EIR-Bericht Nr. 276

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Eidg. Institut für Reaktorforschung Würenlingen
Schweiz

Breeding in Molten Salt Reactors

Lectures at the University of Liège / Belgium
15th May, 1975

M. Taube

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Remerciements

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M. Taube

WHAT IS BREEDING?

WHY IS BREEDING POSSIBLE?

WHAT IS BREEDING GOOD FOR?

Breeding is a process in which two mechanisms are occurring simultaneously. 1) Fissile nuclides are 'burning' and producing energy and neutrons. 2) Some of the neutrons are transforming the so called fertile nuclides into fissile nuclides at a rate greater than the rate at which the fissile nuclides are being consumed.

Breeding is possible because of three factors: 1. Some fissile nuclides have a rather large nett production of neutrons so that more than half of them can be used for breeding. 2. The fertile nuclides are converted to fissile nuclides only by the simple, and energetically not expensive act of neutron capture followed by two spontaneous processes which occur at a much faster rate than the rate of neutron capture. 3. Fertile materials are present in the earths crust at relatively high concentrations. (This also means that these fertile nuclides must be rather stable, beta stable of course, like all heavy nuclides they are alpha unstable. The α-decay rate must be matched to the age of the solar system).

Breeding makes it possible to use not only the uranium-235 (the only naturally occurring fissile nuclide) but also the uranium-238 which occurs in amounts 140 times greater than U-235. These factors permit the use of ores with low uranium and thorium concentrations even down to granites (>50 ppM U+Th).

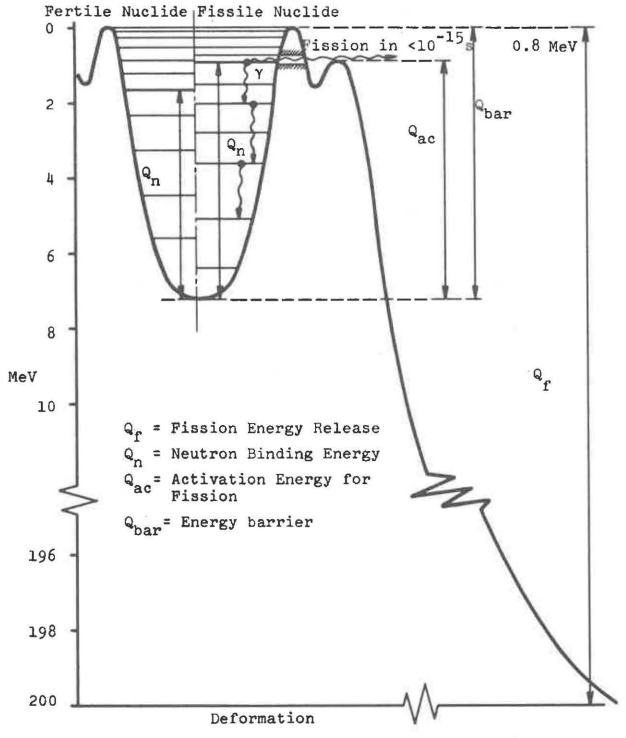
Practically only some reactor types are suitable for effective breeding:

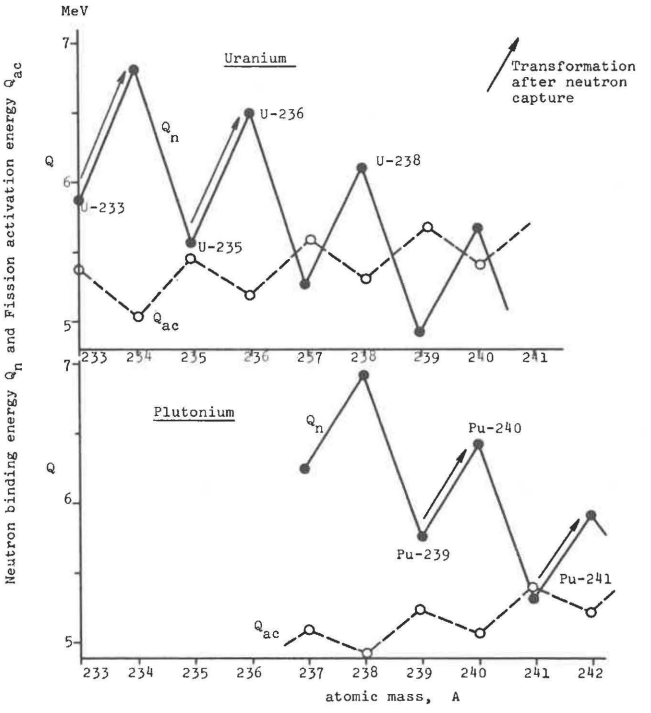
- all reactors with a fast neutron spectrum (e.g. sodium cooled fast reactor, gas cooled fast reactor, molten salt fast reactor)
- one reactor type with a thermal flux spectrum (molten fluoride thermal reactor).

FISSILE AND FERTILE NUCLIDES

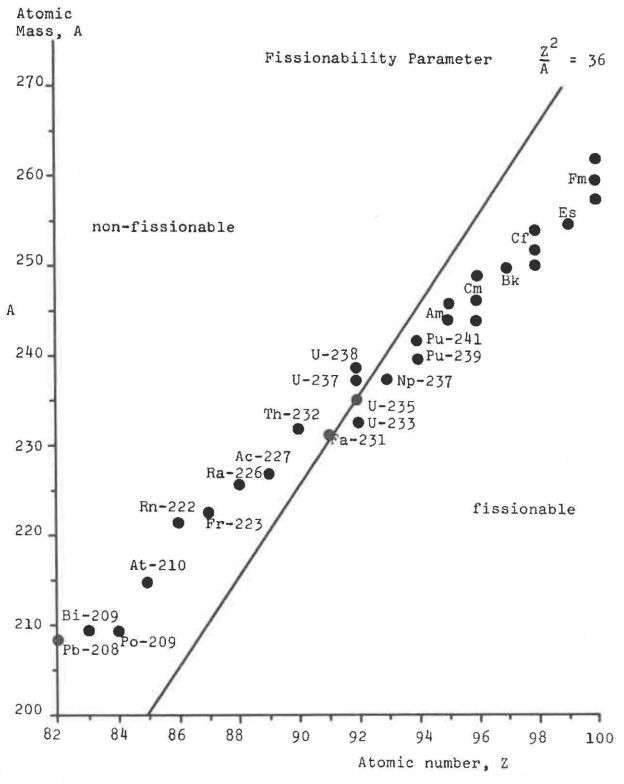
Definitions

	Fissionable Nuclides	
	Fissile nuclides	Fertile nuclides
Characteristics	Neutrons of any energy can produce fission	Only neutrons of high energy (>1 MeV) can induce fission; Neutrons with lower energy are captured and after gamma emission (and in some cases then by beta-decay) a transformation into a fissile nuclide occurs.
Examples	U-233 U-235 Pu-239 Pu-241	Th-232 U-238 U-234 Pu-240
Binding energy of neutrons and barrier to fission	Binding energy of the captured neutron is greater than the fission barrier (more exactly: fission activation energy Q_a) $Q_n > Q_a$	Binding energy of the captured neutron is lower than the fission barrier $Q_n < Q_a$ only fast neutrons with kinetic energy E_c can cause the fission $Q_n + E_c > Q_a$



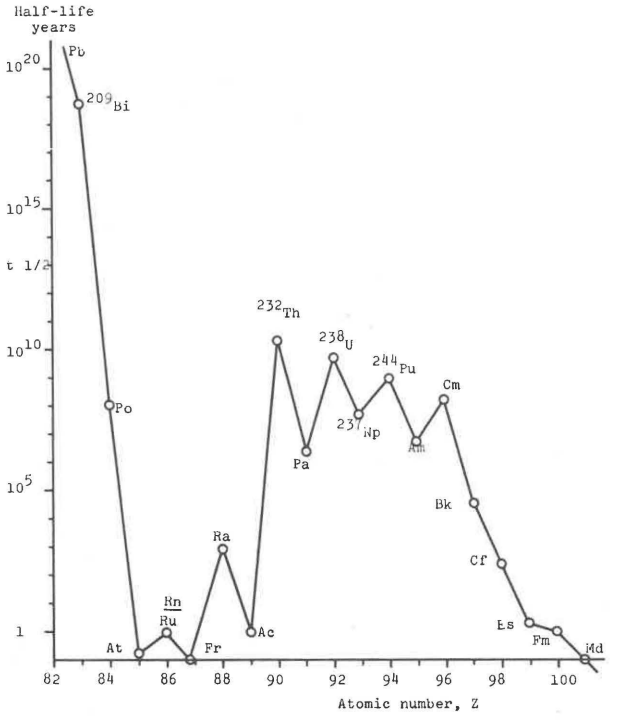


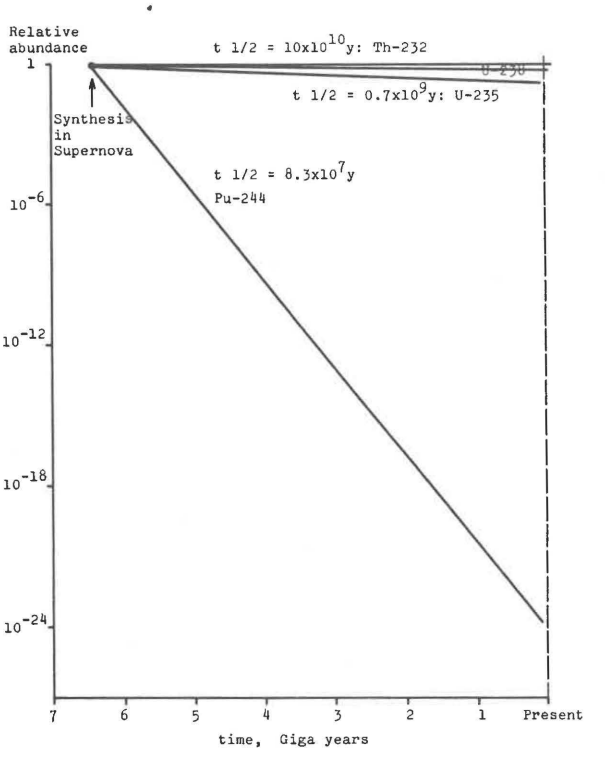
THERE IS ONLY ONE FISSILE NUCLIDE EXISTING IN THE EARTH'S CRUST



for the following reasons

1. The fissile nuclides must have $\frac{Z^2}{A} > 36$ ($\frac{Z^2}{A}$ fissionability parameter)
2. The fissile nuclides must be beta stable, because the half life of beta-decay in this region of A is smaller than 10 years.
3. Because for $\frac{Z^2}{A} > 36$ gives in the realistic case $Z \geq 92$; all fissile nuclides are alpha unstable.
4. To exist in the earth's crust the half life of alpha decay of the nuclide must be of the same order of magnitude as the age of the solar system $\geq 10^9$ years.
5. Only one nuclide fulfills all these criteria: - U-235





ONLY TWO NUCLIDES EXISTING IN THE EARTH'S CRUST CAN PLAY THE ROLE OF FERTILE NUCLIDES

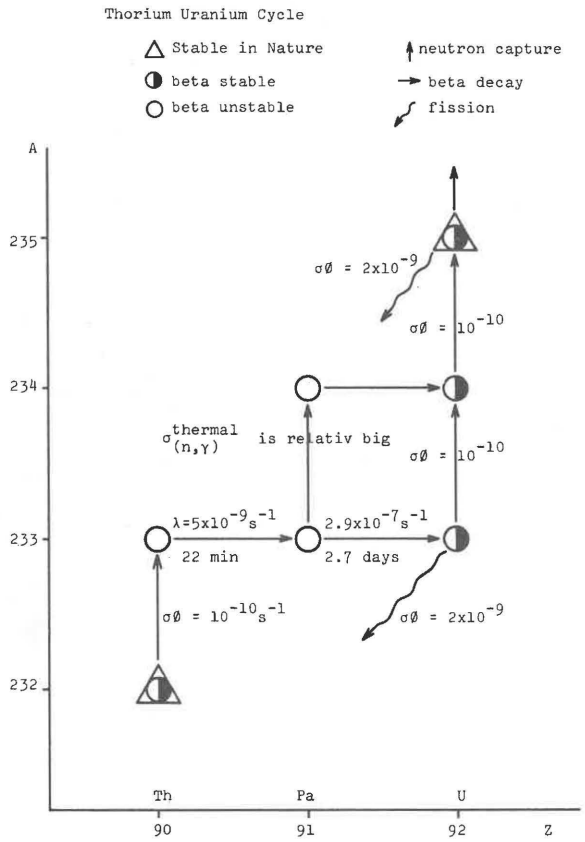
The fertile nuclides must fulfill the following obvious criteria

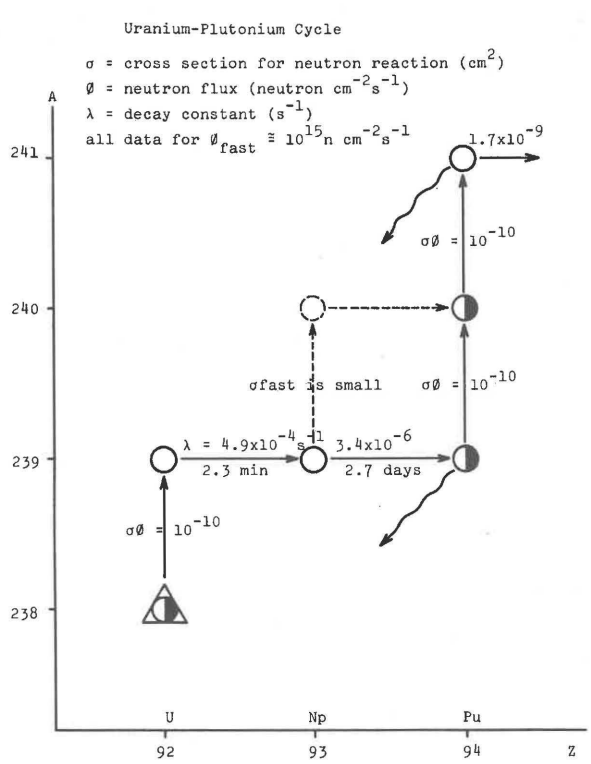
1. They must be abundant on the earth. At least a mean value equivalent to 1 ppM throughout the earth's crust (or more exactly in the outer layer of the earth's crust.
2. Thus they must be beta-stable
3. Thus the Z value must lie between 90 and 94 and be even
4. These are the isotopes of thorium and uranium with t 1/2 $>10^9$ years

The only two 'natural' isotopes are

Th-232 and U-238

These nuclides can be transformed into fissile nuclides by simple neutron capture and spontaneous beta-decay.





