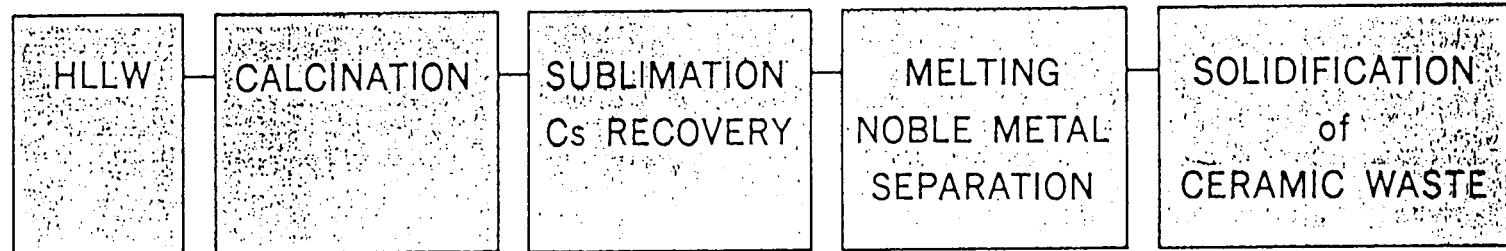


**A POSSIBILITY OF NUCLIDES SEPARATION BY SUPER
HIGH TEMPERATRUE TREATMENT METHOD OF HLLW**

H. HORIE and M. YONEYA

PNC, Japan

PROCEDURE



- CALCINATION ; HLLW IS HEATED, WATER IS VAPORIZED AND FP NITRATES DECOMPOSE TO OXIDES.
- SUBLIMATION ; OXIDES ARE HEATED AT 700°C AND Cs IS REMOVED BY VAPORIZATION.
- MELTING ; NOBLE METALS ARE REDUCED TO METALS DURING MELTING, SEPARATES FROM OXIDE PHASE AND MELT DOWN AT THE CRUCIBLE BOTTOM.
- SOLIDIFICATION ; NOBLE METALS AND OXIDE RESIDUE ARE SOLIDIFIED. SOLIDIFIED OXIDE CONTAINS ALKALI EARTH ELEMENT, RARE EARTH ELEMENTS, Zr AND ACTINIDES.

PRINCIPLES OF THIS METHOD

1 VOLATILIZATION

DIFFERENCE OF BOILING POINT BETWEEN FPS

2 PYROMETALLURUGY

DIFFERENCE OF FREE ENERGY OF OXIDATION BETWEEN FPS

BOILING & MELTING POINT

ELEMENT	BP(°C)		MP(°C)		ORIGEN CODE OUT PUT g/MtU
	METAL	OXIDE	METAL	OXIDE	
SE	885	317	144	340	7.731E01
Rb	666	D	38.9		4.853E02
Sr	1384		789	2430	1.147E03
Y	2927	4300	1495	2410	8.380E02
Zr	3578	4300	1852	2715	4.938E03
Mo	5560	1155	2810	785	4.557E03
Tc	3030	311	2200	118.9	1.019E03
Ru	3900	40	2250	28.4	2.989E03
Rh	3717		983		3.673E02
Pd	3187		1534		1.827E03
Ag	2212	D	981.9		9.241E01
Cd	785	700	321.1		1.465E02
In	-200		156.8		2.824E00
Sn	2270	D	232		1.148E02
Sb	1835	141s	630.7	658	2.778E01
Te	1390		448.8		8.418E02
Cs	880		28.5	480	3.453E03
Ba	1637		729	1923	2.241E03
La	3489	4200	920	2000	1.883E03
Ce	3488		785	1850	3.238E03
Pr	3127		835	2278	1.523E03
Nd	3027		1024	1800	5.521E03
Pm	2730		1035		4.277E01
Sm	1800		1072	2310	1.011E03
Eu	1439		828	2348	1.890E02
Gd	3000		1312	2394	1.830E02
Tb	2800		1358		3.374E00
Dy	2800		1407	2358	1.859E00
Ho	3818		1193	2178	9.420E05
Np	3902		640		8.780E02
Pu	3235		839.5	1750	1.032E04
Am	1800		2850		5.138E02
Cm			1340		3.893E01

FP MORE THAN 1g/MtU IS LISTED UP

MAIN ELEMENTS

	bp(°C)	mp(°C)
ALKALI METAL		
Cs	690	
Rb	688	
ALKALI E.METAL		
Sr	1384	
Ba	1637	
TRANSITION METAL		
Zr		1852
Mo		2610
NOBLE METAL		
Ru		2250
Rh		1983
Pd		1554
RARE EARTH OXIDE		
La		2000
Ce		1950
Pr		2278
Nd		1800
Sm		2310

1. ALKALI METAL MAY BE REMOVED AT TEMPERATURE BELOW 1000°C.
2. ALKALI EARTH METALS HAVE TO BE REDUCED, BECAUSE THESE OXIDE'S bp ARE VERY HIGH.
3. HIGH TEMPERATURE TREATMENT IS NECESSARY TO MELT TRANSITION METALS, NOBLE METALS AND RARE EARTH OXIDES TO SEPARATE METALS FROM OXIDES.

THE CONCEPT OF HIGH LEVEL WASTE TREATMENT

1. CONCENTRATION

THIS AIMS TO VITRIFY ALL FP IN HLLW AND TO RELEASE ONLY MINIMUM VLLW INTO ENVIRONMENT. BUT, MLLW SUCH AS BITUMEN OR CEMENT MATERIALS IS PRODUCED IN REPROCESSING PLANT. THE EFFORT OF MLLW TREATMENT TO SEPARATE INTO HLLW AND VLLW IS CONTINUED.

2. SEPARATION

THE SEPARATION OF ALKALI METAL(Cs), ALKALI "EARTH METAL(Sr), NOBLE METAL(Ru, Rh, PaI), AND TRU IN" HLLW IS INVESTIGATED FOR LONG TIME. THE ADAPTATION OF THIS PROCESS IS NOT YET SUCCEEDED AT ANY PREPROCESSING PLANT.

3. RATIONALIZATION

THIS IS OUR CONCEPT FOR HLLW TREATMENT.

WE ATTEMPT TO OBTAIN THE MOST COMPACT HIGH LEVEL WASTES AND TO SEPARATE MANY ELEMENTS IN HLLW AS BY PRODUCTS.

ISSUES OF THESE CONCEPT

1. CONCENTRATION – VITRIFICATION

- 1) LARGE VOLUME ; THIS HAW CAN NOT CONTAIN FP BEYOND ABOUT 10%, BECAUSE OF FP CONCENTRATION IS LIMITED BASED ON FP VOLUBILITY IN THIS MATRIX AND THIS MATERIAL THERMAL STABILITY.
- 2) THERMAL POWER ; THE THERMAL POWER OF VITRIFIED HAW REQUIRES 30–50 YEAR COOLING TIME TO DISPOSE INTO THE EARTH.

