6 Solid HLW

Properties: activity*, heat, thermal effects

Activity of radionuclides in high-level waste (Ci/canister)

		Time out of Reactor - y			
RN	Half-Life	10	100	1000	10000
90-Sr	29 y	1.4E+5	1.5E+4	3.5E-6	0
137-Cs	30.1 y	2.0E+5	2.4E+4	2.3E-5	0
154-Eu	8.6 y	1.0E+4	210	0	0
210-Pb	22.3 y	0	1.7E-6	1.6E-4	6.5E-3
226-Ra	1600 y	2.5E-7	2.6E-6	1.6E-4	6.5E-3
229-Th	7340 y	9.6E-8	1.7E-6	1.6E-4	1.3E-2
230-Th	7.7E+4 y	4.9E-5	7.4E-5	8.8E-4	8.1E-3
238-Pu	87.8 y	2.4E+2	120	0.28	0
239-Pu	2439 y	3.8	3.8	4.7	9.6
240-Pu	6540 y	10	20	18	7.3
241-Pu	15 y	740	11	0.72	0.34
241-Am	433 y	410	380	81	0.34
243-Am	7370 y	40	40	37	17
242-Cm	163 d	16	11	0.18	0
244-Cm	17.9 y	4.0E+3	130	0	0

Short-lived RI at 10 y : 106-Rh 369 d 1300; 125-Sb 2.73 y 1600; 134-Cs 2.06 y 1.9E+4; 144-Ce 284 d 35; 147-Pm 2.62 y 1.8E+4.

Long-lived RI at 10000 y : 93-Zr 9.5E+5 y 4.3, 93m-Nb 12 y 4.3,

99-Tc 2.1E+5 y 32, 126-Sn 1E+5 y 1.3, 129-I 1.6E+7 y 1.8E-4, 233-U 1.6E+5 y 3.6E-2, 237-Np 2.1E+6 y 0.88

Contribution to heat generation of thermally significant isotopes in PWR spent fuel (%).

time - d 30 90 365 1096 3650
Ba/La-140 13.8 0.93
Zr/Nb-95 23.2 24.5 3.9
Ce/Pr-144 18.0 26.9 35.3 17.3
Cm-242 2.2 3.0 2.36
Cs/Ba-137 1.1 2.0 5.0 14.1 35.3
Sr/Y-90 1.1 2.0 4.9 13.7 33.8
Pu-238 0.33 0.85 2.5 6.9
Cm-244 0.74 2.0 4.5

Phase separation: unstable, T + t : Na2MoO4 (Sr,Cs) soluble, MoO3 lesssoluble, Li2O, 15% B2O3; crystallization: 400-800 C, nucleation, crystal growth, leachability 1000X, waste loading 50-100 kW/m^3, container 0.3 m, T grad 500 C, 1960, P glass 455 C 120 d leaching 100X; BSi glass, devitrification products: Zn2SiO4, (CaSrBa)MoO4, apatite, cracking, porosity +3%, no devitrification if T<450 C;

Waste forms: calcines, glass, glass-ceramics,synthetic minerals

Characteristics of world's solidified high-level wastes.

Solidification process	P	WL	HTF	Density	TC	LL
calcination US	C	100	500	1.0-1.7	0.4-1.0	5E-1
calcination ORNL US	C	90	900	1.2-1.4	0.6-1.0	5E-1
ORNL/WSEP US	BG	30-50	900	2.9-3.1	-	1E-6
WSEP US	G	20-40	1200	3.0	-	1E-4

P GLASS	BNL	US	PG	30	1200	2.7-2.9	2.0-3.5	1E-6
STOPPER		US	S	-	500	-	-	1E-8
THERMALT		US	AS	-	2000	2.9	-	1E-8
FINGAL	AERE	UK	BG	25-40	1050	2.8	2.5-4.0	1E-7
HARVEST	AERE	UK	BG	25	1050	2.6	2.8-4.0	1E-7
Dis. process	CEA	F	BG	20-30	1150	-	2.8-3.6	1E-7
Cont. process	CEA	F	BG	20-30	1150	-	2.8-3.6	1E-7
VERA		Germany	BG	20-30	1200	2.5-2.7	-	1E-7
PHOTO		Germany	PG	25-35	1100	2.6-2.9	2.4	1E-7
LOTES	Eurochemic		PG	30	300	2.1	3.0-4.0	1E-5
Pot solidif.		India	BG	22-28	1050	2.5-3.0	2.5-3.5	1E-6
ESTER		Italy	BG	20-25	1000	2.7-3.0	-	1E-7
ESTER		Italy	PG	20-25	900	2.3-3.5	-	1E-5

F = France, P = Product (A = alumino, G = glass, B = borosilicate, P = phosphate, S = silicate), WL = waste loading %, HTF = Highest Temperature of Formation, TC = Thermal Conductivity in mcal/cm/s/C, LL = Lowest Leachability in $g/cm^2/d$.

