

Nuclear Fuel Cycle

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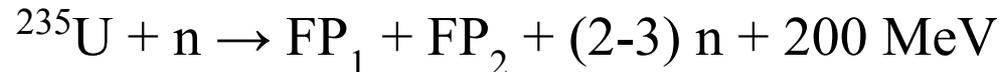


Part 1. Nuclear materials and nuclear fuel

The training course describes **nuclear technologies**,
i.e. the technologies for **handling with nuclear materials (NM)**.

By definition, nuclear materials are those substances
without which it is impossible to initiate
two self-sustainable nuclear reactions
followed by release of huge energy amounts:

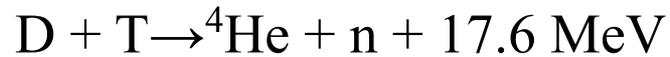
1. Chain fission reaction of heavy nuclei by neutrons



That is why NM include:

1. Natural uranium and natural thorium isotopes.
2. Artificial transuranium isotopes, i.e. isotopes of Pu, Np, Am, Cm,...
3. Artificial uranium isotope ${}^{233}\text{U}$, product of ${}^{232}\text{Th}(\text{n},\gamma){}^{233}\text{U}$ reaction.

2. Thermonuclear fusion reaction of light nuclei



That is why NM include:

1. Hydrogen isotopes: deuterium and tritium.

Natural hydrogen contains 0.015% deuterium but does not contain tritium because of its radioactivity (tritium half-life $T_{1/2} = 12.3$ years).

2. Lithium.

Natural lithium consists of 7.5% ${}^6\text{Li}$ and 92.5% ${}^7\text{Li}$. Lithium isotope ${}^6\text{Li}$ is able to produce tritium intensely in the reaction ${}^6\text{Li}(n,\alpha)\text{T}$. Micro cross-section of ${}^6\text{Li}(n,\alpha)\text{T}$ reaction is 940 barns for thermal neutrons.

Evidently, NM include all chemical compounds of the materials listed above. For example, uranium dioxide UO_2 or heavy water D_2O are nuclear materials too.

Main attention will be given to nuclear materials related with **chain fission reaction** of heavy nuclei induced by neutron irradiation.

Nuclear fuel

is a material that **can be fissioned by neutrons, i.e.**

1. Natural isotopes of **uranium and thorium** (^{235}U , ^{238}U , ^{232}Th).
2. Artificial isotopes of **plutonium and other transuranium elements**.
3. Artificial uranium isotope ^{233}U (product of neutron capture by ^{232}Th).

Primary nuclear fuel contains only **natural fissionable isotopes** (^{235}U , ^{238}U , ^{232}Th).

Secondary nuclear fuel contains **artificial fissile isotopes** (^{233}U , ^{239}Pu , ^{241}Pu).

At present, nuclear power industry is based on the use of natural uranium that consists of the following two isotopes:

1. ^{238}U ; abundance - 99.3%; half-life $T_{1/2} = 4.5$ milliard years.
2. ^{235}U ; abundance - 0.7%; half-life $T_{1/2} = 0.7$ milliard years.

All uranium isotopes are α -emitters and can be fissioned spontaneously.

^{235}U is a sole (!) natural material that can be **fissioned by neutrons of any energy** with generating excessive amount of fast fission neutrons.

Just these excessive neutrons make
the chain fission reaction possible.

Unfortunately, natural uranium contains 0.7% ^{235}U only.
However, nuclear power reactors require the uranium enriched
up to 3-5% ^{235}U .

There are the following uranium types depending on ^{235}U content:

1. **Low-enriched** uranium - $X_{235} < 5\%$.
2. **Medium-enriched** uranium - X_{235} from 5% to 20%.
3. **Highly-enriched** uranium - X_{235} from 20% to 90%.
4. **Weapon-grade** uranium - $X_{235} > 90\%$.

Depleted uranium with ^{235}U content below natural level
(as usual, 0.2-0.3%)
is a by-product of the uranium enriching process.

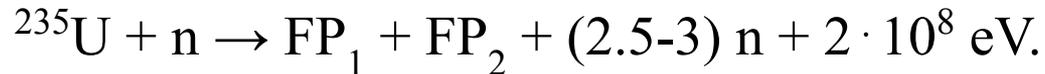
The processes of energy release from nuclear fuel and organic fuels are substantially different.

1. Significantly larger energy content in nuclear fuel.

Incineration of one carbon atom releases thermal energy at the level of **4 eV**:



Fission of one ^{235}U nucleus by neutrons releases thermal energy at the level of **200 MeV**:



Taking difference of atomic weights (235:12) into account,
energy content of ^{235}U fission reaction
exceeds **energy content of ^{12}C oxidation reaction** (per mass unit)
roughly by a factor of **$2.5 \cdot 10^6$** .

The larger energy content of nuclear fuel substantially **decreases fuel mass and volume** needed to produce the same energy amount.
So, nuclear fuel provides **geographical independency** of NPP site placement on site placement of uranium mines and nuclear fuel fabrication plants.

2. It is impossible to burn-up completely full amount of fissile nuclides per one irradiation cycle.

Chain fission reaction can be initiated only if the reactor core contains amount of nuclear fuel **well above its critical mass**.

Per one irradiation cycle it is possible to burn-up **only such a fraction** of nuclear fuel that **exceeds its critical mass** and provides the reactivity margin needed to make up the negative effects from burn-up of fissile nuclides and build-up of fission products (FP).

Fuel burn-up is usually measured as:

1. **FP quantity per total fuel mass.** 10% fuel burn-up means that 10% of fuel mass was burnt-up and converted into 10% of FP mass.
2. **Amount of the released thermal energy per total fuel mass, GWd/t.**

It may be shown that 1% of fuel burn-up equals approximately to thermal energy yield of 10 GWd/t.
Typical fuel burn-up in light-water reactors: 40-50 GWd/t, or 4-5% FP.

3. Possibility for repeat usage (recycle) of fissile and fertile isotopes.

The recycle can reduce significantly the demands for natural uranium mining and its isotope enriching with ^{235}U .

4. Possibility for breeding of fissile isotopes.

Radiative neutron capture by fertile isotope ^{238}U results in build-up of fissile isotope ^{239}Pu .

Radiative neutron capture by fertile isotope ^{232}Th results in build-up of fissile isotope ^{233}U .

The breeding capability is defined by **the breeding ratio (BR)**, i.e. by ratio of the secondary fuel generation rate to the primary fuel incineration rate.

The secondary nuclear fuel can **prolong the reactor lifetime** and produce some **additional amount of thermal energy**.

Depending on the BR value,
the following options of fuel breeding can be marked out:
**partial ($BR < 1$), full ($BR = 1$) and extended ($BR > 1$)
reproduction of nuclear fuel.**

The best conditions for the extended reproduction (breeding) of nuclear fuel
can be formed only **in fast breeder reactors**
fuelled with mixed uranium-plutonium dioxides.

Fast breeder reactors are able to produce so plutonium amount
that is large enough
to meet fuel demands from the reactor-producer (fuel self-sustainability)
and create an initial fuel load for a new reactor-consumer.

If large stockpiles of natural uranium are available,
or if there are no economical incentives for wide NPP deployment,
then fast reactors can operate in **moderate fuel self-sustainability mode**
with the BR value about unity.

5. "Incineration" of nuclear fuel requires no oxidizer.

Incineration of fossil organic fuels in traditional thermal power plant (TPP) requires roughly **three-fold mass of oxygen** taken from the Earth's atmosphere.

Moreover, the incineration is followed by **direct release of toxic wastes** (smoke, ashes, sulphur and nitrogen oxides) into the environment.

"Incineration" of nuclear fuel **does not require an oxidizer at all.** Radioactive fission products and spent fuel can be regarded as **nuclear wastes** but they are **retained within fuel rods for a rather long time.**

Let's compare the daily demands for fuel

from coal-fired TPP and from NPP of the same electrical output (1000 MWe).

The daily energy yield produced by both power plants:

$$1 \text{ GWe} \cdot \text{day} = 4 \text{ GWt} \cdot \text{day} \text{ (at } \eta=25\%) = 2.2 \cdot 10^{33} \text{ eV.}$$

The numbers of carbon atoms and oxygen molecules to be incinerated for production of such an energy yield:

$$2.2 \cdot 10^{33} \text{ eV} / 4 \text{ eV} = 5.5 \cdot 10^{32}.$$

Mass of $5.5 \cdot 10^{32}$ carbon atoms = $(5.5 \cdot 10^{32} / 6 \cdot 10^{23}) \cdot 0.012 \text{ kg} \approx 10^4 \text{ tons}$,
i.e. **about three railway trains a day.**

Mass of oxygen molecules = $(5.5 \cdot 10^{32} / 6 \cdot 10^{23}) \cdot 0.032 \text{ kg} \approx 2.5 \cdot 10^4 \text{ tons}$.