2. SEPARATION – UTILIZATION OF cs AND NOBLE METALS

- 1) HIGH COST ; THE PRICE OF RECOVERED ELEMENTS = PLANT CONSTRU CTION & OPERATION COST/RECOVERED ELEM ENTS \leq THESE PRICE ON THE MARKET. (?)
- 2) 2nd WASTE GENERATION ; NEW SOLVENT WASTE AND/OR ION EXCHANGE RESIN WASTE IS GENERATED. THESE ARE NOT PRODUSED IN PUREX REPROCESSING PLANT.

3. RATIONALIZATION – VERY COMPACT SOLIDIFICATION & SEPARATION AS BY PRODUCTS

OUR CONCEPT MUST ANSWER THE ABOVE MENTIONED ISSUES.

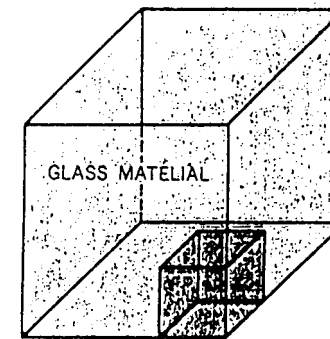
RATIONALIZATION VOLUME REDUCTION

278

WASTE	MATRIX	FP CONTENT
GLASS	Si-B OXIDE	10-20%
SYNROC	Ti OXIDE	10-20%
NEW CERAM	RARE EARTH OXIDE	100%

NUCLEAR RARE EARTH WASTE CERAMICS

VOLUME of WASTE



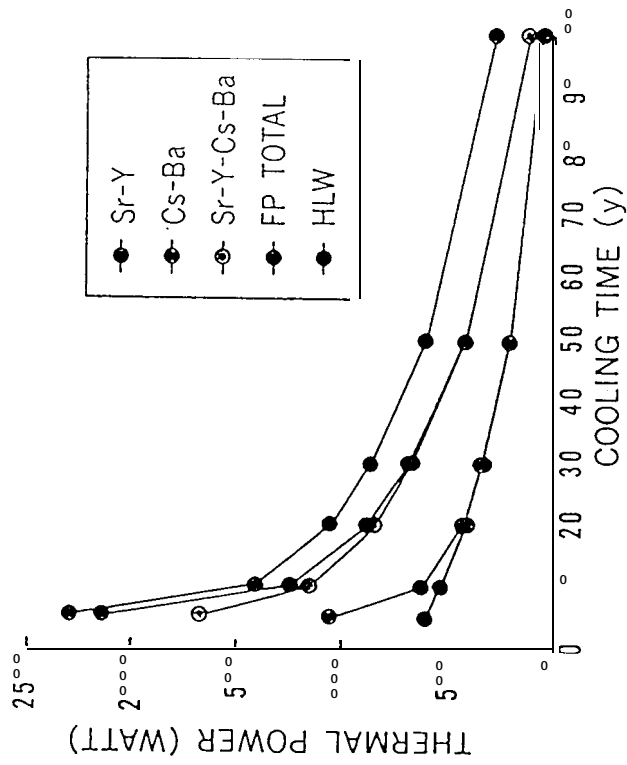
VITRIFICATION



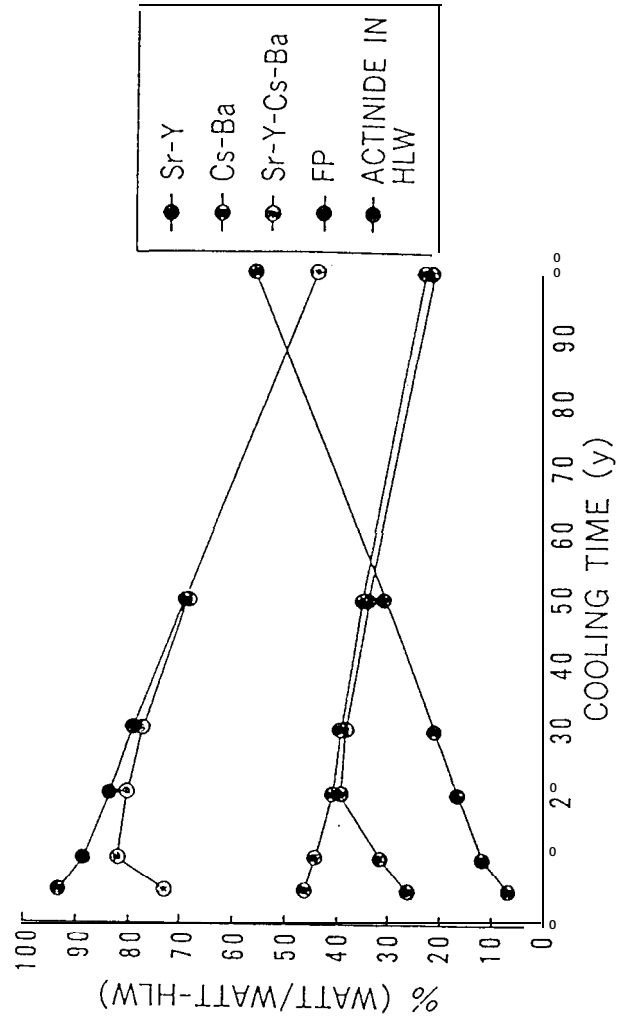
OUR METHOD

RATIGNA IZATION THERMAL POWER

THERMAL POWER



THERMAL POWER RATIO TO HLW



COST OF SEPARATION

1. REPORT BY EXXON NUCLEAR COMPANY(1 978)

REPROCESSING PLANT

CAPACITY ; 2100t/y, BURN UP ; 33,000 Mwd/t

PLANT CONSTRUCTION

Cs	RECOVERY PLANT	" 48M\$
Sr	RECOVERY PLANT	95
Cs + Sr	RECOVERY PLANT	1'12

2. REPORT BY PNL(1977)

REPROCESSING PLANT

CAPACITY ; 5t/d

PLANT CONSTRUCTION

Cs	RECOVERY PLANT	37M\$
Sr	RECOVERY PLANT	37
Cs -t- Sr	RECOVERY PLANT	51

1. THIS HIGH PLANT CONSTRUCTION COST MAKES IT DIFFICULT TO OBTAIN USEFUL ELEMENT IN HLLW AT REASONABLE FEE.
2. SO, USEFUL ELEMENTS IN HLLW MUST BE RECOVERED AS BY-PRODUCT IN ANY OTHER PROCESS.