Calcines: early form, oxides, solubles

Glass: thermodynamically unstable, supercooled liquid +: easy, known, $, durable, variable composition 20% FP -: fragile, unstable; structure: O polyhedra, attraction O-cation, repulsion Cat-Cat;

Ionic field strengths (FS : Z/r^2), charge (C) and ionic radius (IR in 1E-12 m) of cations present in glasses.

	network formers				intermediate ions				network modifiers			
	B	P	Si	As	Be	Al	Ti	Zr	Mg	Li	Ca	Na
C	3+	5+	4+	5+	2+	3+	4+	4+	2+	1+	2+	1+
IR	20	34	41	47	31	50	68	80	65	60	99	95
FS	75	43	24	23	21	12	9	6.3	4.7	2.8	2.0	1.

Oxygen ratio (OR=O/Si): OR = 2 (SiO_2), glass: $2<OR<3$ OR = 4 no glass; leaching: Na+, H+ diffusion and exchange, alkali deficient layer, kinetics: $t^{0.5}$, linear: long t, high T; glass-ceramic: dispersion of crystals, annealing at nucleation T + GG, celsian, diopside, eucrypite, perovskite, borosilicate G

SYNROC and its constituent minerals (weight %, H= Hollandite, Z = Zirconolite, P = Perovskite, BS = Bulk SYNROC).

	H	Z	P	BS
TiO_2	71.0	50.3	57.8	60.3
ZrO_2	0.2	30.5	0.2	10.8
Al_2O_3	12.9	2.5	1.2	6.3
CaO	0.4	16.8	40.6	16.2
BaO	16.0	-	-	6.4

properties: stable, 20 % RW, resistance (mechanical, chemical, radiation); Distribution of high-level waste elements among constituent minerals of SYNROC.

Hollandite : Cs^+, Rb^+, K^+, Ba^{2+}, Fe^{3+}, Cr^{3+}, Ni^{2+}, Mo^{4+}

Zirconolite : U^{4+}, Th^{4+}, Pu^{4+}, Cm^{4+}, Np^{4+}, Act^{3+}, RE, Sr^{2+}

Perovskite : Na^+, Sr^{2+}, Pu^{3+}, Cm^{3+}, Np^{3+}, RE, Act^{4+}

Metal : Ru, Tc, Mo, Ni,Pd, Rh, Te, S, Fe

leaching: removal of C+, C++, Ti Zr rich film, Cs, Ba 1000X, Nd3+,U4+ 10000X less than glass, no new phases; radiation damage: natural Z + P alpha emitters, 1.3E+18 a/g (1000 y) dV +2%, 8E+18 (400 000 y) +3%, Z monoclinic to cubic (CaF2) structure, 8E+19 a/g (4E+8 y) metamict +3% crystalline state, P 20000 y +1.8%; Sri Lanka Z 1E+18 a/g 200 C bulk leach 3E-4 $g/m^2/d$, 8E+18 a/g 2E-3 $g/m^2/d$; preparation: precipitation TIPTi + TBZr + nitrates, slurry, drying 130 C powder, calcination 750 C Ar 4% H2 Cs Ru, HIP ~1150 C ~ 125 MPa, uniaxial HP, 4.5 g/cm^3 more waste, clean; disposal: boreholes 1 m, 4 km, waste : 2.5 km,

seal: 1.5 km 80 GWy, drilling damage, sealing
Interim storage: wet, dry, fuel bays 40 y, 67 US plants "full core reserve" by 2000, dry storage, AFR;
Wet S*: 95% pools 12 m deep, 3 m shielding +: cooling -: dirty; capacity increase: reracking, poisoned rack B, rod consolidation, dismantling FA, storage canister, old fuel
Dry S: used for 20 y by DOE, +: flexibility, passive cooling, cleaner, metal casks, concrete silos**, dry wells (Nevada), buildings*
Large metal dry storage cask characteristics

Characteristic	Castor	TN-24P	MC-10*	NAC 5100
NRC license status	L	U	U	U
Capacity (PWR)	21	24	24	28
Construction materials	iron	steel	steel	SS/Pb/SS
Neutron shielding	PE	BP	BP	SS/Pb/SS
Maximum weight-tons	115	100	100	?

L = Licensed, U = Unlicensed, SS = Stainless steel, PE = Polyethylene, BP = Borated plastic.
AFR: 2 wet facilities Morris (Ill), West Valley (NY), dry AFR Gorleben (G)