Such oxygen mass can be daily made up
by a **forest with 2000 km² in total area, or with 50 km in diameter.**

The same daily energy yield can be produced by

$$2.2 \cdot 10^{33} \text{ eV} / 200 \text{ MeV} \approx 10^{25} \text{ nuclei of } ^{235}\text{U},$$

or by the following **mass of $^{235}\text{U} = (10^{25} / 6 \cdot 10^{23}) \cdot 0.235 \text{ kg} \approx 4 \text{ kg}$.**

6. Accumulation of radioactive FP. Residual heat generation.

Induced radioactivity of structural materials.

FP half-lives cover a broad time range – from milliseconds to millions of years.

Depending on half-lives $T_{1/2}$, the following FP categories can be formed: short-lived (SLFP), middle-lived (MLFP) and long-lived (LLFP) isotopes.

By the end of the cooling time (up to 10 years) in the NPP water pool, isotopic and elemental composition of fission products change remarkably.

Isotopic FP composition can be characterized as follows.

Isotopes with half-lives $T_{1/2}$ longer than 10^{10} years,
may be considered as stable FP.

Isotopes with half-lives shorter than one year may be considered as SLFP.

Isotopes with half-lives within the range $1 \text{ year} < T_{1/2} < 87 \text{ years}$ (^{151}Sm)
may be considered as MLFP.

Isotopes with half-lives longer than 65000 years (^{79}Se)
may be considered as LLFP.

Then, weight percentage of various FP categories is as follows:

Stable FP - 85 %; SLFP – 1 %; MLFP – 6 %, LLFP – 8 %.

Elemental FP composition can be obtained for the following three categories:

1. Elements containing stable isotopes only.
2. Elements containing stable, short-lived and middle-lived isotopes.
3. Elements containing long-lived isotopes.

Then, weight percentage of these FP categories is as follows:

Category 1 (stable isotopes) - 51 %.

Category 2 (stable, short-lived and middle-lived isotopes) - 24 %.

Category 3 (long-lived isotopes) - 25 %.

Main challengers are seven long-lived FP, namely:

^{79}Se , ^{93}Zr , ^{99}Tc , ^{107}Pd , ^{126}Sn , ^{129}I and ^{135}Cs .

Besides fission products,
spent nuclear fuel (SNF) contains **transuranium isotopes**.

Particular attention should be given to the following **Minor Actinides (MA)**:
 ^{237}Np , ^{241}Am , ^{243}Am , ^{244}Cm and ^{245}Cm .

A special category of radioactive wastes (RAW) is produced
at the stage of SNF reprocessing, namely MA-containing RAW.

Minor Actinides are intense heat sources, and so it is very difficult
to handle with MA-containing wastes.

Main channels for MA generation in nuclear reactors:

1. $^{235}\text{U}(\text{n},\gamma)^{236}\text{U}(\text{n},\gamma)^{237}\text{Np}$.
2. $^{241}\text{Pu}(\beta, 14 \text{ years})^{241}\text{Am}(\text{n},\gamma)^{242\text{m}}\text{Am}(\text{n},\gamma)^{243}\text{Am}(\text{n},\gamma)^{244}\text{Cm}(\text{n},\gamma)^{245}\text{Cm}$.
3. $^{242}\text{Pu}(\text{n},\gamma)^{243}\text{Am}(\text{n},\gamma)^{244}\text{Cm}(\text{n},\gamma)^{245}\text{Cm}$.

Residual heat generation by SNF is caused

by natural radioactive decays of fission products and minor actinides.

Time dependency of residual heat generation may be characterized as a rapid exponential slump followed by a gradual approach to a plateau level.

Induced radioactivity of steel in-vessel structures

is mainly caused by the following radioisotopes:

^{55}Fe ($T_{1/2} = 2,7$ years), ^{63}Ni ($T_{1/2} = 100$ years) and ^{60}Co ($T_{1/2} = 5,3$ years).

After the reactor shut-down, the total **induced radioactivity** rapidly decreases and then gradually approaches a plateau level.

Induced radioactivity of metal NPP structures will become

more and more urgent problem

as far as lifetime of NPP currently in operation expires.

Part 2. Nuclear fuel cycle

The technological stages used for fabrication, application and reprocessing of nuclear fuel can be united into a common concept of **nuclear fuel cycle (NFC)**.

Main NFC stages

- 1. Mining of uranium ore** and uranium extraction.
- 2. Fabrication of nuclear fuel** (production of uranium concentrate U_3O_8 , conversion of U_3O_8 into uranium hexafluoride UF_6 , uranium enrichment with ^{235}U , manufacturing of fuel rods and fuel assemblies).
- 3. Use of nuclear fuel** in nuclear reactors.
- 4. Interim storage** of spent fuel assemblies (SFA) in the water storage pools.

The following **two options** can be chosen for the next NFC stages:
open and closed NFC.

In the case of open NFC:

5a. Ultimate disposal of SFA in deep underground geological formations.

In the case of closed NFC:

5b. Radiochemical reprocessing of SFA.

5c. Extraction of radioactive wastes for ultimate disposal in deep underground geological formations.

5d. Extraction of fertile and fissile materials (U and Pu) for multiple repeat use (recycle) in re-fabricated fuel rods and fuel assemblies.

Currently, there are two controversial viewpoints in the world on reasonability of NFC closure:

- 1. The NFC closure is an unreasonable action**, because it assumes SNF reprocessing that includes extraction, transportation and application of regenerated uranium and plutonium for re-fabrication of fresh fuel assemblies. Thus, the NFC closure creates a series of the following technological and political problems:
 - a. Possibility for terrorist groups to steal fissile NM** for manufacturing of nuclear explosive devices.
 - b. Complicacy and jeopardy of SNF reprocessing technologies.**
 - c. Complicacy and jeopardy of RAW treatment for ultimate disposal in geological repositories.**

2. **The opposite viewpoint** does not regard SNF as the wastes suitable only for ultimate disposal. The viewpoint regards **SNF as a valuable NM** containing the primary and secondary nuclear fuel. The primary and secondary fuel can be extracted and multiply recycled at NPP.

The NFC closure is considered as a **main strategic pathway** towards achieving a national energy independence.

Technological difficulties of SNF reprocessing, RAW treatment and ultimate disposal are estimated as complicated and radiation-dangerous problems but all the difficulties **can be successfully overcome** by the methods and tools currently available.

Potential jeopardy of **NM theft and illegal use** is recognized too but the problems of nuclear non-proliferation are resolvable by **domestic and international safeguard systems**.

Part 3. Mining and primary processing of uranium ore

For the beginning, some historical data about uranium discovery

1789 – German chemist M.-F. Klaproth has precipitated a yellow compound from the ores mined in Jachymov (Czech Republic now).

Klaproth erroneously assumed the yellow substance was a new, yet undiscovered chemical element. He named the new element after the planet Uranus.

1841 – French chemist E.-M. Peligot had isolated the first sample of metal uranium. Peligot has evaluated the atomic weight of uranium as 120 a.m.u.

1869 – Russian chemist Mendeleev D.I. has defined more exactly the atomic weight of uranium (240 a.m.u.) and placed uranium in the end of the Mendeleev periodic table.

Because of **strong chemical activity**, uranium is found in the nature in the form of its **complex chemical compounds only**.

In total, nearly **200 uranium-containing minerals** are known today.

Total amount of natural uranium in the Earth's crust is evaluated as 10^{14} tons (about 3 ppm in average).

Total amount of natural uranium in sea and ocean water is evaluated as $4 \cdot 10^9$ tons (~ 3 mg/m³, or about 0.003 ppm in average).

Uranium ores are categorized depending on uranium content:

1. **Very rich ores** – above 1% U.
2. **Rich ores** - from 0.5% to 1% U.
3. **Medium ores** - from 0.25% to 0.5% U.
4. **Ordinary ores** - from 0.09% to 0.25% U.
5. **Poor ores** - below 0.09% U.

In average, the mined ores contain about **0.1% U**, i.e. poor and ordinary ores.

Natural uranium resources are evaluated
on the following two cost categories:

1. **Cheap** uranium costs below 80 US dollars per 1 kg U_3O_8 .
2. **Expensive** uranium costs above 80 US dollars per 1 kg U_3O_8 .

The threshold cost (**80 US dollars per 1 kg U_3O_8**)
differentiates the competitiveness areas of NPP and coal-fired TPP.

If natural uranium costs below 80 US dollars/kg U_3O_8 , then NPP is able to
produce the cheaper electrical energy than TPP does, and vice versa.

The following four categories
of natural uranium resources can be defined
depending on **the completeness of geological information:**

- 1. Reasonably assured resources (RAR).**
- 2. Inferred resources (IR),** i.e. peripheral wings of RAR.
- 3. Prognosticated resources,** the resources expected to exist in well-known uranium provinces.
- 4. Speculative resources,** i.e. the resources expected to exist in geological provinces that may host uranium deposits.

The first and second categories are the most trustworthy ones.

As of January 1, 2017

The reasonably assured uranium resources - $3,87 \cdot 10^6$ tons.

The inferred uranium resources - $2,27 \cdot 10^6$ tons.

Total - $6,14 \cdot 10^6$ tons

that includes $2,28 \cdot 10^6$ tons of **cheap uranium**
and $3,86 \cdot 10^6$ tons of **expensive uranium**.

