A Continuous Transmutation System for Long-lived Nuclides with Accelerator-driven Fluid Targets

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ABSTRACT

An accelerator-driven transmutation system for long-lived nuclides of MA and FP was studied. The system with fluid targets may establish a continuous transmutation system having on-line separation facilities for the elements transmuted by spallation and fission reactions. To realize the effective incineration system MA is designed to be transmuted mainly through fission reactions by fast neutrons and FP of Tc-99 and 1-129 through neutron capture reactions by thermal neutrons. The total system of one accelerator with two fluid targets is discussed.

In the preliminary study molten chloride salt of NaCl-(Pu,MA)Cl3 system is adopted for the target salt of MA transmutation, and Bi-Pb alloy for target fluid of neutron production to transmute the FP with a heavy water blanket. The amounts of MA and FP to be transmuted are estimated by the neutronics and thermal hydraulics calculations. The MA and long-lived FP produced approximately from 10 units of 3000 MWt LWR can be incinerated by about 25mA and 150mA of 1.5 GeV proton beam, respectively.

The principle of the separation of the transmuted elements in the continuous transmutation system is continuously to remove the stable and short-lived transmuted nuclides(elements) without contamination from the long-lived nuclides(elements). The transmuted elements in the molten chloride salt target can be classified into 3 groups considering the chloride formation energy. First group is composed of inert gases and volatile chlorides, 2nd group noble metals and transition elements, and 3rd group alkaline earth metals, lanthanide and yttrium chlorides. The He purge method and Cd extraction method for the on-line separation can be applicable to the 1st and 2nd group, respectively. The cold trapping method may be applicable to 3rd group. The oxidation method and He purge method may be applicable to separate Ru transmuted from Tc, and Xe from I in the FP transmutation system, respectively.

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An accelerator-driven transmutation system for long lived nuclides with fluid target may establish a continuous transmutation system having on-line separation facilities for the elements transmuted by spallation and fission reactions. To realize the effective transmutation system MA is designed to be mainly transmuted through fission reactions by fast neutrons and FPs of Tc-99 and 1-129 through neutron capture reactions by thermal neutrons. In the preliminary study the molten chloride salt of $NaCl-(Pu,MA)Cl_3$ system is adopted for the target salt of MA transmutation, and Bi-Pb alloy for the fluid target of neutron production to transmute the FP with a heavy water blanket. The amounts of MA and FP to be transmuted are estimated by the neutronics and thermal hydraulics calculations.

1. Introduction

Long-lived nuclides such as neptunium, americium and curium of minor actinide (MA), and Tc-99 and I-129 of FP have been received substantial efforts to be separated from the high level radioactive waste (HLW) and to be transmuted to shorter-lived nuclides. An accelerator transmutation system with fluid targets may establish a continuous transmutation system with on-line separation facilities for the elements transmuted by spallation and fission reactions. The advantage of the continuous transmutation system is thought to be able to eliminate the complicated processes being followed by the batch reprocessing for solid spent fuels and targets. The once through process for the transmutation, i.e. to input the long-lived nuclides and to output the stable and short-lived nuclides,

may be established in the accelerator transmutation system with fluid targets,

From the strategic view point a requirement to the transmutation capacity of the unit system is supposed to incinerate such amount of MA and long-lived FP **as produced approximately by 10 units of 3000 MWt LWR. To realize the effective incineration system the** MA is **designed to be incinerated mainly through** fission reactions by fast neutrons and Tc-99 and 1-129 through neutron capture reactions by thermal neutrons considering **the neutron cross sections of MA and** FP of Tc-99 and I-129 as shown in Fig. 1-1 to Fig.1-3 for MA and Fig.2-1 to Fig.2-2 for FP, respectively.

2. MA transmutation system with Molten Salt Target

(1) Target Salt

The molten fluoride salt of $LiF-BeF_2$ system has been studied extensively for many **years at Oak Ridge National Laboratory** as the fuel salt of the molten salt reactor(l) and the target salt of accelerator-diven transmutation system(2). The volubility of thorium and uranium in the salt is high enough to be the fuel and target salts of these systems. On the **other hand volubility of TRU in the** salt has not been reported except PuF_3. The volubility of PuF_3 in the salt is below one mole **percent** at 600 'C(3). It is difficult to estimate the solubilities of Np, Am, Cm in the salt, though, those are not thought to be high enough for the target salt. Moreover, it may be difficult to make the fast neutron system' with LiF-BeF2, since the mass numbers of the constitutional elements of $LiF-BeF_2$ is low enough. From these points, it will be difficult to establish the effective MA **transmutation system with molten salt** of $LiF-BeF_2$, where MA produced approximately from 10 units of 3000 MWt LWR are able to be incinerated by the unit system.

The molten chloride salts have been studied as a solvent in the dry process(4). Recently chloride systems have been received much efforts in the R & D for Integral Fast Reactor at ANL(5), CR IEPI(6), universities(7) and JAERI (8).

Concerning the TRU solubilities in chloride salt systems, several phase diagrams composed of $PuCl_3$ are reported. In the system, $NaCl-ThCl_4-PuCl_3$ is attractive from the view points of Pu volubility and the melting points as shown in Fig.3(9). We adopted to examine the $NaCl-PuCl_3$

system, whose eutectic temperature is 453oC for the composition of 64(m/0)NaCl-36$PuCl_3$, as the target salt in the accelerator transmutation system. The solubilities of MA in this salt are not reported, though, Pu may be replaced by other actinides such as Np, Am, and Cm.

To establish a harder neutron spectrum in the target system, chloride salt may be better than fluoride salt, since mass number of chlorine is about twice of that of fluorine. The parasitic neutron absorption cross section of chlorine is not so large as shown in Fig .4, especially for the fast neutron. Therefore, the amount of sulfur produced by the neutron absorption reaction in the molten salt target may be small enough and its effects to the target salt system will be ignored.

Corrosion problems are important to be solved in application of the molten salts to nuclear systems. Corrosion by chloride is used to be a serious problem, however, low carbon steel may be usable as a structure material, when water concentration in the salt could be controlled to low enough. The mechanism of the corrosion by chloride seems to attribute to formation of complex compounds such as oxychloride under considerable concentration of water in the salt(7).

(2) Target System

Conceptual design studies have been performed to assess the technical feasibility of an accelerator-driven transmutation system with the molten chloride salt target system of the subcritical condition. To , satisfy the requirement for the transmutation capacity of MA produced by about ten units of 3000MWt LWR, namely about 250kg/year, the subcritical target system may need to operate at an effective multiplication factor of around 0.9 or more, considering the reasonable scale of the accelerator and the energy balance of the total system.

The conceptual design of the molten salt target system and its rough scales are shown in Fig.5 and Fig.6, respectively. As shown in Fig.5 and 6, high energy proton beam is injected into the target salt of region I through the beam window. MA is mainly transmuted in this region by the fast fission reaction and spallation reaction. The fission chain reactions may be controlled by the proton current injected. In region II 1, the heat exchangers and centrifugal pumps are located inside the target core to decrease the total volume of the target salt, The target salt containing MA is circulated through the region I to III by the pumps. The total capacity of the heat removal is designed to about 800MW, which

corresponds to the heat generated by the MA incineration velocity of about 250kg/year. From the materials view points, the temperatures of the primary salt at the input and output of the heat exchangers are designed to about 650°C and 550°C, respectively. The region II is a cylindrical neutron reflector to protect the heat exchangers and pumps from the radiation damages.

The region IV is the neutron reflector and outside of which is corresponding to the core vessel. The region V is beam window including gas flow space for cooling. A very high proton flux through the window causes problems of severe radiation damage and excess heating. The preliminary radiation damage analysis on the beam window of HT-9 was conducted.

(3) Calculation for the transmutation

The calculation 'method for the nuclear reaction in the target core is almost same as described in the literature(11). The improved code NMTC/JAERI(12) is used to analyze the spallation reaction. In the calculation a beam power of 1.5GeV, 1 mA is adopted as the reference.

Target salt of the composition 64NaCl-36(Pu,MA)Cl_3 is examined for the calculation. The original composition of the salt is 64NaCl-36$PuCl_3$ and its phase diagram is shown in Fig ,3. The ratio of Pu to MA is assumed to 15 to 85 mole percent. The MA is composed of Np, Am and Cm, and their ratio is as same as those in the spent fuels of the LWR, namely 56: 39:5. The design parameters and the results of the calculation are shown in Table1. The effective multiplication factor is calculated to be 0.92. The thermal output and amount of MA incinerated by the beam current of 1 mA is calculated to be 32MW and 10kg/year, respectively. This result means that the amount of MA produced from 10 units of each 3000MWt can be incinerated by the beam current of about 25mA.

The neutron spectrum and the thermal power density are shown in Fig.7 and Fig.8, respectively. The neutron spectrum in the region I is close to that of the fast reactors. The highest neutron flux is about 10^{14} n/cm^2 s for the current of 25mA at the neutron energy of about 1 MeV. The maximum neutron flux in the region III, where the heat exchanger is located, is about 2 orders of magnitude lower than that in the region I. This result is also recognized from the power distribution in the target

core as shown in Fig .8. The internal reflector may protect the heat exchangers from radiation damage as expected.

(4) On-line separation of transmutation products

[n the target core of effective neutron multiplication factor 0.92, MA more than ninety percent is transmuted by the fission reaction and the several percent by the spallation reaction. The transmutation products in the molten salt target core is not calculated yet. However, those shall be close to the fission products in the fast reactors. The fission reaction of the MA-chloride may produce free chlorine as the following reaction,

$$MACl_3 + n \longrightarrow 3Cl + FPs ,$$

Considerable amount of FPs may react with the free chlorine and become chlorides. The FPs and their major chlorides are shown in Tables2-1 and 2-2 including their free energy of formation and melting point. The chlorides are rearranged in order of the free energy of formation as shown in Table 3. In 'the table the other chlorides such as actinide chloride and alkali chloride are also shown.