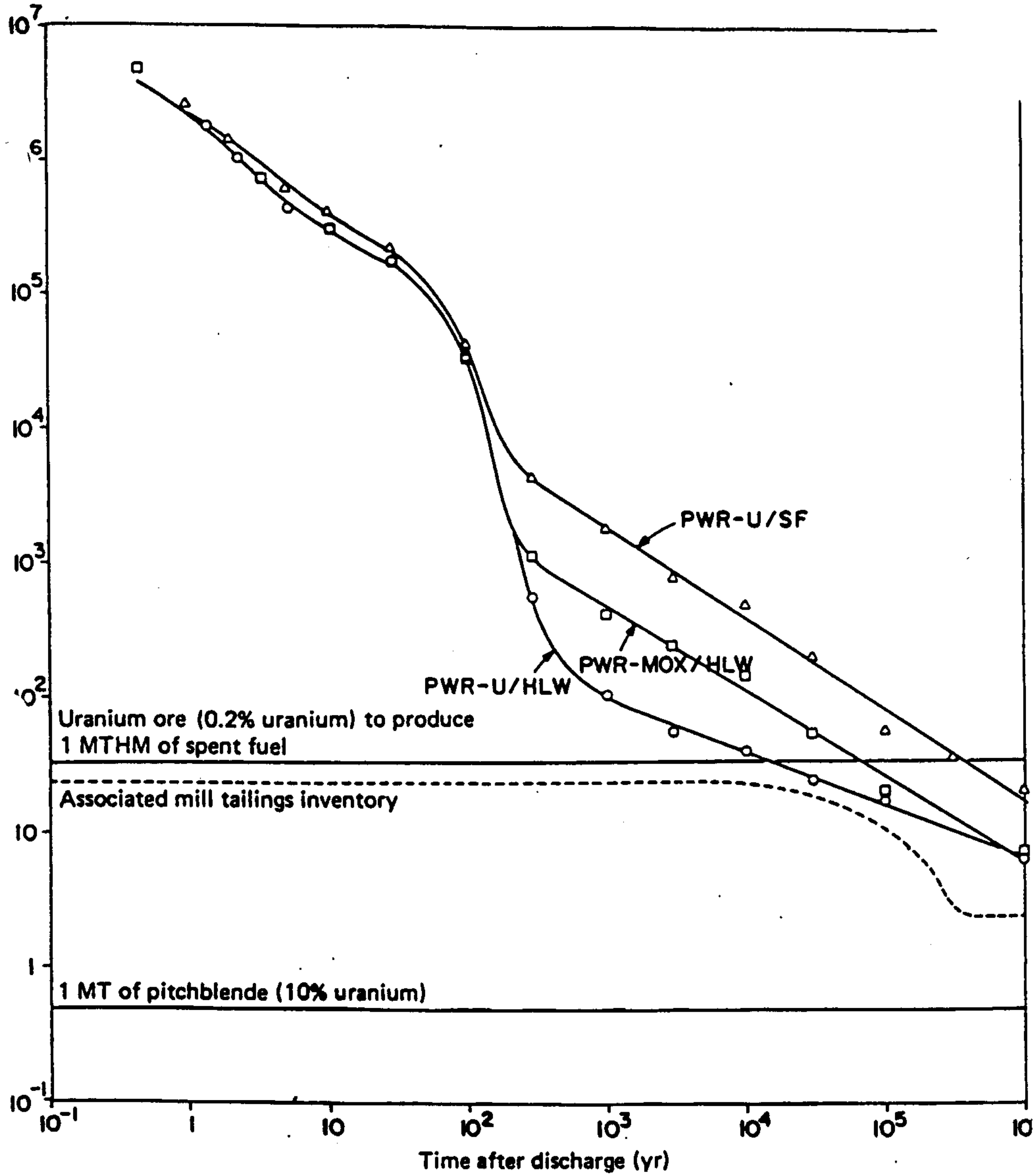


Fig. 1. Radioactive decay of PWR spent fuel and HLW.