TO PERMIT BREEDING THE NUMBER OF NEUTRONS EMITTED PER FISSION SHOULD BE LARGE

The scheme of neutron induced fission of Pu-239

$$^{239}_{94}Pu + n \rightarrow {}^{240}_{94}Pu \xrightarrow{\text{fission}} {}^{137}_{53}I_{84} + {}^{100}_{41}Nb_{59} + \nu\, {}^{1}_{0}n_{1} \text{ (prompt neutron)}$$

$^{100}_{41}Nb_{59} \downarrow \beta^-$ (beta-minus decay)

$^{100}_{42}Mo_{58}$ stable

delayed neutron emission

$^{136}_{53}I_{83} \downarrow \beta^-$ (beta-minus decay)

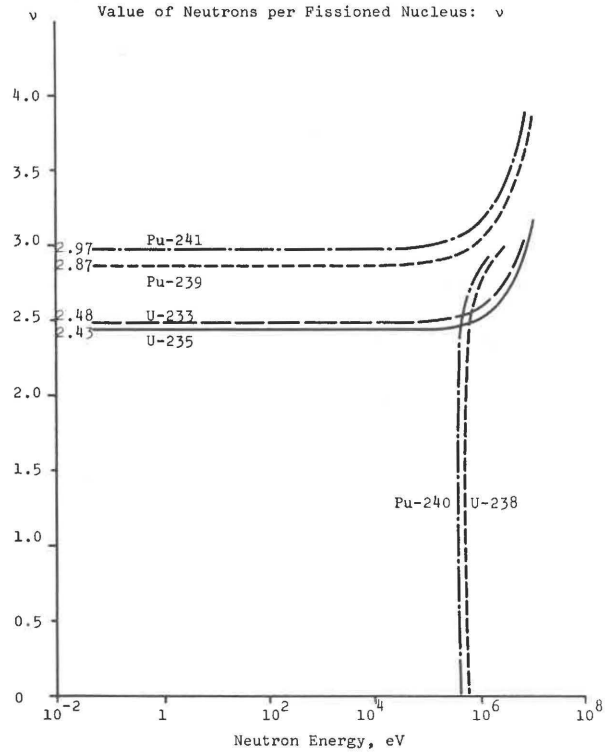
$^{136}_{54}Xe_{82}$ stable

The value of prompt neutrons fission = ν

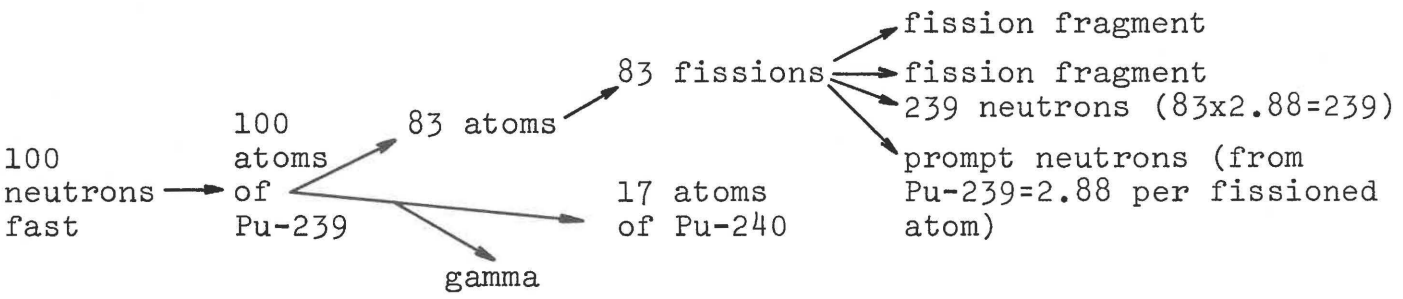
1. The value of ν for uranium isotopes 2.5
2. The value of ν for plutonium isotopes 2.9
3. The value of ν increases when the energy of the captured neutron is ~1 MeV

Table All data approcimate

Nuclide	Thermal reactor		Fast reactor	
	γ	η	γ	η
U-235	2.43	2.09	2.57	2.30
U-233	2.48	2.25	2.51	2.31
Pu-239	2.87	2.08	2.88	2.40
U-238	-	-	2.66	very small
Th-232	-	-	2.36	very small
Pu-240	2.87	0	3.00	1.21
Pu-241	2.97	2.18	3.1	2.06
Pu-242	2.18	0	3.2	1.26



ONLY SOME OF THE CAPTURED NEUTRONS CAUSE FISSION THE OTHERS BRING ABOUT A GAMMA EMISSION. THIS REDUCES THE BREEDING POTENTIAL



The ratio of non-fissioned atoms to fissioned atoms is called α

$$\alpha = \frac{\sigma(n,q)}{\sigma(n,f)} \qquad \text{(in this example } \alpha = \frac{17}{83} = 0.20\text{)}$$

We define: $\sigma_{absorption} = \sigma(n,\ ) + \sigma(n,f)$
The real number of emitted neutrons per neutron absorbed equals:

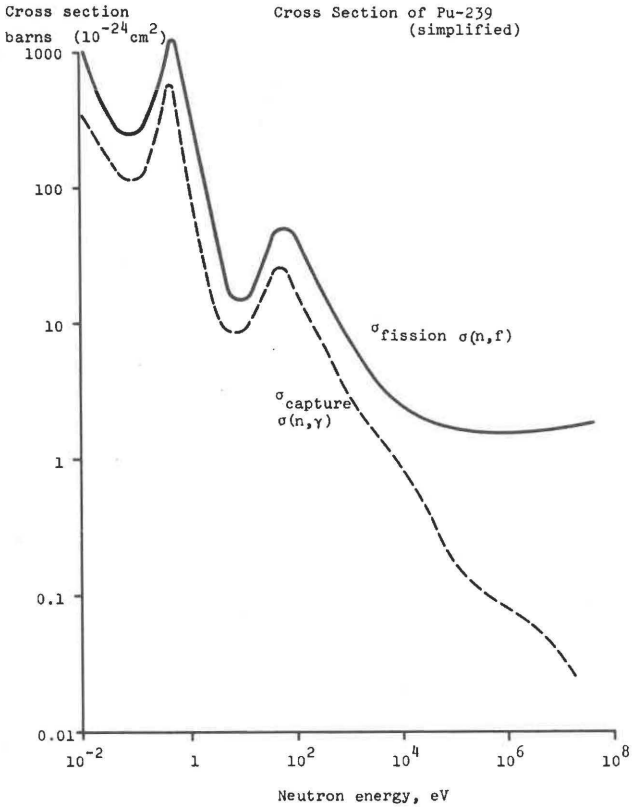
$$\eta = \nu \frac{\sigma(n,f)}{\sigma(n,f) + \sigma(n,\gamma)} = \nu \cdot \frac{1}{1+\alpha}$$

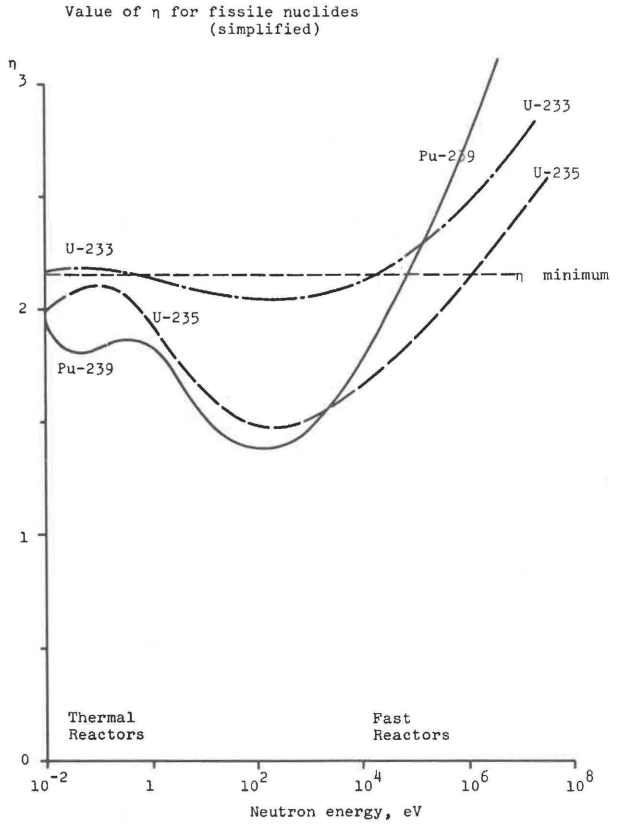
in this example

$$\eta = 2.88 \frac{83}{(83+17)} = 2.40$$

$$\eta = 2.88 \frac{1}{(1+0.2)} = 2.40$$

The value of η is strongly energy dependent
The value of η differs for different fissile nuclides





THE NEUTRON BALANCE FOR FISSION AND BREEDING IS AS FOLLOWS:

Molten Salt (thermal) fluoride breeder for ~100 neutrons

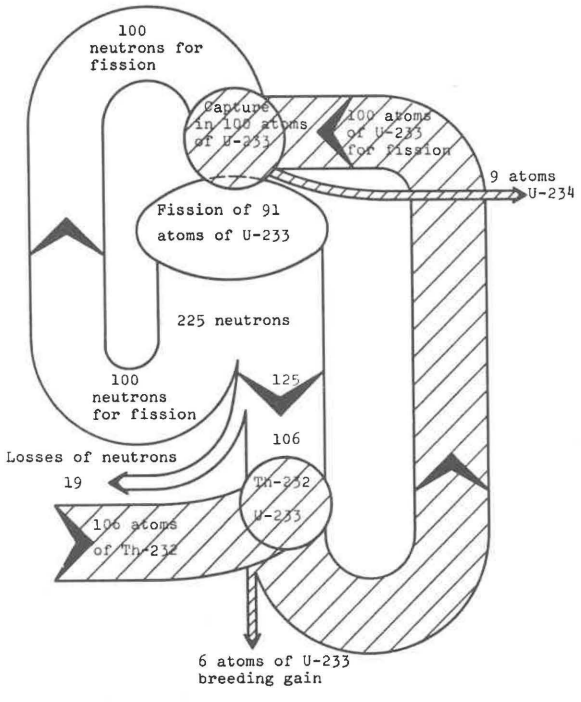
Nuclide	Absorption	Fission
^{232}Th	44.7	0.03
^{233}Pa	0.02	
^{233}U	41.4	92.3
^{234}U	3.7	0.01
^{235}U	3.4	6.8
^{236}U	0.3	
^{237}Np	0.3	
^{6}Li	0.1	
^{7}Li	0.7	
^{9}Be	0.3	0.9
^{19}F	0.8	
Graphite	2.3	
Fission products	0.7	
Leakage	1.0	
(ηE		2.2317)
Breeding ratio (total)		1.0708

Molten salt (fast) chloride breeder for ~100 neutrons

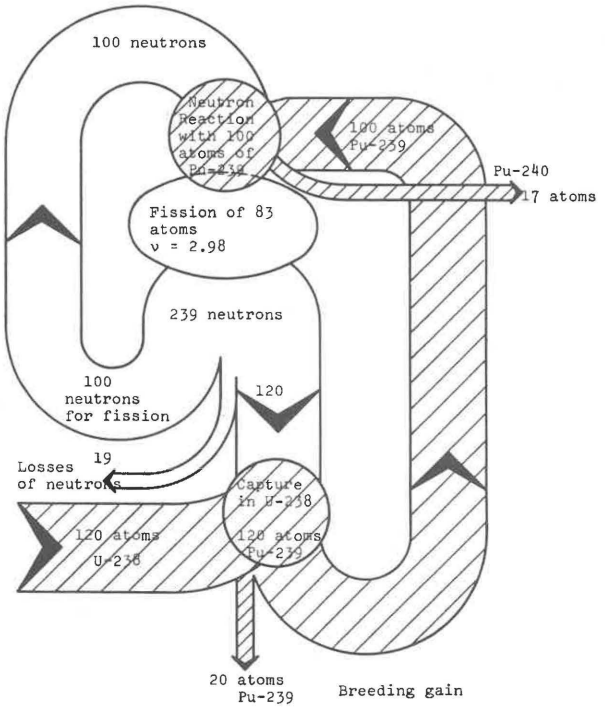
Nuclide	Absorption	Fission	
$^{238}U(n,\gamma)$	22.51		core
(n,f)	2.99	8.23	core
^{239}Pu (n,γ)	5.58		core
(n,f)	28.98	85.55	core
^{240}Pu (n,γ)	2.24		core
(n,f)	1.54	4.72	core
Na	0.26		core
Cl nat	3.16		core
Fe	1.30		core
Mo	2.04		core
Fission products	0.50		core
$^{238}U(n,\gamma)$	23.15		blanket
(n,f)	0.55	1.50	blanket
Na	0.08		blanket
Cl nat	2.22		blanket
Leakage	2.90		blanket

Breeding ratio: core 0.716; blanket 0.670; total 1.386

Balance for Thermal Fission U-233



Balance for Fast Fission of Pu-239
(Fission Products not shown)



DEFINITION OF BREEDING RATIO AND BREEDING GAIN

$$BR = \frac{\text{average rate of production of fissile nuclides}}{\text{average rate of loss of fissile nuclides}}$$

$BR_{maximum} \cong$ Breeding potential $= \eta - 1$

$G =$ Breeding gain $= BR - 1 = \eta - 2$; for breeder $G > 0$

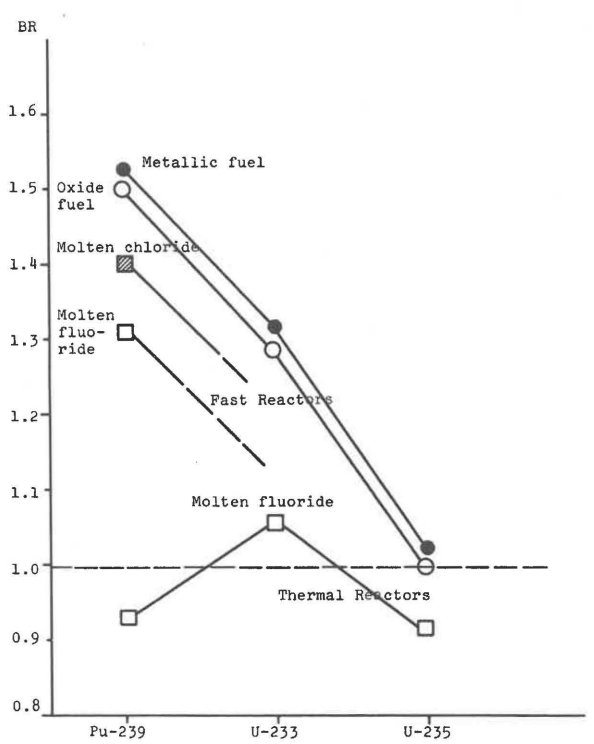
1) for typical fast reactors; value of breeding gain, G

oxide fuel	0.25	(at present for 300 MWe LMFBR; G = 0.12 ± 0.03)
nitride fuel	0.30	
carbide fuel	0.4 ÷ 0.47	(gas cooled FBR)
molten chloride	0.35	