Under the consideration of the chloride formation energy the FPs can be qualitatively grouped in the following 3 groups as shown in Table 4.

Group I : Inert gas or volatile chloride,
Xe, Kr, I, $TeCl_4$, $ZrCl_2$
(about 23°/0 of total FP)

Group 2: Noble metals and transition metals,(the free energy of formation is smaller than that of Cd-chloride in absolute value)
Nb, Te, Mo, Tc, Rh, Pd, Ru
(about 33°/0 of total FP)

Group 3 : Alkaliearth metals, Lanthanide and Y, (the free energy of formation is large in absolute value)
Ba, Rb, Sr, Cs, Sm, La, Pr, Ce, Nd, Eu, Gd, Y
(about 44°/0 of total FP)

The schematic image of on-line separation method for the FP is shown in Fig.9. For the group-1 ,the He gas purge method will be applicable. In

this method He gas is blown into the salt and purges away the gaseous FP with He. For the inert gases this method has been examined successfully in R & D of MSBR at ORNL(13). $TeCl_4$, $ZrCl_2$ and I are also expected to be purged away but the experiment was not performed yet. For the group-2, a reductive extraction method with liquid Cd metal will be applicable. In the extractor of Fig.9, the target salt and liquid **Cd metal are contacted, and the chlorides of group-2 are reduced** to metals by Cd. The metallic elements in the molten salt phase can be extracted to the liquid Cd metal phase owing to their distribution coefficients between the salt phase and the metal. The elements solved in the Cd metal can be removed by the cold trapping continuously as shown in Fig.9. In the metal elements separated by the cold trapping, Tc-99 will be contained. Tc can be separated from other elements by using the oxidation and volatilization method of Tc_2O_7, since its vapor pressure is much higher than the other oxides. The elements in the group-3 will instantly become stable chlorides after produced by the transmutation reactions. These chlorides can not be reduced by Cd metal. The volubility of these chloride in the target salt is uncertain. The cold trapping, however, might be applicable to separate the chlorides of the group-3, since the melting points of these chlorides are high enough comparing to the target salt matrix. The separation methods for the three groups of FP and their fraction to the total FP are listed in Table 4. The importance of the FP removal from the target salt is to remove the stable and short lived FP without contamination from the long-lived nuclides. If the contamination is low enough, the FP waste removed may be easily disposed.

3. Transmutation of the Long-lived FP

The long-lived FP of Tc-99 and 1-129 can be transmuted to stable nuclides of Ru and Xe, respectively, through neutron absorption reactions. The reactions and those cross sections are shown in Fig. 10, The cross sections of Tc-99 and 1-129 for thermal neutron are 20 burns and 31 burns, respectively. These values are larger than those for the fast neutron in 2 orders of magnitude.

The transmutation velocity of the nuclides dN/dt in the neutron flux@ is depicted in equation (1).

$$dN/dt = -N\lambda - N\Phi\sigma \qquad (1),$$

where

λ = disintegration constant

σ= neutron absorption cross section

The number of nuclides at time t is obtained from the equation (1),

$$N(t) = No \exp(-\lambda' t) \qquad (2)$$

where

$\lambda' = \lambda + \Phi\sigma$:effective disintegration constant

The effective half lives ($ln2/\lambda'$) of Tc-99 and 1-129 are shown in Fig.11 as a function of neutron flux. The effective half lives of Tc-99 and I-129 for the $\Phi = 10^{15}$ n/cm^2 s are calculated as 1.1 year and 0.7 year, respectively.

The schematic concept of the FP transmutation system is shown in Fig. 12. The high energy proton of 1.5 GeV is injected to the Bi-Pb flowing target. The spallation neutron produced at the Bi-Pb target passes through a wall of the container to the heavy water blanket. The neutron in the blanket losses its kinetic energy during collision with the heavy water and transmute the Tc and I to the stable nuclides, which are contained in the heavy water. Tc is contained in the water as a slurry of TcO_2 and I is solved as ion from solution of AlI_3. The transmutation products of Ru in the slurry may be separated from the TcO_2 slurry by the volatilization method of Tc_2O_7. On the other hand Xe from the I-129 can be removed easily from the heavy water by He-purge method. The number of neutrons produced from the spallation reaction of 1.5 GeV proton with Bi-Pb target is estimated approximately to be 50. According to this value the proton current requested to transmute the FPs produced from 10 units of 3000 MWt LWR is more than 150mA(for 60% efficiency 250mA is requested). The radiation damage and corrosion to the wall of the Bi-Pb vessel are the serious problems. The austinitic stainless steel, however, is thought to be applicable if the temperature of the wall can be controlled under 300°C. In the case of solid target it will be difficult to control the temperature of the wall/boundary materials between target and blanket under 300°C, through which high flux of neutrons are passing.

The transmutation reactions of these FPs are heat absorption reactions. To hold the energy balance as a total system, the electric

power for the FP transmutation shall be supplied by the margin of the power produced by the MA transmutation system, whose image is shown in Fig. 13.

4. Conclusion

Accelerator-driven transmutation system for long-lived nuclides of MA and FP was studied. In the preliminary study, molten chloride salt of $NaCl-(Pu,MA)Cl_3$ system was adopted for the target salt of MA transmutation, and the Bi-Pb fluid target with the heavy water blanket for FP transmutation. The amounts of MA and FP to be transmuted were estimated by the neutronics and thermal hydraulics calculations. The MA and long-lived FP produced approximately from 10 units of 3000 MWt LWR can be incinerated by about 25mA and higher than150mA of 1.5 GeV proton beam current, respectively. The on-line separation methods for the transmuted elements were discussed to establish the continuous transmutation system. The transmuted elements in the molten chloride salt can be classified into 3 groups considering the chloride formation energy. First group is composed of inert gases and volatile chlorides, 2nd group noble metals and transition metals, and 3rd group alkaline earth metals, lanthanide and yttrium chlorides. The He purge method and Cd-metal extraction method for the on-line separation can be applicable to 1st and 2nd group, respectively. The cold trapping method may be applicable to 3rd group. To separate Ru transmuted from Tc, and Xe from I in the FP transmutation system the oxidation method and He purge method may be applicable, respectively.

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Table 1 Design parameters of target system and results of **the** calculation for MA transmutation

Target Salt
Composition : 63NaCl-36(Pu, MA)Cl_3
(pu : MA= 15: 85)
(MA : Np, Am, Cm)
Volume :2,6 m3
Weight :9 ton
TRU inventory :5 ton
Effective Multification Factor
k_{eff} = 0.92
Beam Power :1.5 GeV, 25 mA
Thermal Output :800 MW
Transmutation Rate of MA :250 kg/y

Table 2-1 FP and its chloride

FP	* (g/MtHM)	* (wt %)	Chloride	-A Gf(at1000K) (kcal/g · Cl)	MP (°C)
Kr	1.0 E3	0.7			
Rb	8.9 E2	0.6	RbCl	81.2	715
Sr	1.9 E3	1.3	SrCl2	81.0	856
Y	1.0 E3	0.7	YCl3	61.2	700
Zr	1.1 E4	7.3	ZrCl2	49.2	310
Nb	1.7 E2	0.1			
Mo	1.7 E4	11.3	MoCl2	8	
Tc	3.4 E3	2.3	TcCl3	7	
Ru	1.3 E4	8.7	RuCl3	1.4	
Rh	3.8 E3	2.5	RhCl	5.8	
Pd	1.1 E4	7.3	PdCl2	3.8	
Ag	1.1 E3	0.7	AgCl	19	457
Cd	9.6 E2	0.6	CdCl2	30.4	569
(FPtotal	1.5 E5	100%)			

* WHC-EP-0268(1990).75 %U-25 %Pu

Table 2-2 FP and its chloride

FP	* (g/MtHM)	* (wt%)	Chloride	-ΔGf(at1000K) (kcal/g-Cl)	MP (℃)
Te	2.7 E3	1.8	TeCl4	17.1	224
I	1.5 E3	1			
Xe	1.9 E4	13			
Cs	1.6 E4	10.7	CsCl	80	646
Ba	6.6 E3	4.4	BaCl2	83.4	960
La	5.0 E3	3.3	LaCl3	67	846
Ce	9.0 E3	6.0	CeCl3	66.3	
Pr	4.6 E3	3.1	PrCl3	66.3	
Nd	1.5 E4	10	NdCl3	64.2	758
Pm	3.4 E2	0.2	PmCl3		
Sm	4.7 E3	3.1	SmCl3		668
Eu	5.1 E2	0.3	EuCl3		
Gd	5.3 E2	0.4	GdCl3		593
(FPtotal	1.5 E5	100%)			

* WHC-EP-0268 (1990).7 5%U—25%Pu

Table 3 Chlorides in target salt

Chloride	−ΔGf	Chloride	−ΔGf	Chloride	−ΔGf (kcal/g·Cl)
BaCl2	83.4	AmCl3	60.4	CdCl2	30.4
KCl	81.4	CmCl3	58.8	FeCl2	26,6
RbCl	81.2	PuCl3	58.5	TeCl2	17.1
SrCl2	81.0	MgCl2	57.7	MoCl2	8.0
CsCl	80.0	NpCl3	54.1	TcCl3	7.0
SmCl2	80.0	UCl3	51.8	RhCl	5.8
LiCl	78.8	SnCl2	51.3	PdCl2	3.8
CaCl2	77.9	ZrCl2	49.2	RuCl3	1.4
NaCl	75.7				
LaCl3	67.0				
PrCl3	66.3				
CeCl3	66.3				
NdCl3	64.2				
YCl3	61.2				