The world nuclear power in 2016 (391 GWe)
has consumed about 62,3 thousand tons of natural uranium.

Under such a consumption rate,
the cheap uranium resources are sufficient for 37 years,
the expensive uranium resources can prolong this time period on 62 years.

Thus, **total cheap and expensive uranium resources** are able to meet demands
of the global nuclear power for natural uranium during about **100 years**.

Global distribution of main uranium resources (2017)

	Country	Uranium resources, thousand tons
1	Australia	1818
2	Kazakhstan	842
3	Canada	514
4	Russia	486
5	South Africa	322
6	Brasilia	277

Total – $4.26 \cdot 10^6$ tons of $6.14 \cdot 10^6$ tons, i.e. 70%

Uranium production rate (2016)

	Country	Production rate, thousand tons
1	Kazakhstan	24,7
2	Canada	14,0
3	Australia	6,3
4	Namibia	3,6
5	Niger	3,5
6	Russia	3,0

Total – $55.1 \cdot 10^3$ tons of $62.1 \cdot 10^3$ tons, i.e. 89%

The world nuclear power (2016)

	Country	Total nuclear power, GWe	NPP share, %
1	USA	99,8	20
2	France	63,0	72
3	Japan	39,8	30
4	China	31,4	3,5
5	Russia	26,9	18
6	South Korea	23,1	30

Total – 284 GWe of 391 GWe, i.e. 73%

**The following four methods
are mainly used for recovery of natural uranium**

- 1. Underground recovery of uranium ore from mines.**
- 2. Recovery of uranium ore from open-cast mines.**
- 3. Underground leaching, or in-situ leaching.**
- 4. Recovery of uranium from seawater.**

When U-containing minerals are recovered from the Earth's crust with application of the first two methods, solid uranium ore undergoes **the hydro-metallurgical treatment.**

Main stages of hydro-metallurgical treatment of uranium ore

- 1. Crashing and physical concentration** of uranium ore by removal of barren (dead) rocks.
- 2. Leaching (dissolution)** of uranium ore in acidic or carbonate solutions.
- 3. Selective recovery of uranium** from the solutions with application of the following methods: **sorption-desorption, extraction - re-extraction, chemical precipitation.**
- 4. Production of dry uranium concentrate.**
- 5. Production of pure (refined) uranium compounds** with application of **the affinage technologies.**

Methods for separation of U-bearing minerals from the barren rocks

1. Radiometrical separation

The ore pieces are monitored by radiometers to detect natural gamma-radioactivity.

Non-radioactive pieces of the barren rocks are removed (about 50%).

2. Gravitational separation

The gravitational method is based on **different densities** of U-bearing minerals ($6.5-10.5 \text{ g/cm}^3$) and the barren rocks ($2.5-2.7 \text{ g/cm}^3$)

If pieces of uranium ore are put into a **water-filled vessel**, then **the heavier U-bearing pieces sink onto bottom**.

3. Floatation separation

The floatation method is based on **different densities and different abilities to be moistened by water** of the U-bearing minerals and the barren rocks.

The pieces of uranium ore are put into a **water-filled vessel**, and the **air flow is pumped** through the vessel from its bottom (the air barbotage process).

The **lighter pieces of the barren rocks** are sticking to the air bubbles and going up to the **water surface**.

The **heavier pieces of the U-bearing minerals** are gradually sinking **onto the vessel bottom**.

**The next stage of hydrometallurgical treatment:
leaching of uranium compounds from uranium ore**

Depending on **chemical composition of uranium ore**, the following **two types of the leaching reagents** can be used, namely **acidic or carbonate solutions**.

The **acidic leaching** is a widely used technology. Sulphuric acid (H_2SO_4), nitric acid (HNO_3) or hydrochloric acid (HCl) can be used as a leaching reagent.

The carbonate leaching is applied only if uranium ore contains **large amount of impurities** which can **interact actively with acidic solutions**.

Soda NaHCO_3 , sodium bi-carbonate Na_2CO_3 or ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$ can be used as a leaching reagent.

**The next stage of hydrometallurgical treatment:
the increase of concentration and
the recovery of uranium compounds from solutions**

The following three technologies are used to increase concentration and derive uranium compounds from solutions:

- 1. Sorption – desorption** with application of organic ion-exchange resins.
- 2. Extraction – re-extraction** with application liquid organic extractants.
- 3. Chemical precipitation** of uranium compounds from solutions.

The first and second methods are able to increase uranium concentration in solutions while the third method is able to derive solid uranium from solutions.

The sorption – desorption process

The sorption process

is based on the ability of some organic ion-exchange resins to sorb selectively uranium compounds on their surface.

Small granules of the ion-exchange resin

are mixed with U-bearing solution, and the granules sorb uranium compounds primarily.

The **uranium washing off** the granules is named as a **desorption, or elution process**.

Neutral or alkaline soda solutions are used as eluents.

Multiple application of the sorption – desorption process can increase uranium concentration in solution.

The extraction – re-extraction process

The extraction process

is based on the property of some liquid organic substances (extractants) **to form stable chemical compounds with uranium salts.**

When U-bearing solution contacts with organic extractant, **the most uranium quantity goes into organic fraction.**

The light organic fraction and heavy aqueous fraction are separated, and **the process of uranium re - extraction** from organic fraction is carried out.

Light water or low-concentrated nitric acid HNO_3 can be used as **re – extractants.**

Multiple application of the extraction – re-extraction process can increase uranium concentration in solution.

Chemical precipitation of uranium compounds

Uranium compounds can be precipitated from solutions by admixing some **suitable reagents (precipitants)** into the U-bearing solutions.

The following substances can be used as **precipitants**: hydrogen peroxide H_2O_2 , ammonium hydrate NH_4OH , caustic soda NaOH , etc.

The chemical precipitation process produces **insoluble hydrates of uranium oxides $(\text{UO}_x) \cdot n\text{H}_2\text{O}$** , which fall as a sediment onto the vessel bottom.

Thermal treatment converts the sediment to the **dry uranium concentrate** consisting mainly of U_3O_8 .

The **uranium concentrate is a final product** of the hydrometallurgical technology.

The in-situ leaching process

consists of the following steps:

1. **Drilling** of the injection and output wells (boreholes) into the uranium ore.
2. **Injection** of liquid dissolvents into the uranium ore body for leaching (dissolution) of uranium compounds.
3. **Pumping out** of the produced solutions through the output wells.

Then, the U-bearing solutions undergo the procedures of the hydrometallurgical treatment:

sorption – desorption, extraction – re-extraction, chemical precipitation.

Seawater can be also regarded as a very low-concentrated (~ 0.003 mg/l) U-bearing solution suitable for the hydrometallurgical treatment.

The affintage process

Final product of the hydrometallurgical treatment of natural uranium ore is a dry uranium concentrate consisting of 95-96% U_3O_8 and **4-5% impurities**.

Unfortunately, there are **strong neutron absorbers (B, Cd, Hf)** in the impurities. They **must be removed** from the uranium concentrate.

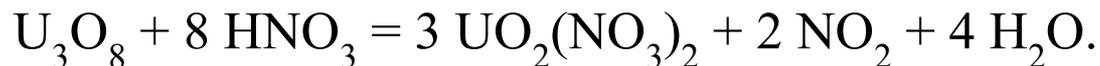
The most developed **purification (affintage) technology** is based on the aqueous extraction process with application of **tri-butyl-phosphate (TBP)** as a top-quality extractant.

The most important property of TBP consists in its excellent ability to **extract selectively uranium compounds** from U-bearing solutions.

TBP can extract uranyl-nitrate $UO_2(NO_3)_2$ from its aqueous solution by **four orders of magnitude more effectively** than impurities.

Main stages of the extraction affinage process

1. Dissolution of uranium concentrate in nitric acid:



2. Mixing of uranyl-nitrate solution with TBP:



3. Separation of organic and aqueous phases.

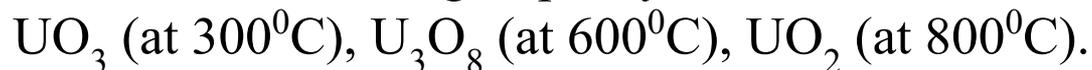
4. Derivation of pure uranyl-nitrate from organic phase

by the chemical precipitation process. Two precipitants can be used:

- Precipitation by **hydrogen peroxide** H_2O_2 produces hydrate of uranium peroxide $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ as a solid deposit.
- Precipitation by **ammonium bicarbonate** NH_4HCO_3 produces ammonium-uranyl-carbonate (AUC) - $(\text{NH}_4)_4\text{UO}_2(\text{CO}_3)_3$ - as a solid deposit.

Calcination of these deposits

produces the following impurity-free uranium oxides:



Part 4. Isotope uranium enrichment

The world nuclear power is based on the use of **enriched uranium**.

Thermal light-water reactors

(the major type of nuclear power reactors in the world)
are fuelled with **low-enriched uranium (2-5% ^{235}U)**.

All the uranium enrichment technologies are based on the mass difference of main uranium isotopes ^{235}U and ^{238}U .