2) for thermal breeder

molten fluoride	0.06
all other fuels solid and liquid	<0.00

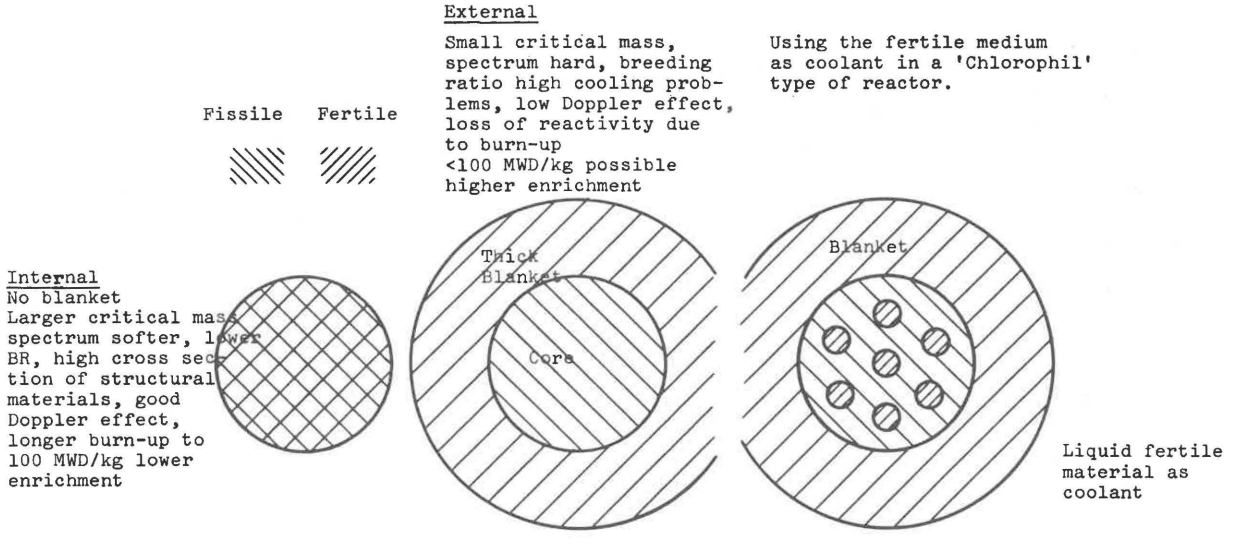
BR =	Mechanism	Typical value for Pu fuelled fast reactor
$(+\nu$	No. of neutrons per fission	(+2.96
-1	one neutron for fission claim	- 1
$-\alpha$	loss due to absorbtion in Pu-239	- 0.24
$-A$	losses in structural material, etc.	-(0.1÷0.25)
$-L$	leakage of neutrons	-(0.04÷0.06)
$-T$	losses due to absorbtion in FP	-(0.01÷0.015)
$+F.$	rate of fission of U-238	+(0.19÷0.22).
$.(\nu-1))$	neutrons from U-238 fission	.(2.70-1))
$\left(\frac{1}{1+\alpha}\right)$	rate of absorbtion in Pu-239 in (n,γ) reaction	$\left(\frac{1}{(1 + 0.24)}\right)$
$BR_{fast} =$		1.25 ÷ 1.40



FOR THE CHEMIST, THE POSSIBILITY OF INTERNAL OR EXTERNAL BREEDING IS OF IMPORTANCE

	Primary Step			Secondary Step	
Cycle	Fertile	Intermediate	Fissile	Intermediate	Fissile
Thorium	Th-232 90	Pa-233 91	U-233 92	U-234 92	U-235 92
Uranium	U-238 92	Np-238 93	Pu-239 94	Pu-240 94	Pu-241 94

Fissile and Fertile Materials
Micro-mixing $(U,Pu)O_2$
Macro-mixing UO_2 particles + PuO_2 particles
In fused salt: $PuCl_3$ in fuel, UCl_3 in coolant/fertile material



Note: for ~3000 MW(th) radius of core is ~100 cm
thickness of blanket is ~100 cm

DEFINITION OF DOUBLING TIME

Doubling time T_o is the period of time (years) in which a breeder produces enough fresh fissile material to fuel a new breeder react with the same power level (T_{eff} includes the inventory of fissile materials out of core e.g. cooling, being transported and reprocessed). The compound doubling time T^{eff}_{comp} takes into account that in a breeder system, the new breeder can be fuelled with fissile material coming from the total system and not only from one reactor.

$$T_o = \frac{\text{Specific inventory (gram fissile/MWth)}}{(1 + \alpha) \cdot G} \text{ (days)}$$

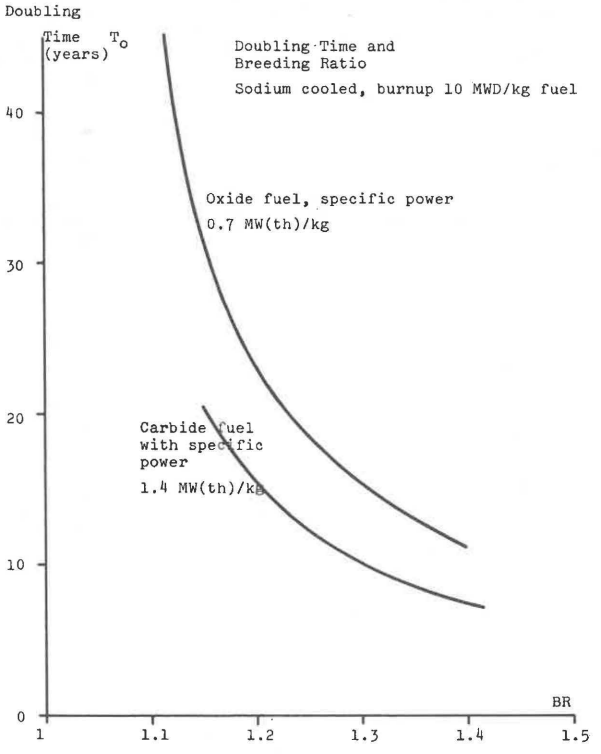
G = BR-1; breeding gain

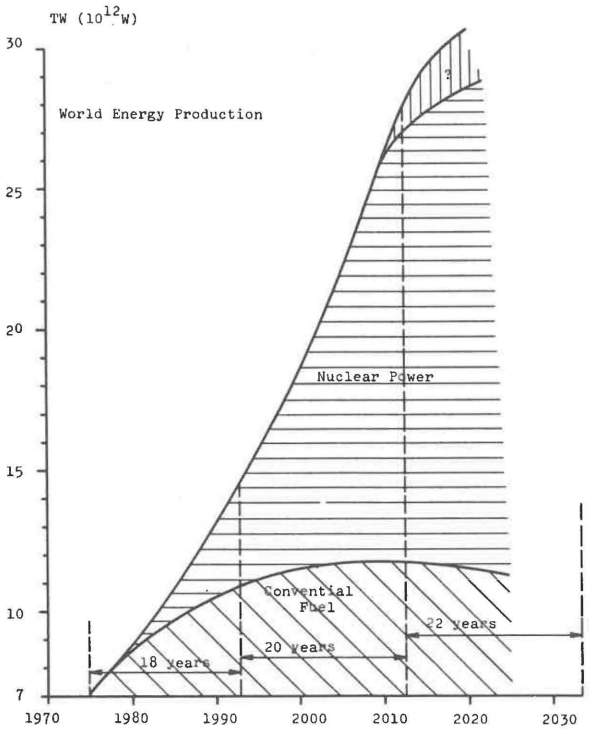
r = fuel inventory out of core

L = load factor (hours per 8760 hours in year)

F = fraction of fission in fertile nuclide

$$T^{eff}_{comp} = T_o \frac{(1+F)}{L(1-r)} \cdot \ln 2$$

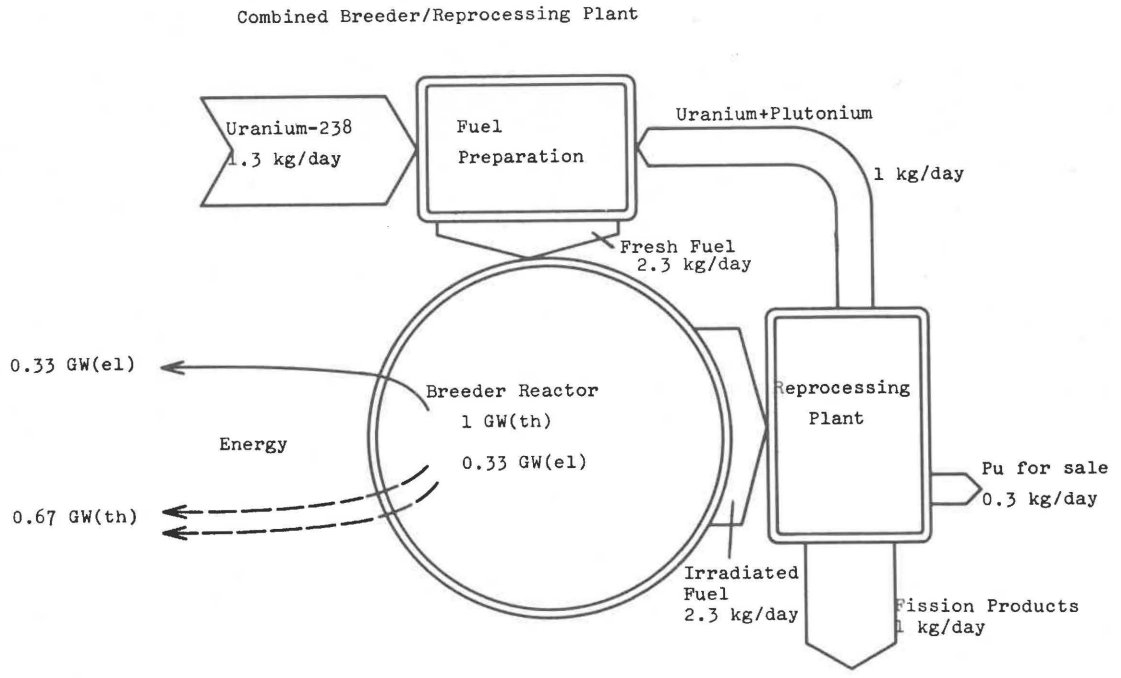




DOUBLING TIME IS COUPLED WITH FUTURE ENERGY DEVELOPMENT

The rate of doubling (doubling time) of the total energy consumption is ~18 years and may increase in the future.

Doubling time of electrical energy consumption is ~9 years.
Doubling time of nuclear power capacity is less than 9 years.
Doubling time of breeders should be of the same magnitude.
In the future, civilization should reach a steady state when the doubling time for the breeder will satisfy the demand with $T_s >$ ~30 years.



BREEDERS ARE NECCESSARY BECAUSE THE WORLD RESOURCES OF 'GOOD' URANIUM ORES ARE RATHER LIMITED

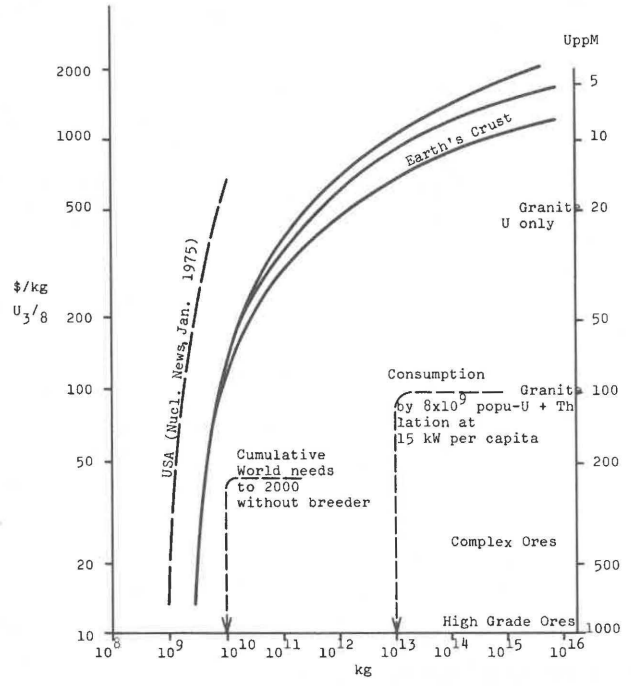
A tremendous increase in available uranium ores occurs if one considers not only the classical ores (>1000 ppM uranium) but the very abundant granites with 80 ppM uranium and thorium.

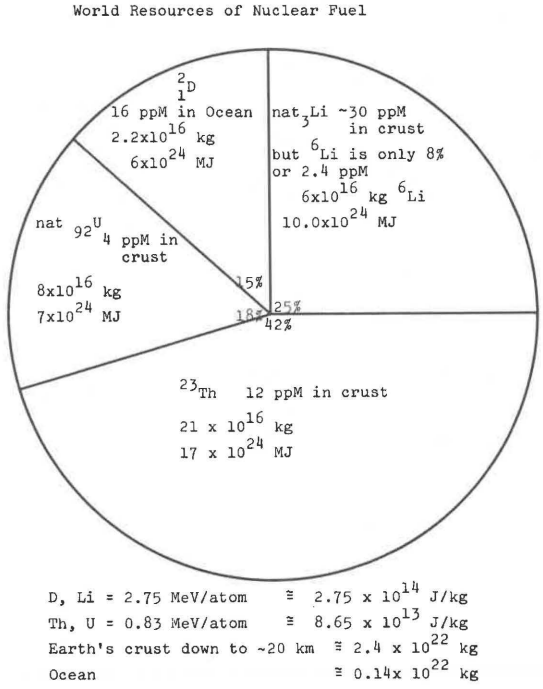
Even if the price of uranium should increase a hundred fold the price of the raw fuel per kWhr will be no higher than it is now for light water reactors (since the uranium contains only ~0.4% of burnable U-235).

1 kWhr (e) ≅ 3 cents US, of this fuel ≅ 0.8, from this plutonium ≅ 0.5 cents.

1 g Pu ≅ 1 MWDth = 24000 kWhr(th) = 8000 kWhr(e) ≅ 40$/g Pu
for 1 g Pu ≅ 1.5 g natU

present price 1 kg U ≅ 30 $; 1 g ≅ 3¢
assume future extreme price 1 kg U = 2000 $ 1 g = 2 $
1 g Pu will require 3 $ worth of Unat
Each gram of Pu will be not 40 $ but 42 $ per g.
The price of electrical energy increases to 3.25 ¢/kWh(e)





D, Li = 2.75 MeV/atom ≅ 2.75 x 10^{14} J/kg
Th, U = 0.83 MeV/atom ≅ 8.65 x 10^{13} J/kg
Earth's crust down to ~20 km ≅ 2.4 x 10^{22} kg
Ocean ≅ 0.14x 10^{22} kg

FUTURE ENERGY NEEDS COULD BE VERY GREAT BUT WOULD STILL BE MET FROM NUCLEAR SOURCES IN THE FIRST INSTANCE

TODAY: 3.8×10^9 people x 2 kW/cap. = 7.6 TW = 2.4×10^{20} J/year

FUTURE: 8×10^9 people x 15 kW/cap. = 120 TW = 38×10^{20} J/year
1 gram (U,Th) = 1 MW/day = 8.64×10^{10} J

38×10^{20} J/year 4.4×10^{10} g/year = 44000 tons Uranium and/or Thorium per year

But granite contains 80 ppM U+Th so the annual need for granites as 'fissile' ores will be 550 million tons.
At the present time coal production alone is 4 times greater!

