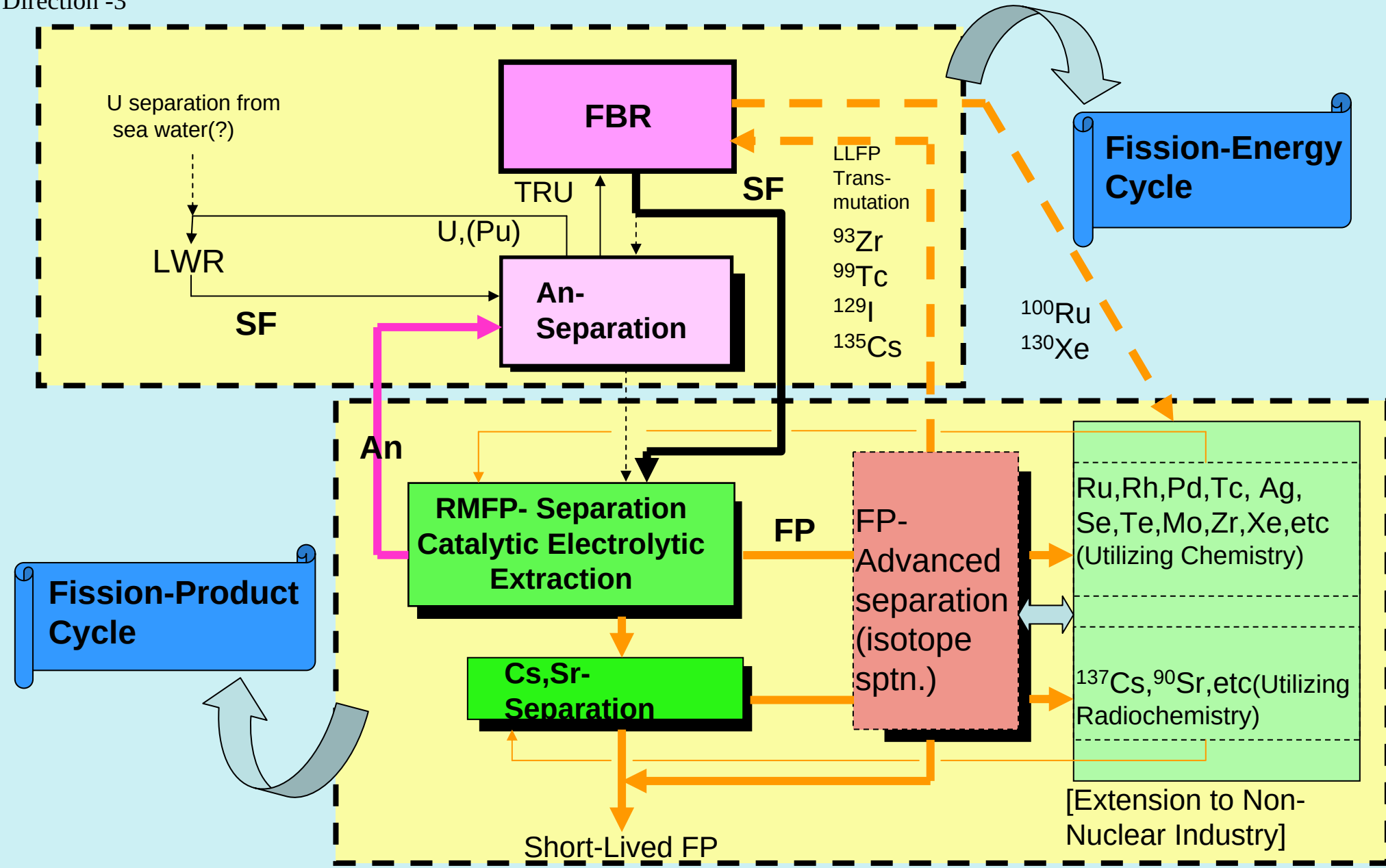


Fig. New Back-End Concept ; *Fission-Energy Cycle* and *Fission-Product Cycle*

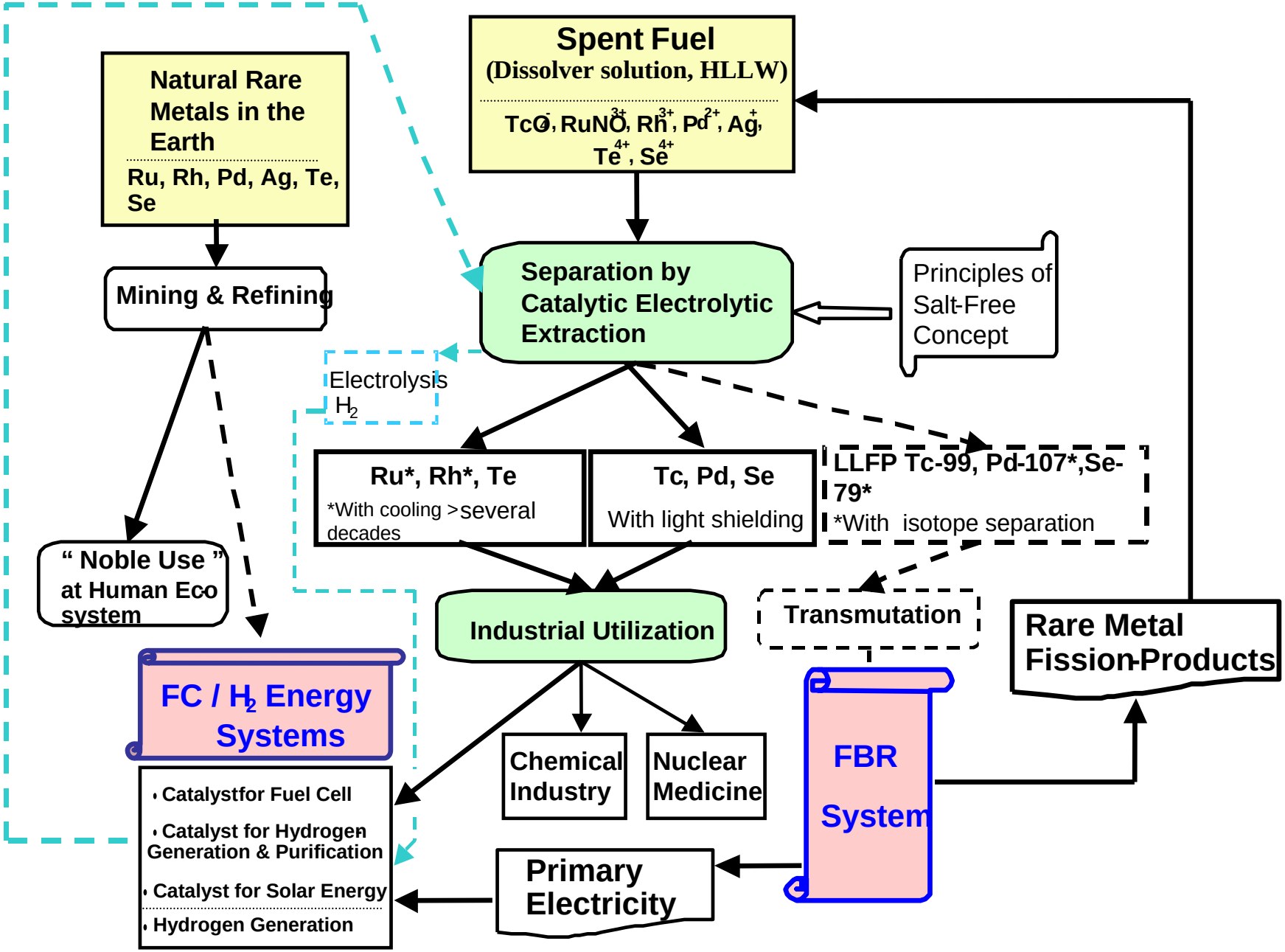


Fig. Symbiotic Energy System by Hydrogen and Nuclear, Bridging by RMFP

Conclusions

Separation and Fabrication

- Abundance of RMFP (Ru, Rh, Pd, Tc, Se, Te) in Spent Fuel
- Applicable of Catalytic Electrolytic Extraction (CEE) Method

Utilization

- RMFP as Catalysts of H_2 Production and Fuel Cell
- Excellent Ability of Quaternary, Pd-Ru-Rh-Re deposit Pt or Ti electrodes for Electrolysis of either Alkaline or Sea Water
- Expectation of ^{99}Tc and Re in this direction of Utilization