E X P E R I M E N T

1. SPENT FUEL CALCULATION

CODE ORIGEN 2
SPENT FUEL
BURN UP 45,000 Mwd/MtU
COOLING TIME 5y

2., SIMULATED HLLW

'ELEMENT >1 g/MtU
Tc IS REPLACED BY Re.
Pm IS REPLACED BY Ce.
SOLUTION : NITRIC ACID SOLUTIN

3. CALCINATION OF HLLW

TEMPERATURE 700°C

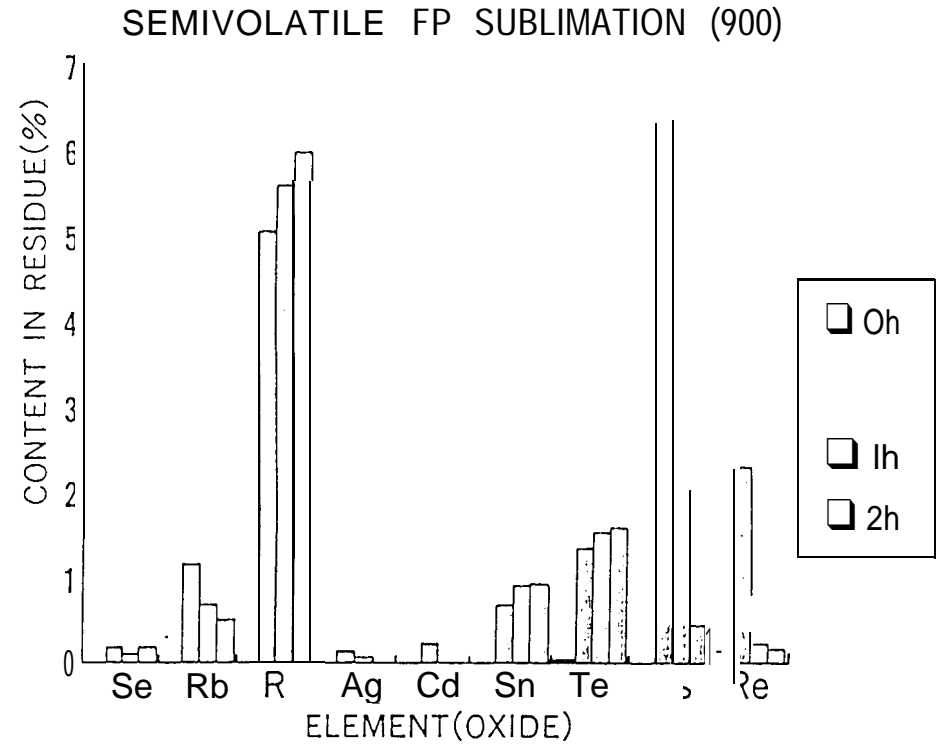
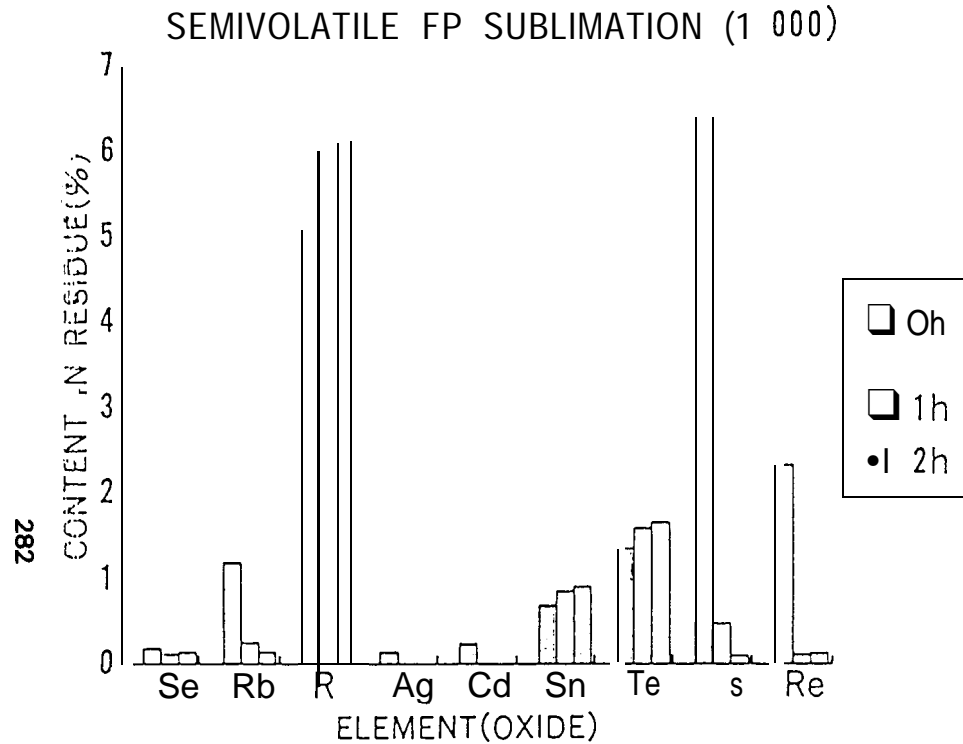
4.SUBLIMATION OF CALCINED HLLW