Granite: Energy cost for 15 ppM U and 60 ppM Th.
Granite is the main constituent of the earth's crust (up to 20 km deep)

$$1000 \text{ kg granite} = \frac{10^6 \text{ g}}{68.6 \text{ g/mol}} = 1.46 \times 10^4 \text{ mol}$$

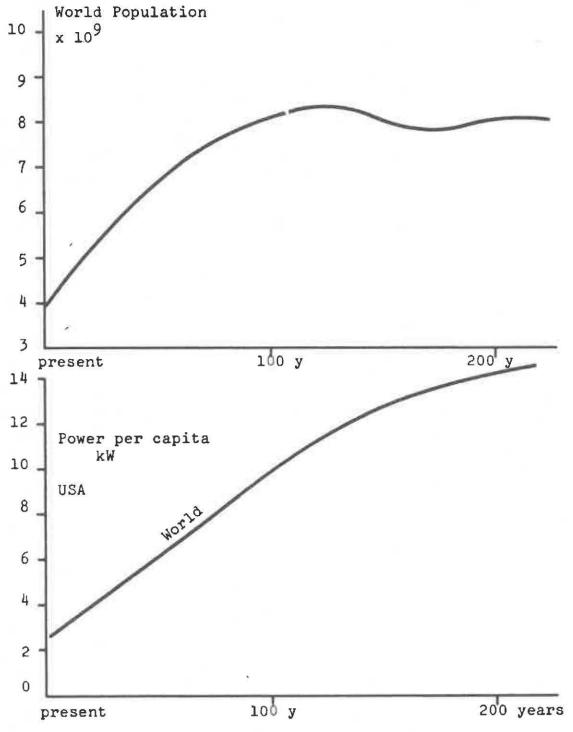
Free enthalpy of formation of granite = 210 kcal/mol ' 8.8×10^5 J/mol

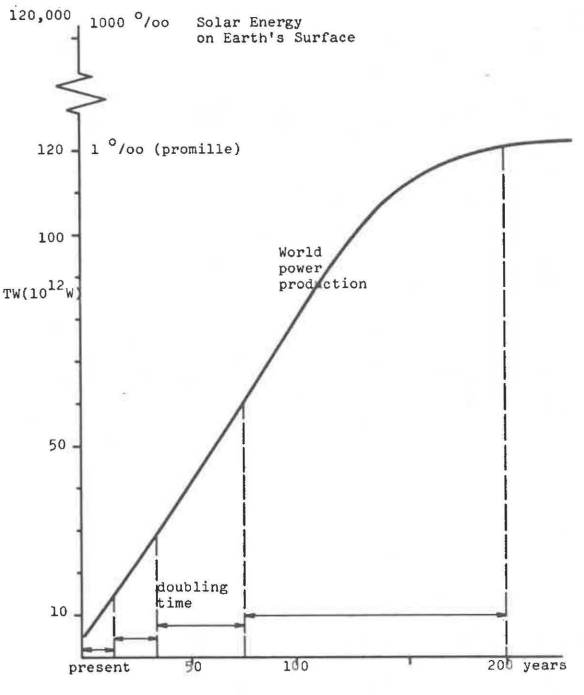
Technological free energy (electrolysis?) = 1.8 $MJ_{elec/mol}$ + 1.8 $MJ_{therm/mol}$

Technological free energy for 1 ton granite = 5.2×10^{10} J.

Amount of uranium and thorium = 75 ppM = 75 g = 75MWD total = 6.48×10^{12} J

Amount of electricity at 40% efficiency = 2.6×10^{12} J





ONE OF THE BIGGEST CONSTRAINTS TO FISSION ENERGY IS THE PROBLEM OF FISSION PRODUCT MANAGEMENT

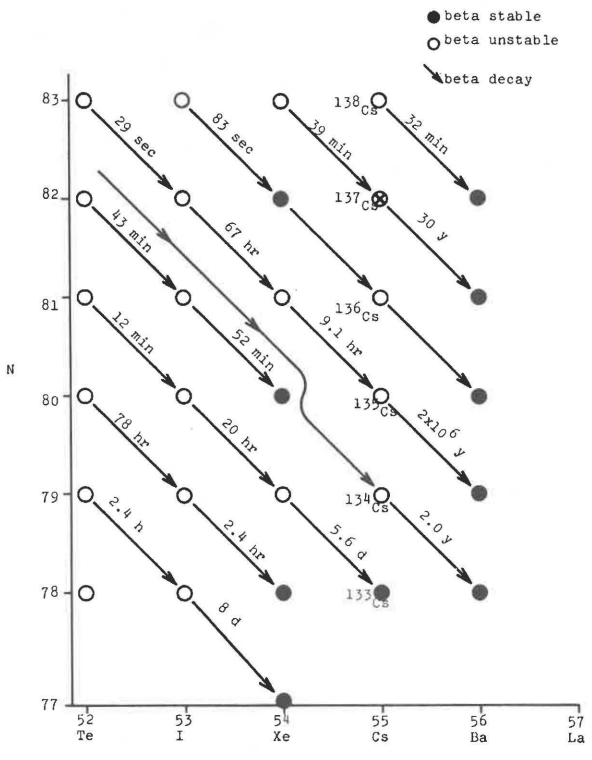
Each fission releases ~200 MeV; 1 Joule = 3.1×10^{10} fissions.

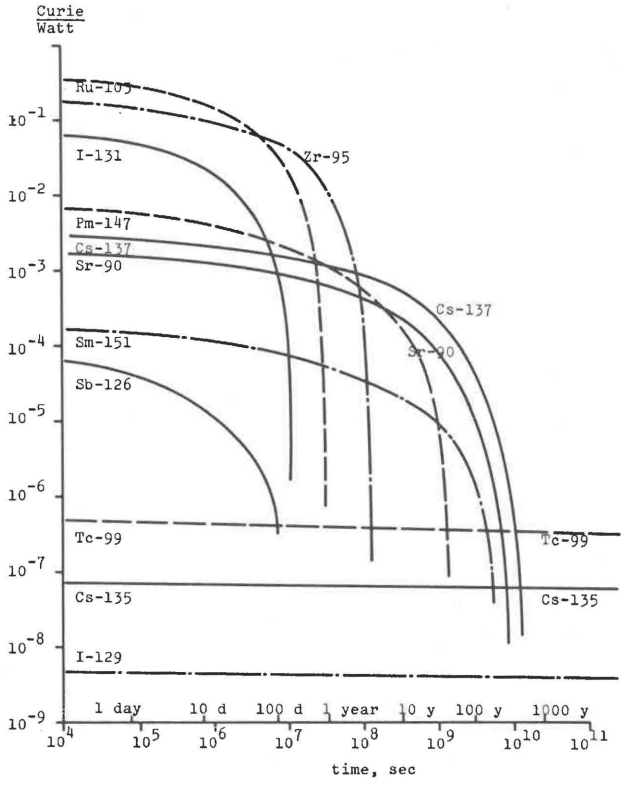
1 watt = 3.1×10^{10} fissions per second equivalent to 6.2×10^{10} fission product atoms per second.

In steady state very roughly 1 Watt of power ~1 Curie of fission products (1 Curie = 3.7×10^{10} disintegrations per sec).

All fission products are beta unstable (neutron rich nuclei)

Some fission products are long lived, comparable with a human life span or even the life span of an element of social organisation.





THE PROBLEM OF FISSION PRODUCT MANAGEMENT IS VERY DIFFICULT AND REQUIRES A SOPHISTICATED SOLUTION

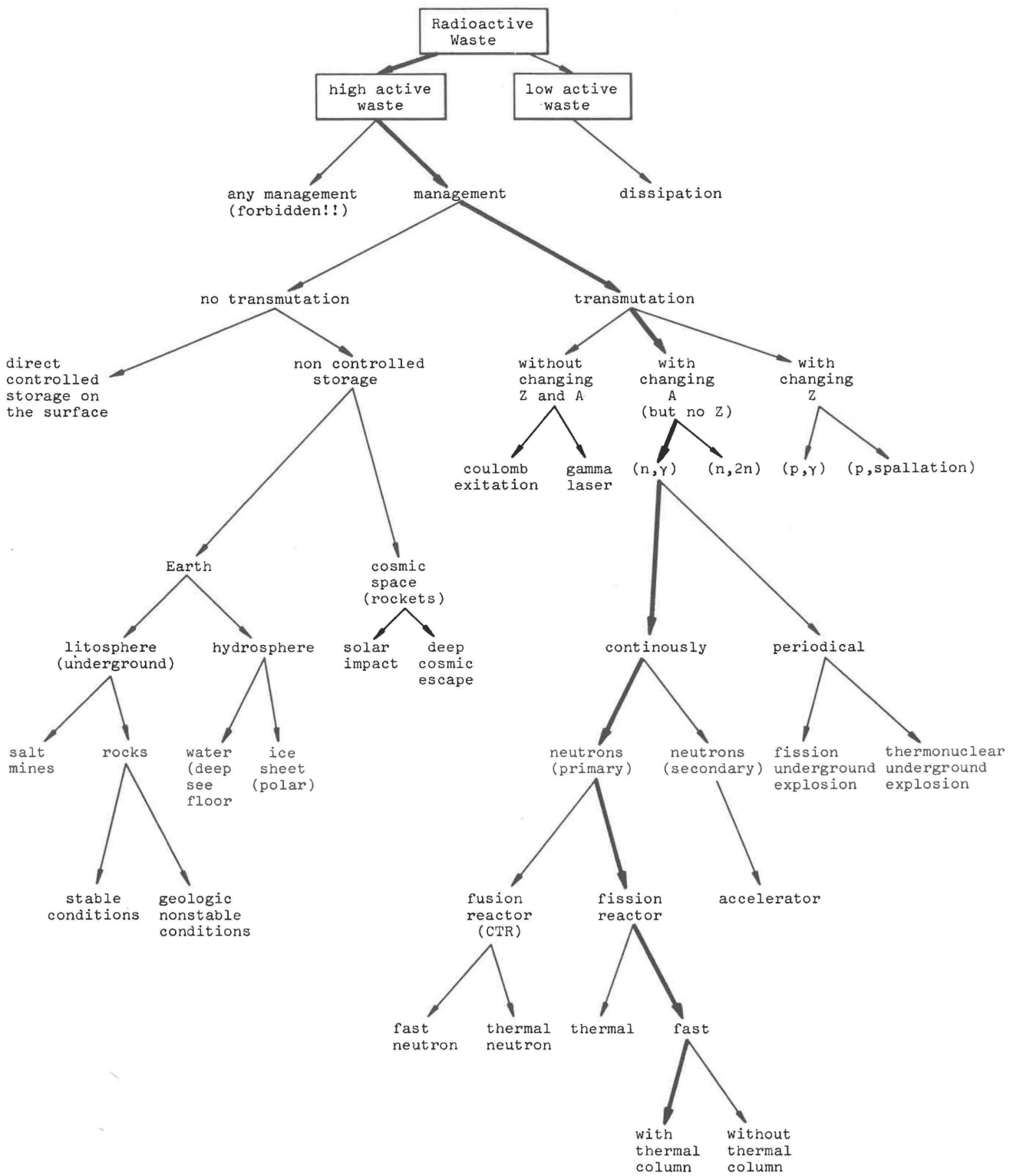
The possibilities of radioactive waste management are:

1. Without the use of nuclear transmutation; that is the fission product nuclides are not changed, but merely removed and isolated; as for example a rocket to the sun, in discused salt mines or in the polar ice-cap.

2. By using nuclear transmutation in which the nuclear properties are so fundamentally changed that the transmuted products are short living nuclides which decay after a short retention time to a stable nuclide.

In this second class of waste management techniques a number of exotic methods have been discussed

- gamma laser excitation (does not exist)
- underground neutron irradiation due to fission or thermonuclear explosion (e.g. more than 3000 explosions of 100 kT per year in USA 2000 only)
- bombarding by protons (e.g. a 10 GeV accelerator with 1 Amp)
- neutron irradiation in a thermo-nuclear fission reactor (does not exist)
- neutron irradiation in a fission reactor (only pessimistic opinions).


Radioactive Waste
high active waste
low active waste
any management (forbidden!!)
management
dissipation
no transmutation
transmutation
direct controlled storage on the surface
non controlled storage
without changing Z and A
with changing A (but no Z)
with changing Z
coulomb exitation
gamma laser
(n,γ)
(n,2n)
(p,γ)
(p,spallation)
Earth
cosmic space (rockets)
litosphere (underground)
hydrosphere
solar impact
deep cosmic escape
continously
periodical
salt mines
rocks
water (deep see floor
ice sheet (polar)
neutrons (primary)
neutrons (secondary)
fission underground explosion
thermonuclear underground explosion
stable conditions
geologic nonstable conditions
fusion reactor (CTR)
fission reactor
accelerator
fast neutron
thermal neutron
thermal
fast
with thermal column
without thermal column

THERE IS A METHOD FOR 'INCINERATION' OF THE MOST DANGEROUS FISSION PRODUCTS

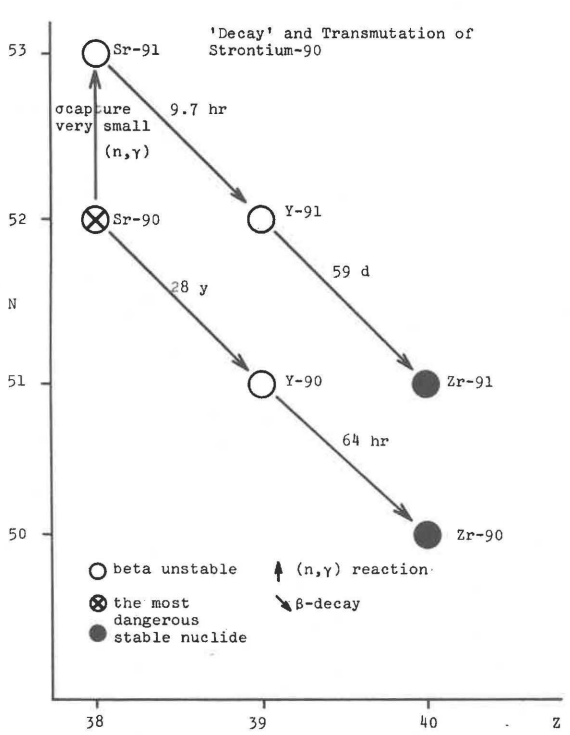
Shown here are the most dangerous nuclides: per 100 fissioned atoms.

