HIGH TEMPERATURE ACTINIDE PARTITIONING CHEMISTRY

Charles C. McPheeters

Chemical Technology Division
Argonne National Laboratory

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Presentation by **Mr. McPheeters**

In opening his presentation Mr. McPheeters noted that the fuel cycle facility attached to EBR-II had reprocessed some 35000 fuel pins since it started up in the 1960s. The cell had now been decontaminated and refurbished ready for the installation of new equipment for the IFR fuel cycle. It was intended to start this up in September 1991. There is to be one electro-refiner unit with two cathodes, each with a capacity for collecting 10kg of uranium and thus, in full-time operation able to support a reactor of 600MWe.

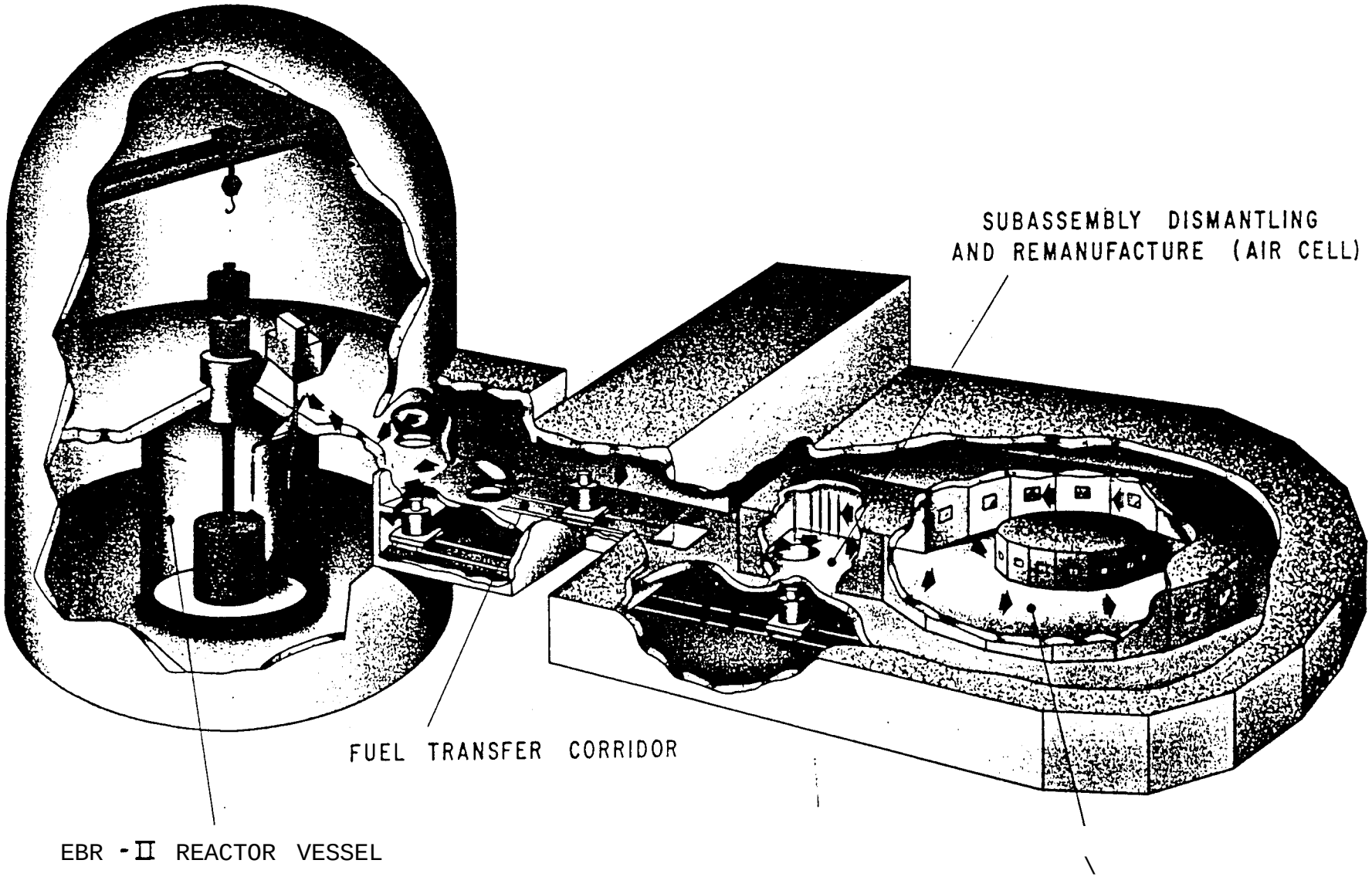
In describing the electro-refining process Mr. McPheeters noted that the distribution coefficients he was using were the inverse of those used by Japanese presenters earlier in the meeting, i.e. he was using the ratio of concentration in the chloride to concentration in the metal phase. After reporting some results using a lithium, sodium, calcium, barium chloride electrolyte he added that recent work on a lithium/potassium chloride system gave distribution coefficients of 35 and above for the rare earths, 3.4 for americium and curium and 1.9 for neptunium and plutonium.

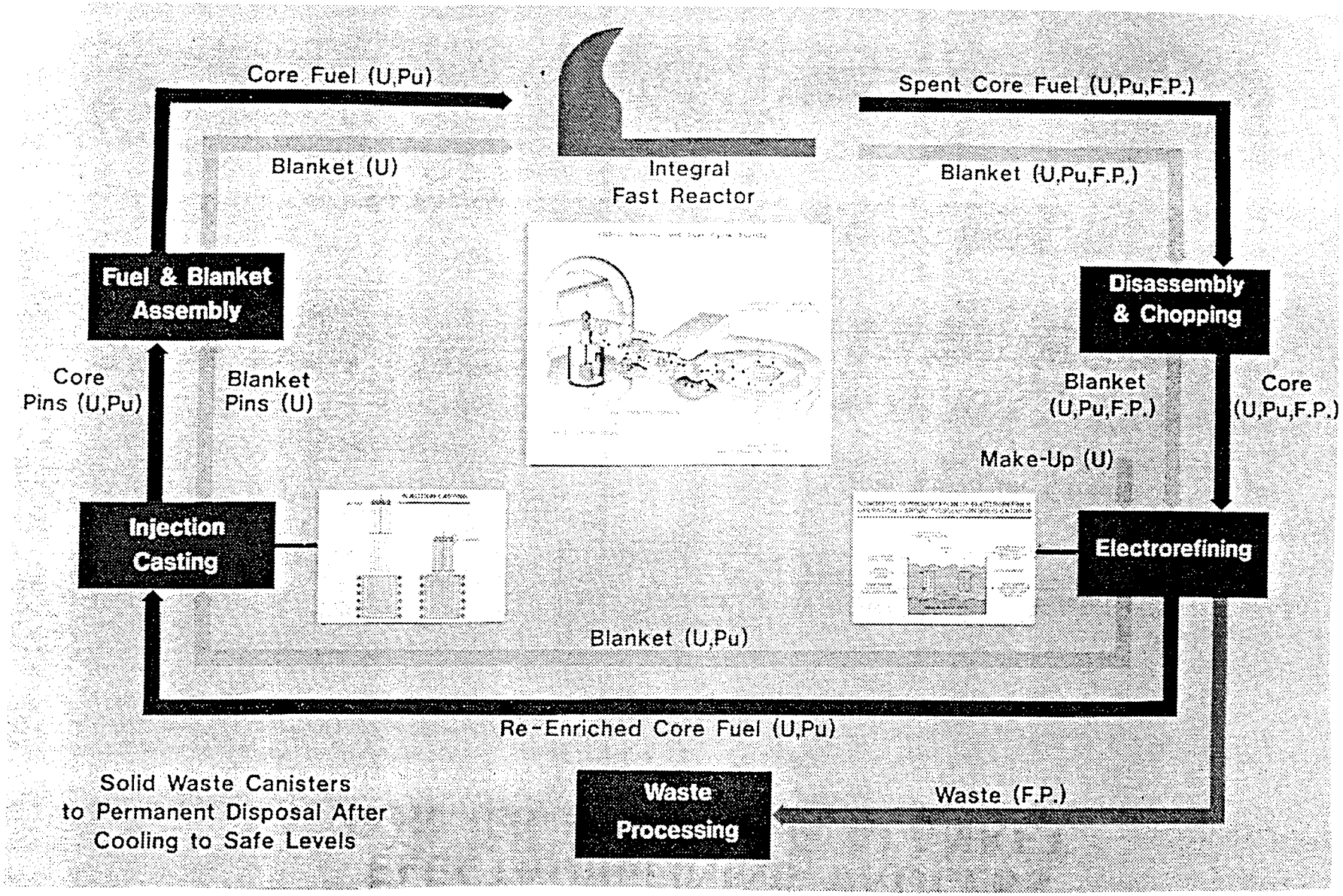
After outlining the waste treatment processes he suggested that with further successful development of the process, after stripping the transuranics from the salt wastes it would be possible to reduce plutonium to less than 100 nanoCi/g of salt and perhaps even to less than 10 nanoCi/g.

Consideration was being given to using spent LWR fuel as a source for fuelling the LMR. Small scale work had been undertaken on a flowsheet involving an initial reduction by calcium with two alternative processes for separating the TRU and rare earths using either salts or magnesium as an extracting medium.