TEMPERATURE 800 — 1000°C
ATMOSPHERE Ar GAS

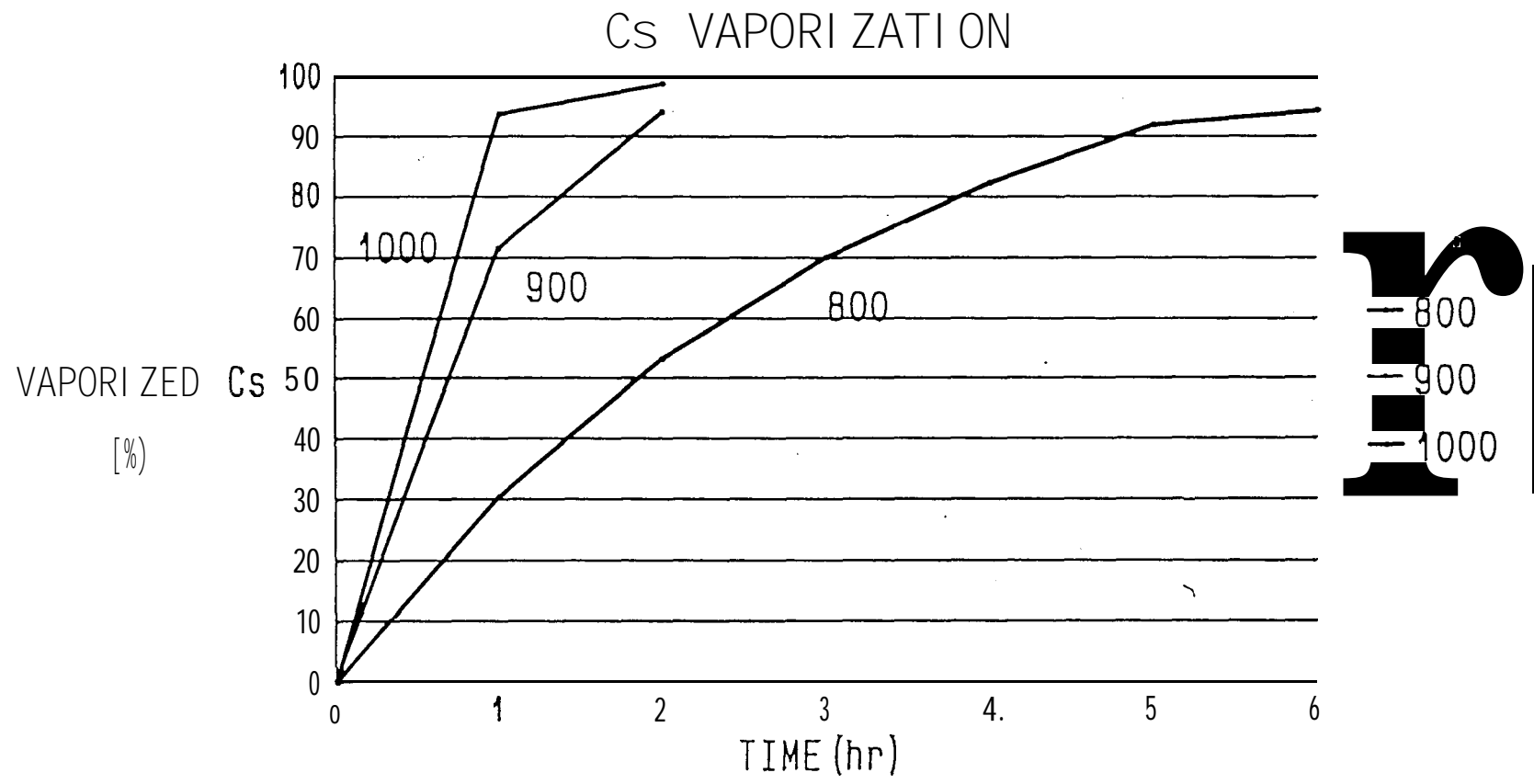
5. MELTING

TEMPERATURE 1800°C
ATMOSPHERE Ar GAS

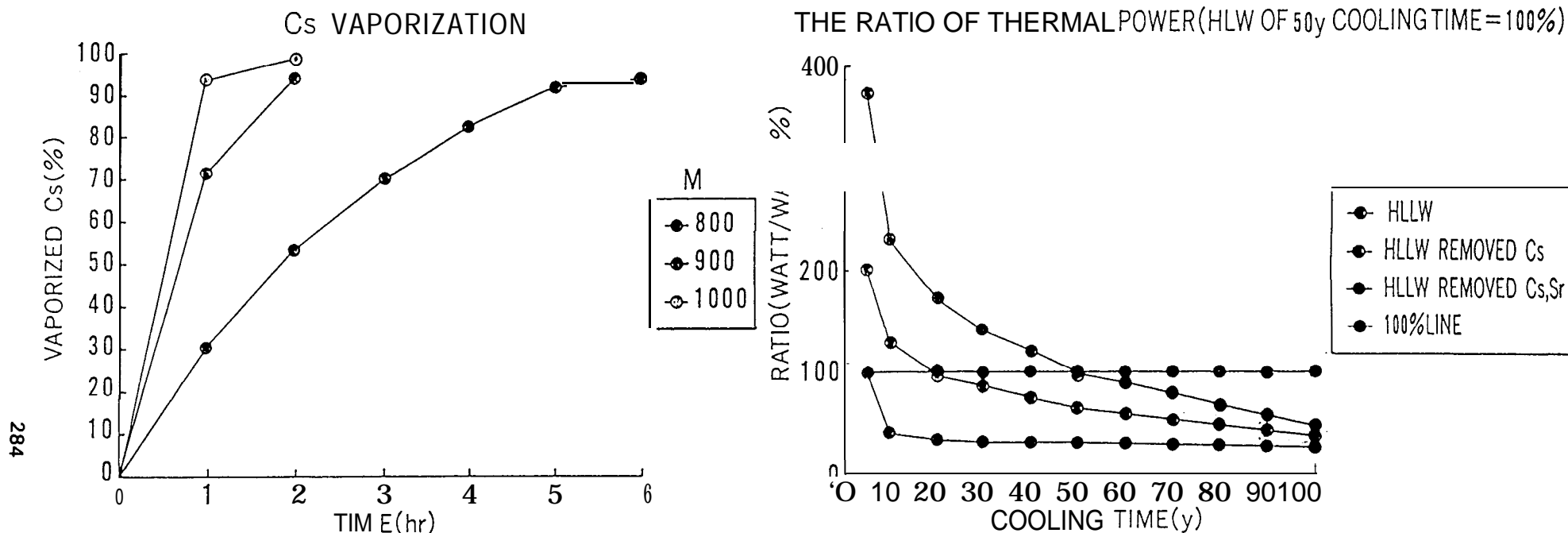
SUBLIMATION EXPERIMENTS OF SIMULATED CALCINED HLLW



1. Rb, Ag, Cd, Cs, AND Re SUBLIMED.
2. Se, Ru, Sn AND Te DID NOT SUBLIME.
3. Ru IS THE MOST SUBLIMABLE ELEMENT AS THE CHEMICAL FORM RuO₄ IN VITRIFICATION PROCESS. IN THIS EXPERIMENTS CARRIED OUT UNDER Ar GAS, Ru WAS NOT OXIDIZED AND NOT VAPORIZED.
4. THIS EXPERIMENT SHOWS THAT Cs, THE HIGHEST THERMAL POWER ELEMENT, IS ABLE TO BE SEPARATED.