The mass difference ($\Delta m = 3 \text{ a.m.u.}$) defines
different behavior of uranium isotopes in a **magnetic field**,
in a **centrifugal field**,
different probabilities to penetrate through a porous wall, etc.

Quality of isotope separation (enriching) technologies can be characterized by two main parameters, namely:
efficiency and energy consumption.

Efficiency of an enriching technology is defined by its ability to increase abundance of necessary isotope after one step of the enriching process.

Energy consumption of an enriching technology is defined in the terms of energy expenses per a separative work unit (SWU).

General layout of the uranium enrichment process can be shown in the following way.

Initial uranium mass F and ^{235}U content X_F are main input parameters.

Main output parameters of the process:

1. **Mass of enriched uranium P and ^{235}U content X_P .**
2. **Mass of depleted uranium W and ^{235}U content X_W .**

Equations of NM mass balance in the process of uranium enriching

1. **Balance of uranium mass:** $F = P + W$;
2. **Balance of ^{235}U mass:** $X_F \cdot F = X_P \cdot P + X_W \cdot W$.

This is a system of **two equations with three unknown values** (F, P, W).

Having divided both equations by P,
the system can be transformed into the resolvable system
of **two equations with two unknown values** (F/P and W/P):

$$F/P = 1 + W/P;$$

$$X_F \cdot F/P = X_P + X_W \cdot W/P.$$

Having resolved the system, one can find:

- a. Factor of natural uranium consumption** per a product mass unit:

$$F/P = (X_P - X_W)/(X_F - X_W);$$

- b. Factor of waste production** per a product mass unit:

$$W/P = (X_P - X_F)/(X_F - X_W);$$

- c. Division factor** of uranium feed flow θ :

$$F = P + W = \theta \cdot F + (1 - \theta) \cdot F; \text{ where } \theta = P/F = (X_F - X_W)/(X_P - X_W).$$

Examples:

a. Production of weapon-grade uranium from natural uranium:

$$X_F = 0.7\%; X_P = 90\%; X_W = 0.25\%.$$

$$\text{Then, } F/P = (X_P - X_W)/(X_F - X_W) = 89.75 / 0.46 \approx 195.$$

This means that production of 25 kg
(mass of weapon-grade uranium for one nuclear explosive device)
requires nearly 5 tons of natural uranium, or 5000 tons of natural uranium ore.

b. Production of reactor-grade uranium from natural uranium:

$$X_F = 0.7\%; X_P = 4\%; X_W = 0.25\%.$$

$$\text{Then, } \theta = (X_F - X_W)/(X_P - X_W) \approx 0.12;$$

This means that 120 kg of low-enriched uranium (4% ^{235}U)
and 880 kg of depleted uranium (0.25% ^{235}U)
can be obtained from 1000 kg of natural uranium.

The following parameters may be helpful to characterize the uranium enrichment process:

1. Relative concentrations of ^{235}U
in the feed (natural uranium), product (enriched uranium)
and waste (depleted uranium):

$$R = X_F/(1 - X_F); R' = X_P/(1 - X_P); R'' = X_W/(1 - X_W).$$

2. The single-stage separation factor: $\alpha = R'/R = [X_P/(1-X_P)]/[X_F/(1-X_F)]$.

3. The single-stage depletion factor: $\beta = R/R'' = [X_F/(1-X_F)]/[X_W/(1-X_W)]$.

4. The single-stage enrichment gain: $\varepsilon' = \alpha - 1$.

5. The single stage depletion gain: $\varepsilon'' = \beta - 1$.

The separative works

English physicists R. Peierls and P. Dirac have developed **the methodology for quantitative evaluation** of the works needed to enrich uranium with ^{235}U .

They have introduced **a function** that could characterize **the “value” of an isotope composition.**

For example, **the “value” function of the feed uranium U_F** is defined as a product of the feed mass F and a dimensionless function $V(X_F)$, **where $V(X)$ – the separation potential function, i.e. $U_F = F \cdot V(X_F)$.**

Before the enrichment process

the “value” of the feed uranium $U_F = F \cdot V(X_F)$.

After the enrichment process

the “value” of enriched uranium $U_P = P \cdot V(X_P)$,

the “value” of depleted uranium $U_W = W \cdot V(X_W)$,

i.e. the total “value” of materials increased on:

$$\Delta U = U_P + U_W - U_F = P \cdot V(X_P) + W \cdot V(X_W) - F \cdot V(X_F).$$

The “value” gain ΔU defines a scope of the separative works needed to divide the initial binary isotope mixture into two new materials: **enriched uranium and depleted uranium.**

The exact formula for the potential separation function $V(X)$ can be obtained after the following mathematical operations with equation for the “value” gain ΔU :

1. The equation must be re-written into the form containing the feed mass only:
$$\Delta U = \theta \cdot F \cdot V(X_p) + (1 - \theta) \cdot F \cdot V(X_w) - F \cdot V(X_f);$$
2. The separation potentials $V(X_p)$ and $V(X_w)$ must be expanded in the Taylor series in the vicinity of X_f point including the first three terms only.
3. It is assumed that the single-stage separative work is independent on the feed concentration X_f .

Then, the following **second-order differential equation** is obtained:

$$d^2V/dX^2 = 1/[X^2 \cdot (1 - X)^2];$$

with the solution: $V(X) = (2X - 1) \cdot \ln[X/(1 - X)]$.

So:

$$\Delta U = P \cdot V(X_P) + W \cdot V(X_W) - F \cdot V(X_F).$$

If the material masses are measured in kilograms,
then the separative works scope can be also measured in the SW-kilograms,
or, by definition, **1 SW-kilogram = 1 SWU (Separative Work Unit).**

Specific scope of the separative works η_{SWU}
can be defined as the work scope
needed to produce one kilogram of enriched uranium:

$$\eta_{\text{SWU}} = \Delta U / P.$$

As is shown above:

$$F = P \cdot [(X_P - X_W) / (X_F - X_W)]; \quad W = P \cdot [(X_P - X_F) / (X_F - X_W)].$$

Therefore:

$$\eta_{\text{SWU}} = V(X_P) + V(X_W) \cdot (X_P - X_F) / (X_F - X_W) - V(X_F) \cdot (X_P - X_W) / (X_F - X_W).$$

**Gaseous uranium hexafluoride UF₆
as an initial material for uranium enriching**

Some **attractive properties** of uranium hexafluoride:

1. Natural fluorine consists of **only one stable isotope** ¹⁹F.
That is why uranium hexafluoride can be considered as a **binary mixture** of only two gases, namely **heavy gas** ²³⁸UF₆ and **light gas** ²³⁵UF₆.
2. Uranium hexafluoride can exist in the **solid, liquid and gaseous states** under **moderate temperature and pressure** conditions.
3. Uranium hexafluoride **can be sublimated** from the solid state into the gaseous state, omitting the liquid state, **by a slight warming-up**.

Strong chemical activity is a main disadvantage of uranium hexafluoride.

Conversion of uranium concentrate into uranium hexafluoride

Uranium concentrate U_3O_8 is usually fluorinated by means of the following two-step technology:

1. Reaction of U_3O_8 with gaseous fluorine to produce uranyl-fluoride UO_2F_2 :



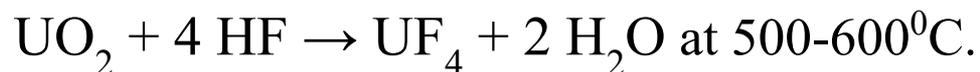
2. Reaction of uranyl-fluoride with gaseous fluorine to produce uranium hexafluoride UF_6 :



In the closed option of nuclear fuel cycle
uranium dioxide UO_2
extracted from spent nuclear fuel
can be used as an initial material for conversion into uranium hexafluoride.

Uranium dioxide UO_2 is usually fluorinated
by means of the following **two-step technology**:

- 1. Reaction of uranium dioxide with hydrofluoric acid** to produce uranium tetra-fluoride UF_4 :



- 2. Reaction of uranium tetra-fluoride with gaseous fluorine** to produce uranium hexafluoride UF_6 :



Gas diffusion (GD) technology of uranium enrichment

**The GD-technology is based
on different thermal velocities**

of light molecules $^{235}\text{UF}_6$ and heavy molecules $^{238}\text{UF}_6$

As light and heavy molecules have the same kinetic energy:

$$m_{\text{LM}} \cdot V_{\text{LM}}^2 = m_{\text{HM}} \cdot V_{\text{HM}}^2,$$

velocity of light molecules is higher than that of heavy molecules:

$$V_{\text{LM}} = V_{\text{HM}} \cdot (m_{\text{HM}}/m_{\text{LM}})^{1/2}.$$

The higher velocity of light molecules allows them to penetrate through a porous wall with the larger probability.

It was **theoretically shown** the **maximal single-stage separation factor** α_{max} for two gases diffusing through a porous wall is equal to:

$$\alpha_{\text{max}} = V_{\text{LM}}/V_{\text{HM}} \approx 1 + 0.5 \cdot \Delta m / m_{\text{LM}} = 1.0043.$$

So small value of the single-stage separation factor requires to pass the gas flow through **many successive GD-stages (GD-cascade)**.

The **energy consumption rate** of the GD-technology: **~ 2500 kWh/SWU**.