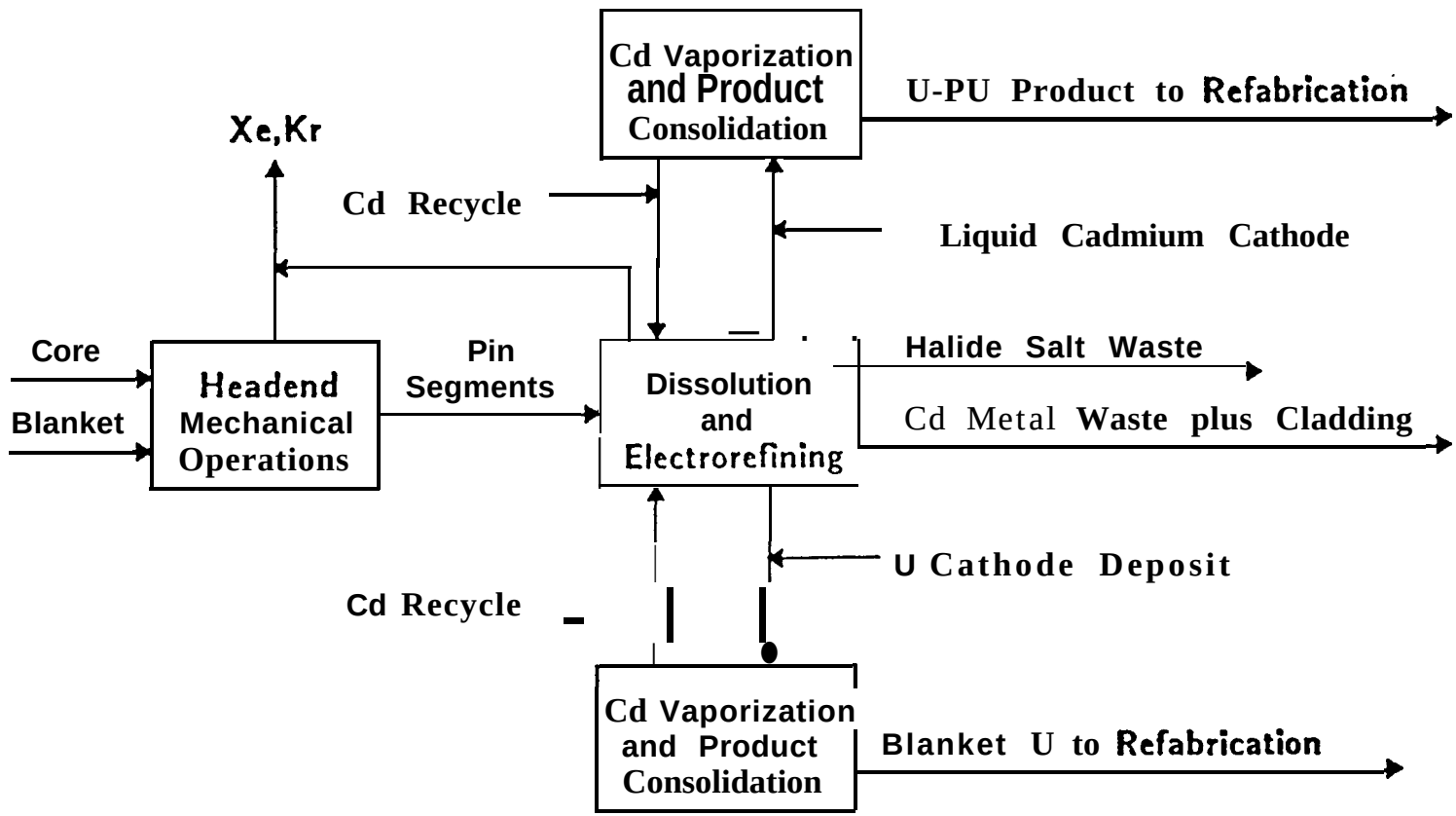
Responding to a question, Mr. McPheeters said that the decontamination factor for rare earths was about 20 in the IFR process.

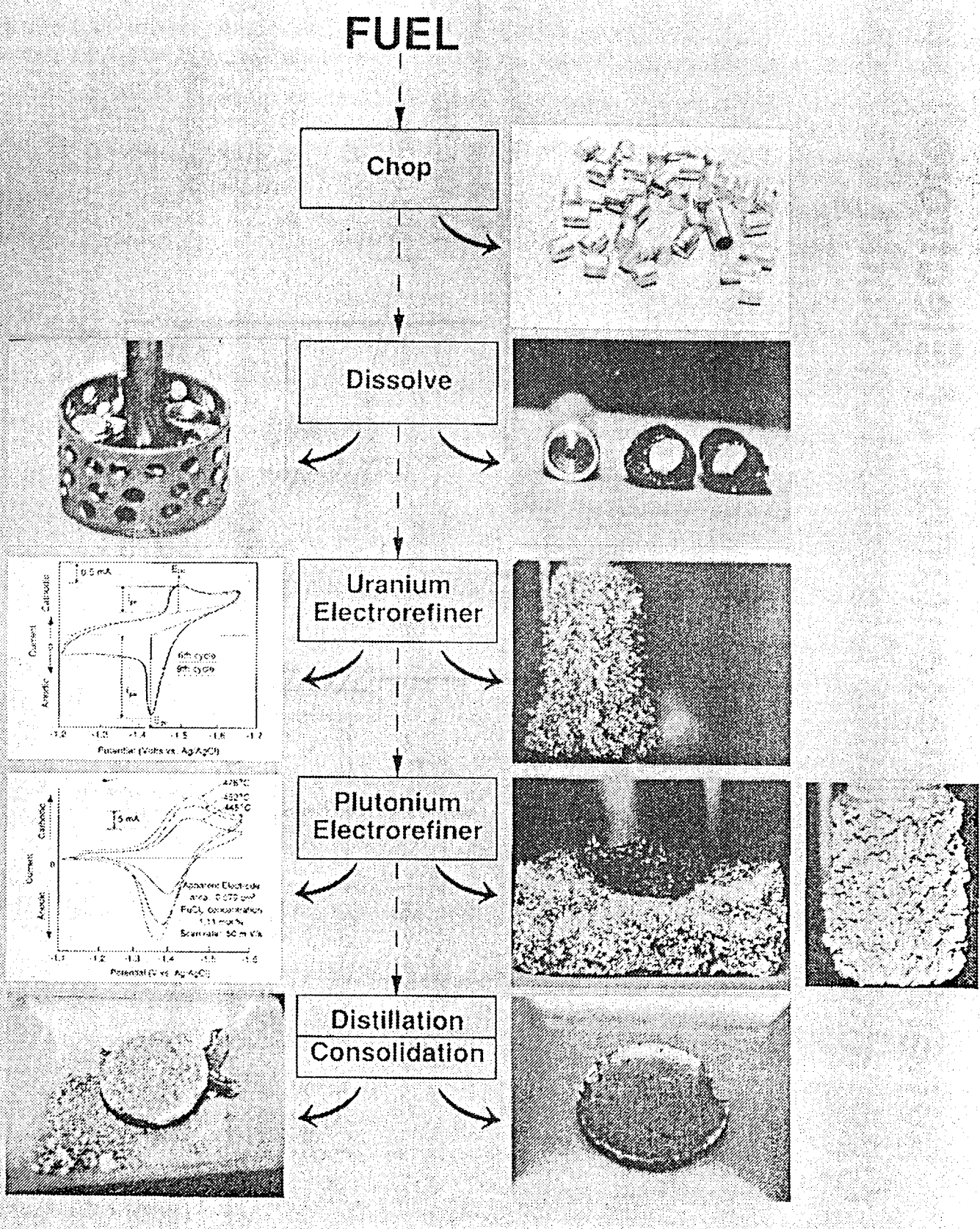
EBR-II Reactor and Fuel Cycle Facility




Core Fuel (U,Pu)
Spent Core Fuel (U,Pu,F.P.)
Blanket (U)
Integral
Fast Reactor
Blanket (U,Pu,F.P.)
Fuel & Blanket
Assembly
Disassembly
& Chopping
Core
Pins (U,Pu)
Blanket
Pins (U)
Blanket
(U,Pu,F.P.)
Core
(U,Pu,F.P.)
Make-Up (U)
Injection
Casting
Electrorefining
Blanket (U,Pu)
Re-Enriched Core Fuel (U,Pu)
Solid Waste Canisters
to Permanent Disposal After
Cooling to Safe Levels
Waste
Processing
Waste (F.P.)