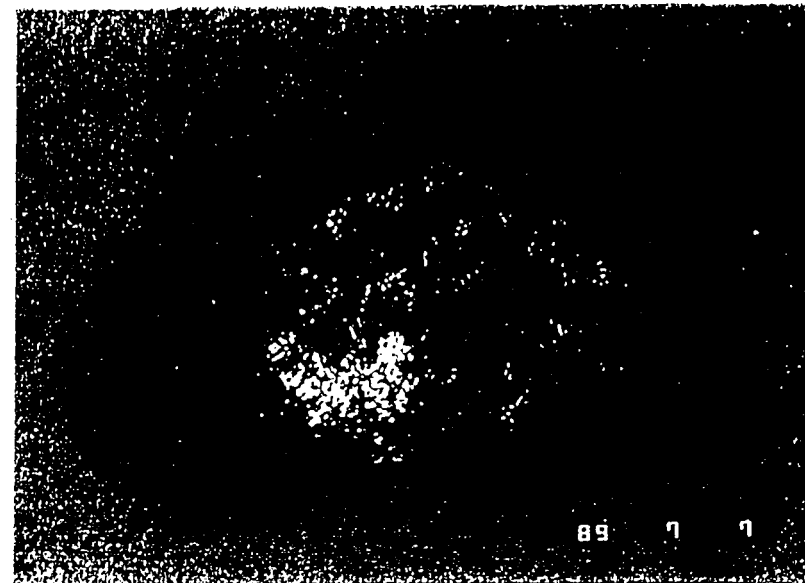
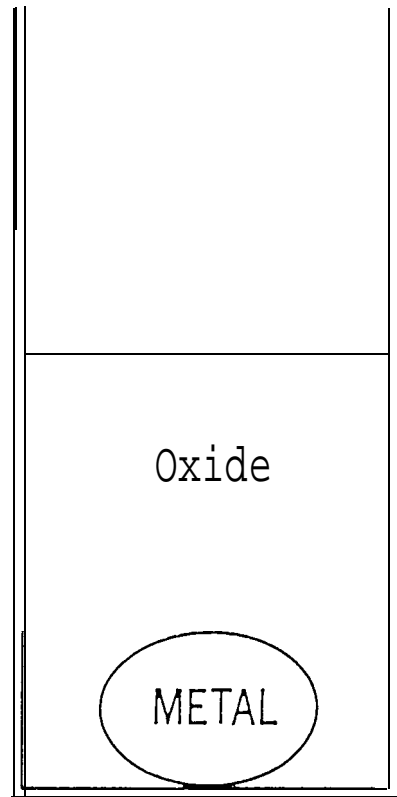
THE EFFECT OF Cs SEPARATION



284

1. THIS FIGURE SHOWS THERMAL POWER RATIO ON THE BASIS OF 50y COOLING HLLW'S THERMAL POWER.
2. THE 23y COOLING HLLW SEPARATED Cs HAS EQUAL VALUE TO 50y COOLING HLLW. IT IS SAID THAT 30-50 STORAGE IS NECESSARY TO LOWER HAW THERMAL POWER TO PREVENT HEATING UP THE ROCK AROUND DISPOSAL PIT.
3. Cs SEPARATION FROM HAW BY OUR METHOD SHORTENS ABOUT 25Y OF THE STORAGE TIME.

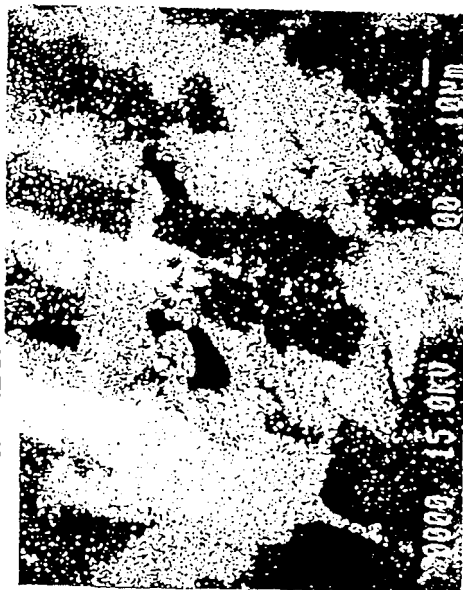
MELTING EXPERIMENT OF CALCINED HLLW



1. THIS FIGURE ILLUSTRATES THE SECTION OF CRUCIBLE AFTER MELTING OF CALCINED HLLW.
2. THIS IS A PHOTOGRAPH OF THE METAL OBTAINED BY MELTING OF CALCINED HLLW.
3. THUS, CALCINED HLLW WAS SEPARATED TO METAL PHASE AND OXIDE PHASE DURING METLTING PROCESS.