Cascading of the GD-process

System of the successively linked GD-stages constitutes the GD-cascade.

The GD-cascade consists of the following two branches:

- a. **The enriching branch** where relative ^{235}U content can be increased from 0.71% in natural uranium to 5-90% in enriched uranium.
- b. **The depleting branch** where relative ^{235}U content can be reduced from 0.71% in natural uranium down to 0.2-0.3% in depleted uranium.

Each GD-stage has two outputs for the gas flow:

1. The gas flow with increased content of ^{235}U enters the next stage of the enriching branch.
2. The gas flow with reduced content of ^{235}U enters the next stage of the depleting branch.

Cascading of the GD-process

The numbers of the GD-stages
are quite different in the **enriching and depleting** branches.

Evidently, reduction of ^{235}U content **from 0.71% in natural uranium**
down to 0.2-0.3% in depleted uranium
will require the smaller number of the depleting stages

while elevation of ^{235}U content **from 0.71% in natural uranium**
up to 5% (reactor-grade uranium)
or up to 90% (weapon-grade uranium)
will require the larger number of the enriching stages.

Cascading of the GD-process

The number of the GD-stages in the enriching branch N_p
can be evaluated by such a way:

It follows **from the definition of the single-stage enrichment gain**
that **after the first stage** of the enriching branch:

$$X_p/(1 - X_p) = (1 + \varepsilon') \cdot X_F/(1 - X_F).$$

After N_p stages of the enriching branch:

$$X_p/(1 - X_p) = (1 + \varepsilon')^{N_p} \cdot X_F/(1 - X_F).$$

Then:

$$N_p \approx (1/\varepsilon') \cdot \ln \{ [(X_p/(1-X_p))] / [X_F/(1-X_F)] \}.$$

Cascading of the GD-process

The number of the GD-stages in the depleting branch N_w
can be evaluated in a similar manner:

It follows **from the definition of the single-stage depletion gain**
that **after the first stage** of the depleting branch:

$$X_w/(1 - X_w) = (1 + \varepsilon'')^{-1} \cdot X_F/(1 - X_F).$$

After N_w stages of the depleting branch:

$$X_w/(1 - X_w) = (1 + \varepsilon'')^{-N_w} \cdot X_F/(1 - X_F).$$

Then:

$$N_w \approx (1/\varepsilon'') \cdot \ln \{ [(X_F/(1-X_F))] / [X_w/(1-X_w)] \}.$$

Evaluation of the numbers of the GD-stages

in the enriching and depleting branches of the GD-cascade

Let assume that **weapon-grade uranium** ($X_p = 90\%$)
must be produced **from natural uranium** ($X_F = 0.71\%$)
at ^{235}U content in depleted uranium $X_w = 0.2\%$.

Then, **the numbers of the enriching and the depleting GD-stages**
are equal to $N_p \approx 1660$, $N_w \approx 290$, respectively.

Let assume that **reactor-grade uranium** ($X_p = 4\%$)
must be produced **from natural uranium** ($X_F = 0.71\%$)
at the same ^{235}U content in depleted uranium ($X_w = 0.2\%$).

Then , **the number of the enriching stages drops down to $N_p \approx 410$**
at the same number of the depleting stages ($N_w \approx 290$).

Uranium enriching in gas centrifuges (GC)

If a cylindrical vessel (**centrifuge**) containing a binary mixture of light and heavy gases ($^{235}\text{UF}_6$ and $^{238}\text{UF}_6$) rotates with a large angular velocity ω , then heavy molecules are driven back to the vessel wall while light molecules remain in the central zone.

The **centrifugal force** F acts on elementary volume of the gas mixture:

$$F(r) = \gamma(r) \cdot \omega^2 \cdot r.$$

The **pressure** on the gas components:

$$dP(r)/dr = F(r) = \gamma(r) \cdot \omega^2 \cdot r.$$

Densities of the gas components can be derived from the **Mendeleyev-Clapeyron equation**:

$$\gamma(r) = m/V = P(r) \cdot M/RT$$

Then, differential equation for the gas pressure can be re-written:

$$dP(r)/dr = P(r) \cdot M \cdot \omega^2 \cdot r / 2RT,$$

and solved:

$$P(r) = P(0) \cdot \exp(M \cdot \omega^2 \cdot r^2 / 2RT) = P(0) \cdot \exp(M \cdot V^2(r) / 2RT).$$

Contents of light and heavy gas components are proportional to the radial pressure distribution:

$$\begin{aligned} X_{235}(r) &= X_{235}(0) \cdot \exp(M_{LM} \cdot V^2(r)/2RT); \\ X_{238}(r) &= X_{238}(0) \cdot \exp(M_{HM} \cdot V^2(r)/2RT). \end{aligned}$$

As it follows from these formulas,
content of the heavy gas component (depleted uranium)
is larger on the centrifuge periphery
while **content of the light gas component (enriched uranium)**
is larger in a central zone.

So, **the single-stage enrichment factor and the single stage enrichment gain**
can be determined by such a way:

$$\begin{aligned} \alpha(r) &= [X_{235}(0)/X_{238}(0)] / [X_{235}(r)/X_{238}(r)] = \\ &= \exp(\Delta m \cdot V^2(r)/2RT) \approx 1 + \Delta m \cdot V^2(r)/2RT. \\ \varepsilon' &= \alpha - 1 \approx \Delta m \cdot V^2/2RT. \end{aligned}$$

As is seen, **the single-stage enrichment gain**

$$\varepsilon' = \alpha - 1 \approx \Delta m \cdot V^2/2RT.$$

is proportional to the squared linear velocity of the centrifuge rotation.

The **rotation velocity** of the contemporary centrifuges reaches the values of 500-700 m/s.

The **GC-technology** can provide the following velocity-dependent values of **the single-stage enrichment gain**:

$$\varepsilon' = 0.098 \text{ at } V = 400 \text{ m/s};$$

$$\varepsilon' = 0.152 \text{ at } V = 500 \text{ m/s};$$

$$\varepsilon' = 0.300 \text{ at } V = 700 \text{ m/s}.$$

The following **materials** are currently used to make the gas centrifuges:

1. Aluminum-based alloys at $V \leq 350$ m/s.
2. Titanium-based alloys at $V \leq 450$ m/s.
3. Alloyed steels at $V \leq 500$ m/s.
4. Glass-fiber plastics reinforced by graphite at $V = 500-700$ m/s.

The **energy consumption rate** of the GC-technology: **~ 200 kWh/SWU.**

Laser technologies of uranium enriching

The laser technologies rely on the slightly **different excitation energies of electronic shells** around of ^{238}U and ^{235}U nuclei.

The energy difference may be used **to excite selectively uranium atoms or U-containing molecules** by the laser light tuned properly to a necessary wavelength.

The excited state of electronic shell **can selectively enhance** some **physical or chemical reactions** of U-containing materials.

This **enhancement can promote separating** the excited ^{235}U atoms and the non-excited ^{238}U atoms.

Conditions for the laser-induced isotope separation

1. The electronic excitation scheme must contain **a line belonging to one isotope only.**
2. **The line must be far enough from other lines** of the desirable isotope and from all the lines of other isotopes.
3. **High-quality laser must be developed** and finely tuned to a necessary wavelength.
4. **Physical or chemical processes must be found** to separate the excited and non-excited U-containing materials.
5. **Laser-induced impact** on the isotope mixture must be a **main excitation mechanism.**

Atomic Vapor Laser Isotope Separation (AVLIS) technology

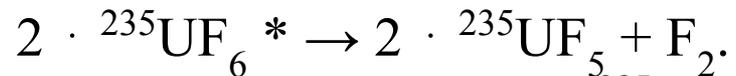
The AVLIS technology includes the following stages:

- 1. High-temperature vacuum evaporation of uranium atoms:**
Accelerated electron beam knocks uranium atoms out of U-Re alloy.
- 2. Irradiation by xenon laser ($\lambda \sim 3780 \text{ \AA}$, ultraviolet range).**
 ^{235}U atoms are selectively excited./
- 3. Irradiation by krypton laser ($\lambda \sim 3500 \text{ \AA}$, ultraviolet range). The excited**
 ^{235}U atoms are selectively ionized.
- 4. Collection of ^{235}U ions on an electrically charged plate.**

Molecular Laser Isotope Separation (MLIS) technology

The MLIS technology includes the following stages:

1. **Uranium hexafluoride UF_6 is cooled down to 30 K without condensation.**
2. **Irradiation by infrared laser ($\lambda \sim 16\,000\ \text{\AA}$). Molecules of $^{235}UF_6$ are selectively excited.**
3. **Irradiation by ultraviolet laser ($\lambda \sim 308\ \text{\AA}$). The excited $^{235}UF_6$ molecules are selectively dissociated:**



White powder of uranium pentafluoride $^{235}UF_5$ (“laser snow”) precipitates from the gas flow.

The single-stage enrichment gains are very large for both laser technologies (from 3 to 15).

The energy consumption rate of the laser technologies $\sim 20\ \text{kWh/SWU}$.