Table 4 Separation methods **for** FP

He **Purge Method** (Group -1) 23 0/0		**Reductive Extraction Method** (Group-2) 33 %		**Cold Trap Method** (Group, - 3) 44 %	
	('Ye)		(%)		(%)
Kr	0,7	Nb	0,1	Rb	0.6
Xe	13 ·	Mo	11.3	Sr	1,3
Te(TeCl4)	1.8	Tc	2.3	'f	0.7
I .	1,0	Ru	8,7	Cs	10.7
Zr(ZrCl2)	7.3	Rh	2.5	Ba	4.4
		Pd	7.3	La	3.3
		Ag	0.7	Ce	6.0
				Pr	3.1
				Nd	10 "
				Pm	0.2
				Sm	3.1
				Eu	0.3
				Gd	0.4

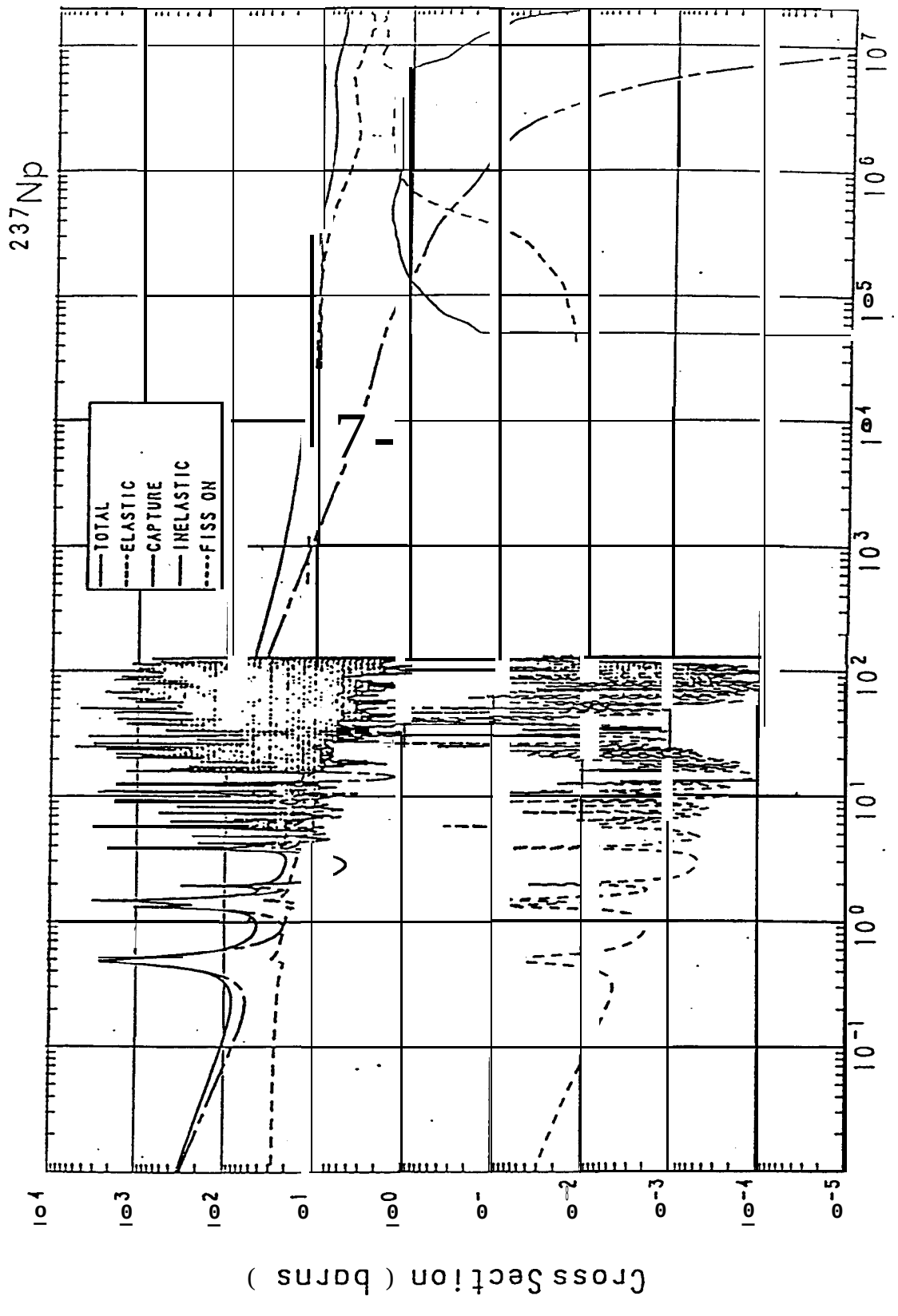


Fig 1-1 Cross Section of Np-237

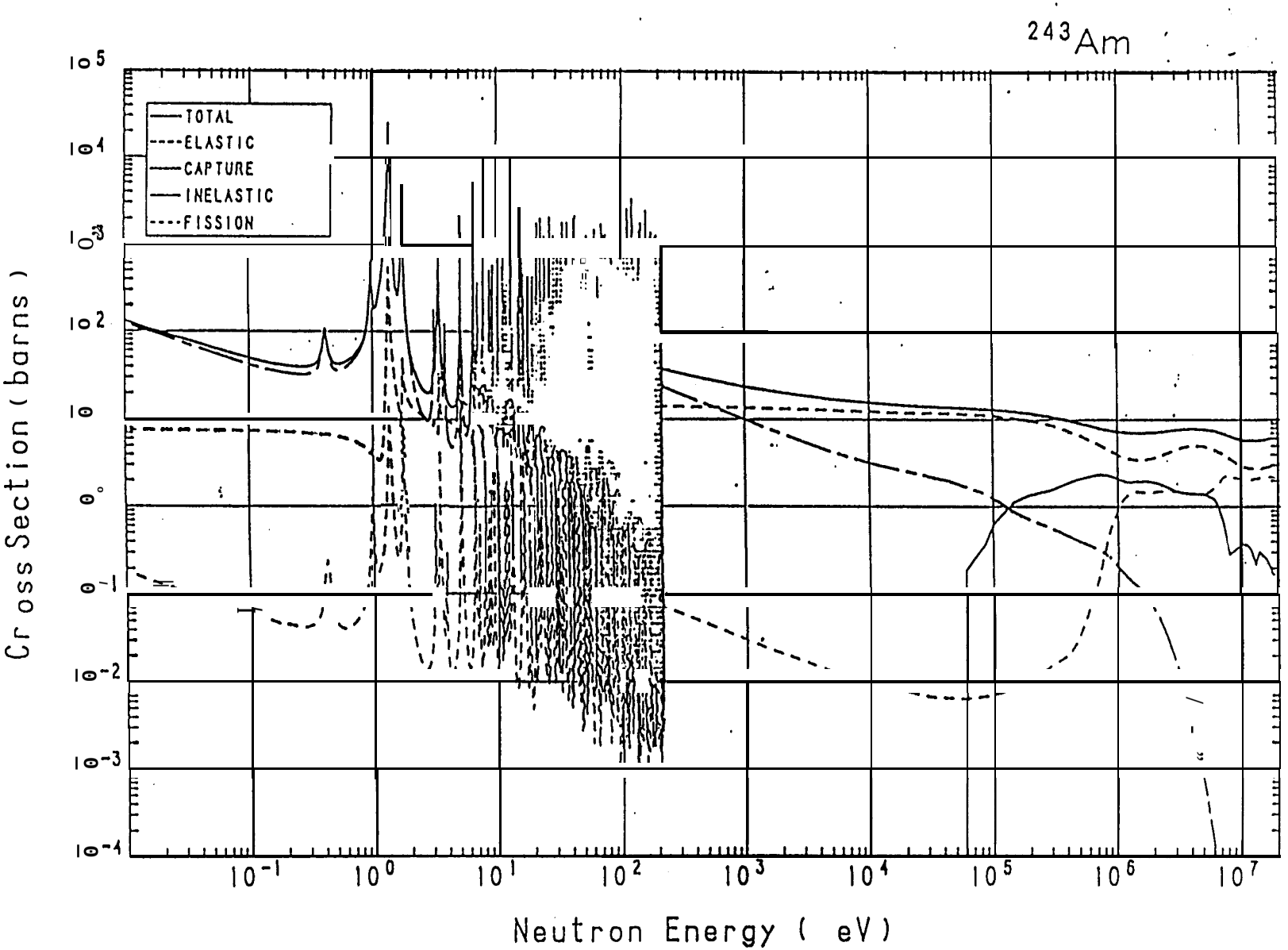


Fig.1-2 Cross Section of Am-243