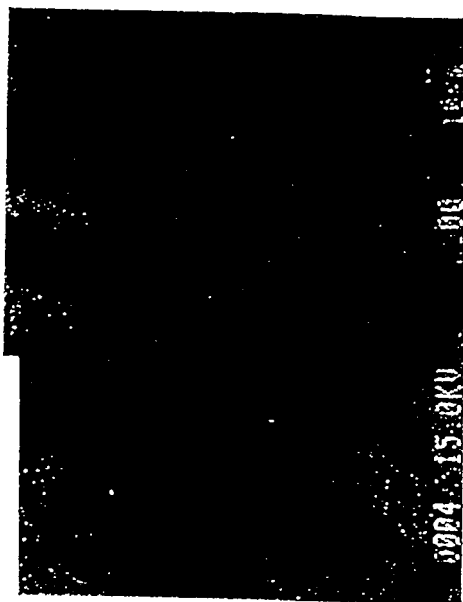
METAL PHASE
EFMA ANALYSIS

BN-M Ru-La



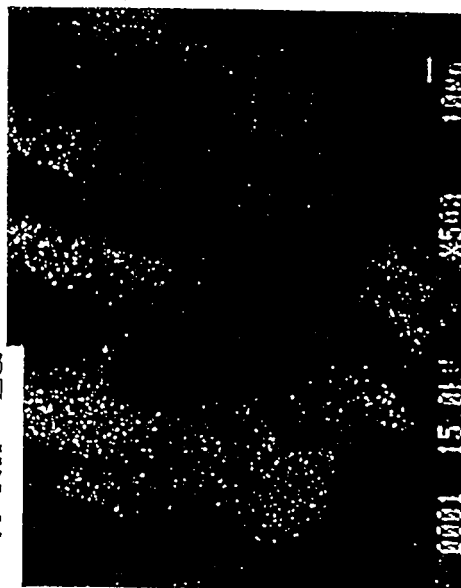
Ru

BN-M Mo-La



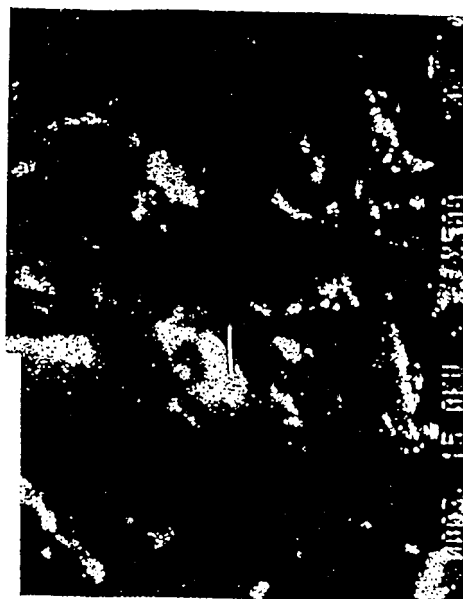
Mo

BN-M Rh-La



Rh

B M

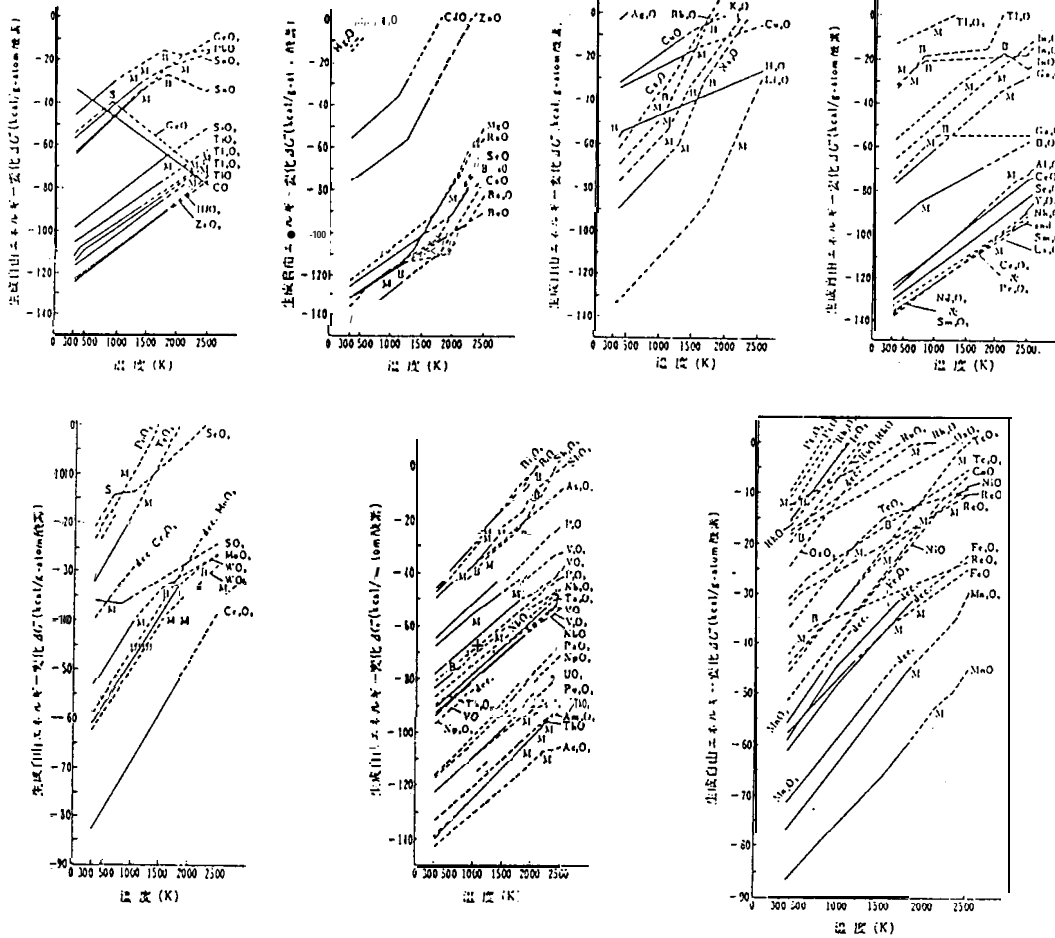


Pd

REDUCTION OF NOBLE METALS

STANDARD FREE ENERGY OF OXIDE FORMATION

Ellingham Diagram



FREE ENERGY OF MAIN ELEMENT IN HLLW
(1800°C)

ELEMENT	FREE ENERGY OF OXIDE FORMATION (kcal/g-atom Oxygen)
NOBLE METAL	
Ru	>0
Rh	>0
Pd	>0
TRANSITION METAL	
Zr	-92
Mo	-32
Tc	-15
ALKALI EARTH" METAL	
Sr	-100
Ba	-95
RARE EARTH METAL	-90~-110
TRU	-90~-100

287

1. IN OUR EXPERIMENT CONDITION, ELEMENTS WHICH HAVE FREE ENERGY MORE THAN THAT OF Mo ARE REDUCED.

NOBLE METAL RECOVERY

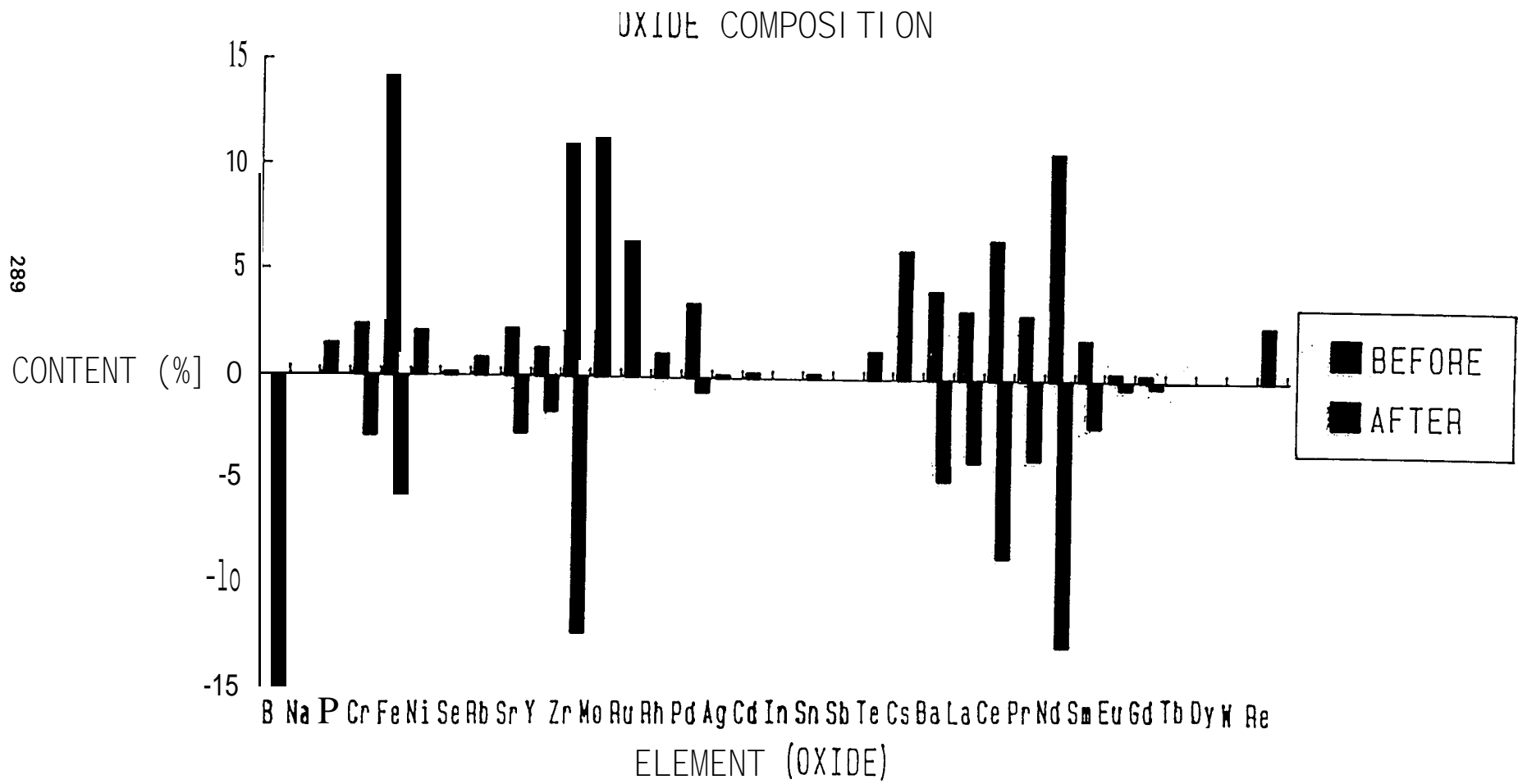
NOBLE METAL RECOVERY
(ANALYSIS)