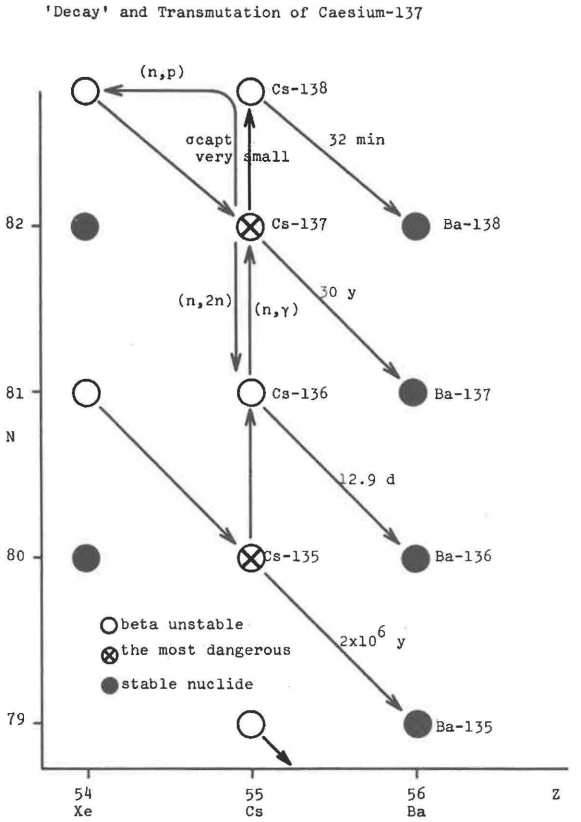
Caesium	133 (stable)*	6.91	21.14	33.18
	135 (2×10^6 years)	7.54		
	137 (30 years)	6.69		
Strontium	88 (stable)*	1.44	3.62	
	90 (28 years)	2.18		
Iodine	127 (stable)	0.38	1.55	
	129 (1.7×10^7 y)	1.17		
Technetium	99 (2.1×10^5 y)	5.81		
Krypton	83 (stable)	0.36	2.47	
	84 (stable)	0.56		
	85 (10.7 years)	0.672		
	86 (stable)	0.882		

*problem of isotopic separation

The incineration is possible due to irradiation in a very high neutron flux, which gives, for example

$$\text{Cs-137 } (n,\gamma) \text{ Cs-138} \xrightarrow[\beta^-]{32 \text{ min}} \text{Ba-138 (stable)}$$





THE NEUTRON TRANSMUTATION OF F.P. NEEDS A VERY HIGH THERMAL NEUTRON FLUX OF 5×10^{16} n $cm^{-2}s^{-1}$

The efficiency of the transmutation is limited by the criteria that the probability of the bombardement of an atom by a neutron is ~10 times greater than the probability of spontaneous beta decay.

$$\lambda(\text{neutron capture}) \geq 10 \cdot \lambda \text{ (beta decay)}$$

We know that for a neutron flux Ø (n $cm^{-2}s^{-1}$) and the capture cross section σ_c (cm^2/particle) the probability of reaction equals.

$$\lambda \text{ reaction} = Ø \cdot \sigma; \quad \text{therefore } Ø \cdot \sigma > \lambda \text{decay}$$

For caesium-137 we have

$$\lambda \text{decay} = 7.7 \times 10^{-10} s^{-1}$$

$$\sigma \text{capture (thermal)} \cong 0.06 \times 10^{-24} \text{ cm}^2$$

$$\sigma \text{capture (fast)} \cong 0.01 \times 10^{-24} \text{ cm}^2$$

For the postulated neutron reaction probability

$$Ø > \frac{\lambda \text{decay}}{\sigma \text{cap}} > Ø\text{fast}; \quad Ø\text{fast} = \frac{7.7 \times 10^{-10}}{0.01 \times 10^{-24}} = 8 \times 10^{16}; \quad Ø\text{thermal} = \frac{7.7 \times 10^{-10}}{10.6 \times 10^{-24}} =$$

$$= 1{,}2 \times 10^{16}$$

	Flux
	Thermal / Fast
Power rating (W/cm^3)	80 / 500
Fissile concentration (N)	3% / 10%
Nuclei per cm^3	8×10^{20} / 30×10^{20}
$\sigma_{fission}$ (10^{-24} cm^{-2})	700 / 2
Flux Ø $ncm^{-2}s^{-1}$, Ø =	6.2×10^{12} / 2.6×10^{15}
Fluence, Ø.t t = (days) Ø.t = (ncm^{-2})	700 / 100 3.7×10^{20} / 2.2×10^{22}

Possibilities of transmutation		
Source of Particles	Particles	
	Protons	neutrons
Accelerator ~30 MeV	30 MeV protons for (p,γ)(p,n)	-
Accelerator >1 GeV	1 GeV protons for (p,xn) (p,spall)	(secondary) High flux of neutrons
Nuclear explosion	-	primary very high flux in very short time
C.T.R. (controlled thermonuclear reactor	-	High flux, continously
Fission reactor	-	Very high flux continuously

IT MAY BE POSSIBLE TO COUPLE A BREEDING SYSTEM WITH A HIGH FLUX TRANSMUTATION FISSION REACTOR

We postulate a system with breeding potential and with transmutation potential.
The compound doubling time Ts must be at least 30 years,

since; $Ts(year) = \frac{1000}{365} \cdot \frac{M.(1+F)}{(BR-1)(1+\alpha)} L \cdot \ln 2 = 30$ years

from this; $_{min}BR = 1 + 2.75 \cdot \ln 2 \cdot \frac{M.(1+F)}{(30.(1+\alpha)} \cdot L$

for typical values;

$$_{min}BR = 1.077$$

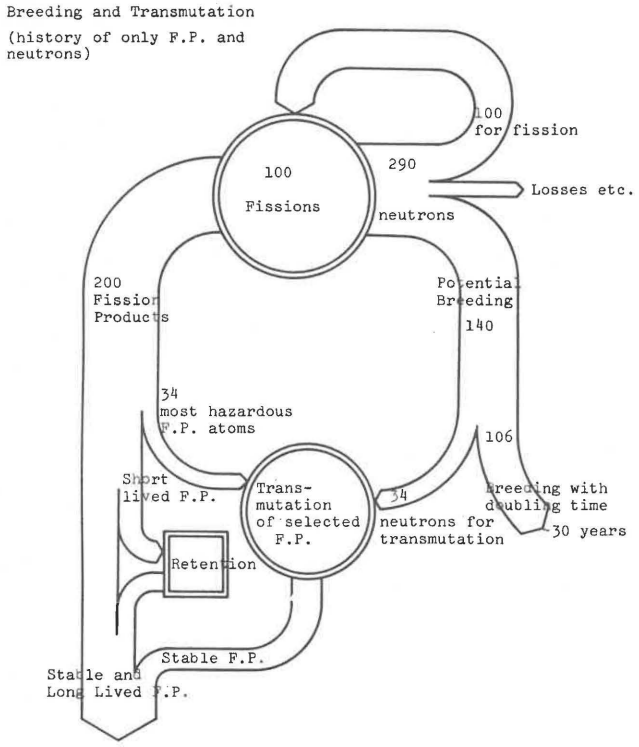
we know that: $_{max}BR = \frac{\nu-1-\alpha-(A+L+T)+F(\nu-1):}{(1+\alpha)}$ when T is very small (T=transmutation rate)

For the desired $BR_{min} = 1.077$ we obtain:

$$T = \nu-1-\alpha-BR(1+\alpha)-A-L+F(\nu-1)$$

For typical values: T = 0.364

That is, for a breeding system with a breeding potential of BR = 1.4 and for a compound doubling time of 30 years, approx. 0.36 of FP nuclides could be transformed in the fast system.



Organisation of transmutation and breeder system

Our system is:
- breeding system with compound doubling time 30 years.
- breeding potential $BR_{pot} = 1.4$
- transformation rate 0.36
- 1 burner reactor for transmutation
- breeder power reactors

We obtain:

$$X.BR_{max} = (X+1)BR_{min}$$

but we know $BR_{max} = BR_{min} + \frac{T}{(1+\alpha)}$

from this, for typical values

$$X = BR_{min} \frac{1+\alpha}{T} = 3.7$$

Result: for about 3.7 power units of breeder reactors and 1 power unit of the breeder transmutation reactor 0.36 of FP nuclides of all reactors can be 'incinerated'.

WHAT IS THE CONNECTION BETWEEN BREEDING AND THE FUEL CHARACTERISTICS (PHYSICAL STATE: SOLID/LIQUID, CHEMICAL STATE: METALLIC, CERAMIC, SALT)?

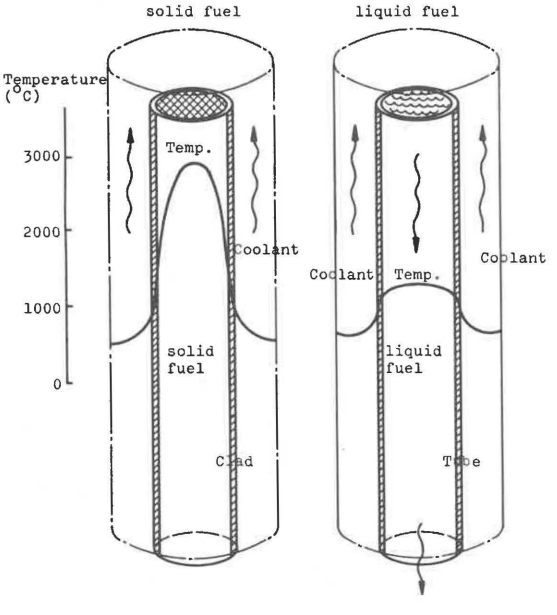
Breeder reactors are feasable using both thermal and fast neutrons. But for thermal neutrons, breeding is possible only in a very limited region the thorium-232/uranium-233 cycle in a liquid fuel reactor.

	Breeder Reactors			
Neutrons	Thermal		Fast	
Fertile/fissile Cycle	Th-233	U238/Pu239	Th232/U239	U238/Pu239
Potential Breeding gain G=BR-1-losses	~0.1	< 0	~0.3	~0.45
Impact of intermediate molecule	Pa-233 σ^{th}_{ab}=large	breeding not possible	Pa-233 σ^{fast}_{ab}=small	Np-239 σ^{fast}_{ab} negligible because t1/2 small
Consequence	Continuous Pa extraction	-	no limitations, periodic rechanging possible	
Results	liquid fuel (aqueous or molten)	-	no limitations, solid fuel possible	
Maximum losses in core structural material and coolant	~0.1	-	~0.2	~0.3
Consequences	Moderator D_2O or graphite	-	Metals possible, graphite forbidden	
Consequences	No metallic tubes in the core	-	metallic tubes in the core possible	
Impact of cooling system	out of core	-	no limitations, in core cooling possible	
Fuel system	liquid fuel only, cooled out of core	-	solid and liquid fuel, cooling in/or out of core. Solid fuel: ceramis, metals; liquid fuel: chlorides only.	
Example only for liquid fuel reactors	molten salt ^{7}LiF BeF_2 ThF_4 UF_4 graphite / aqueous solution suspension UO_2/ThO_2 in D_2O	-	molten salt NaCl $^{232}ThCl_4$ $^{233}UCl_3$	molten salt NaCl $^{238}UCl_3$ $^{239}PuCl_3$

THE LIQUID FUEL REACTOR ALSO HAS OTHER ADVANTAGES IN RELATION TO THE CLASSICAL SOLID FUEL REACTOR

	Solid Fuel	Liquid Fuel
Pressure	pressure of volatile fission products	no FP pressure: Very low pressure of fuel components
Cooling Problems	cooling only in the core	cooling in the core or out of core
Burn-up	periodic recharging typical case PWR: specific power 40 KW/kg fuel, burn-up 30000 KWd/kg fuel, dwell time 750 days	continuously recharging e.g. MSBR: 22 KW/litre dwell time 10 days
Reprocessing	periodic	continous

Heat Transport in the Core



thermal / fast				Fuel: ambient pressure, liquid	Fuel: overpressure, solid
Coolant	unpressurised	liquid	metal (Na)	projected	now not possible / LMFBR
			salt	MSBR (fluoride) / MSFBR Chlorophyl (chloride)	– / –
	pressurised		water	– / not possible	LWR HWR / not possible
		gas	CO_2	– / No	English French GCR / No
			He	– / –	HTGR HHT / GCFBR

GCR = Gas Cooled (thermal) Reactor
GCFBR = Gas Cooled Fast Breeder Reactor
HHT = High Temp. Helium (thermal) Reactor
HWR = Heavy Water (thermal) Reactor
LMFBR = Liquid Metal Fast Breeder Reactor
LWR = Light water (thermal) Reactor
HTGR = High Temp. Steam Turbine Reactor
MSBFBR = Molten Salt Fast Breeder Reactor
MSBR = Molten Salt (thermal) Breeder Reactor

MOLTEN SALT FUEL APPEARS TO BE THE BEST LIQUID FUEL

Only limited possibilities exist for choosing a fuel to operate in the liquid state in a reactor.

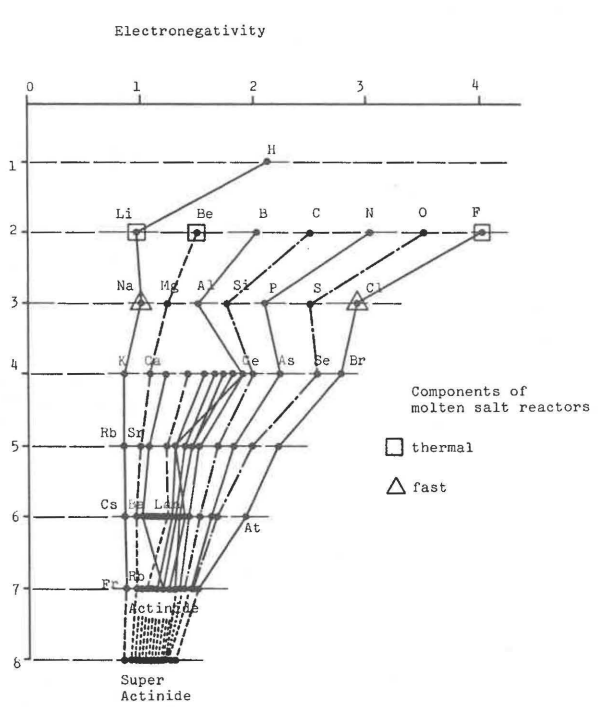
The limiting criterium seems to be the radiolysis in the extremely high field of neutrons, fission fragments and gamma rays.

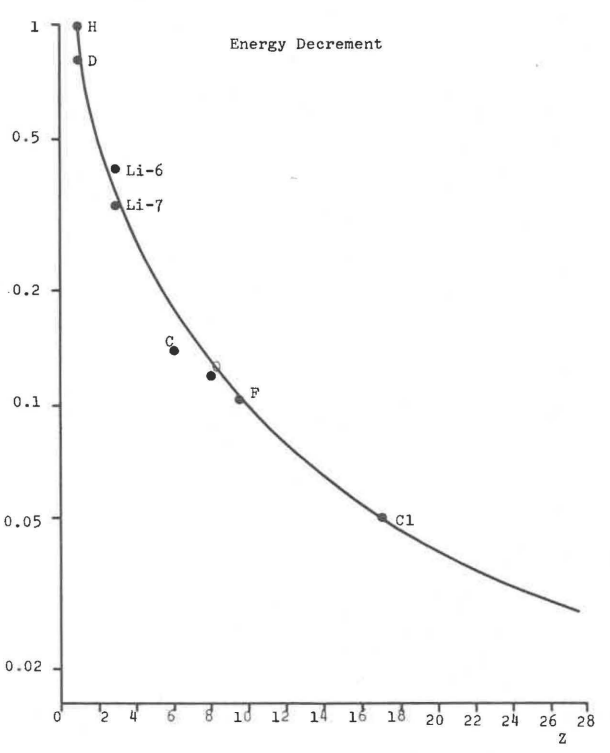
In addition the chemical stability of the dissolved species of thorium, uranium and/or plutonium in the presence of the products of radiolysis is a severe problem. The ionic liquids, that is the molten ionic salts seem to be the most appropriate media for fission fuel (see table of electronegativity overleaf).