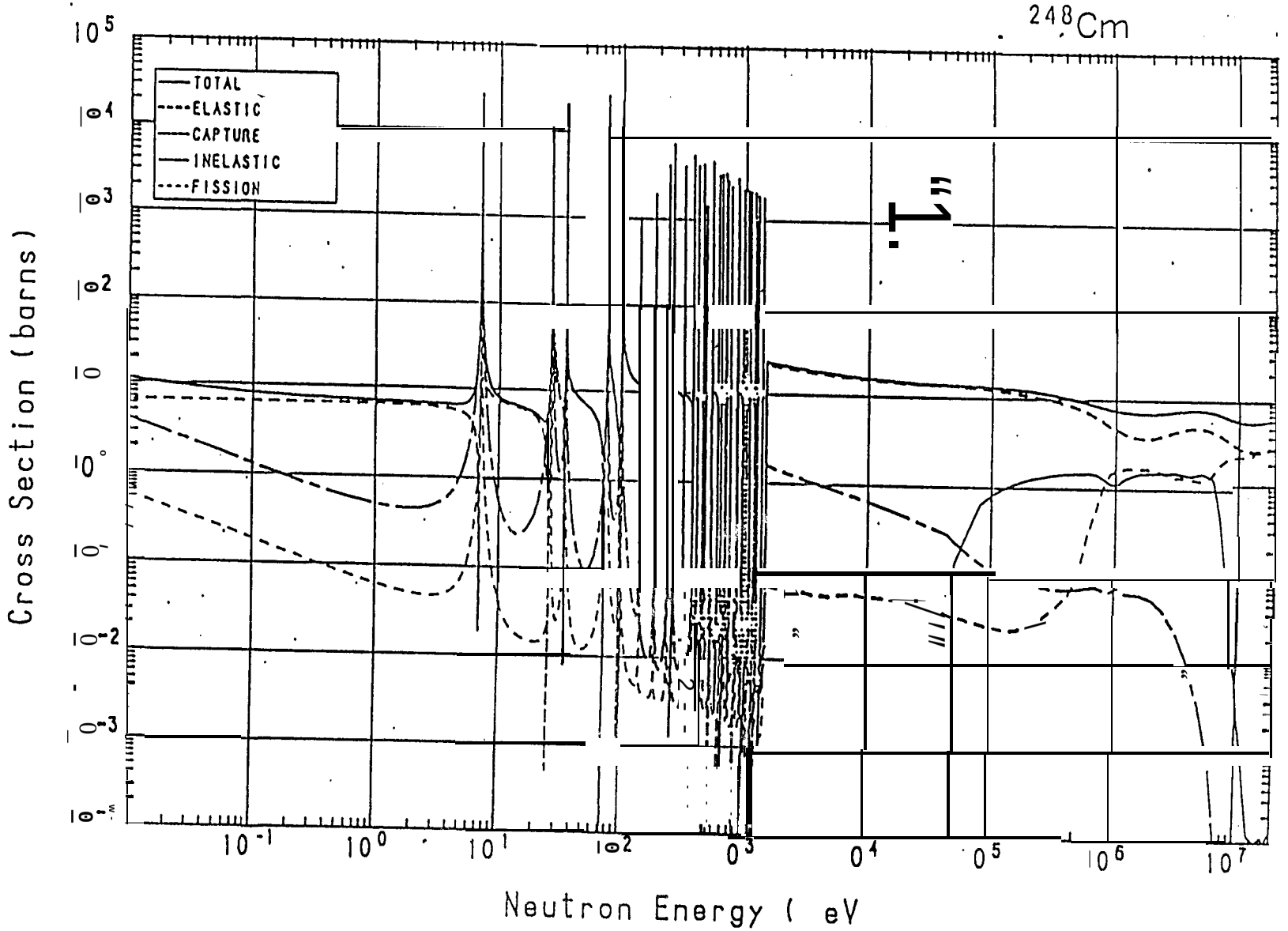


Fig.1-3 Cross Section of Cm-248

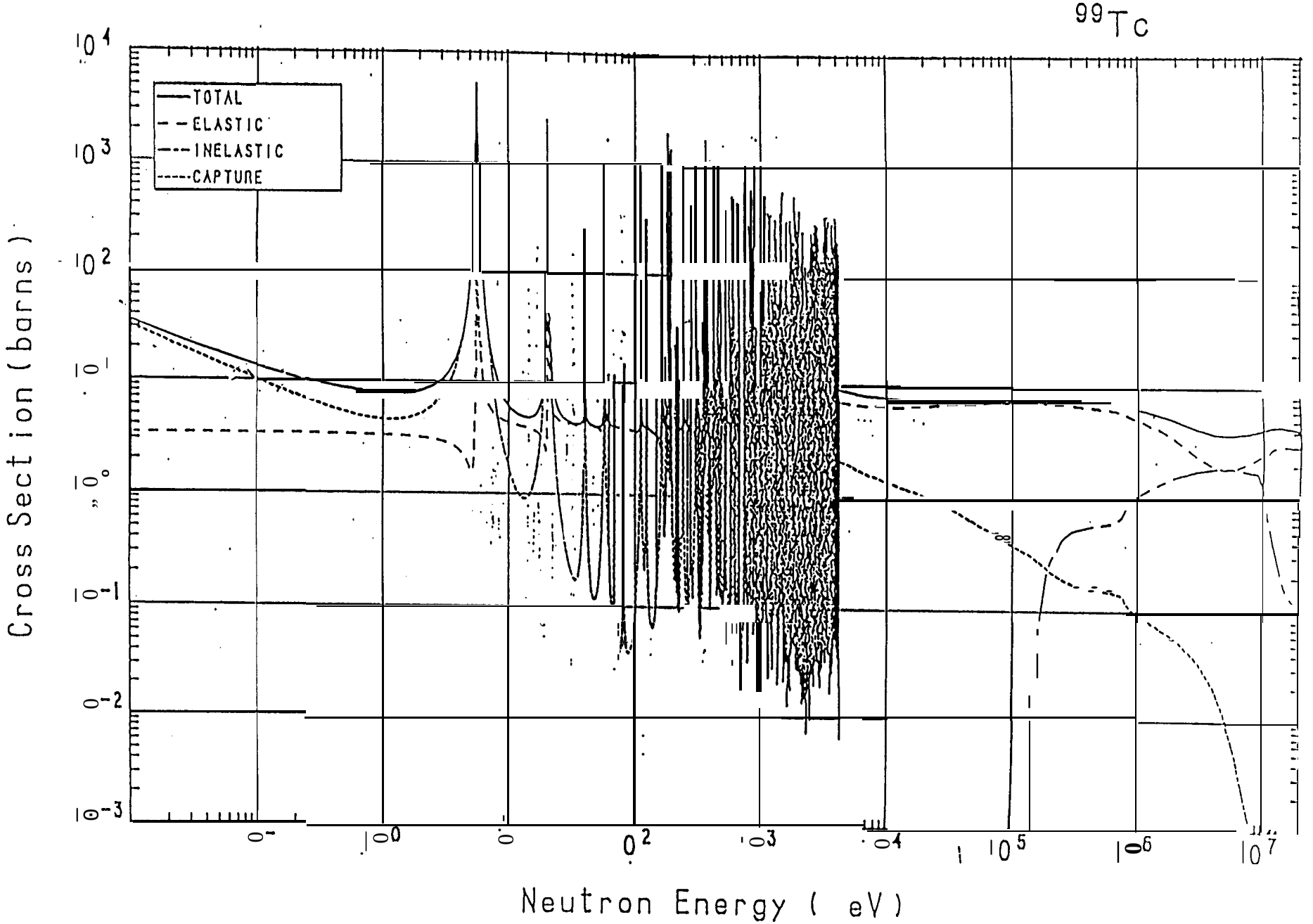


Fig.2-1 Cross Section of Tc-99

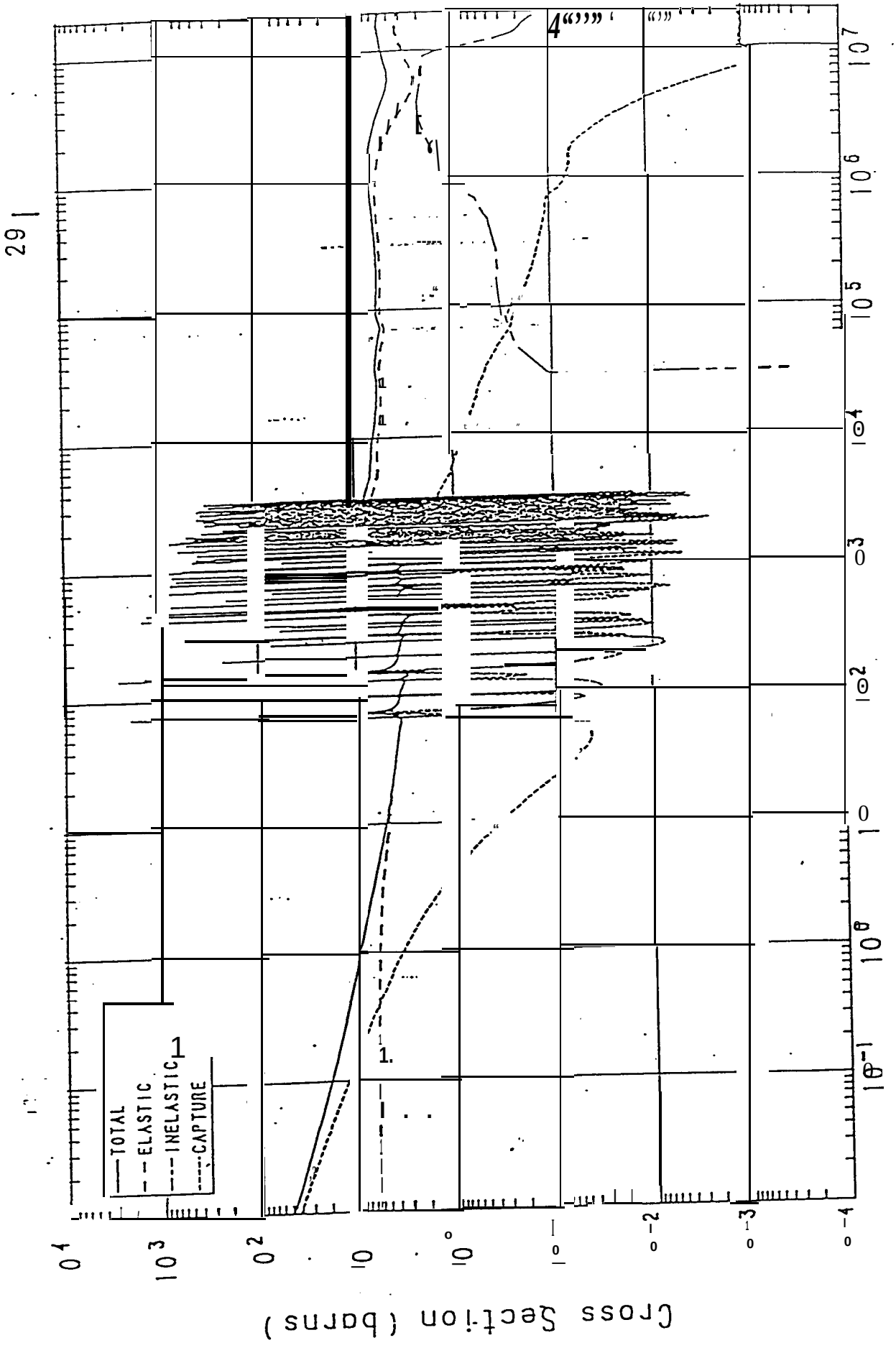
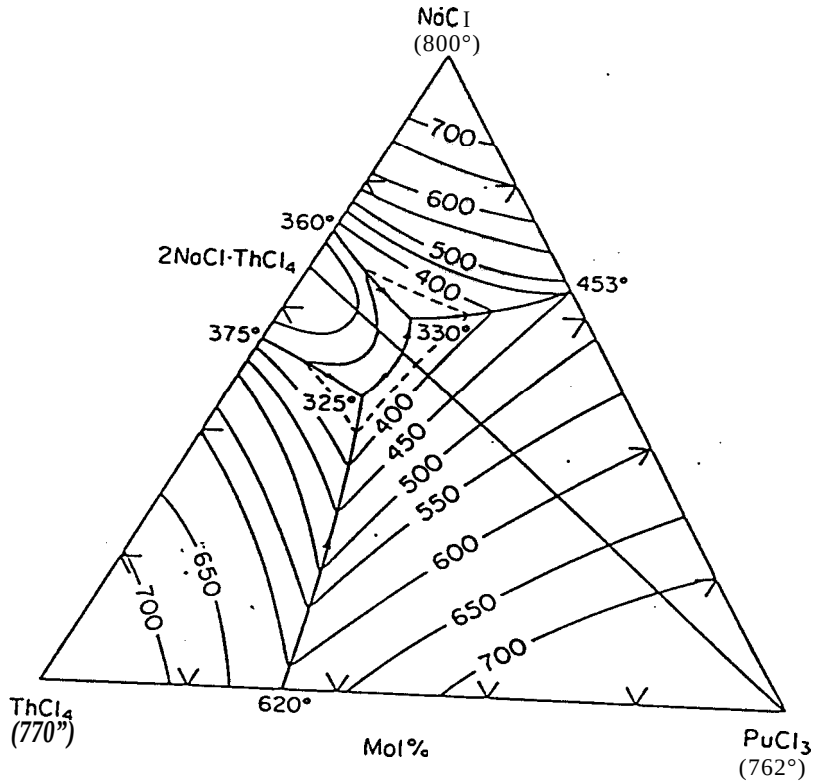


Fig.2-2 Cross Section of I-129



Temp. (°C)	Type	Composition (mol%)		
		NaCl	$PuCl_3$	$ThCl_4$
330	Eutectic	58.5	18.5	23.0
325	Eutectic	46.5	18.5	35.0

The section $2NaCl·ThCl_4$-$PuCl_3$ was found [o be binary with a minimum that occurs at 370°, 52% NaCl, 22%$PuCl_3$, 26%$ThCl_4$.

Fig.3 Phase diagram of NaCl-$PuCl_3$-$ThCl_4$(9)