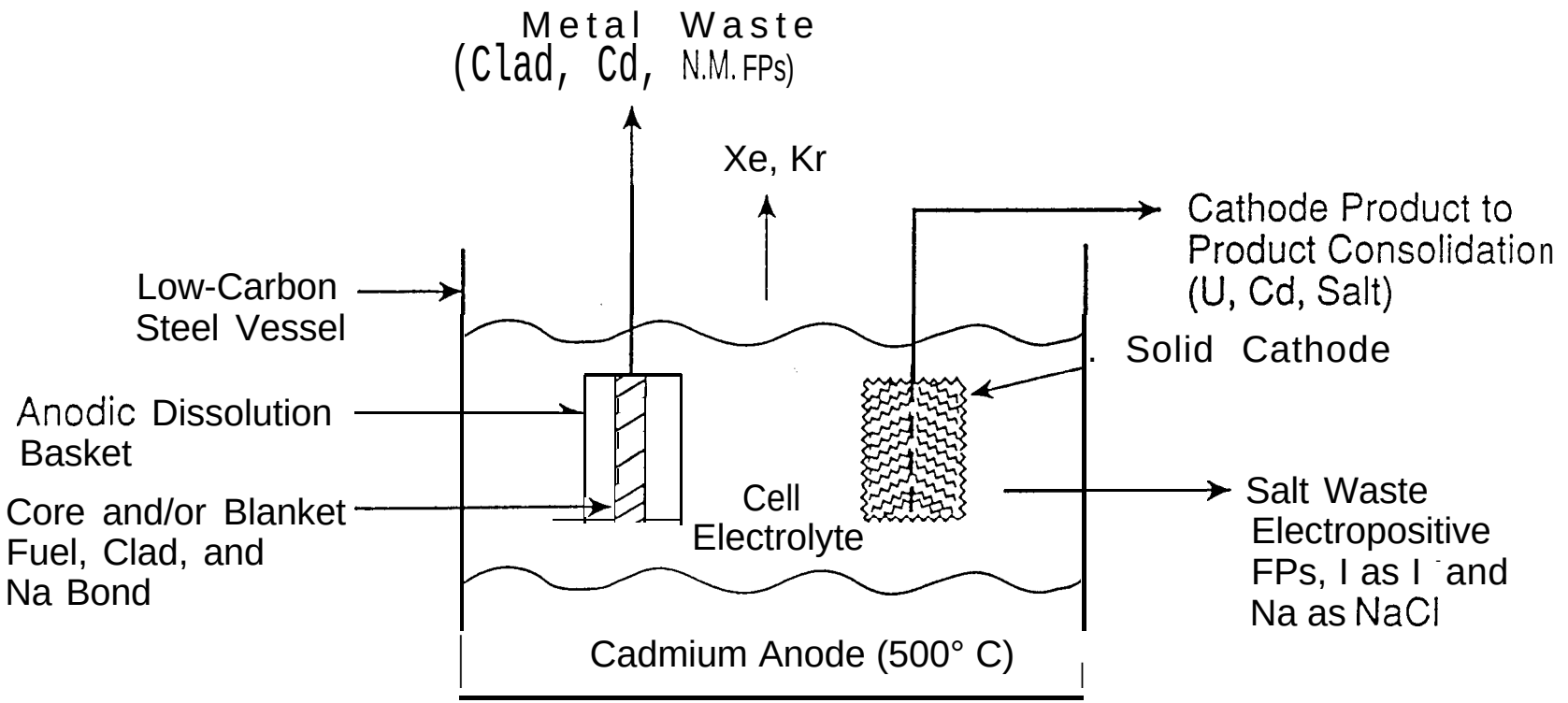
ELECTROREFINING PROCESS FOR IFR CORE AND BLANKET





ELECTROREFINING PROCESS

Schematic Representation of **Electrorefiner** Operation – Anodic Dissolution/Solid Cathode



Free Energies of Formation of Chlorides at 773°K, $-\Delta G^{\circ}_{f}$, kcal/g-equiv. Cl

$BaCl_2$	87.9	$CmCl_3$	64.0	$CdCl_2$	32.3
$CsCl$	87.8	$PuCl_3$	62.4	$FeCl_2$	29.2
$RbCl$	87.0	$MgCl_2$	62.1	$NbCl_5$	26.7
KCl	86.7	$NpCl_3$	58.1	$MoCl_2$	16.8
$SrCl_2$	84.7	UCl_3	55.2	$TcCl_3$	11.0
$LiCl$	82.5	$ZrCl_2$	46.6	$RhCl$	10.0*
$NaCl$	81.1			$PdCl_2$	9.0
$CaCl_2$	80.7			$RuCl_3$	6.0*
$LaCl_3$	70.2				
$PrCl_3$	69.0				
$CeCl_3$	68.6				
$NdCl_3$	67.9				
YCl_3	65.1				