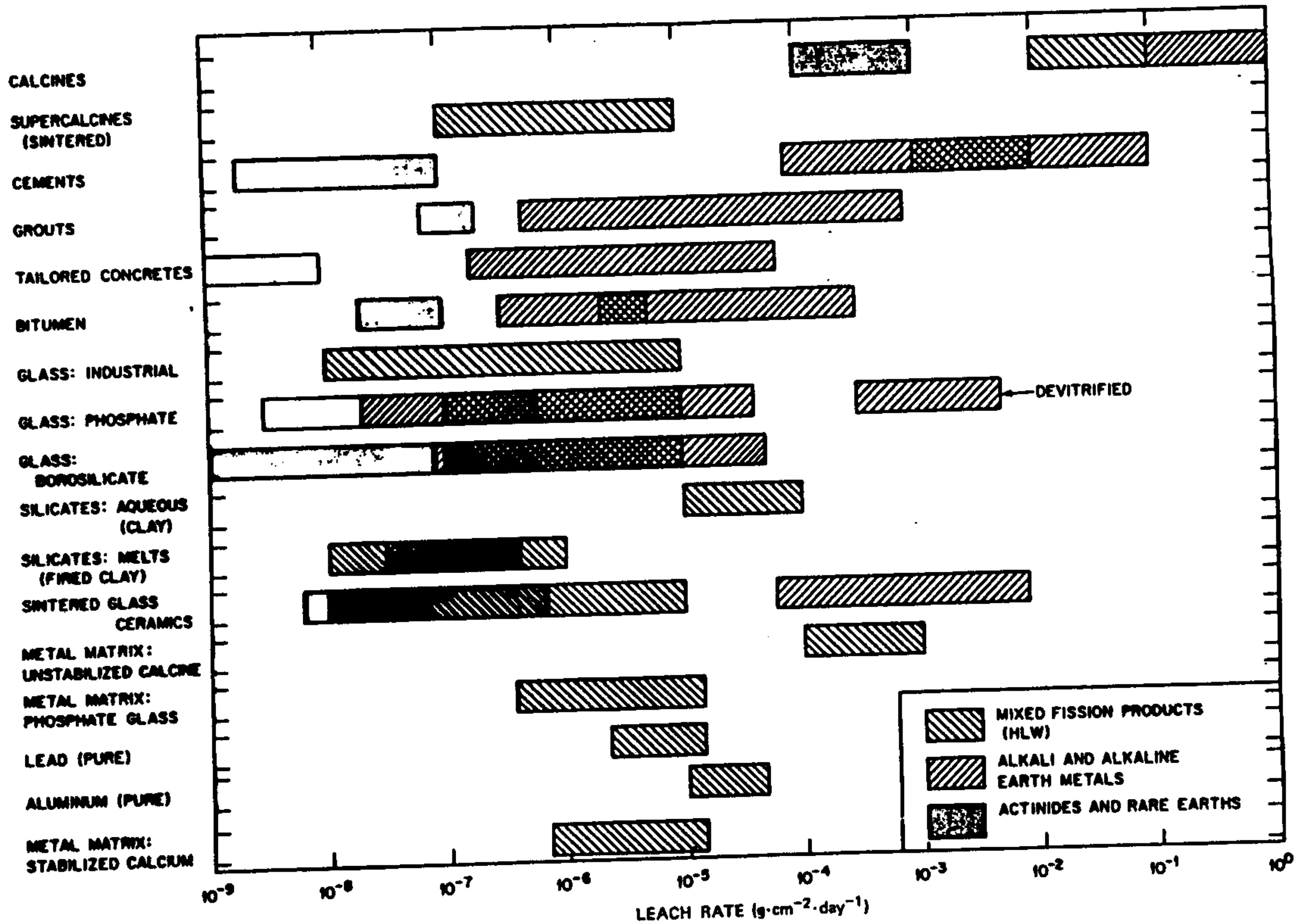
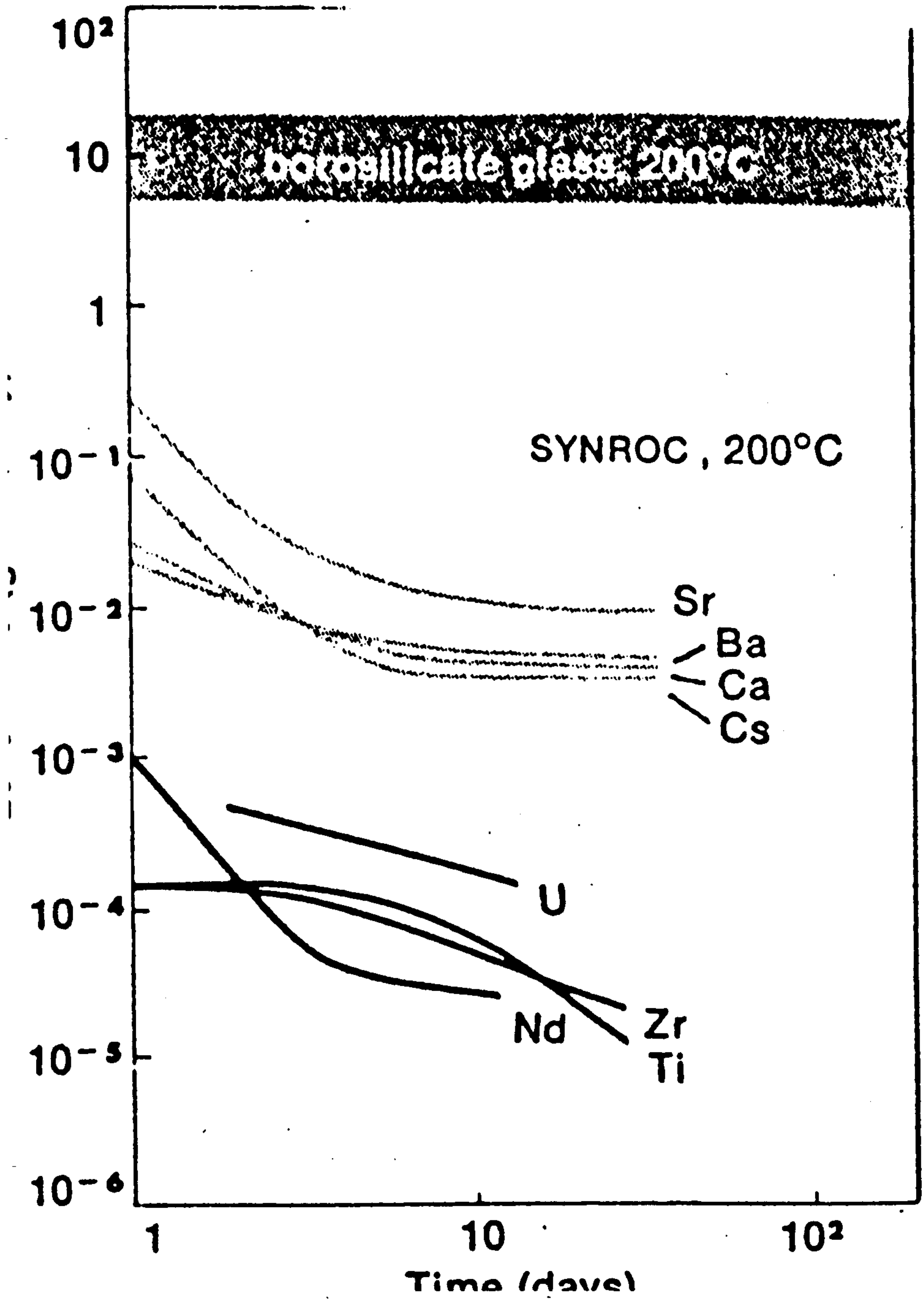


Fig. 5. Some reported leach rates for various radionuclides in several matrix materials.