Liquid state	Range of liquid state (°C)	Stability	Reactor type	
			Thermal	Fast
Aqueous solution	0<T<300 with pressure	Radiolytic decomposition. Instability of U and Pu salts in aqueous solution	Possible but negative experience with homogeneous thorium reactor	no possible due to neutron moderation
Organic solution or suspension	-50<T<300 decomposition	Radiolytic decomposition. Very unstable compound of Pu and U	Possible (?) but no experience	
Metallic solution or suspension	-50<T<2000	Very stable, some limitations in the solubility of U_{met} and Pu_{met}	Possible. Some experiments in Brookhaven Nat.Lab. USA	Possible. LAMPRE, Reactor Experiments (with Pu alloys? Los Alamos USA
Molten salt solution	400<T<1000	Stable to irradiation but corrosive!	Possible using fluorides. MSBR Experiment (Oak Ridge, USA). 8 MW(th)	Possible using chlorides. No experimental experience EIR Switzerland
Ceramics	1500<T practically impossible	-	-	-

BOTH THERMAL AND FAST FLUX MOLTEN SALT BREEDER REACTORS ARE POSSIBLE

	Thermal	Fast
Breeding ratio	max. 1.06	1.3 - 1.5 (?)
Possibility of transmutation	no	yes, 0.35
Fuel cycle	Th-U_{233} only because, in this case only, is η thermal >1.2	U-Pu_{239} and/or Th-U_{233}
Chemistry of molten salt	Fluorides only. positive experience exists	Chlorides, or fluorides (?) no experience with chlorides
Structural materials	Only graphite-direct contact, no metals (no parasitic capture)	metals in core permitted.
Cooling	Out of core cooling	Either in core or out of core cooling
Present day development	USA - Oak Ridge; France Fontenay aux Roses; India - Trombay?	UK., -Harwell, Winfrith (?); Switzerland: Würenlingen EIR
Moderation of neutrons	Fluoride in large amounts acts as a weak moderator	The moderation factor for chlorine is 3 times lower and the concentration is also smaller





MOLTEN FLUORIDE VERSUS MOLTEN CHLORIDE FUEL - I

Criteria for molten salt as fuel:

Melting point: lower than 500-600°C

Boiling point higher than 1500°C (partial pressure)

Density: as high as possible, $\rho = 3\ gcm^{-3}$

Capture cross section low $\sigma^{thermal}_{capture}$ <0.16; σ^{fast}_{capt} small

Cross section for nuclear reactions low; e.g. for $^{35}Cl\ (n,p)^{35}S$

Elastic scattering: high for thermal, low for fast (see previous page)

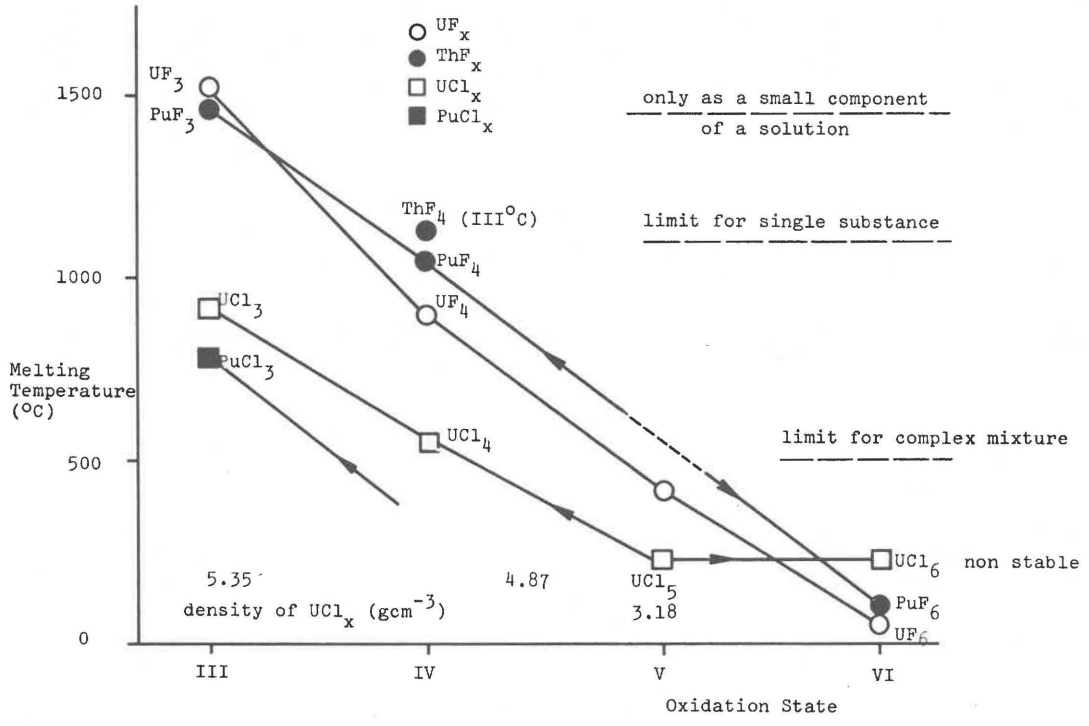
Radiolytic stability high and fast recombination (previous page)

Chemically stable (large free enthalpy of formation), no precipitates

Simple technology, low corrosivity

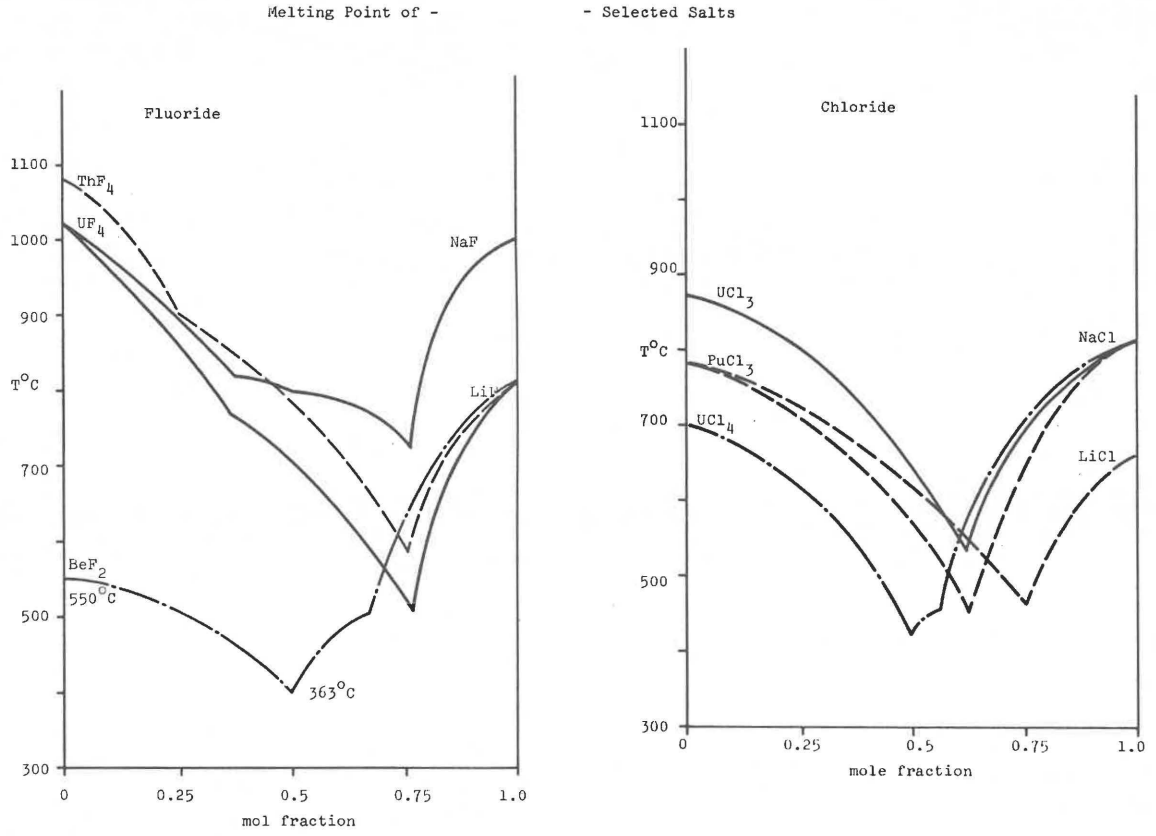
Low viscosity (low pumping requirements) ~1 centipoise

Low price, good availability, non poisonous



MOLTEN FLUORIDE VERSUS MOLTEN CHLORIDE FUEL - II MELTING POINTS

		Fluoride	Chloride
Reactor Type		Thermal (fast possible)	only fast because σ_{capt} Cl is large
Components -	fertile	ThF_4 only	UCl_3 or UCl_4 (unstable!)
	fissile	UF_4 or UF_3	$PuCl_3$ only
	dilutent	LiF Possible but also BeF_2 plays the role of moderator NaF forbidden since T_{melt} is too high	LiCl forbidden since $BeCl_2$ they act as moderators NaCl possible
Moderator		Li.F, BeF_2 not sufficient. Graphite is necessary: does not react with molten fluoride	none
Metallic tubes in the core		not permitted due to neutron balance	permitted, e.g. a molybdenum/iron duplex



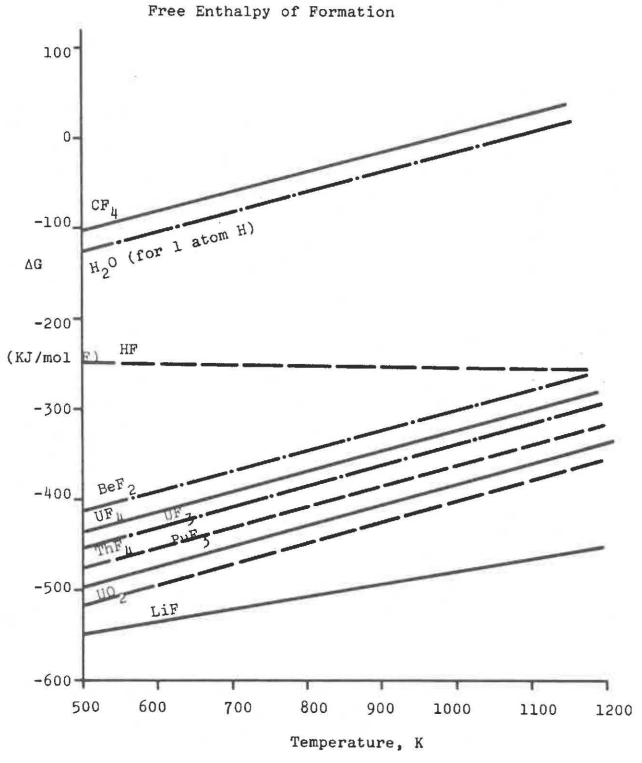
MOLTEN FLUORIDE VERSUS MOLTEN CHLORIDES FUEL - III CHEMICAL STABILITY

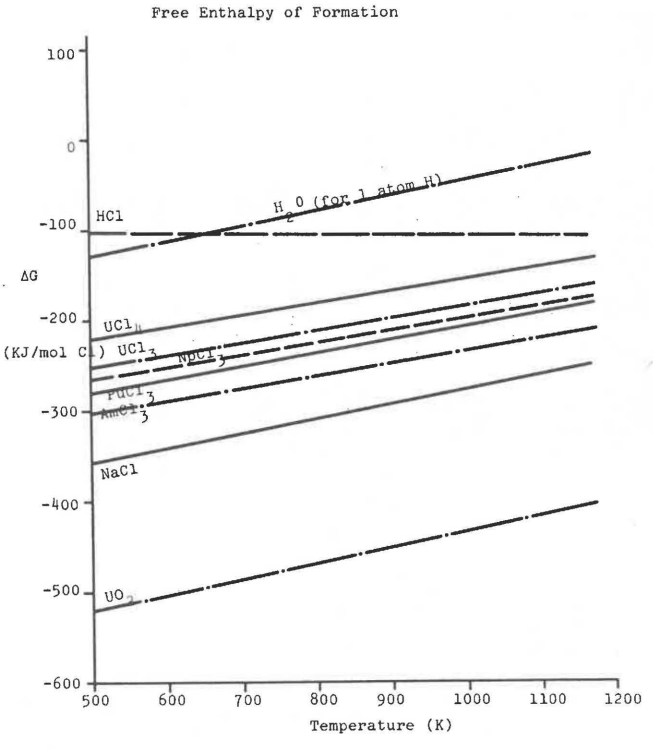
The free energy of formation for fluorides is greater than that for chlorides.

The formation of oxides of uranium is retarded in fluorides.

The ratio ΔG (HF/H_2O) is not the same as ΔG (HCl/H_2O).

Carbon tetra-fluoride is a product of graphite and fluorides.