Part 5. Technologies for fabrication of fuel rods and fuel assemblies

Uranium dioxide UO_2 is the most widely used type of nuclear fuel.

Main advantages of uranium dioxide

1. **High melting temperature** (2780°C).
2. **High chemical stability** in contacts with main coolants.
3. **Satisfactory compatibility** with main cladding materials.
4. Feasibility for manufacturing of **high-density fuel pellets**.
5. Acceptable **radiation resistance** under high neutron fluxes and fluences.
6. **Isotropy** of crystalline lattice.

Main shortcomings of uranium dioxide

1. **Low heat conductivity**, especially at the elevated temperatures.
As a result, large temperature jumps (up to $\sim 1500^\circ\text{C}$) take place in very thin ($R \sim 3 \text{ mm}$) fuel pellets.
2. **High hygroscopicity** by wet air.

Pelletization of uranium dioxide UO_2

1. Conversion of uranium hexafluoride into uranium dioxide:

a. Barbotage of uranium hexafluoride UF_6 through aqueous solution of ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$.

Solid deposit of ammonium-uranyl-carbonate (AUC) - $(\text{NH}_4)_4\text{UO}_2(\text{CO}_3)_3$ - precipitates from the solution.

b. Heat treatment of AUC at 600°C .

Thermal AUC dissociation produces finely dispersed UO_2 powder.

The powder is unsuitable for pressing because of too small dimensions (~ 0.5 micron) of the powder particles.

2. Mixing of UO_2 powder with organic plasticizers.

3. Hydro-compaction for production of the powder-plasticizer briquettes.

4. Granulation of the briquettes by milling.

5. Annealing at 700°C for removal of the organic plasticizers.

6. Cold pressing and sintering of UO_2 pellets.

Manufacturing of fuel rods and fuel assemblies: technological stages

1. Preparation of nuclear fuel:

- a. Conversion of uranium hexafluoride into uranium dioxide powder.
- b. Granulation, annealing and sintering of fuel pellets.

2. Preparation of tubular cladding and end caps.

3. Manufacturing of fuel rods:

- a. Insertion of fuel pellets into tubular cladding.
- b. Installation of end caps, filling up with helium.
- c. Sealing of fuel rods by welding.

4. Preparation of the completing details for mounting of fuel assemblies.

5. Assemblage of fuel rods into a single fuel assembly.

6. Quality control and testing.

Part 6. Technologies for the use of nuclear fuel in nuclear reactors

Before the reactor operation starts up, the reactor is a super-critical facility.

The reactivity margin ($K_{\text{EFF}} - 1$) is suppressed by the control rods.

Fuel burn-up and build-up of fission products, early or late, will convert the reactor into the sub-critical state ($K_{\text{EFF}} < 1$).

To continue the reactor operation, a certain **corrective action (refueling)** must return the reactor to **the super-critical state ($K_{\text{EFF}} > 1$).**

The major refueling mission is to replenish the reactivity margin.

The supplementary refueling mission is to flatten spatial shape of heat generation rate.

The following measures can perform the refueling missions:

- 1. Full or partial substitution** of fresh fuel assemblies for spent ones.
- 2. Transpositions (shuffling) of irradiated fuel assemblies** with different values of fuel burn-up.
- 3. Any combinations of two measures** mentioned above.

The refueling technologies

The reactor can be re-fuelled:

1. After the reactor shutdown, cooldown and removal of the reactor head.
2. After the reactor shutdown, without cooldown and removal of the reactor head.
3. Without the reactor shutdown, at the reduced or full power level.

Light-water reactors are re-fuelled according to **the first option**.

Once a year the reactor is shutdown (4-5 weeks), the reactor head is removed, spent fuel assemblies are transferred to the fuel storage pool, fresh fuel assemblies are introduced into the reactor core.

All the refueling operations are carried out under a thick water layer.

Sodium-cooled fast reactors are re-fuelled according to **the second option**.

Two rotating eccentric plugs located on the reactor head can bring the in-vessel transfer machine (IVTM) to any fuel assembly.

The fuel assembly is grappled by the IVTM manipulator and transferred to the in-vessel storage zone.

Spent fuel assemblies are removed from the reactor through a special hoist.

Heavy-water CANDU-type reactors are re-fuelled without the reactor shutdown, at full power.

Fuel bundles are placed in horizontal pressure tubes.

Two **fueling-refueling machines (FRM)** are connected to a fuel channel at its opposite sides.

One FRM inserts fresh fuel bundles while another FRM receives spent fuel bundles as they are ejected from the channel.

RBMK-type reactors can be also re-fuelled in a continuous manner, without the reactor shutdown, at full power.

1. **The FRM attaches onto the fuel channel** to be re-fuelled.
2. **Pressures** in the fuel channel and in the FRM cask **are equalized**.
3. **Spent fuel assembly** is grappled by the FRM manipulator and **withdrawn from the fuel channel**.
4. **Passability** of the fuel channel is **checked up** with a special imitator.
5. **Fresh fuel assembly is inserted** into the fuel channel.
6. **The FRM and the fuel channel are disconnected**.

Part 7. Transportation of spent nuclear fuel

The spent fuel transport casks can weigh about 100 tons.

The spent fuel assemblies take only 2-5% of the total weight.

The remaining 95-98% of the total weight belong to the safety systems.

A typical spent fuel transport cask looks as follows:

- 1. Large hollow thick-walled cylinder in vertical or horizontal position.**
(1.5-2 m in diameter, 4-6 m in height, 40 cm thick).
The casks are made of **steel, cast iron or concrete**.
- 2. Outer surface of the cask** is covered by special fins to extend the heat removal area ($\sim 30 \text{ m}^2$). The outer fins can extend the heat removal area approximately twice.
- 3. Inner surface of the cask** is lined by stainless steel to enhance corrosion-resistance. The steel liners can include the layers of **neutron absorbers and neutron moderators** (borated polyethylene, for example).

4. Metal shelves are placed in the inner cavity for disposition of spent fuel assemblies.

During shipment, **the inner cavity is filled up with coolant.**

The decay heat is removed from spent fuel assemblies either **by natural convection or by forced circulation** of coolant.

5. The transport casks are hermetized with application of the reinforced densifiers.

6. The transport casks are equipped with a **control system** for permanent monitoring of the inner cavity parameters (radioactivity, residual heat generation rate, temperature and pressure) and with an **accidental decontamination system.**

Main requirements to designs of the transport casks:

1. **Radiation safety** of the staff members, population and the environment (metal vessel containing neutron absorbers and neutron moderators).
2. **Nuclear safety** (metal shelves containing strong neutron absorbers).
3. **Reliable heat removal** (the finned outer surface, forced coolant circulation in the inner cavity).
4. **Reliable hermetization** even under severe accidental conditions.

The hermeticity tests include:

- **Drop test** from 9-m height onto a steel plate.
- **Puncture test** from 1-m height onto a vertical metal rod.
- **Water immersion test** (depth - 15 m, duration - 8 hours).
- **Fire resistance test** – in-flame staying for 30 minutes at 800⁰C plus 2-hour staying without cooldown.

Part 8. Technologies for reprocessing of spent nuclear fuel

The following aims are pursued by the technologies used for reprocessing of spent nuclear fuel (SNF)

- 1. Recovery of uranium and plutonium** for the repeated use (recycle).
- 2. Separation of fission products (FP) and minor actinides (MA)** for further treatment and ultimate disposal as radioactive wastes (RAW).

Classification of SNF reprocessing technologies

1. Aqueous (wet) technologies:

- a. Solvent-extraction processes:** selective recovery of uranium and plutonium from SNF-containing solutions by organic extractants.
- b. Precipitation processes:** formation of insoluble uranium and plutonium compounds by introduction of appropriate precipitants into SNF-containing solutions.

2. Non-aqueous (dry) technologies:

- a. Pyrochemical processes:** for example, the fluoride volatility technology based on different volatility and sorption of uranium fluorides, plutonium fluorides and FP fluorides.
- b. Pyrometallurgical processes:** for example, the electrochemical refinement technology based on different transport properties of uranium, plutonium and fission products in molten salts.

The aqueous solvent-extraction technologies
are the most widely used and industrially matured processes.

Main stages of the aqueous solvent-extraction
PUREX-technology
(PUREX means Plutonium-Uranium-Extraction)

1. **Dismantling** of spent fuel assemblies and **chopping** of spent fuel rods.
2. Preliminary SNF oxidation (**voloxidation**).
3. **SNF dissolution**, preparation of the SNF solution for uranium and plutonium extraction.
4. **The extraction – re-extraction cycles.**

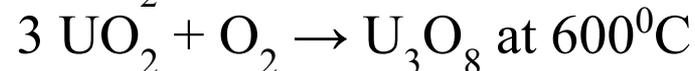
Dismantling of fuel assemblies and chopping of fuel rods

1. **Removal** of end caps, wrappers and spacers, dismantling of fuel lattice.
2. **Shearing operation** that chops long fuel rods into short (~ 5 cm) pieces in inert gas atmosphere (nitrogen or argon).

Preliminary SNF oxidation (voloxidation)

The voloxidation process is a **high-temperature SNF-oxygen reaction**.