10²
10
1
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
borosilicate glass, 200°C
SYNROC , 200°C
Sr
Ba
Ca
Cs
U
Nd
Zr
Ti
1
10
10²
Time (days)

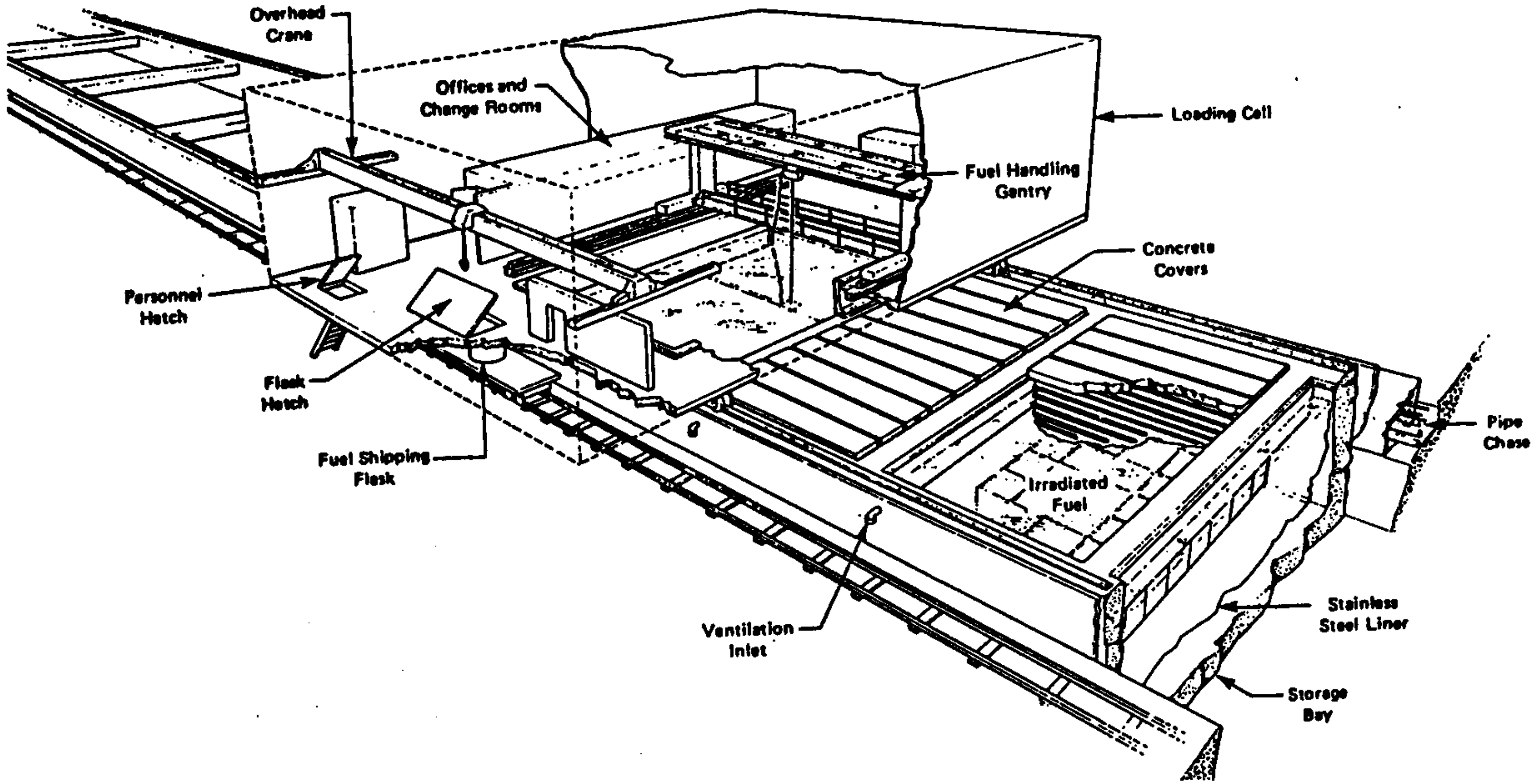
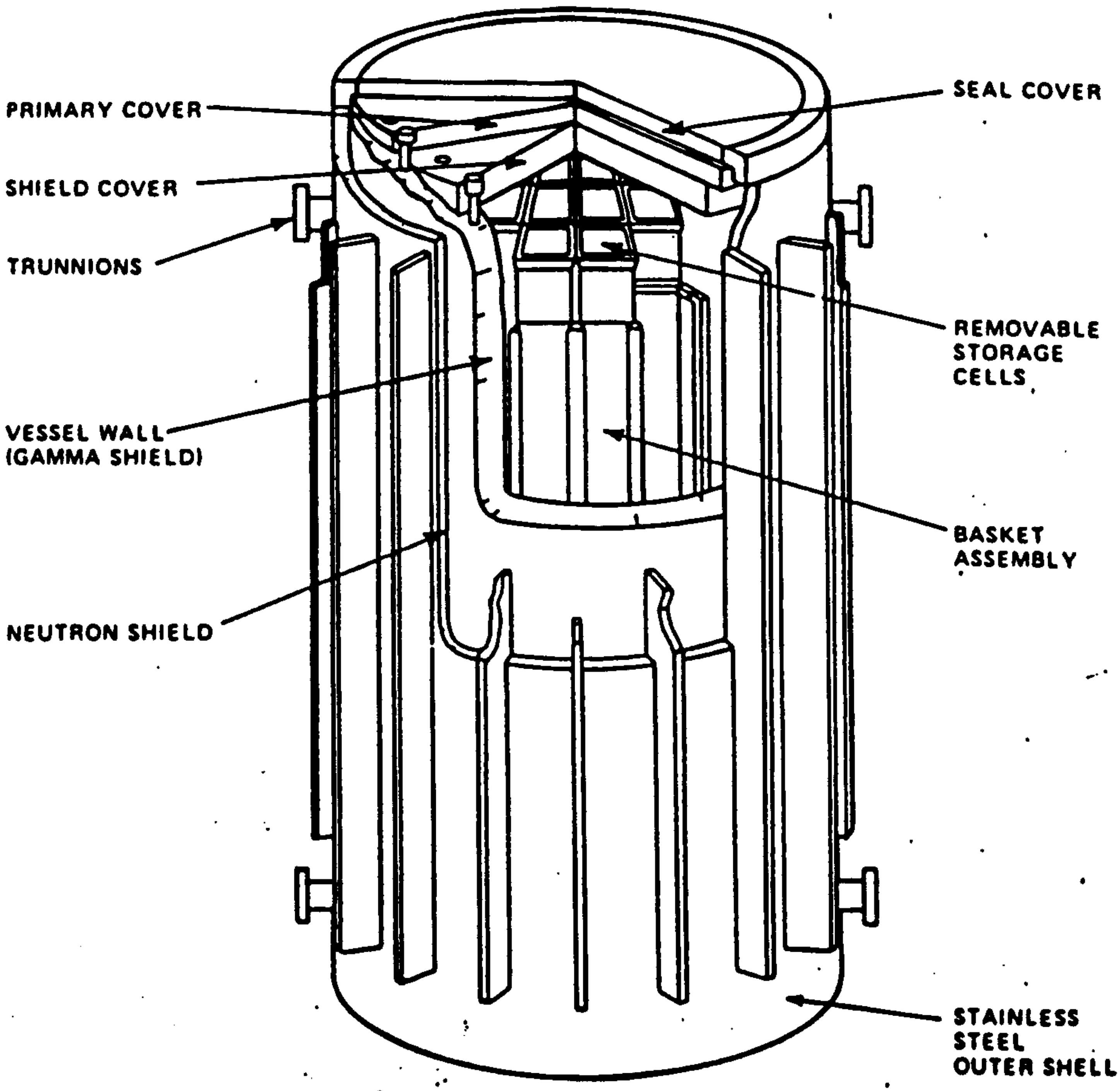
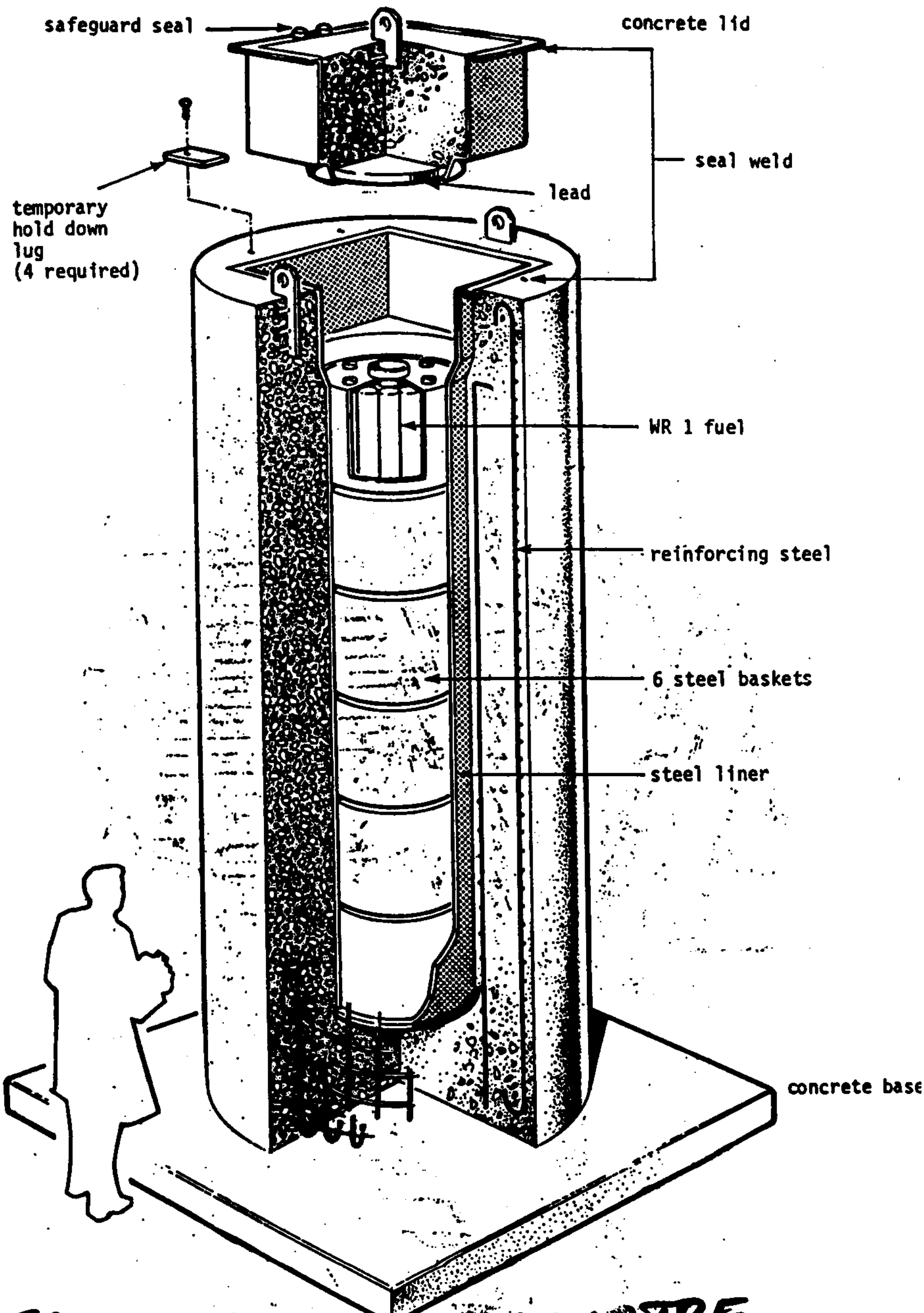