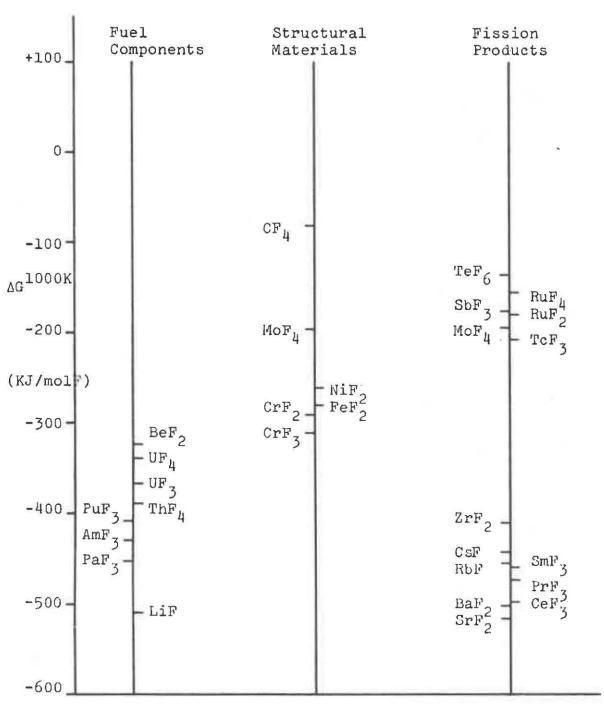
MOLTEN FLUORIDE VERSUS MOLTEN CHLORIDES FUEL - IV

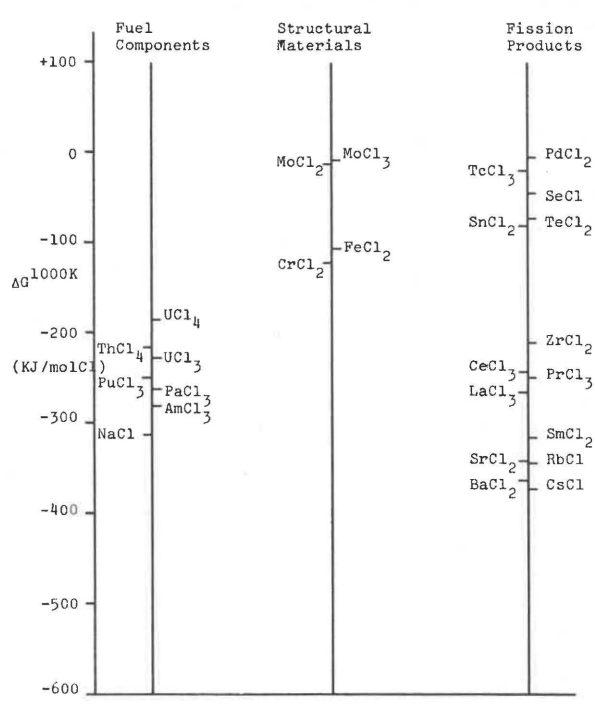
STABILITY AGAINST FISSION AND CORROSION PRODUCTS

For molten fluoride the crucial mechanism

$$UF_4(d) + 1/2\ Cr(Ss) \quad UF_3(d): \quad K^{900K} = 1.38 \times 10^{-4}$$

Numerical Values given for ΔG^{1000K} in $2LiF\text{-}BeF_2$ solution





MOLTEN SALT FLUORIDE BREEDER (THERMAL) POWER REACTOR

1 GW(el), MSBR (Oak Ridge concept)

Fuel: ^{7}LiF (71.7 mol%), BeF_2 (16%), ThF_4 (12%), $^{233}UF_4$ (0.3%)

T_{fuel} = 839-978 K T_{melt} = 772 K

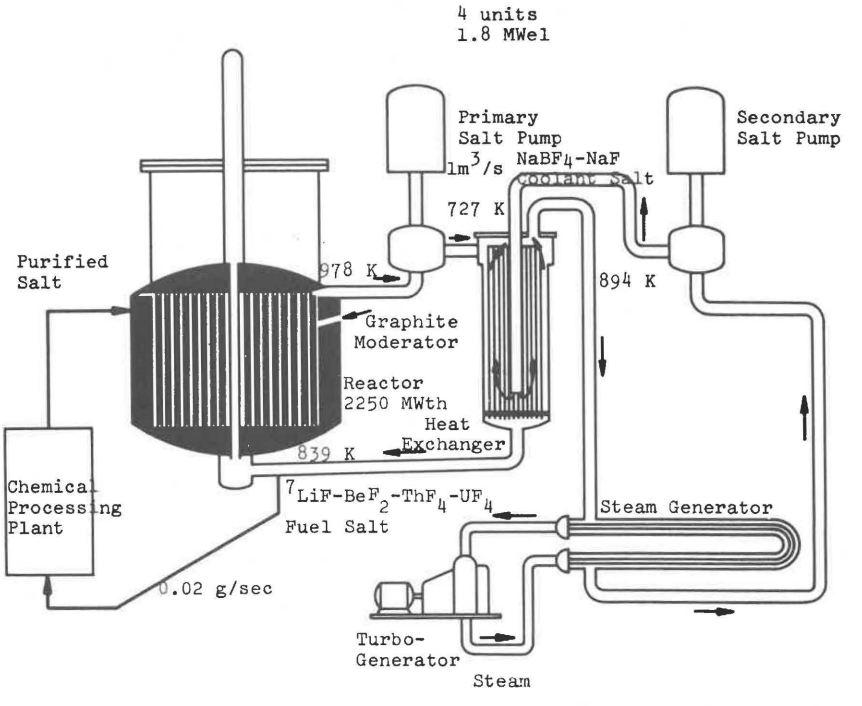
Breeding ratio = 1.06 Doubling time = 22 years

Density (~908 K) = 3330 kg/m^3. Heat Capacity = 1.36 J $g^{-1}K^{-1}$

Viscosity (~908 K) = 0.01 N s m^{-2}

Structural material: graphite (in core)
Hastelloy N

Problem of delayed neutron precursors.

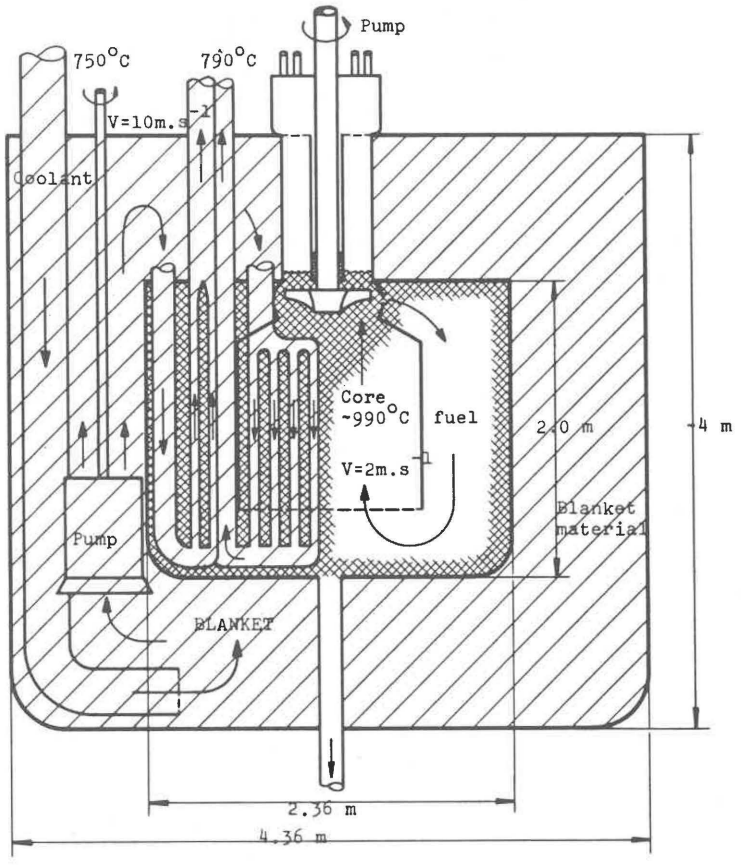


A FAST BREEDER REACTOR WITH MOLTEN CHLORIDES COULD HAVE IN CORE COOLING

Total power: 2050 MW(th) Core volume 7.75 m^3 (2m x 2.36 m)
Fuel: $PuCl_3$ (15 mol%) NaCl (85 mol%). T_{melt} = 685°C; ρ = 2.34 gcm^{-3}
Coolant, fertile: $^{238}UCl_3$ (65 mol%) NaCl (35 mol%) T_{melt} = 710°C;
ρ= 4.00 gcm^{-3}
Specific power: 220 W/cm^3 core; 705 W/g Pu
Velocity: Fuel 2 m s^{-1}; coolant 9 m s^{-1}
Number of tubes in the core: 20,000 (1.26/1.20 cm dia.)
Reprocessing: continous, 3 gs^{-1}; dwell time: 10 days
Breeding ratio: internal 0.716; outer 0.67
total 1.386 (corrected)
Mean fast flux across core: 7 x 10^{15} n $cm^{-2}s^{-1}$
fast flux in the centre: 1.2 x 10^{16}n $cm^{-2}s^{-1}$

Temperature reactivity coefficent ($\delta k(\%)/\delta T(^{\circ}C)$)
fuel = 3.8 x 10^{-2}; coolant +1.29 x 10^{-2}

Structural material: Fe (1.45 kg/l): Mo(0.465 kg/l)

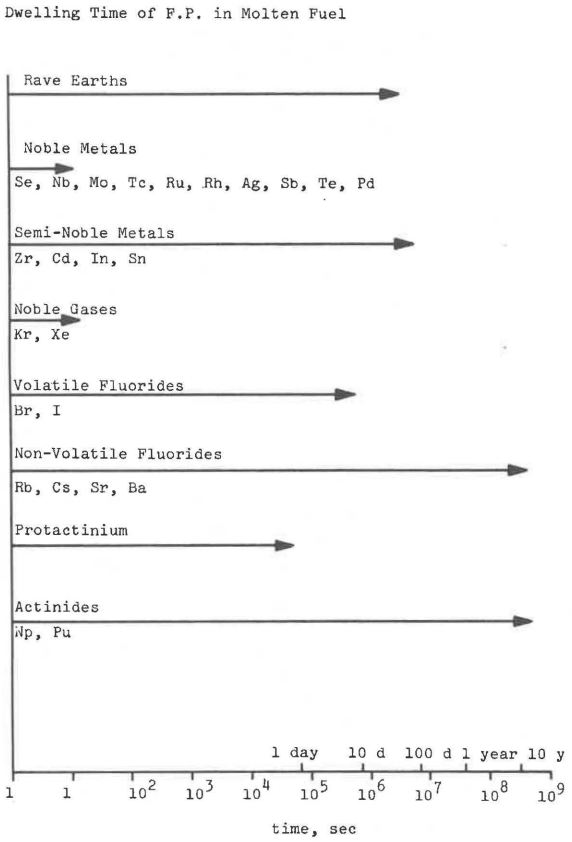


THE VERY COMPLEX PROBLEM OF CONTINOUS REPROCESSING OF THE FUEL IN A MOLTEN FLUORIDE REACTOR HAS BEEN SOLVED

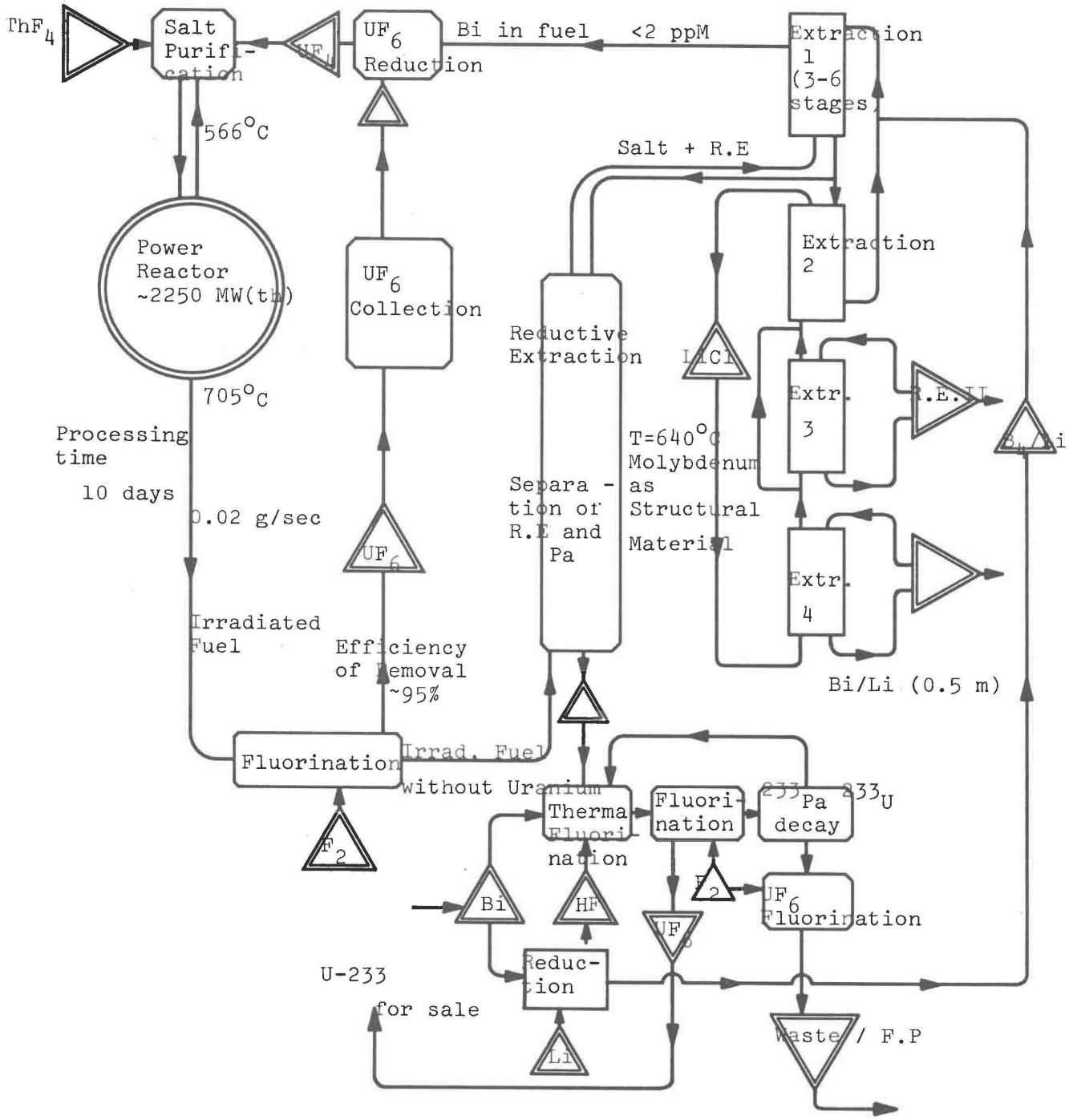
The operation of a molten salt thermal reactor as a high performance breeder is made possible by the continuous reprocessing of the fuel salt in a plant located at the reactor site. The most important operation consists in removing fission products (rare-earths) and isolating Pa-233 from the high flux region during its decay to U-233 in order to reduce neutron absorption.

It is also neccessary for:
- the removal of excess U-233
- addition of fresh amounts of Th-232
- the proper redox potential to be maintained
- the oxides to be removed
- corrosion products to be maintained at tolerable levels

In order to achieve the breeding ratio of 1.06 - 1.07 the following fission products must be removed as shown.



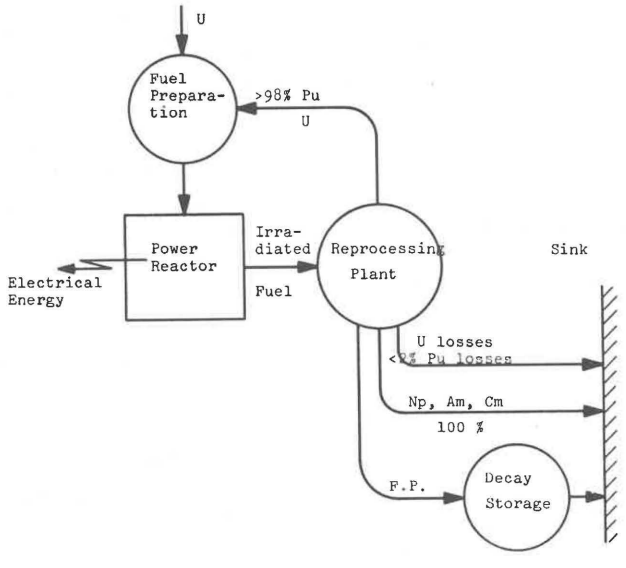
Reprocessing in MSBR



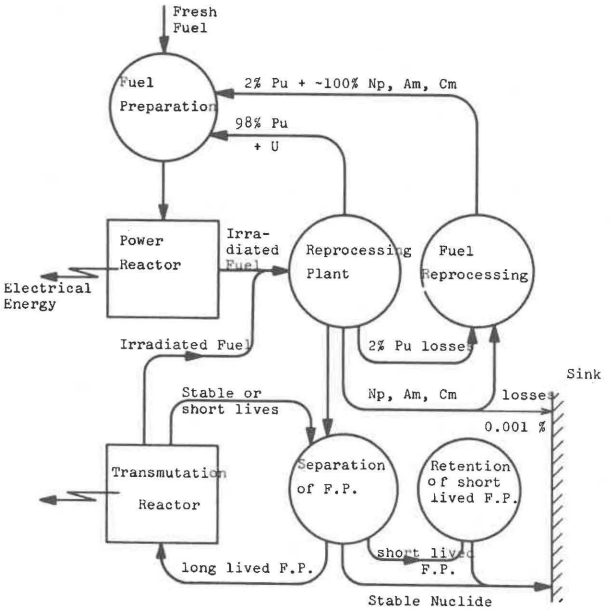
THE EXISTING REPROCESSING SCHEME IS TOO CONSERVATIVE.
IT DOES NOT TAKE INTO ACCOUNT THE PROBLEMS OF RADIOACTIVE WASTE MANAGEMENT

	PRESENT STATE	POSSIBLE FUTURE FORM
Reprocessing	periodic	quasi-continuous
Removal of F.P.	in a mixture	as individium
Transmutation of hazardous F.P.	no	possible in a special central station
Actinides (Np, Am, Cm..)	removal to radioactive waste	recycled in a special power reactor?