ELEMENT	'YIELD
Ru	101.7%
Rh	88.2
Pd	100.4
Mo	95.2

1. HIGH RECOVERY YIELD OF NOBLE METAL IS CARRIED OUT."
2. RECOVERED NOBLE METAL. IS ALLOY WITH ANOTHER TRANSITION METAL.
3. THIS ALLOY IS BETTER FORM FOR SAVING IT FOR EMERGENCY BECAUSE OF IT'S LOW RADIO ACTIVITY.

FEATURE IN NOBLE METAL RECOVERY

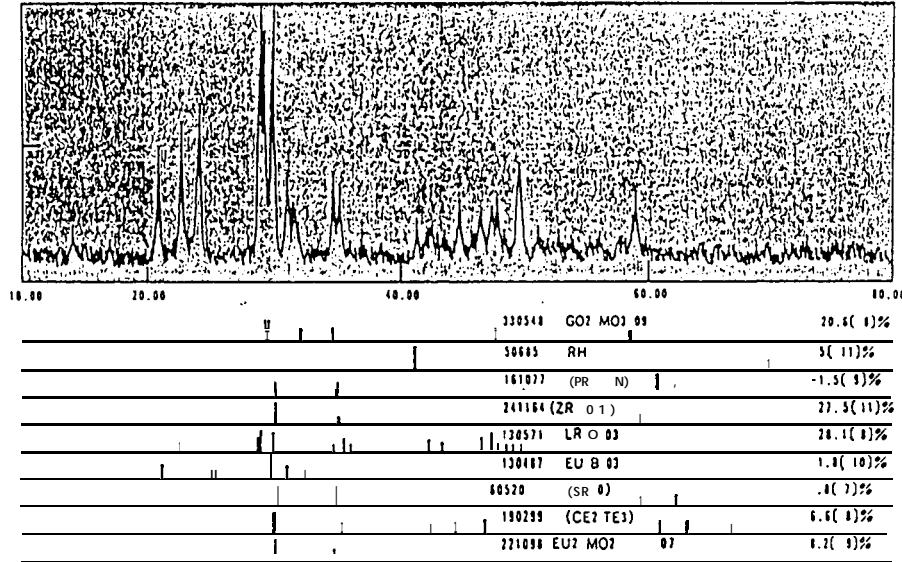
	FORMER METHOD	NEW METHOD
N. M. PRODUCT	MAIN PRODUCT	SUB PRODUCT
METHOD	EXTRACTION	PYROMETAL
REAGENT	NEW REAGENT	ALMOST UNNECESSARY
WASTE	2nd WASTE (NEW REAGENT)	NO 2nd WASTE
OTHER R&D	2nd WASTE TREATMENT & DISPOSAL	UNNECESSARY
COST	RECOVERY & MANAGEMENT OF 2nd WASTE	RECOVERY (AS BY-PRODUCT)



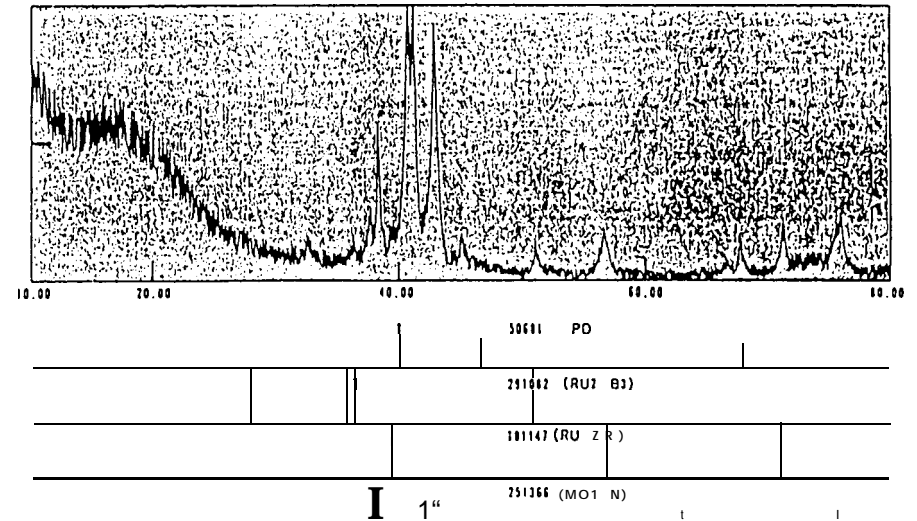
X-RAY DIFFRACTION SPECTRA

RESULTS OF 2nd SEARCH MATCH

Sample Name :BN-1-M1800 (File name : BN-1100)