*Estimated Value

Basic Theory

- Equilibrium between metal-salt phases

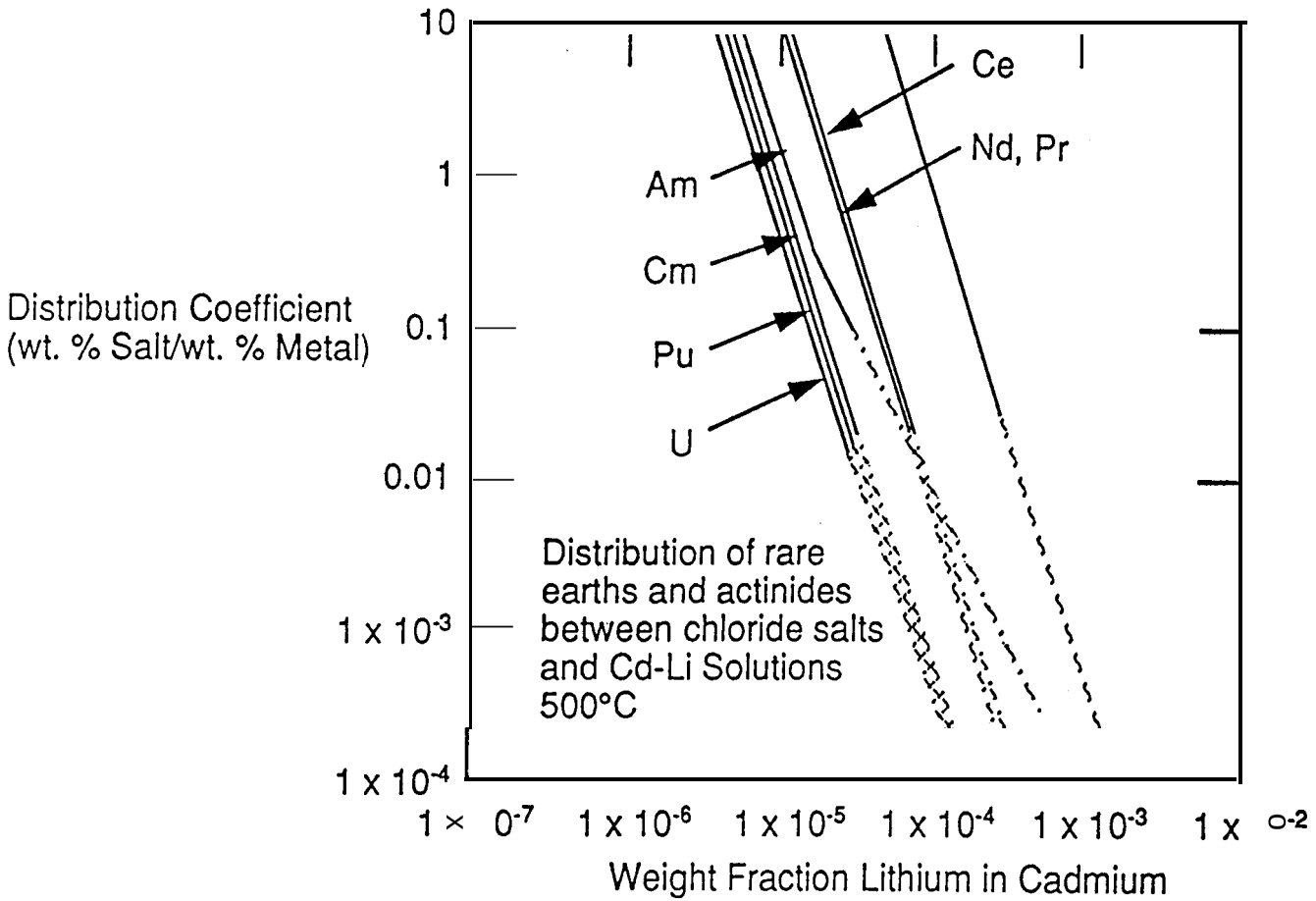
  $U + PuCl_3 = UCl_3 + Pu$

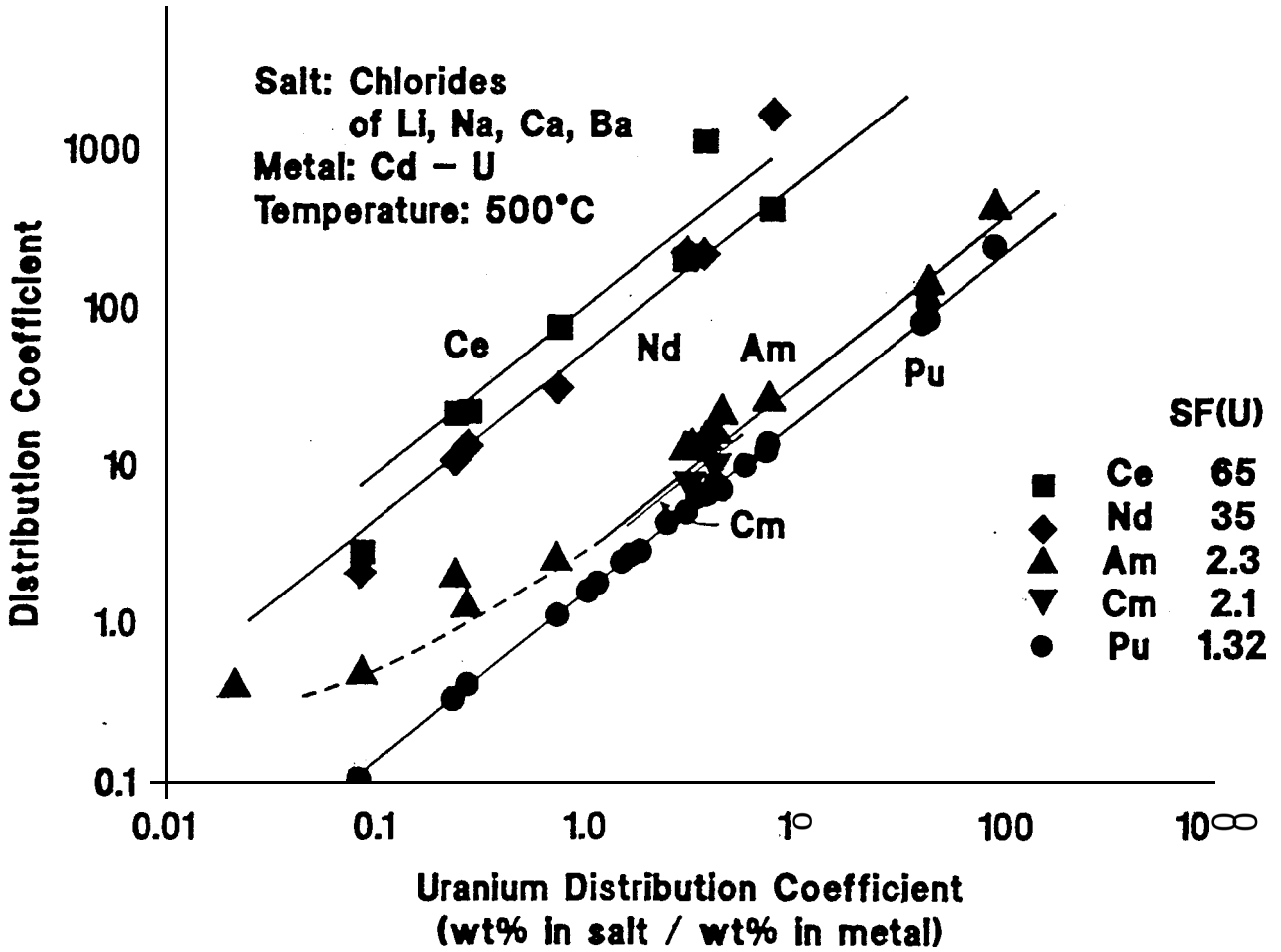
- Distribution coefficients:

$$\frac{X_{UCl_3}}{X_U} = \left[\frac{X_{PuCl_3}}{X_{Pu}}\right]\left\{\left[\frac{\gamma_{PuCl_3}}{\gamma_{UCl_3}}\right]\left[\frac{\gamma_U}{\gamma_{Pu}}\right]\left[\exp\left[-\frac{\Delta G^\circ}{RT}\right]\right]\right\}$$

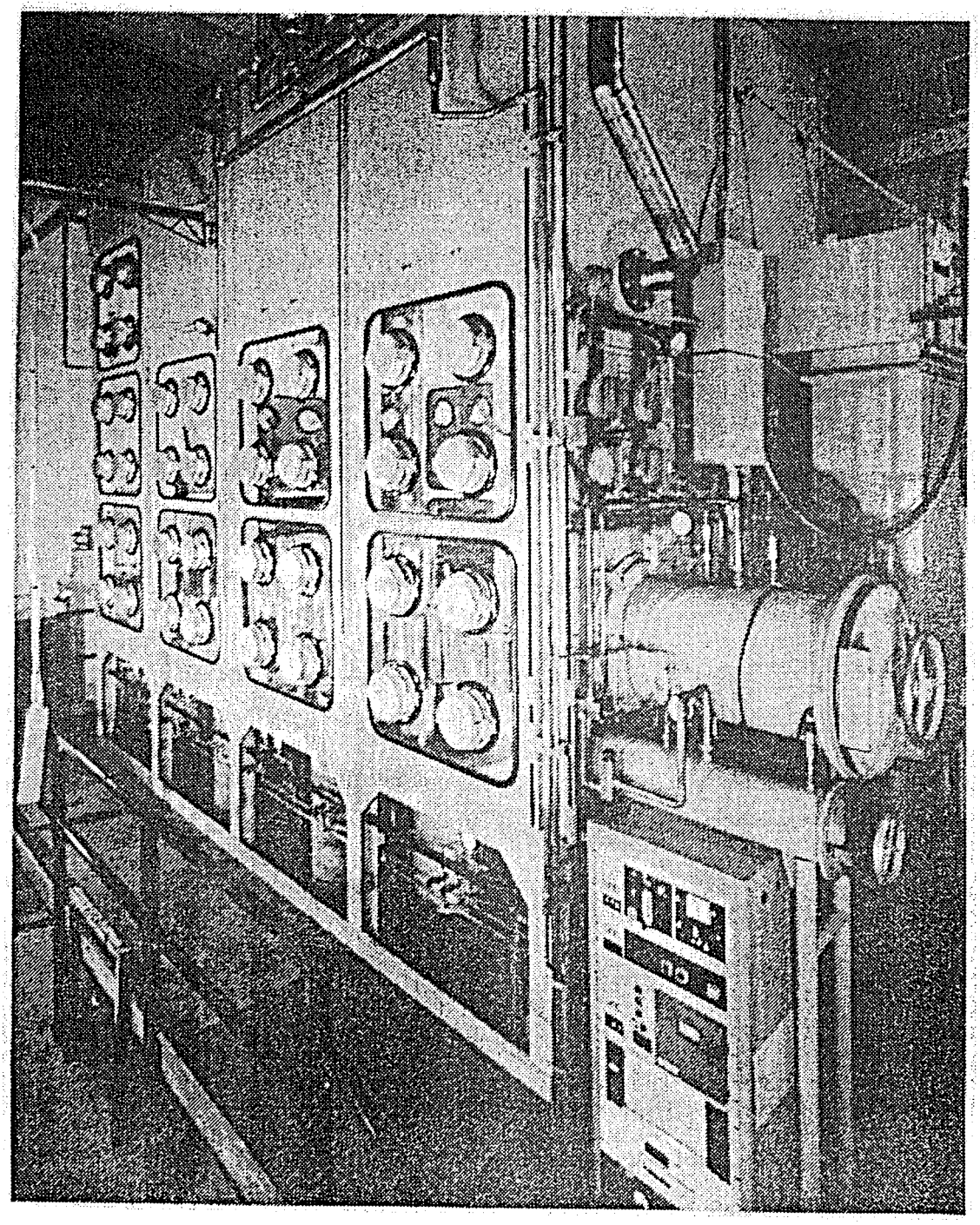
$$\alpha_U = (\alpha_{Pu})(D_{Pu}) = (\alpha_{Am})(D_{Am}) = (\alpha_{Nd})(D_{Nd}) \ldots$$

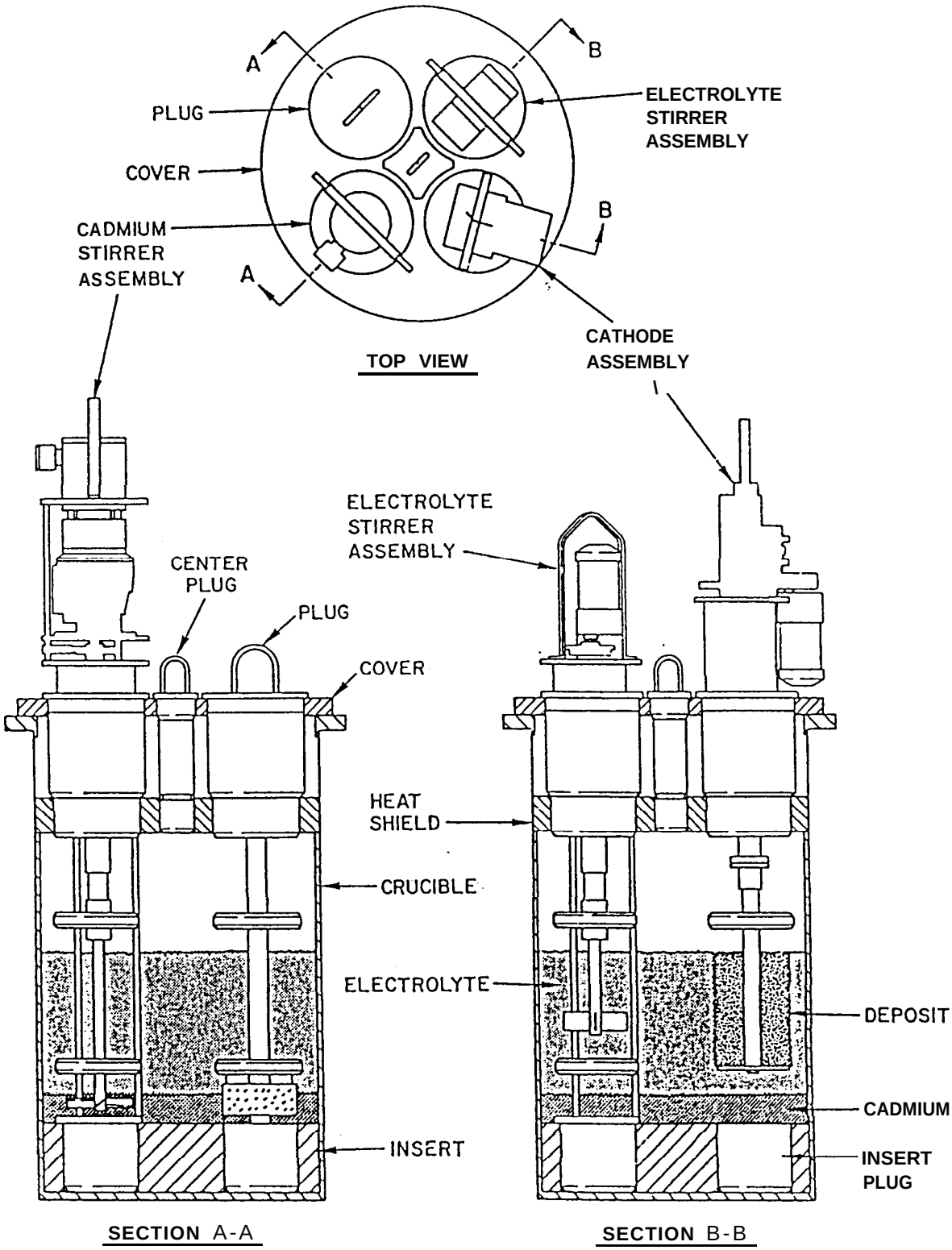
$$= \left[(\alpha_{Li})\left(\frac{X_{LiCl}}{X_{Li}}\right)\right]^3 = \left|(\alpha_{Li})\left(\frac{0.5}{X_{Li}}\right)\right|^3$$