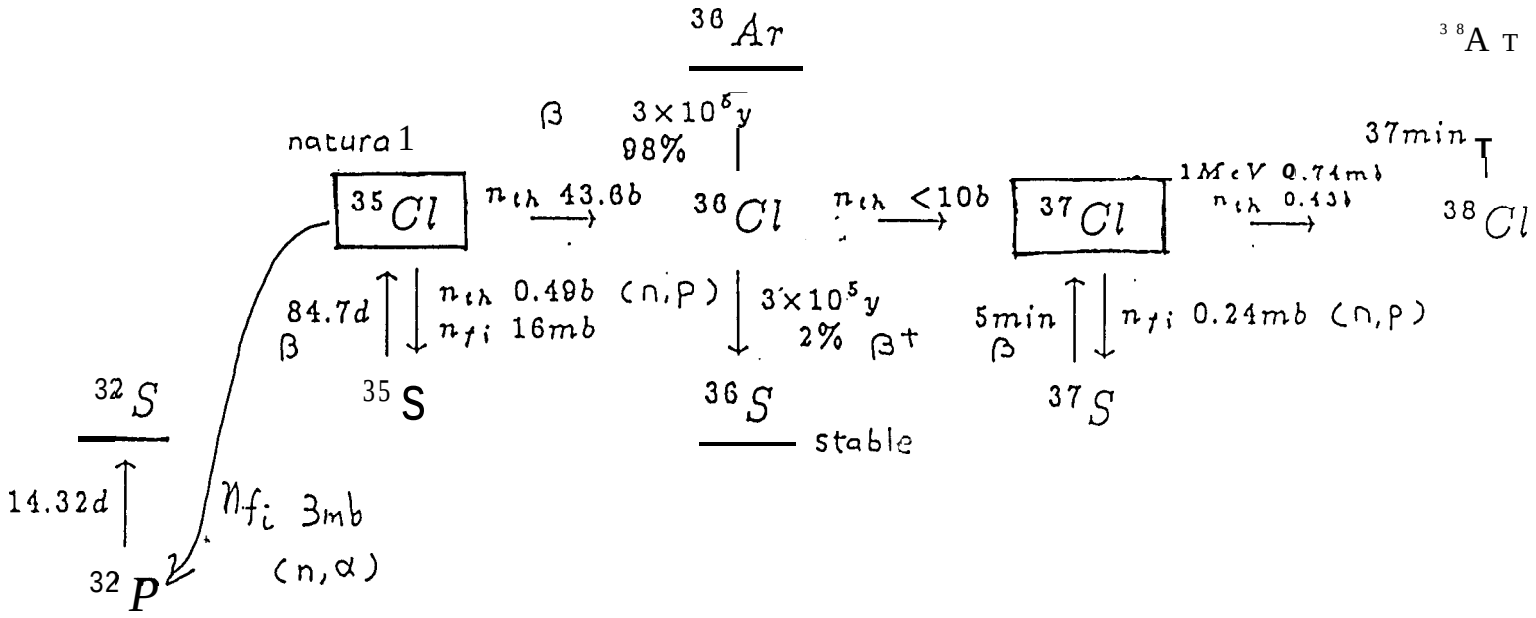


Fig.4 Chloride nuclear reactions

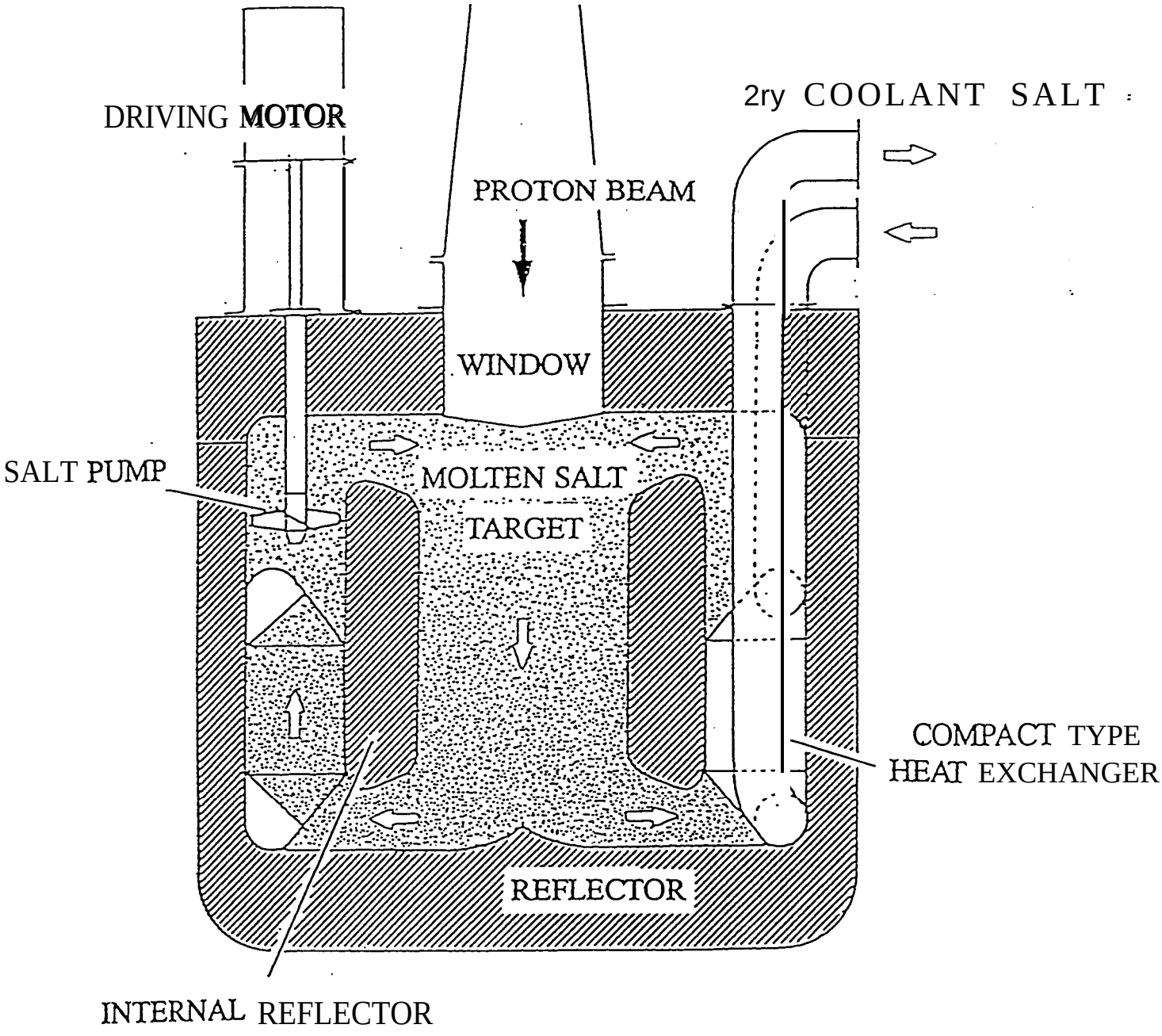
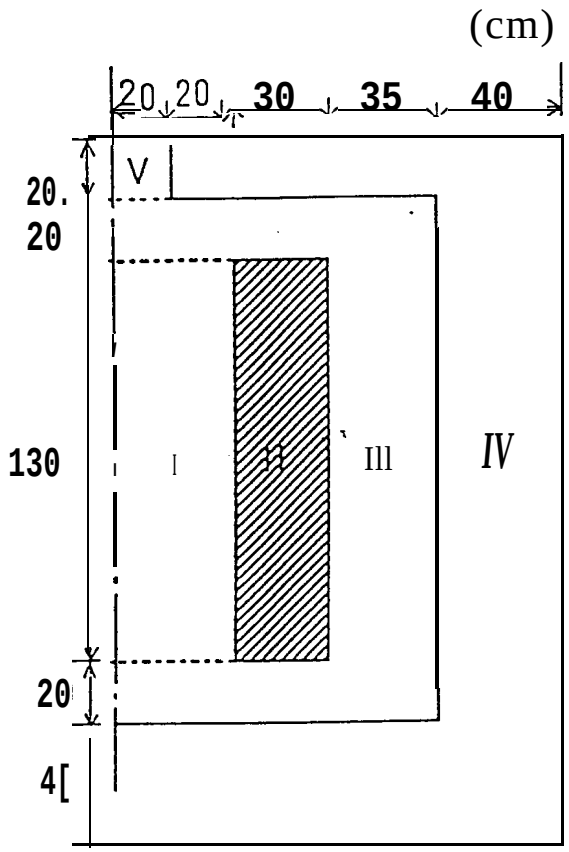


Fig.5 Concept of the molten salt target system



REGION

1 : Target Molten Salt
II : Internal Reflector
III : Heat Exchanger Region
N: Reflector
V: He (Beam Window)