Reprocessing today



Reprocessing in the Future



THE LONG TERM HAZARDOUS TRANSPLUTONIUM ELEMENTS CAN BE FULLY BURNED-UP IN A FISSION REACTOR

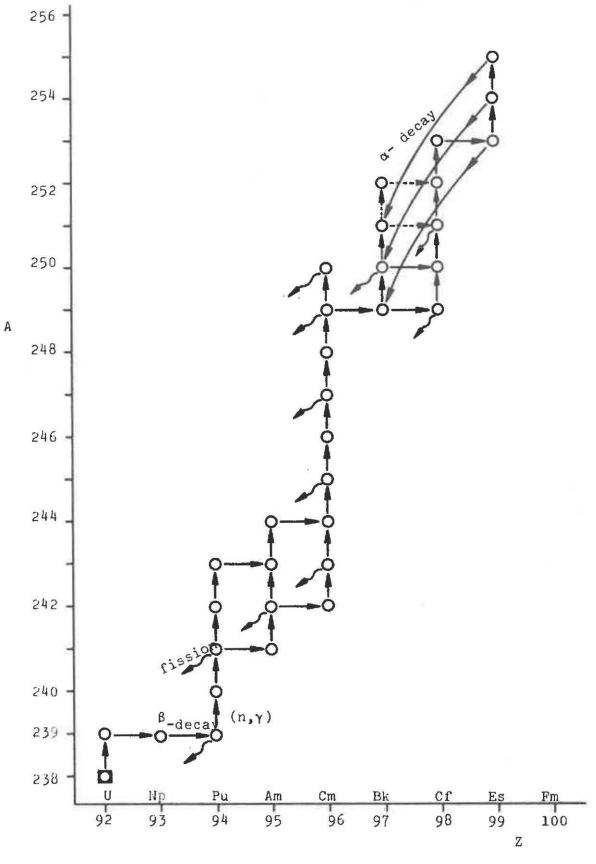
Parallel to the burning of U and Pu also synthesis of Np, Am, Cm, Bk and Cf is going.

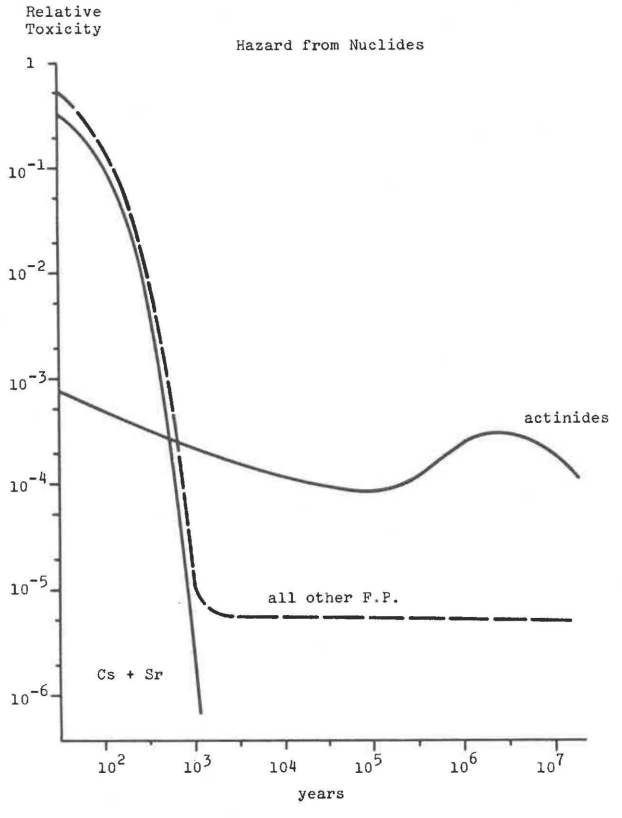
At present time the actinides, other than U and Pu, are removed to the waste.

The problem of the hazard from these actinides in long term must be solved.

The recycling of actinides bach to the power reactors gives the solution of problem.

The methods of the recycling must be developed.





CHEMISTRY OF FLUORIDE FUEL

Fluorides are the only salts with acceptable σ_{abs}, requisite stability (ΔG) and melting point.

Oxidation state: UF_3 due to stability and low T_{melt}
PuF_3 the most stable } but in both cases
ThF_4 the only one } T_{melt} is very high

Components:
1) ^7LiF and BeF_2 for lowering T_{melt}
2) for moderating
3) ^7Li because: $^6_3Li(n,\alpha)$ T, σ_{th} = 953 barn
4) LiF/BeF_2 for low viscosity

Tritium production: in spite of ^7Li the products are (for ~1 GW(el))
$^{233}U(n,f)$ ternary: 30 Ci/day
$^7Li(n,\alpha n)\ ^3T$: 1200 "
$^6Li(n,\alpha)\ ^3T$: 1200 "

Graphite - as moderator and structural material (ρ = 1.9 gcm^{-3})

$4\ UF_4 + C \quad CF_4 + 4UF_3$: e.g. pressure $CF_4 = 10^{-8}$ bar.

The problem of xenon-135: This F.P. is adsorbed in the open pore volume in the graphite; accesible void volume ~10% graphit replacement in the core ~each 2 years

Disproportionation

$4UF_3(d) \quad 3UF_4(d) + U$: $K^{900K} = 6.3 \times 10^{-7}$

Instability in the presence of oxygen-containing materials:

$UF_4 + O_2 \quad UO_2 + ...$

solubility of UO_2 in molten salt ~40 ppM
also precipitation of Pa_2O_5, PuO_2

FLUORIDES

F.P. Balance: $UF_4 \rightarrow$ 2 atom F.P. + $4F \rightarrow$

$\rightarrow Me^{I}F + Me^{II}F_2 + Me^{III}F_3 + Me^{o} + \sim + F_2$

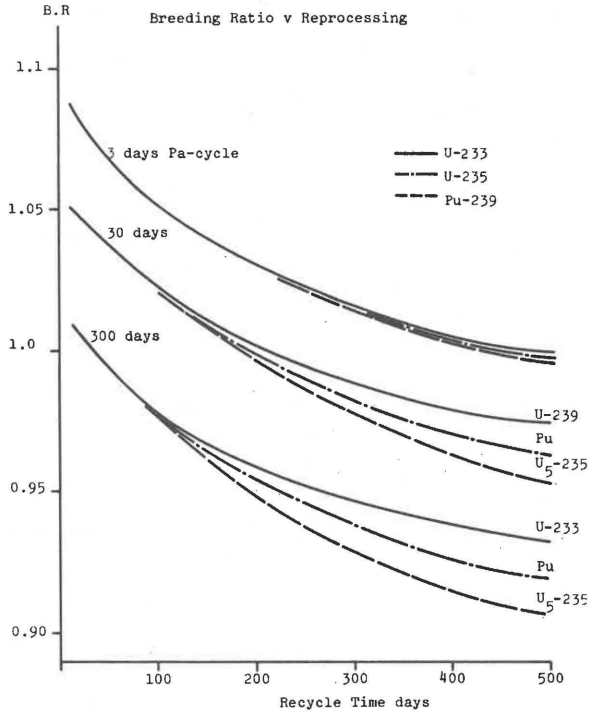
The Breeding Ratio is very sensitive to the removal rate of RE and Pa-233.

Structural material for reprocessing: TZM: molybdenum alloy

for fuel system Hastelloy N (modified) (wt%)

Ni	75	Si	0.1	C	0.06
Mo	12	W	0.1	P	0.015
Cr	7	Al	0.1	S	0.015
Fe	4	Ti	1.0	B	0.001 (10 ppM)
Mn	0.2	Co	0.2		
Hf	1.0	Ta	2.0		

Cost of salt 57$/pound, in this U-233 $13/g; total cost 23×10^6 $



ANALYTICAL PROBLEMS FOR MOLTEN FLUORIDE FUELS ARE OF THE HIGHEST IMPORTANCE

In order to fully exploit the unique features of the molten salt reactor concept it will be neccessary to carry out all analyses automatically on line with transducers located directly in the salt streams in the reactor and reprocessing plant. The most significant items to be measured are

- Redox conditions of the fuel: the U^{3+}/U^{4+} ratio which influences the rate of corrosion and the distribution of certain fission products and tritium in the reactor. This is due to the disproportionation

  $4UF_3 \rightarrow 3UF_4 + U^o$ (only in molten state)

  (by spectrophotometric methods also voltammetry)
- corrosion product concentration (Cr^{+2} Ti^{+3}, voltammetry)
- oxide levels (by hydrofluorination: $MeO + HF \rightarrow H_2O + MeF_x$) 50 ppM precision
- bismuth (polarographic method 50 ppG)
- hydrogen and tritium (diffusion to Pd-electrode some ppM)
- protactinium
- certain fission products (remote gamma spectrometry and for noble metals mass spectrometry)

Note: Most of these techniques are carried out in hot laboratories. The electrochemical technique appears to be the prime candidate for practical on-line fuel analysis because of the simplicity of its transducers.

The analytical and general chemical problems in the molten chlorides are also of interest because an important step in the continuous reprocessing technique is the liquid bismuth/molten chloride reduction extraction metal transfer process.

IN A HIGH NEUTRON FLUX CHLORINE TRANSFORMS TO SULPHUR AND PHOSPHOROUS

Chlorine 35 reacts with neutrons: $^{35}Cl(n,p)$; $^{35}Cl(n,\alpha)^{32}P$

Separation of $^{35}Cl/^{37}Cl$ is relatively easy because

1 ^{37}Cl in the naturally occurring Cl is 24.5%

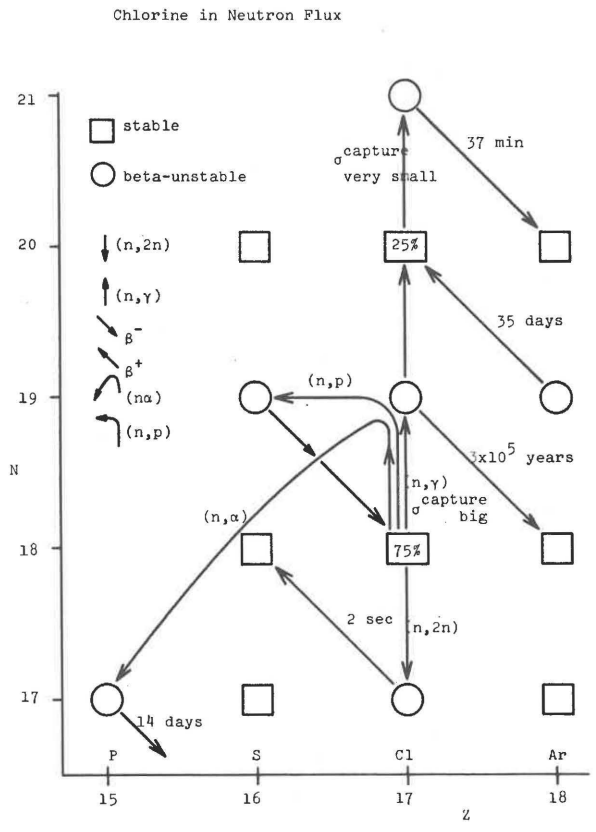
2 the ratio $\frac{37-35}{35} = 0.057$

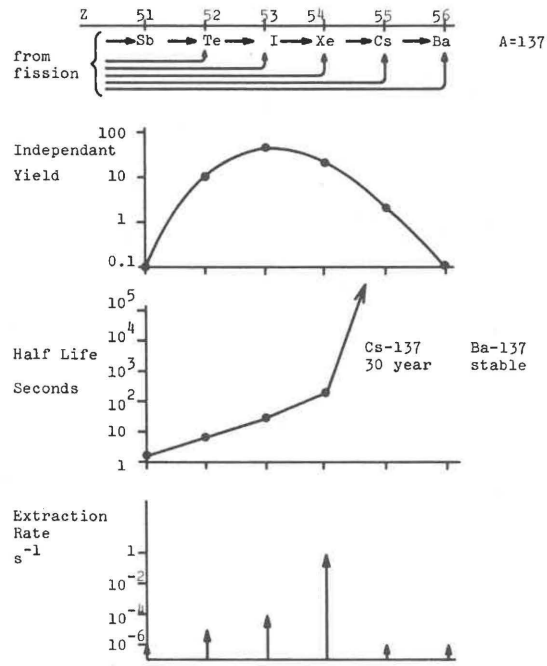
3 Chlorine is volatile

WITH MOLTEN CHLORIDE FUEL IT SEEMS THAT A CONTINUOUS GAS EXTRACTION SYSTEM IS POSSIBLE

Iodine isotopes as precursors of delayed neutrons

Isotopic separation e.g. Caesium





THE BALANCE OF CHLORINE DURING THE FISSION PROCESS IS "NEGATIVE"

$$PuCl_3 \xrightarrow{(n,f)} E' + E'' + 3Cl$$

$$100\ PuCl_3 \xrightarrow{(n,f)} 0.008\ Se + 0.003\ Br + 0.942\ Kr + 1.05\ RbCl + 5.49\ SrCl_2 + 3.03\ YCl_3 + 21.5\ ZrCl_3 + 0.29\ NbCl_5(?) + 18.16\ MoCl_2 + 4.01\ Tc + 31.45\ Ru + 1.73\ Rh + 12.66\ Pd + 1.88\ AgCl + 0.66 + 0.66\ CdCl_2 + 0.06\ InCl + 0.325\ SnCl_2 + 0.67\ SbCl_3 + + 7.65\ TeCl_2 + 6.18\ I + 21.23\ Xe + 13.35\ CsCl + 9.50\ BaCl_2 + 5.78\ LaCl_3 + 13.98\ CeCl_3 + 4.28\ PrCl_3 + 11.87\ NdCl_3 + 1.44\ PmCl_3 + 3.74\ SmCl_3 + 0.60\ EvCl_2 + 0.03\ CdCl_3$$

$$100\ PuCl_3 \xrightarrow{(n,f)} 200\ ECl_{1.5}$$

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LITERATURE

For molten salt reactors only, estimated to the recent publication

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