Strategic View

- Symbiotic Energy System by hydrogen and Nuclear, bridging by RMFP
- New Distribution of Precious Rare Metal
  Natural RM ⇒ "Noble" Use, RMFP ⇒ Industrial Use
- New Back-End Fuel Cycle
  Fission-Energy cycle and *Fission-Product cycle*

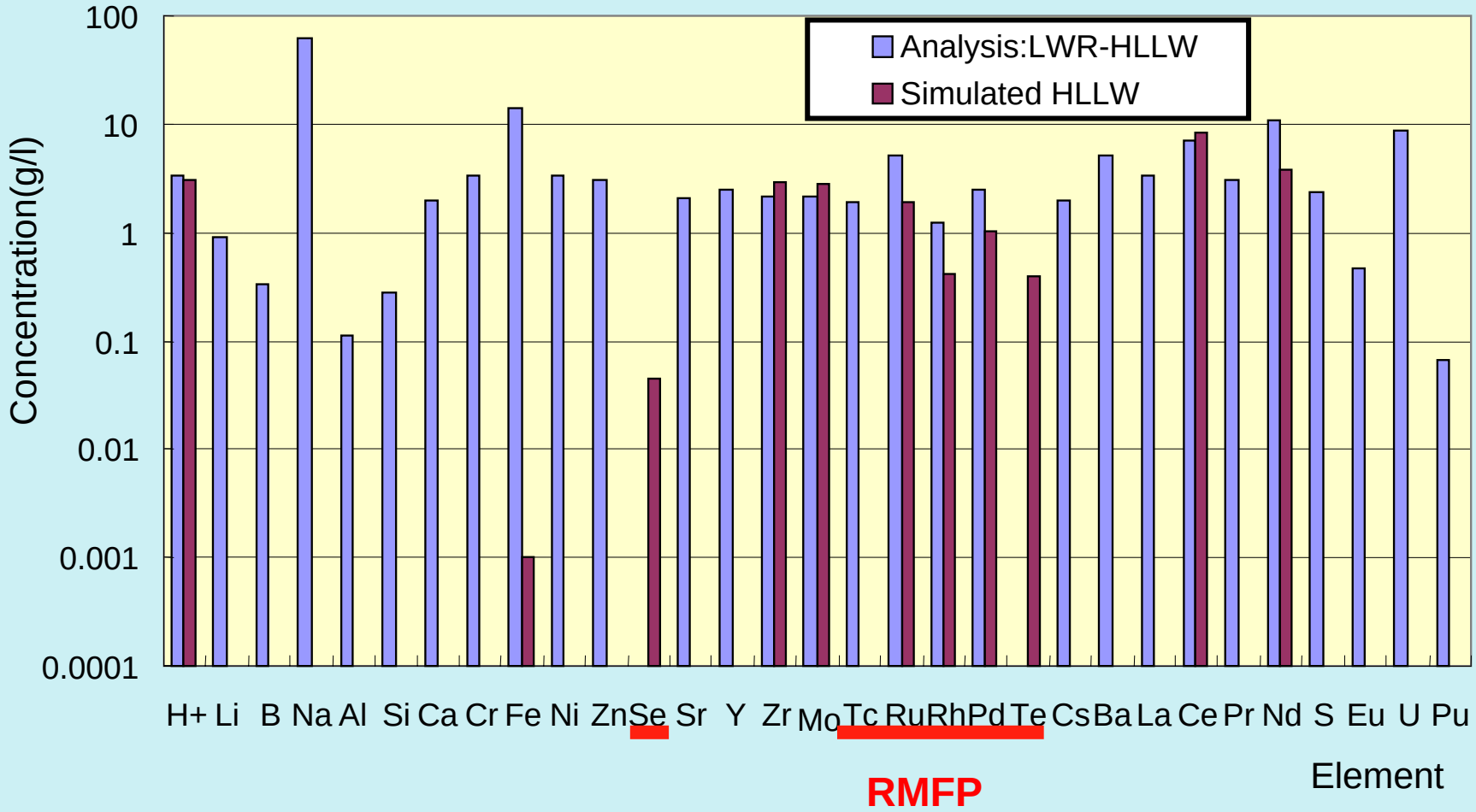
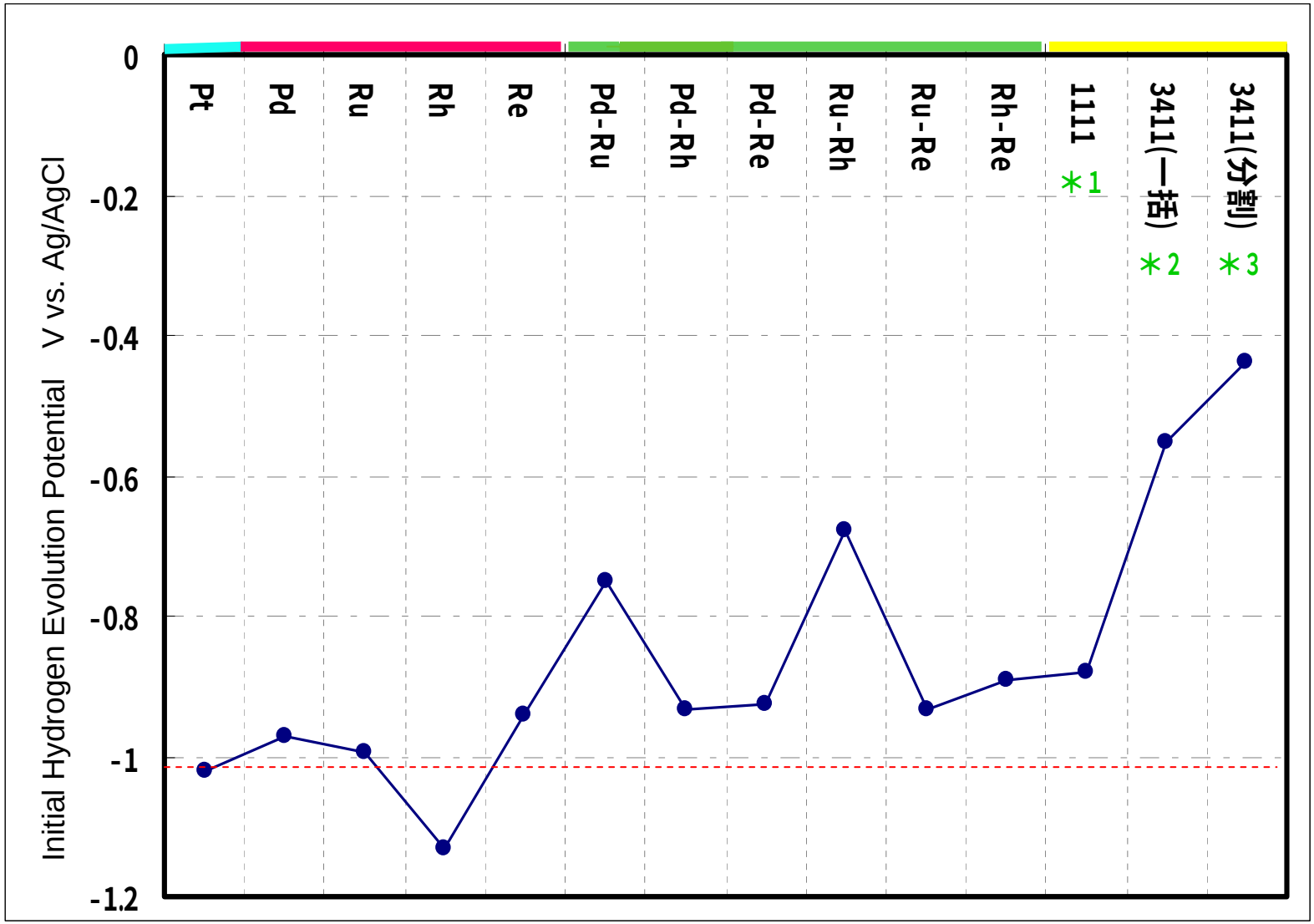