Fig.6 Scales of the molten salt target core

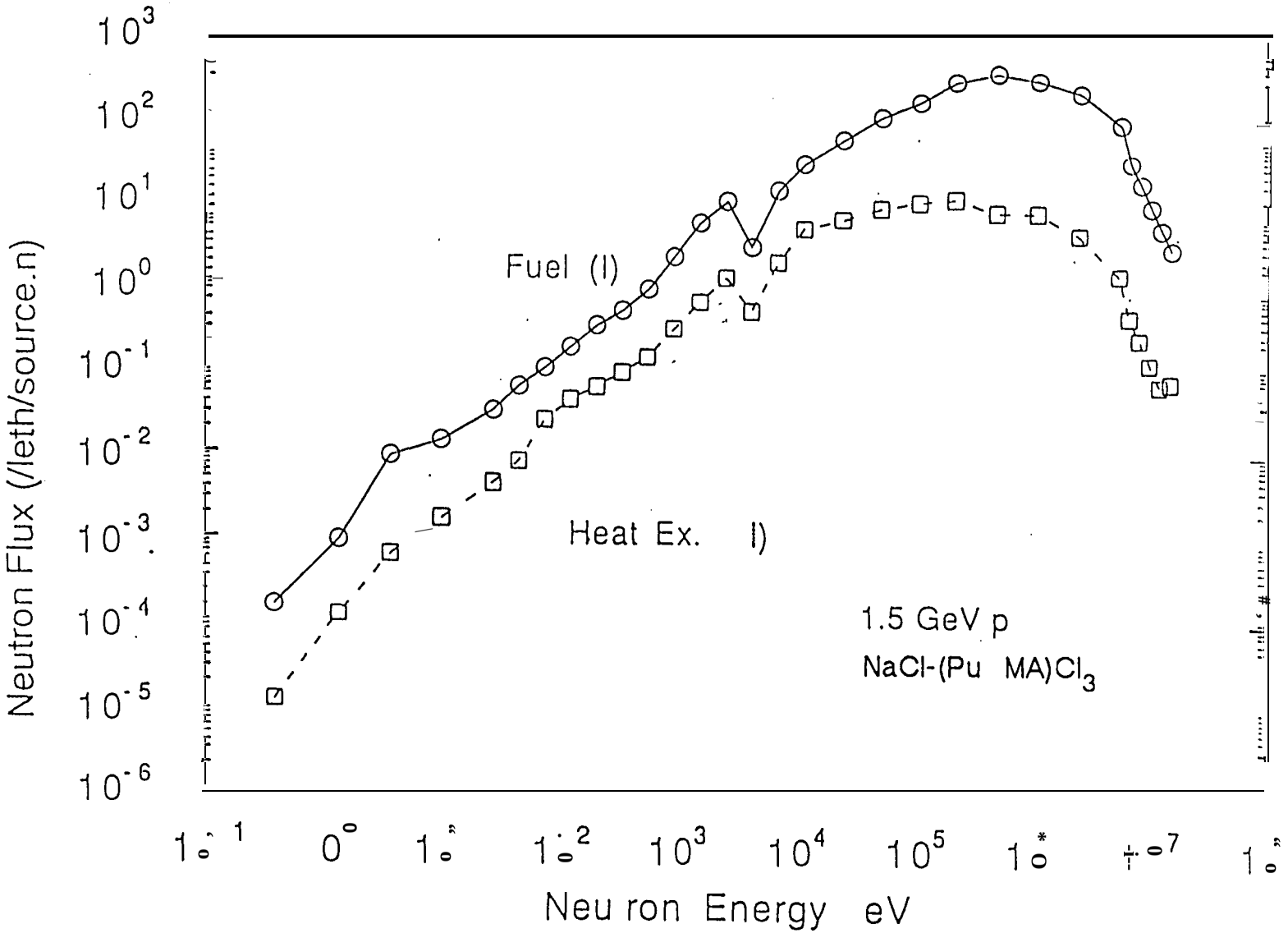


Fig.7 Neutron spectrum in the target core

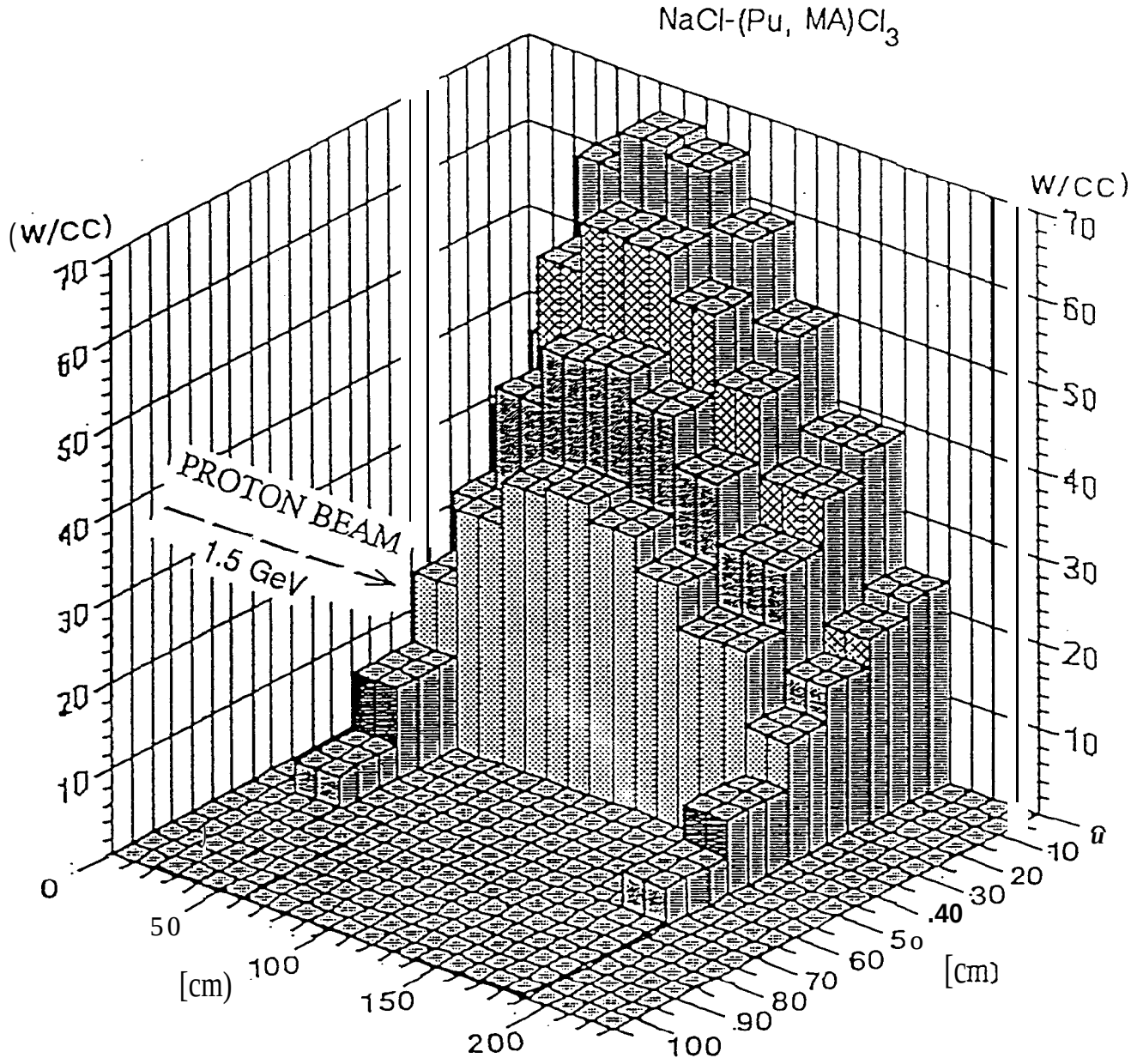