Uranium dioxide UO_2 converts into uranium octa-oxide U_3O_8 :



The conversion leads to the following positive effects:

- a. Fuel density** decreases (on ~ 30%) due to different densities of UO_2 (~11 g/cm³) and U_3O_8 . (~8.3 g/cm³).
Fuel volume consequently increases, fuel becomes more porous and friable.
As a result, the further SNF dissolution is significantly simplified.
- b. Fuel crystalline lattice** undergoes substantial changes.
- c. Intense release of gaseous and volatile fission products.**

SNF dissolution

SNF pieces are dissolved by boiling nitric acid HNO_3 :



Metal claddings of fuel rods remain undissolved.

They are removed and treated later as solid radioactive wastes.

Extraction

The solvent-extraction process is a separation of materials between two different fractions: light organic fraction and heavy aqueous fraction.

The extraction process takes place in two connected vessels: **mixer and settler**.

SNF solution and organic extractant (TBP) are pumped into the mixer.

The mixture is pumped later into **the settler**.

The light organic fraction (extract), containing U, Pu and TBP, raises to upper zone of the vessel.

The heavy aqueous fraction (raffinate), containing fission products, lowers to bottom zone of the vessel.

Re-extraction

The re-extraction process takes place also in two connected vessels:
mixer and settler.

The extract and the aqueous washing solution are pumped into **the mixer.**

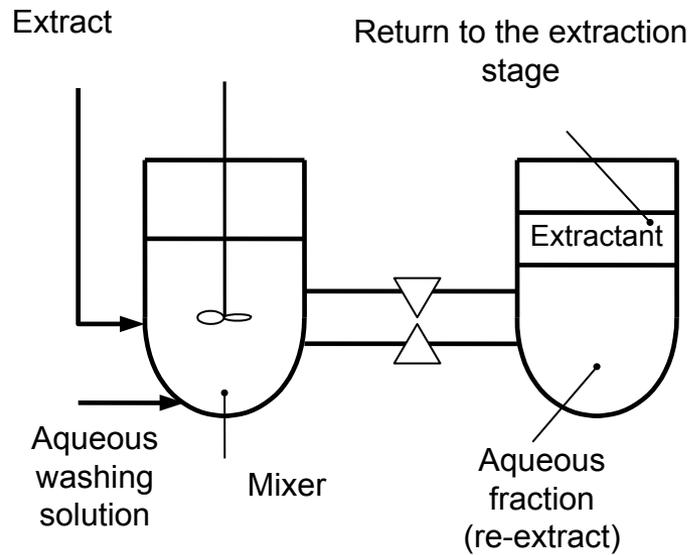
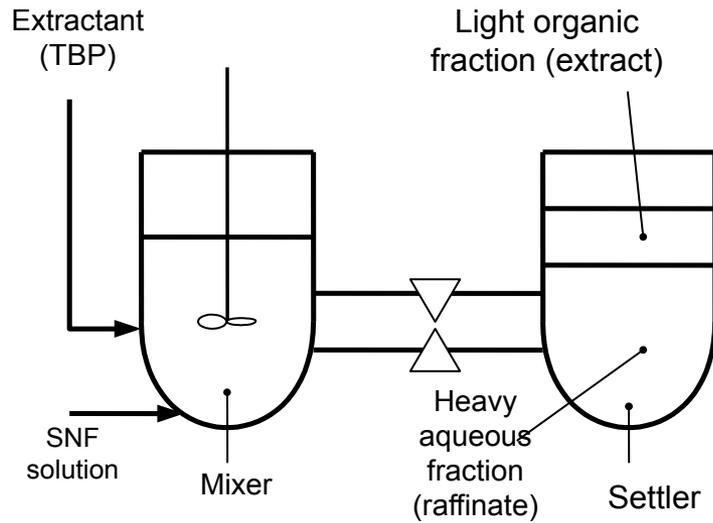
The mixture is pumped later into **the settler.**

The light organic extractant and the heavy aqueous fraction (re-extract)
can be easily separated.

Thus, uranium and plutonium in the re-extract
are separated from fission products.

The organic extractant can be used again in the extraction process.

The extraction – re-extraction process



Separation of plutonium from uranium

Uranium and plutonium are recovered from SNF solution as the following **uranium-TBP and plutonium-TBP solvates**:

1. $\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{ TBP}$ for six-valent uranium.
2. **$\text{Pu}(\text{NO}_3)_3 \cdot 3 \text{ TBP}$ for trivalent plutonium.**
3. $\text{Pu}(\text{NO}_3)_4 \cdot 2 \text{ TBP}$ for four-valent plutonium.
4. $\text{PuO}_2(\text{NO}_3)_2 \cdot 2 \text{ TBP}$ for six-valent plutonium.

Uranium-plutonium separation is based on the **minimal solubility of trivalent plutonium solvate** $\text{Pu}(\text{NO}_3)_3 \cdot 3 \text{ TBP}$ in the light organic fraction.

Therefore, **six- and four-valent plutonium solvates** should be reduced to the **trivalent state and washed out** from the organic fraction.

Composition of the reducing solution can include potassium nitrite KNO_2 , compounds of bivalent iron and so on.

Thus, **one cycle of the extraction – re-extraction process with uranium-plutonium separation** consists of the following stages:

1. **SNF dissolution** by nitric acid.
2. **Extraction of uranium and plutonium** from the acidic SNF solution by organic extractant. Uranium and plutonium are jointly separated from fission products.
3. **Re-extraction of plutonium** from the organic fraction by the aqueous reducing solution. Six- and four-valent plutonium solvates are reduced to trivalent state and transferred to the aqueous fraction. Thus, plutonium is separated from uranium.
4. **Re-extraction of uranium** from the organic fraction by diluted nitric acid. Uranium goes into the aqueous fraction.

Aqueous Safeguarded Fabrication and Reprocessing (SAFAR) technology

Input material – the **acidic SNF solution after two cycles** of FP separation.

Then, the following **operations** are performed:

- 1. Infusion of the SNF solution** into a water-absorbing organic material (ethyl-benzoate, for instance). The SNF solution is converted into the colloid-like substance $(U,Pu)O_2(OH)_{0.4}(NO_3)_{1.6}$.
- 2. Injection of the colloid-like substance** into an ammonia-based organic material for further dehydration. The colloid-like substance is converted into the jelly-like spherical granules $(U,Pu)O_2(OH)_2 \cdot 0.5 NH_3 \cdot 0.5 H_2O$ with sizes within the range of 40-100 microns.
- 3. Thermal treatment of the granules** under gradually elevated temperatures. The thermal treatment evaporates all the organic materials and ultimately calcines the solid granules at $\sim 500^{\circ}C$.

The aqueous SAFAR-technology

is estimated as a **proliferation-resistant technology**

because of the following reasons:

1. **Joint recovery of uranium and plutonium.**
2. Uranium and plutonium are recovered from SNF by only two cycles of the solvent-extraction technology. So, **uranium and plutonium are deliberately contaminated with radioactive fission products.**
3. Final product of the SNF reprocessing - $(U,Pu)O_2$ granules – are characterized by the **enhanced radioactivity and heat generation rate.**

Non-aqueous (dry) technologies for SNF reprocessing

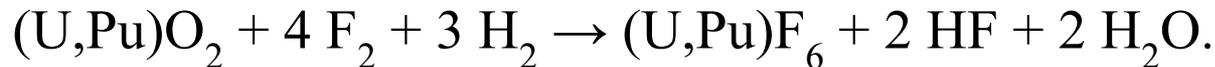
The pyrochemical gas-fluoride technology

is based on **different boiling points, volatilities and sorption** of uranium, plutonium and FP fluorides by sodium fluoride NaF.

Main stages of the gas-fluoride technology:

1. Thermal melting of fuel cladding at 1600⁰C.

2. The SNF fluorination at 400⁰C:



The most fraction of FP fluorides (up to 85%) remains
in the non-volatile sediment.

Well-volatile fluorides of uranium and plutonium go out from SNF.

3. The gas flow passes through the column filled up with NaF granules.

U, Np and Tc fluorides are sorbed by NaF granules at 100⁰C.

Pu, Ru, Zr and Nb fluorides are sorbed by NaF granules at 400⁰C.