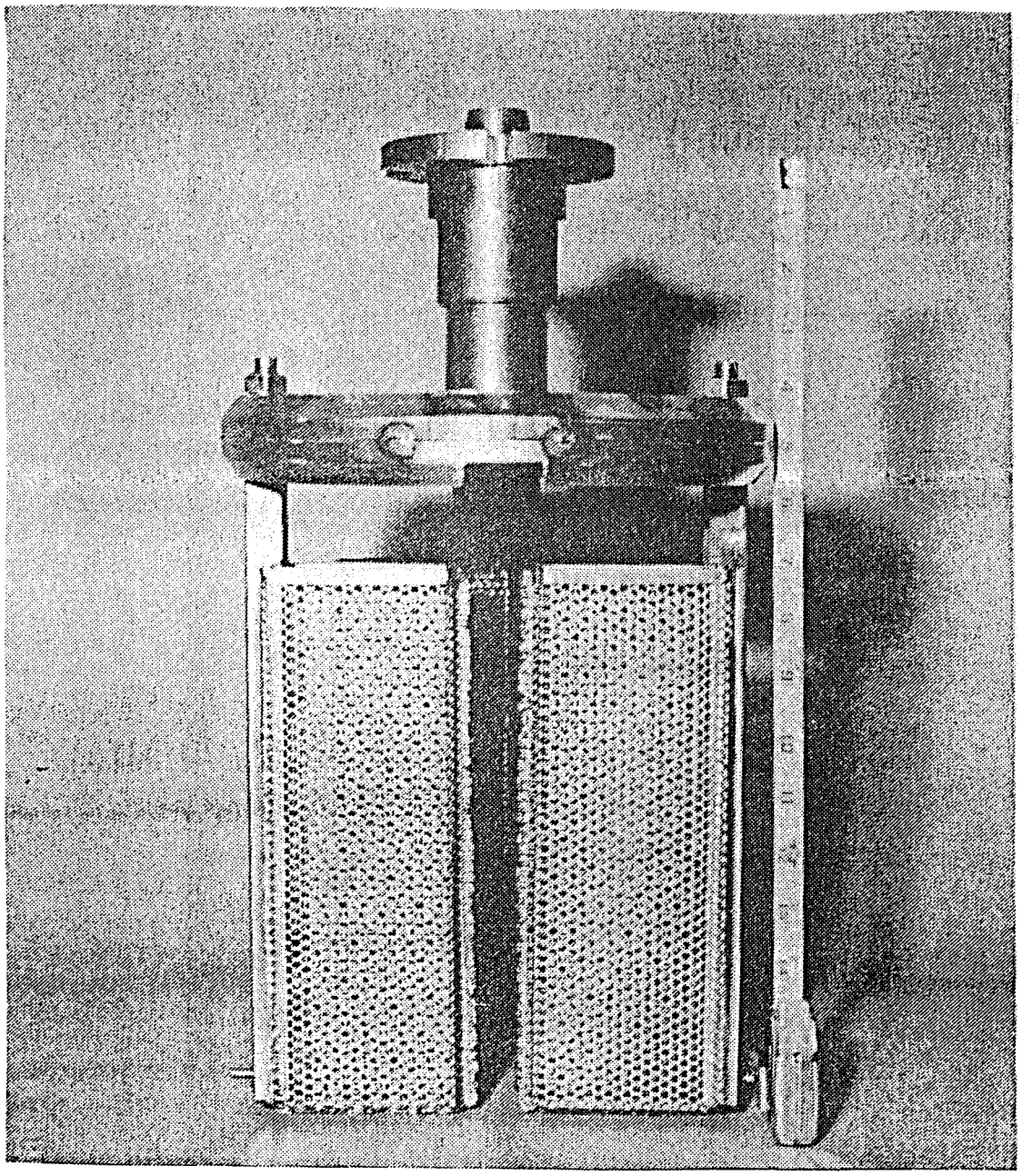

Distribution Coefficient
(wt. % Salt/wt. % Metal)
10
1
0.1
0.01
1 x 10-3
1 x 10-4
Ce
Nd, Pr
Am
Cm
Pu
U
Distribution of rare earths and actinides between chloride salts and Cd-Li Solutions 500°C
1 x 10-7
1 x 10-6
1 x 10-5
1 x 10-4
1 x 10-3
1 x 10-2
Weight Fraction Lithium in Cadmium


Salt: Chlorides
of Li, Na, Ca, Ba
Metal: Cd – U
Temperature: 500°C
Ce
Nd
Am
Pu
Cm
SF(U)
Ce 65
Nd 35
Am 2.3
Cm 2.1
Pu 1.32
Distribution Coefficient
1000
100
10
1.0
0.1
0.01
0.1
1.0
1⁰
100
10⁰⁰
Uranium Distribution Coefficient
(wt% in salt / wt% in metal)

ARGON ATMOSPHERE GLOVE BOX FOR TESTING THE ENGINEERING-SCALE (10 kg) ELECTRO-REFINER




A
B
PLUG
ELECTROLYTE
STIRRER
ASSEMBLY
COVER
CADMIUM
STIRRER
ASSEMBLY
B
A
CATHODE
ASSEMBLY
TOP VIEW
ELECTROLYTE
STIRRER
ASSEMBLY
CENTER
PLUG
PLUG
COVER
HEAT
SHIELD
CRUCIBLE
ELECTROLYTE
DEPOSIT
CADMIUM
INSERT
INSERT
PLUG
SECTION A-A
SECTION B-B



Anodic Dissolution Basket Assembly
(Three of four baskets used are shown.)

ANL Neg. 5634K, Frame #6

ELECTROTRANSPORT REACTION

Anode (Cadmium)

$$U \longrightarrow U^{+3} + 3e^-$$

$$Pu \longrightarrow Pu^{+3} + 3e^-$$

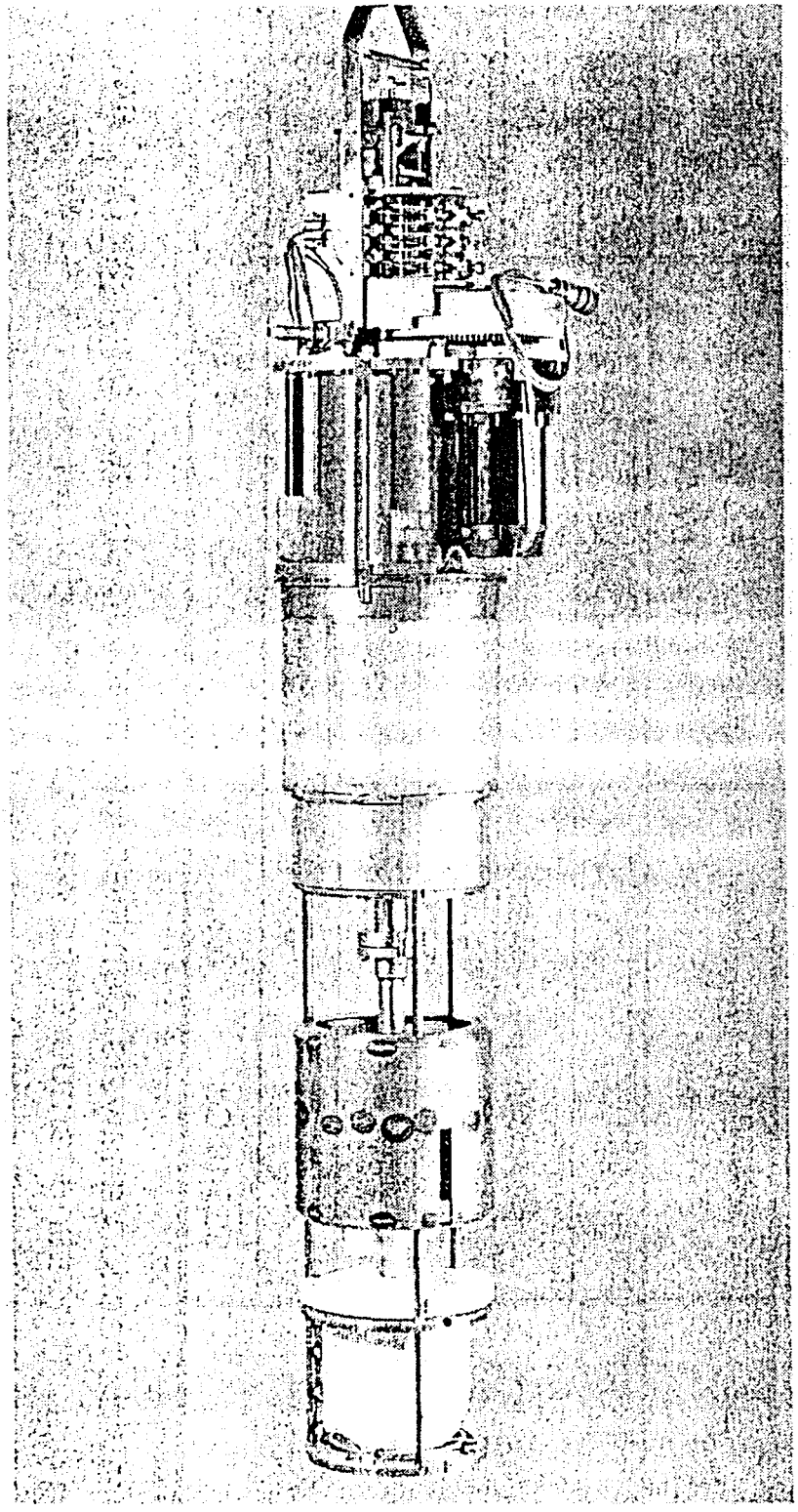
Cathode (Solid Mandrel)