Fig.8 Power density in the target core (< 5MeV, at 1 mA proton beam)

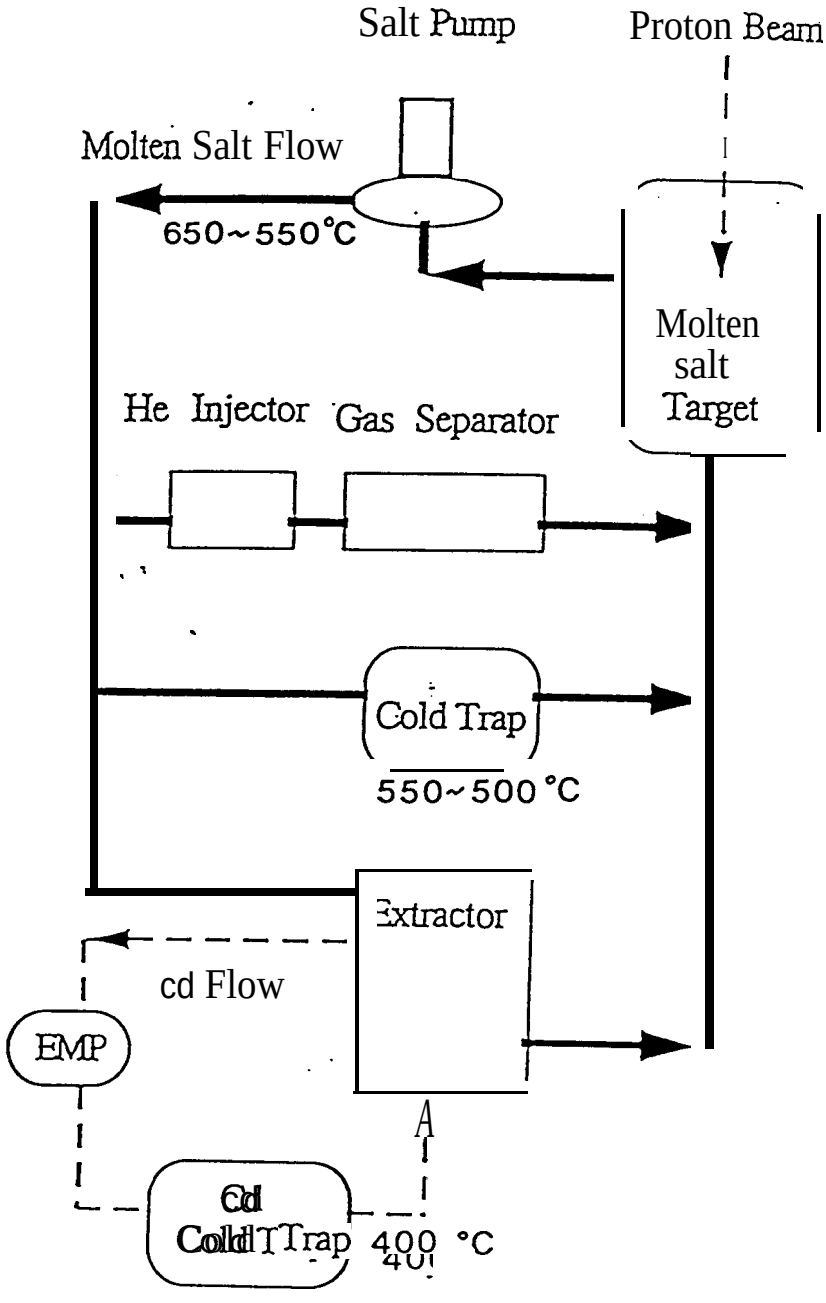
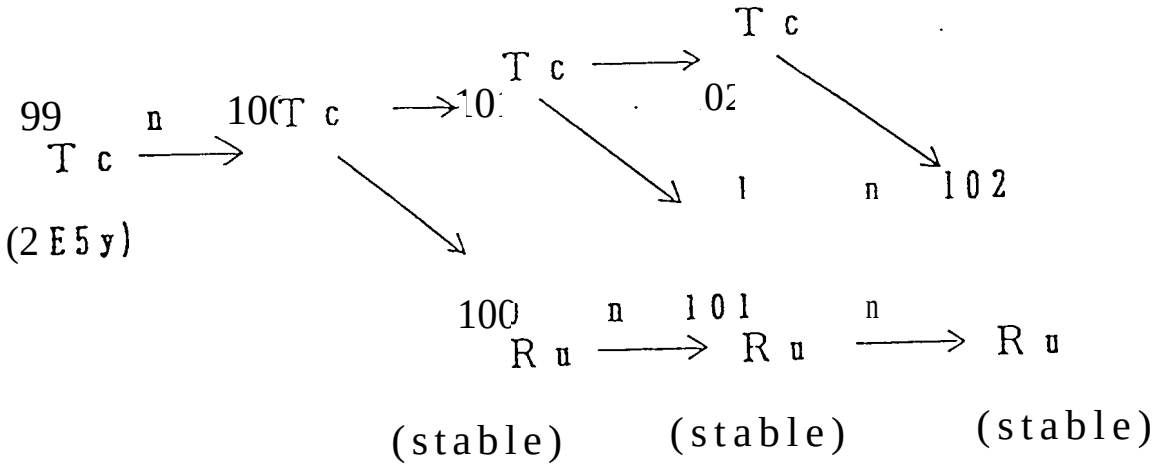
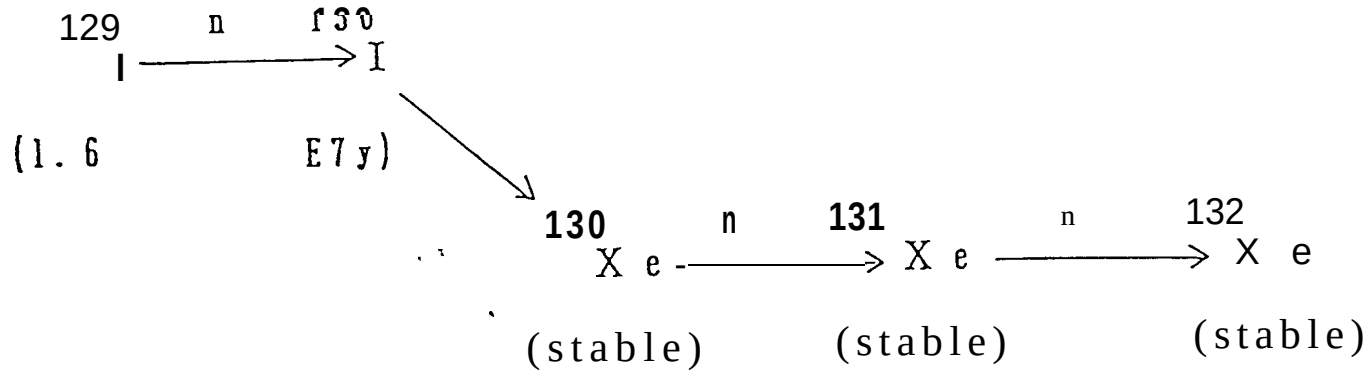