X-RAY DIFFRACTION SPECTRA FOR OXIDE PHASE

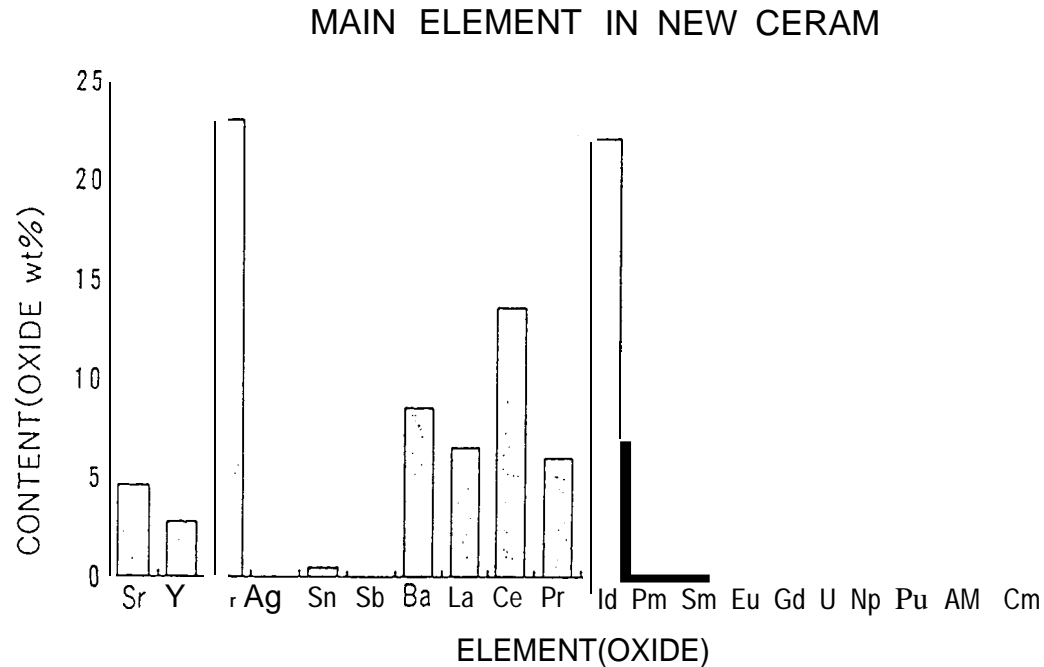


X-RAY DIFFRACTION SPECTRA FOR METAL PHASE

29 °

1. THE SHARP PEAK OF OXIDE PHASE SHOWS THAT THIS PHASE IS CRYSTAL AND NOT GLASS. THIS PHASE CONSISTS IN THREE PHASE, ALKALI EARTH OXIDE, ZIRUKONIA AND RARE EARTH OXIDE. DETAIL ANALYSIS IS UNDER INVESTIGATION.
2. METAL PHASE CONSISTS IN NOB E METAL AND TRANSITION METAL. X-RAY DIFFRACT ON ANALYSIS INDICATES Ru IS METAL FORM AND DIOXIDE. IN THE VITRIFICATION Ru PRECIPITATES AS DIOXIDE. AS ABOVE MENT ONED, Ru IS NOT VAPORIZED. IN OUR PROCESS, Ru MAY BE EASILY REDUCED.

COMPOSITION OF NEW CERAM



COMPOSITION OF NEW CERAM

ELEMENT	CONTENT
ALKALI EARTH	14.2%
Zr	20.8
RARE EARTH	58.48
TRU	5.52
TOTAL	98.98

1. FIGURE AND TABLE SHOW THE COMPOSITION OF NEW HAW OXIDE ON THE BASE OF CALCULATION USING ORIGEN CODE.
2. COMPOSITION OF NEW HAW OXIDE IS SIMPLIFIED AS SHOWED IN TABLE.
3. THE MAJOR ELEMENT OF NEW HAW OXIDE IS RARE EARTH ELEMENT. SO IT IS NAMED NEW CERAM(NUCLEAR RARE EARTH WASTE CERAMIC).

NEW CERAM PROPERTIES

PROPERTIES	NEW CERAM	GLASS
MATR *	RARE EARTH OXIDE	SI-B GLASS
DENSITY(t/m ³)	4.8	2.7
weight(kg/t-U)	28.8	395
VOLUME(m ³ /t-U)	6	146
LEACH RATE(kg/m ² d)	6 * 10 ⁻⁴	2 * 10 ⁻⁴

1. NEW CERAM HAS HIGHER DENSITY THAN GLASS, SO ITS VOLUME IS VERY SMALL.
2. ON THE LEACH RATE, IT MUST BE CONSIDERED THAT LOSS MATERIALS OF NEW CERAM ARE FEWER AND THAT GLASS IS MORE RADIOACTIVE MATERIALS.

ALL ELEMENT

	I a	II a	III a	IV a	V a	VI a	VII a	VIII	I b	II b	III b	IV b	V b	VI b	VII b	O
1	H															He
2	Li	Be									B	C	N	O	F	Ne
3	Na	Mg									Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru Rh Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	RARE E	Hf	Ta	W	Re	Os Ir Pt	Au	Hg	Tl	Pb	Bi	Po	As	Rn
7	Fr	Ra	U, URJ													

ELEMENTS SPENT FUZZ

	I a	II a	III a	IV a	V a	VI a	VII a	VIII	I b	II b	III b	IV b	V b	VI b	VII b	O
1	H															He
2	Li	Be										C				
3																
4										Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru Rh Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Rf Rf E								Tl	Pb	Bi	Po	As	Rn
7			U, TRU													

E L E M E N T
A F T E R . S U B L I M A T I O N T R E A T M E N T

	I a	II a	III a	IV a	V a	VI a	VII a	VIII	I b	II b	III b	IV b	V b	VI b	VII b	o
1																
2		Be														
3																
4										Zn	Ga	Ge	As	Se		
5		Sr	Y	Zr	Nb	Mo	Tc	Ru Rh Pd	Ag	Cd	In	Sn	Sb	Te		
6		Ba	RARE E.								Tl	Pb	Bi	Po	As	
7			U, TRU													

ELEMENT AFTER REDUCTION TREATMENT

	I a	II a	III a	IV a	V a	VI a	VII a	VIII	I b	II b	III b	IV b	V b	VI b	VII b	O
1																
2		Be														
3																
4																
5		Sr	Y	Zr												
6		Ba	RARE E													
7			U, Th													

CONCLUSION

WE INVESTIGATED NEW HLLW TREATMENT METHOD AND FOUND NEXT.

- (1) Cs SUBLIMES ALMOST PERFECTLY AT 1000°C.
- (2) NOBLE METAL (AND TRANSITION METAL) IS REDUCED TO METAL AND RECOVERED.
- (3) RESIDUAL OXIDE IS THE MOST COMPACT HAW.
- (4) ALMOST FPs BEHAVE AS EACH SINGLE OXIDE AND COMPLICATED BEHAVIOR BY
FORMATION OF THESE COMPLEX OXIDES DOES NOT BE OBSERVED IN THIS PROCESS.
- (5) IT MAY BE ABLE TO SAY THAT ACTINOID, ALKALI EARTH AND RARE EARTH ACT
IN ACCORDANCE WITH EACH THERMOCHEMICAL DATA AT REDUCTION AND SUBLIMATION.
- (6) SO, THESE ELEMENT GROUP **MAYBE** SEPARATED EACH OTHERS.