$$U^{+3} + 3e^- \longrightarrow U\ (s)$$

$$Pu^{+3} + 3e^- \longrightarrow Pu(s)$$

$$UCl_3 + Pu(s) \longrightarrow PuCl_3 + U(s)$$

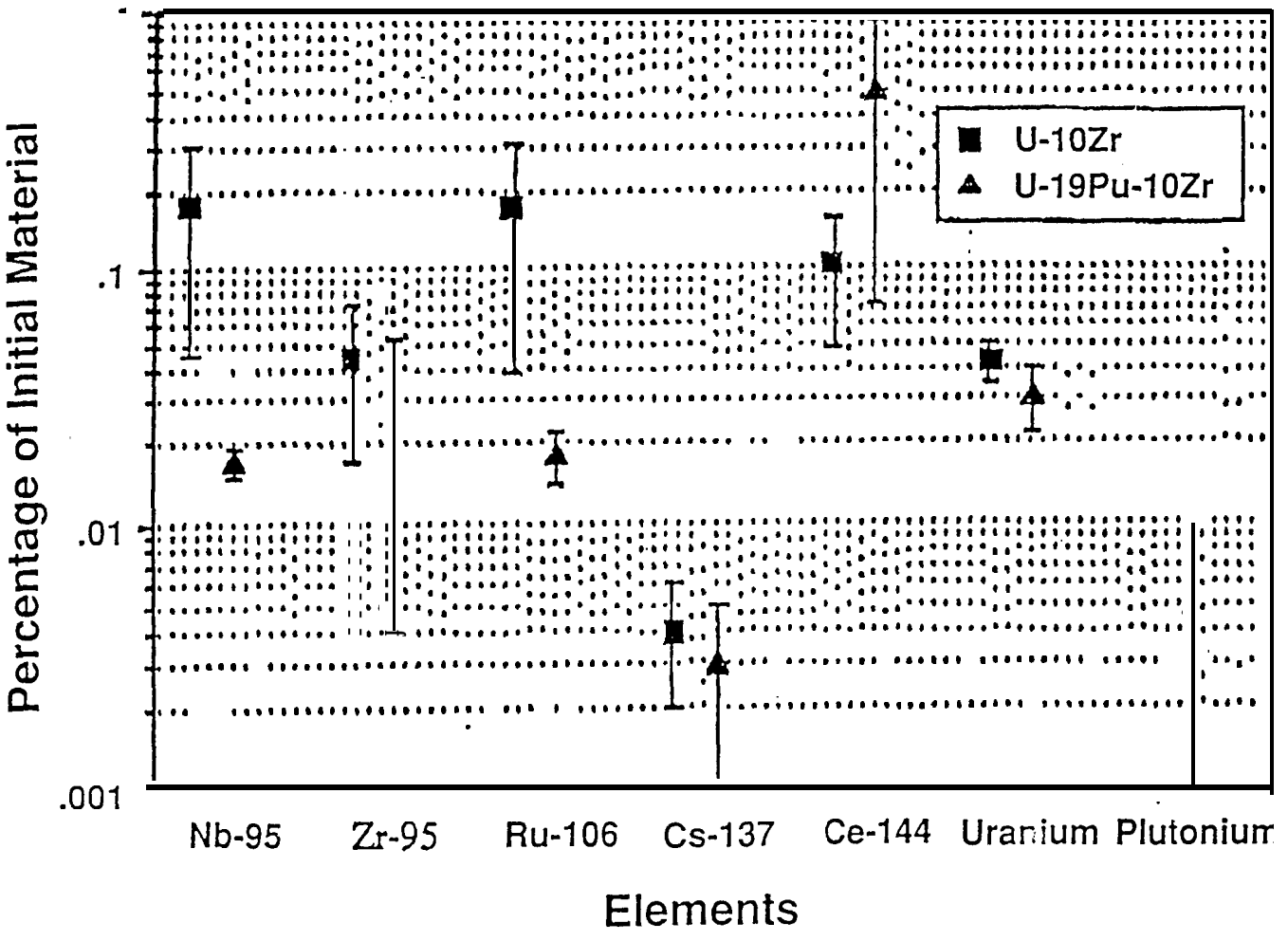
LIQUID CADMIUM CATHODE ASSEMBLY FOR COLLECTING PLUTONIUM IN THE ELECTRO-REFINER



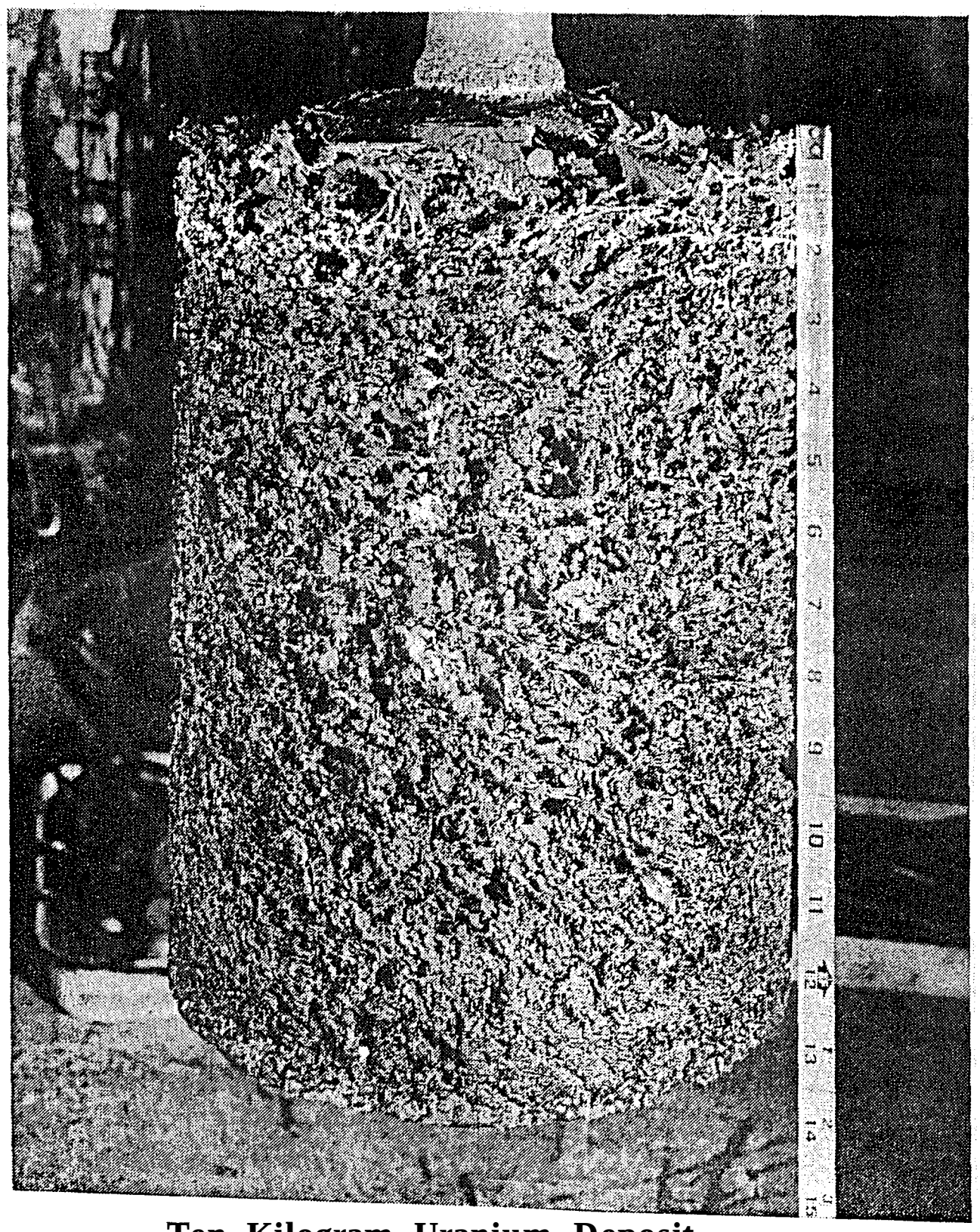
STARTING, INTERMEDIATE, AND FINAL COMPOSITIONS FOR PRODUCT PURIFICATION AND CONSOLIDATION