Fig.9 Concept of the on-line separation system





Isotope	σ (thermal)	σ (fast)
Tc99	20 barns	0.2 barns
I129	31	0.2

Fig.1O Nuclear reactions of Tc-99 and 1-129

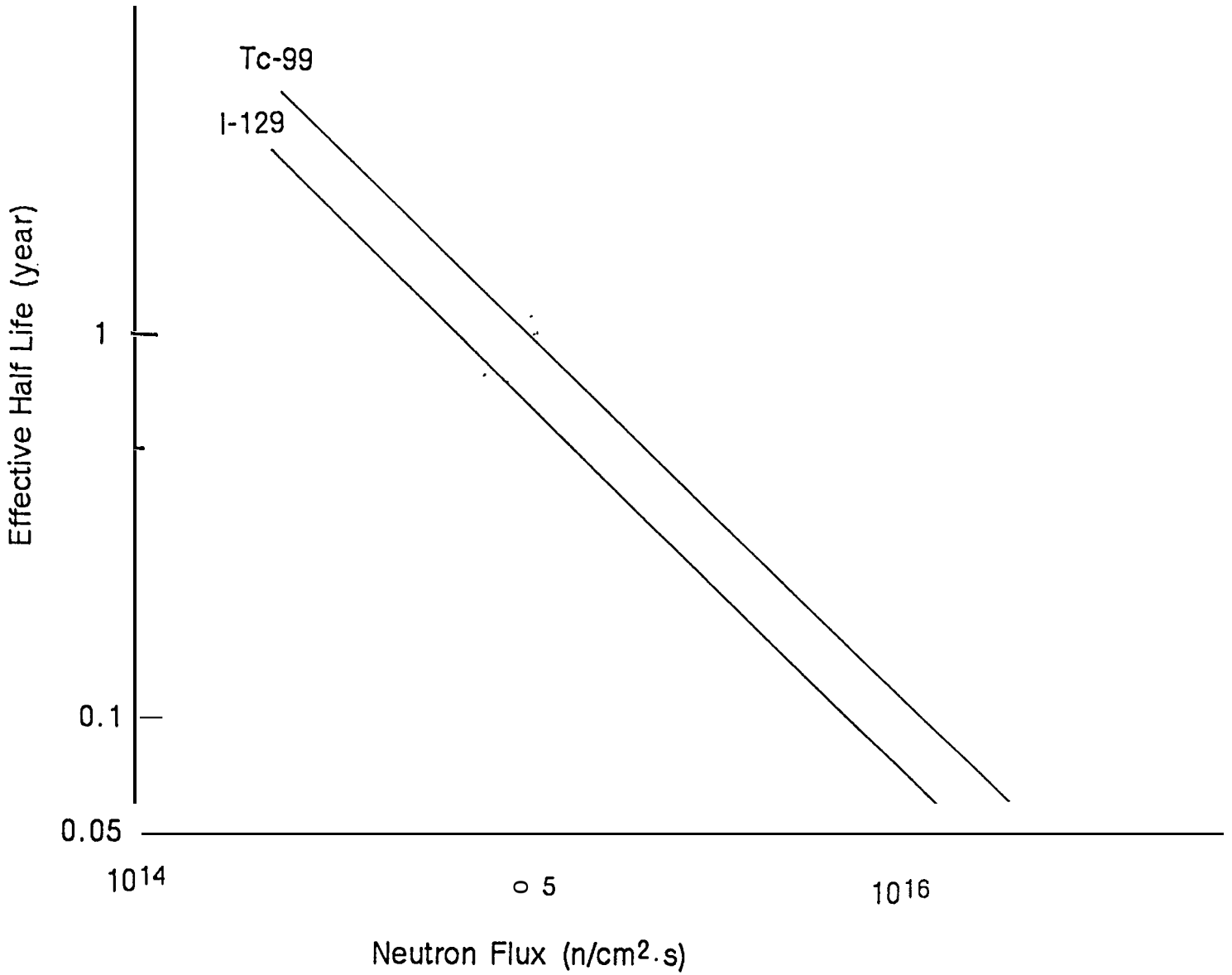


Fig.1 Effective half-lives and neutron flux for Tc-99 and I- 29

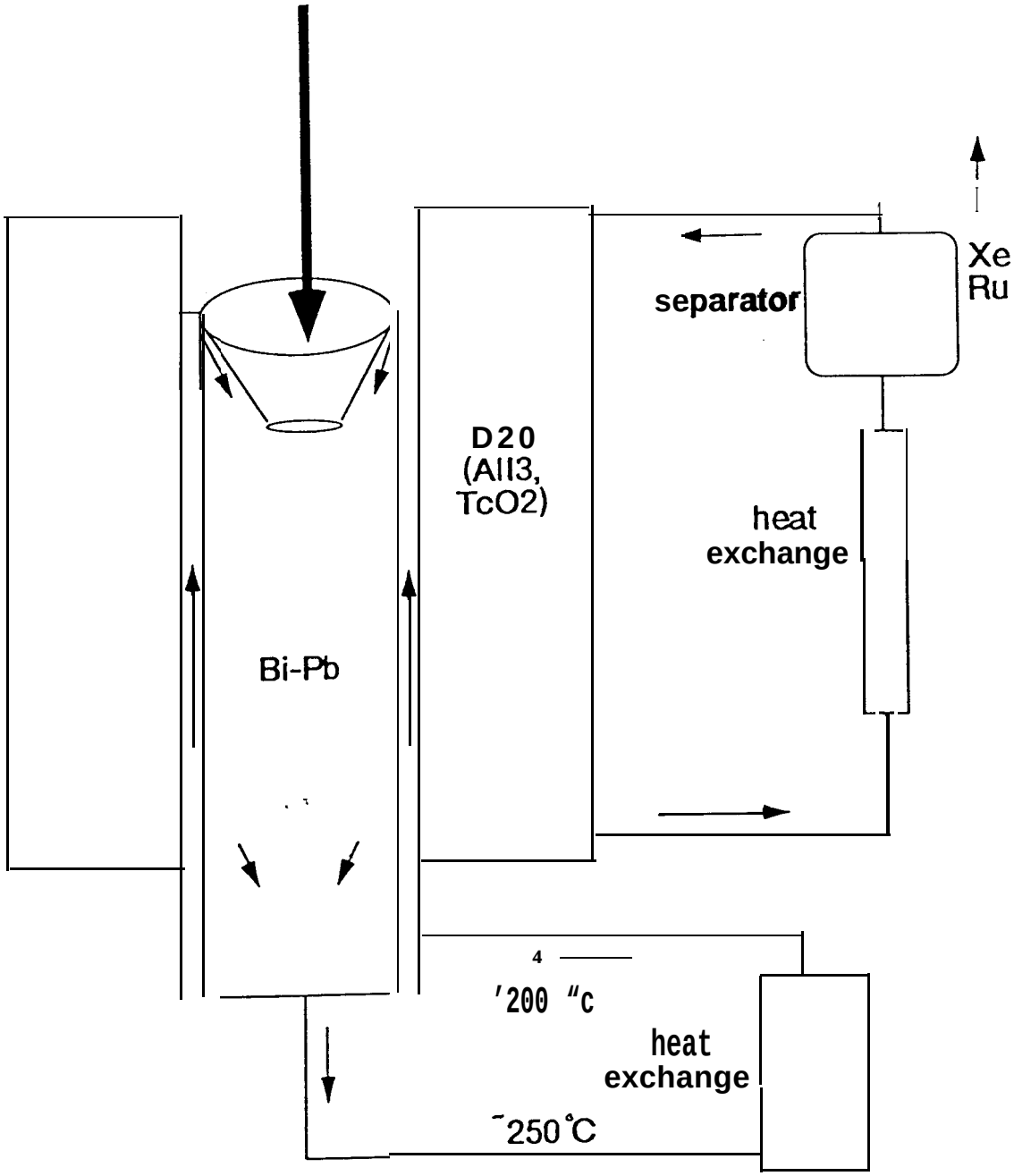


Fig-12 Accelerator transmutation system of Bi-Pb target with D20 blanket

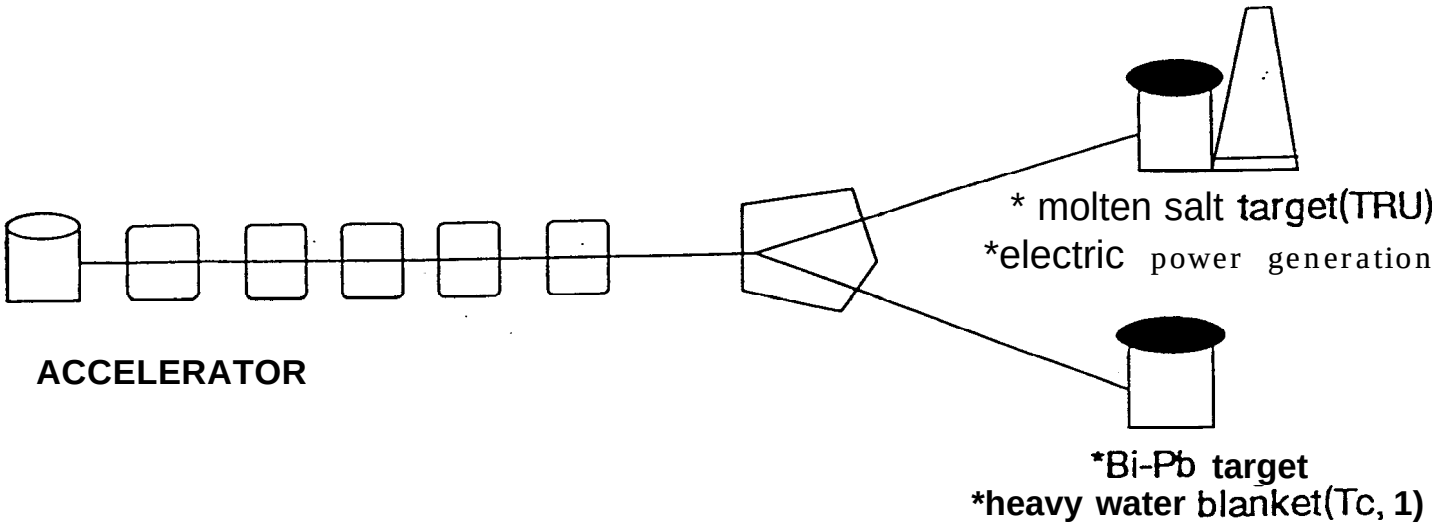


Fig. 13 Accelerator Transmutation System for long-lived MA and FP