FIGURE 3: CENTRAL POOLS - CUTAWAY (From Ref. 5). AECL 6191



e 5-18 Westinghouse MC-10 cask. (Reprinted from *Nuclear News*



F2 CONCRETE CANISTRE

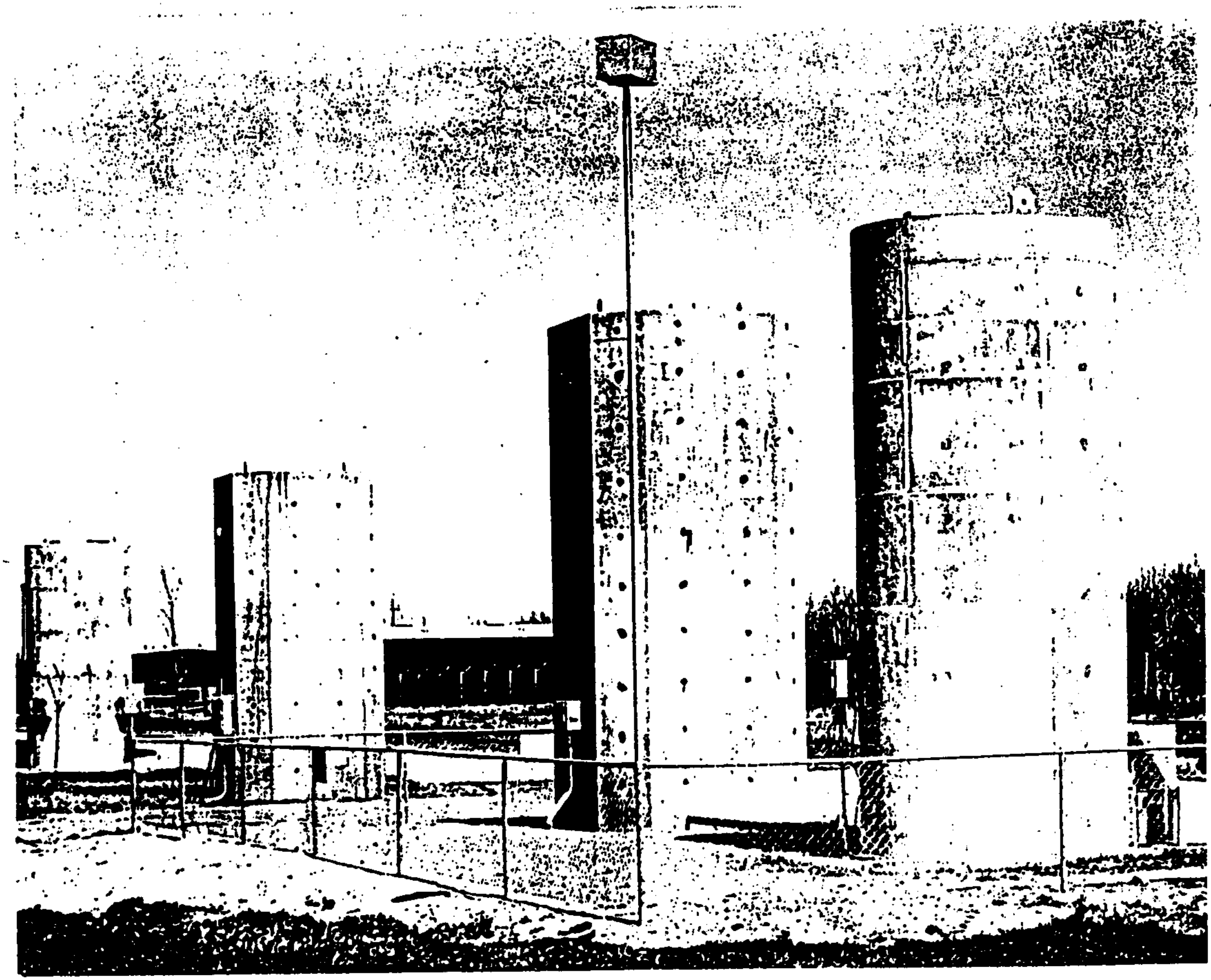


FIGURE 10: CANISTERS IN OPERATION. AECL6191

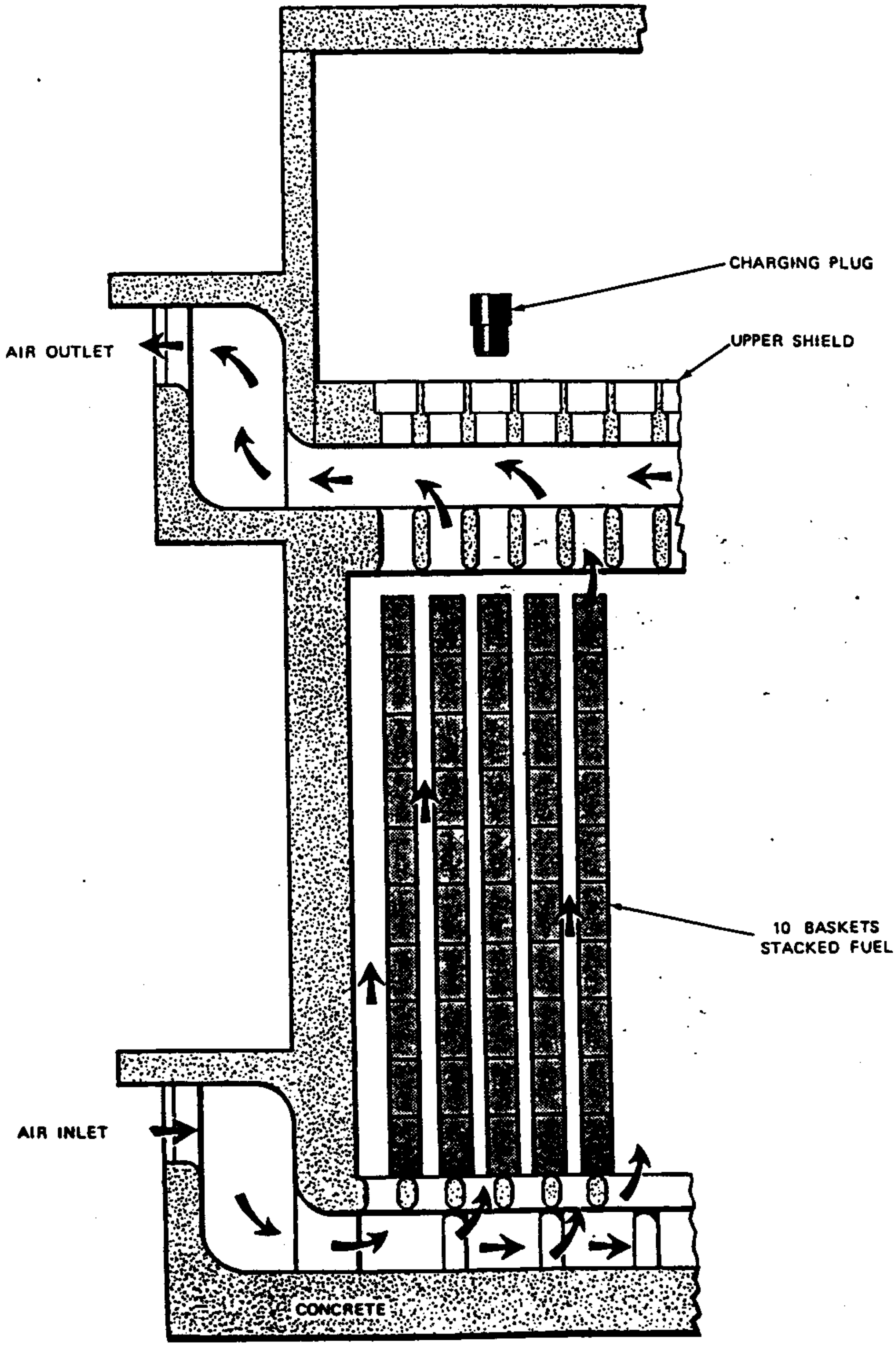


FIGURE 5: DRY STORAGE FACILITY - CONVECTION COOLING. AECL6(