	Starting Composition, g (Wt %)		Intermediate[a,b] Composition, g (Wt %)		Final Composition, g
Run #1	100.42 U-Zr	(21.75)	100.42 U-Zr	(52.60)	.129.33
	28.92 pu	(6.26)	28.92 pu	(15.15)	U-Pu-Zr[c]
	332.40 Cd	(71,.99)	61.56 Cd	(32.25)	
Run #2	128.21 U	(26.08)	128.21 U	(75.28)	156.28
	28.07 Pu	(5.71)	28.07 Pu	(16.48)	U-Pu[d]
	335.19 Cd	(68.21)	14.03 Cd	(8.24)	

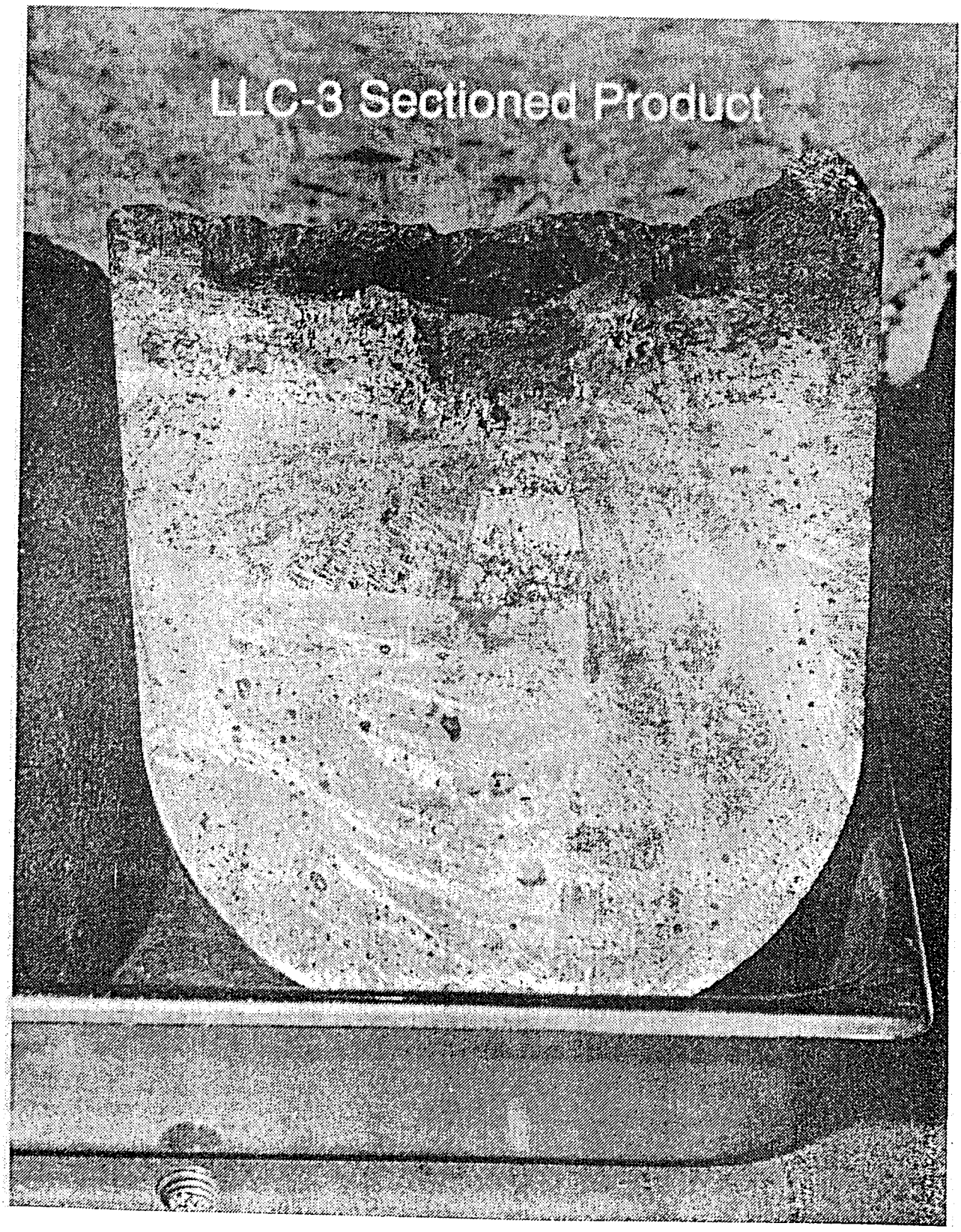
[a] X-ray diffraction analysis identified intermediate phases to be alpha-U and $PuCd_6$.
[b] Maximum heating temperature was 668°C for Run #1 and 702°C for Run #2.
[c] Product contained <150 ppm Cd and Be.
[d] Product contained 54 ppm Cd and 287 ppm Be.



Dissolution of Irradiated Fuel Segments



Ten Kilogram Uranium Deposit - 1990
(ANL Neg. 9132)



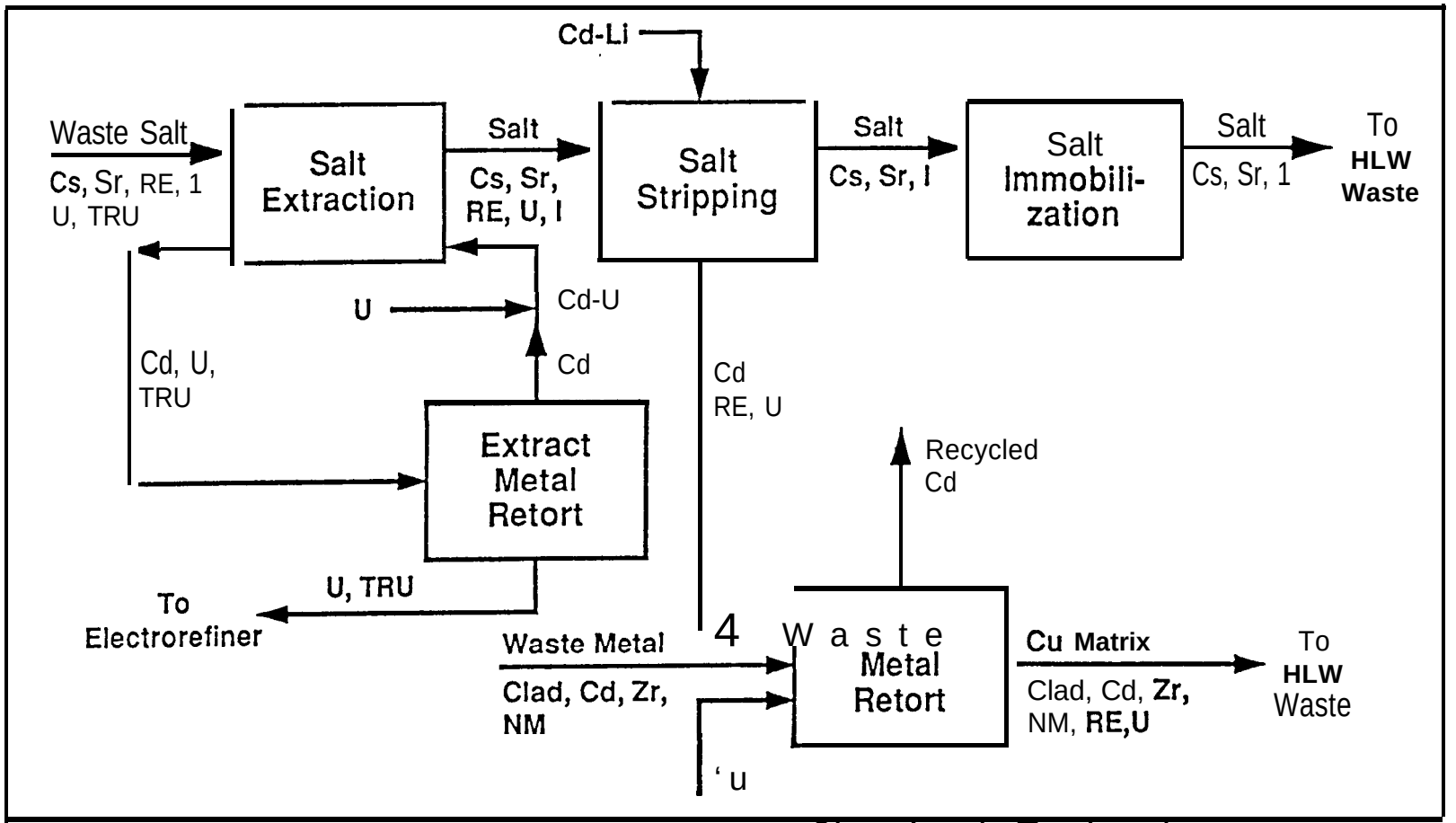
(ANL Neg. 5384K **Frame** #12)