Fig. Elemental Composition of High Level Liquid Waste (HLLW)

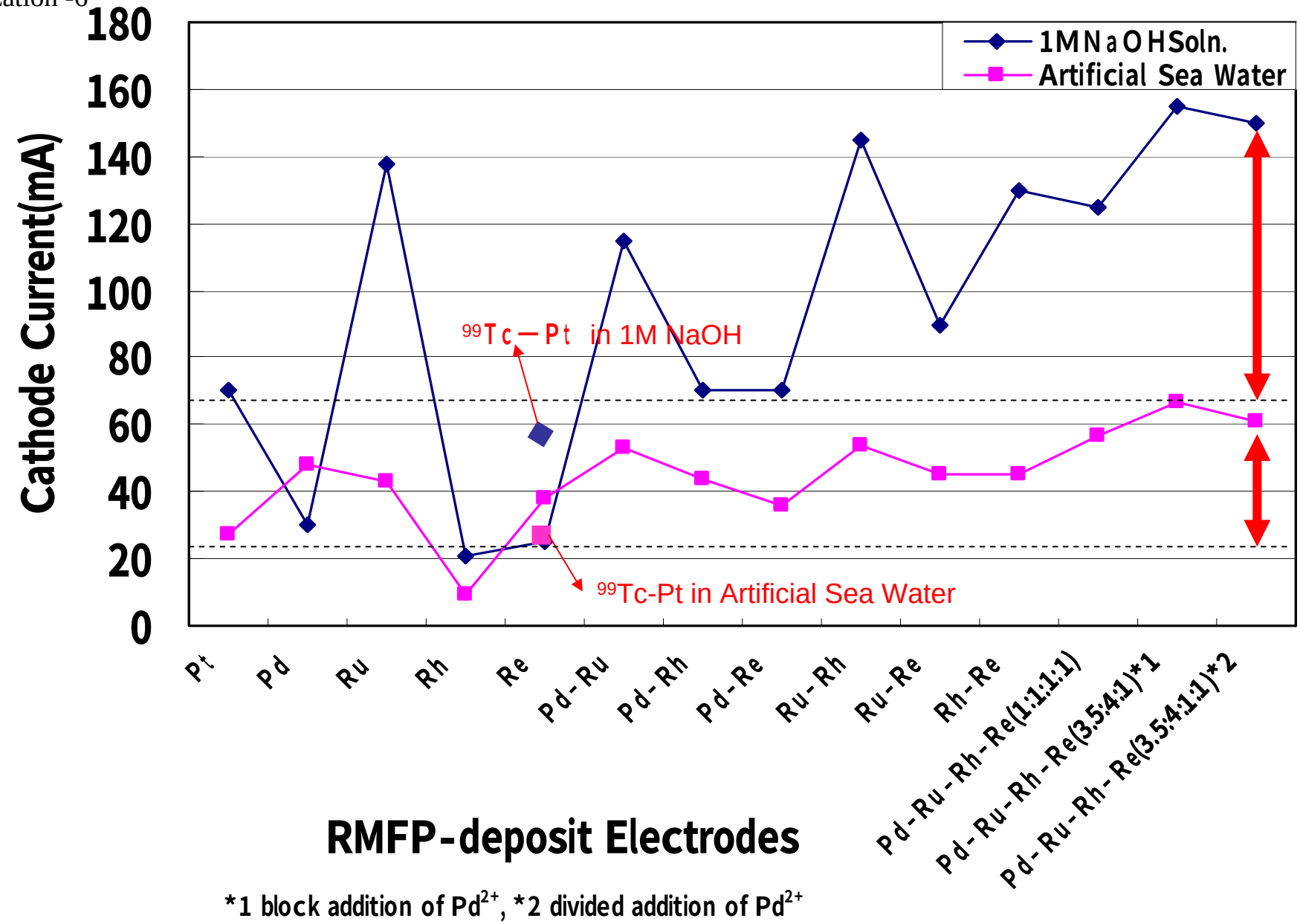
(H+ : mol/l)



*1 Pd-Ru-Rh-Re=1-1-1-1 *2 Pd-Ru-Rh-Re=3-4-1-1 ; Pd/(Ru+Rh+Re)=1.6 Bloc Addition of Pd2+

*3 Pd-Ru-Rh-Re=3-4-1-1 ; Pd/(Ru+Rh+Re)=1.6 Continuous Addition of Pd2+

Fig. The Initial Hydrogen Evolution Potentials on Various RMFP-deposited Pt Electrodes



*1 block addition of Pd^{2+}, *2 divided addition of Pd^{2+}

Fig. Cathodic Currents for Hydrogen Evolution of RMFP deposit Pt Electrodes at ϕ-1.25V (V vs.Ag/AgCl)) in 1M NaOH and in Artificial Sea Water