ELECTRODEPOSITION OF URANIUM INTO LIQUID, CADMIUM CATHODE

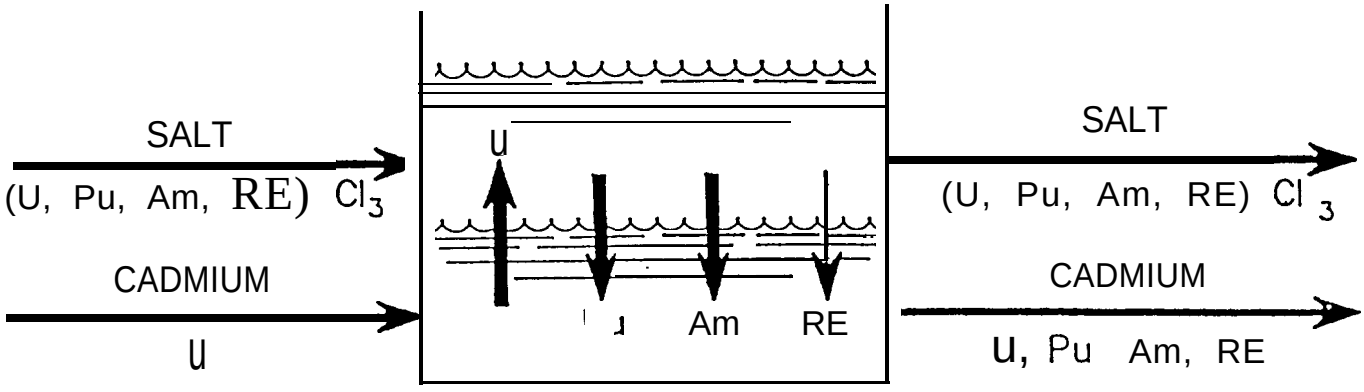
	LCC-1	LCC-2	LCC-3	LCC-4	LCC-5
Deposition Current, A	25	26	25-30	64	170
Cutoff Voltage, V	-1.0	-1.0	-1.0	-1.0	-1.0
Deposition Time, h	56	68	130	33	18
Cathode Efficiency, %	73	54	46	49[a]	b
Cadmium Load, kg	8.7	12.5	12.2	9.6	16,0
Uranium Collected, kg	3.0	2.8	4.4	3[a]	b
Vol. Fraction Uranium, %	14	10	12	8.5[c]	b

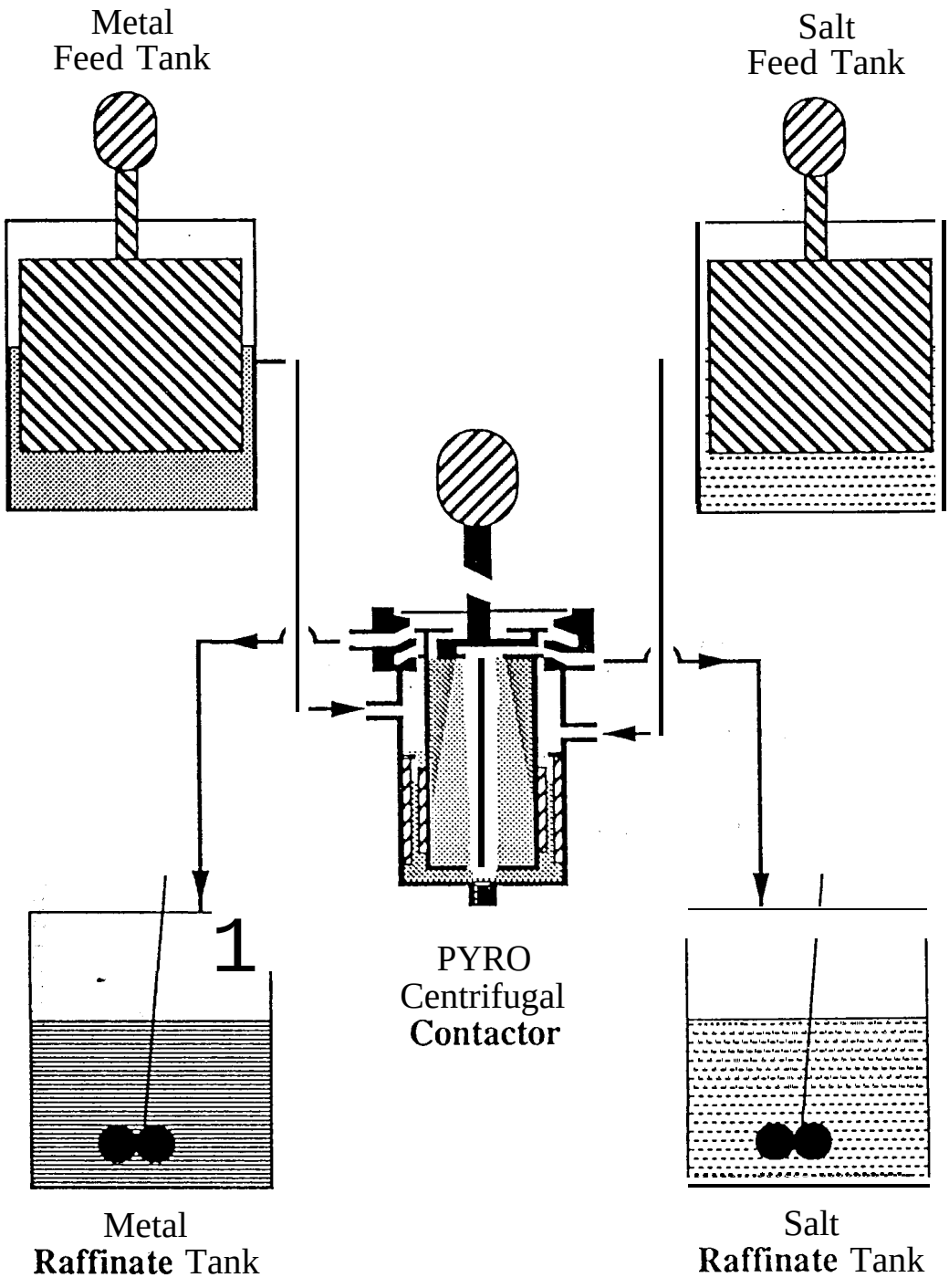
[a] Based on increased weight of cathode at end of run.
[b] Chemical analysis of samples from the liquidcadmium cathode product has not been completed.
[c] Based on measured volume of liquid cadmium cathode.

TRU Recovery and Waste Treatment



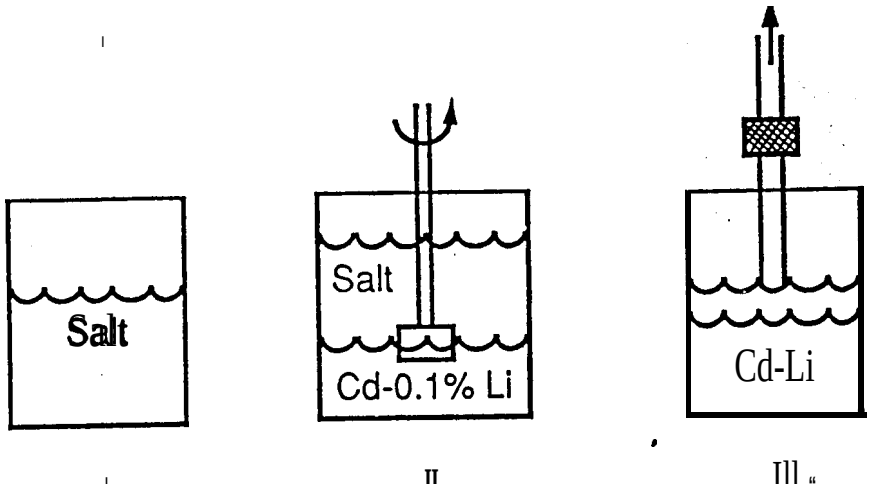
EXTRACTION OF TRU ELEMENTS FROM SALT BY CD – U ALLOY





Pyrocontactor Salt Treatment Test Facility

Laboratory Demonstration of Salt Stripping



	I Initial Salt	II Stripped Salt	III Filtered Salt
U	1.0 Wt %	10 ppm	1 ppm
Pu	0.2%	0.4 ppm	0.03 ppm
Am	3 µCi/g	0.3 nCi/g	0.3 nCi/g
Cm	10 µCi/g	cO.5 nCi/g	<0.5 nCi/g
Ce, Nd	0.5%	<0.01 0/0	<0.01 %

PACKAGING SALT FOR DISPOSAL

Candidate Waste Forms

- Alter Chemical Form (e.g., glass)

  Messy

- Mortar Matrix

  H_2 generated by water **radiolysis**

- Ceramic Matrix

  Fair strength
  Slows leaching
  Incorporate absorbents for Cs and Sr

SUMMARY AND CONCLUSIONS

- ANODIC DISSOLUTION OF METAL FUEL (U-Zr and U- Pu-Zr) IS RAPID, EFFICIENT, AND COMPLETE.
- ELECTROCHEMICAL DEPOSITION OF 10-kg URANIUM ON A SOLID CATHODE HAS BEEN ACHIEVED IN 27 h.
- ELECTROCHEMICAL DEPOSITION OF U-Pu (URANIUM AND $PuCd_6$) IN A LIQUID CADMIUM CATHODE HAS BEEN DEMONSTRATED.
- PRODUCTION OF NO N-TRU SALT WASTE HAS BEEN DEMONSTRATED ON A SMALL SCALE.
- WE THINK THAT NON-TRU SALT AND METAL WASTE FORMS CAN BE DEVELOPED THAT WILL BE SUITABLE FOR DISPOSAL IN A GEOLOGICAL REPOSITORY.