4. Desorption of UF₆ and PuF₆ from NaF granules by F₂-N₂ mixture at 400⁰C.

Non-aqueous (dry) technologies for SNF reprocessing

The pyrometallurgical technology of the electrochemical refining

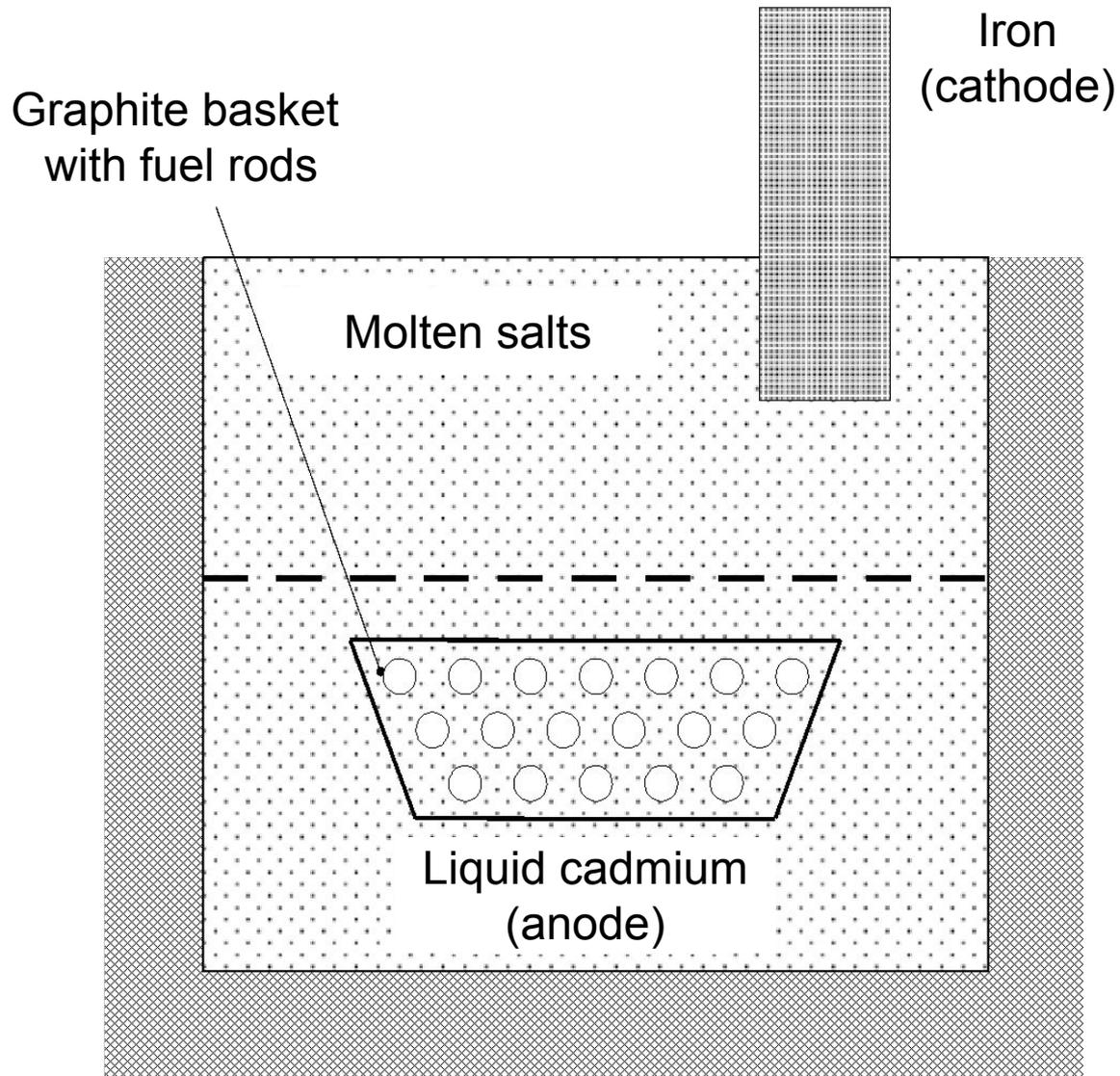
is based on **different transport properties of uranium, plutonium and FP**
when electric current passes through the molten salts.

The electrochemical refining vessel

is filled up with liquid cadmium in the bottom part
and with molten salts
(mixture of K, Na, Ca and Ba chlorides)
above the cadmium layer.

Iron rod is introduced into the molten salts from the vessel top.

Electrochemical SNF refining



Main stages of the electrochemical SNF refining:

1. **Fuel rods are chopped** and their pieces are loaded into a perforated graphite basket.
2. **The graphite basket** is loaded into the liquid cadmium layer. Fuel is dissolved by liquid cadmium. Fuel claddings remain in the basket.
3. **Spent fuel and fission products** are distributed in liquid cadmium and molten salts by such a way:
 - a. **Gaseous and volatile FP** escape the molten materials.
 - b. **Solid FP** escape the liquid cadmium and enter the molten salts.
 - c. **Uranium and plutonium** are present in both layers.
4. **When electric current is switched on** between the liquid cadmium (anode) and the iron rod (cathode), uranium, plutonium and some FP precipitate on the iron cathode.

The cathode deposition

is taken off and used to fabricate a fresh nuclear fuel.

DUPIC-technology

(DUPIC means Direct Use of spent PWR fuel in CANDU)

The SNF discharged from light-water PWR-type reactors can be used in heavy-water CANDU-type reactors because **spent PWR fuel contains large enough amount of fissile isotopes:**
residual uranium enrichment $\sim 0.9\%$ ^{235}U ,
 $\sim 0.7\%$ of reactor-grade plutonium
(about 70% of fissile isotopes ^{239}Pu and ^{241}Pu).

Total content of fissile isotopes in spent PWR fuel is about **1.4%**.
CANDU reactors can be fuelled even with **natural uranium (0.7% ^{235}U)**.

The **two-fold content** of fissile isotopes in spent PWR fuel makes operation of CANDU reactors feasible.

The DUPIC-technology provides spent PWR fuel reprocessing **with application of thermal and mechanical procedures only.**

Main stages of the DUPIC-technology:

- 1. Dismantling of spent fuel assemblies.**
- 2. Transversal chopping of fuel rods.**
- 3. Longitudinal slitting of fuel claddings to weaken them.**
- 4. Voloxidation (thermal treatment by oxygen) at 400⁰C.** Uranium dioxide UO_2 converts into uranium octa-oxide U_3O_8 , fuel volume increases on $\sim 30\%$, and **fuel rods throw their previously weakened cladding.**
Fuel becomes more porous, partially powder-like material, **some gaseous and volatile FP escape the porous fuel.**
- 5. OREOX-treatment (Oxidation-Reduction of Oxide fuel) with multiple interchange of the following reactions:**
 - a. Oxidation by air at 450⁰C** - UO_2 converts into U_3O_8 .
 - b. Reduction by hydrogen at 700⁰C** - U_3O_8 converts into UO_2 .
 - c. Multiple interchange of the oxidizing and reducing reactions** produces the dispersed UO_2 powder. All gaseous FP escape the fuel.
- 6. Pelletization of UO_2 powder** by pressing and sintering.
- 7. Manufacturing of fuel rods and fuel bundles** for CANDU-type reactors.

Specific features of the DUPIC-technology

- 1. Full absence of any liquid solvents and extractants.** Consequently:
 - **Small volume of radioactive wastes** (gaseous FP, fuel claddings).
 - **Compact reprocessing facility**, i.e. a real opportunity for co-allocation of NPP and the reprocessing facility in a single site.
- 2. No uranium-plutonium separation and no fuel-solid FP separation.**
Only gaseous and volatile FP are released from the fuel.

So, it becomes possible to formulate
the main criteria for proliferation resistance
of the SNF reprocessing technologies:

- **Co-extraction (joint recovery) of uranium and plutonium.**
- **Deliberate contamination of the reprocessed fuel with radioactive FP.**
- **Compactness of the reprocessing facility** making it possible to co-allocate NPP and the reprocessing facility in a single site, the absence of lengthy transportations.

Part 9. Technologies for processing of radioactive wastes

The radioactive substances,
whose profitable applications **are not feasible yet,**
should be regarded as **radioactive wastes (RAW).**

General strategy of RAW management

is a **total RAW isolation** from the environment and food chains
by creating **multiple barriers** against RAW migration.

Specific RAW feature

is a **principal impossibility of their extermination** by traditional technologies
(incineration, conversion into other chemical form).

Only natural radioactive decay, i.e. only time,
is able to make RAW harmless.

The general strategy is a strategy of passive defense
against negative RAW properties (radioactivity, heat generation, toxicity).

RAW classification

1. According to **RAW aggregation state** (liquid, solid and gaseous RAW).
2. According to **RAW specific radioactivity** (low-level, middle-level and high-level RAW).

Treatment of high-level wastes (HLW)

There are two HLW forms:

1. **Spent fuel assemblies** discharged from nuclear power reactors.
2. **HLW from radiochemical reprocessing of spent nuclear fuel.**

These wastes are **mainly liquid RAW** because the SNF reprocessing is primarily based now on **the solvent-extraction PUREX-like technologies.**

Main stages of the HLW treatment

1. Interim storage.

- a. **Spent fuel assemblies** are placed into the **water storage pools** at NPP.
- b. **Liquid HLW** are poured into the **steel storage tanks**.

2. Evaporation of liquid HLW.

The HLW evaporation provides ~ **200-fold reduction of the HLW volume**.

3. Solidification of the evaporated HLW.

Main mission of the HLW solidification
is to **implant the HLW into a stable inert matrix**
that can prevent the HLW migration into the environment.

**At present, the HLW vitrification
(the HLW implantation into glass compositions)
is considered as the most suitable technology for the HLW immobilization.**

Main stages of the HLW vitrification

- a. Ultimate HLW evaporation.**
- b. Calcination of the evaporated HLW at 300-400⁰C.**
- c. Mixing of the calcined HLW with the glass-producing additives.**
- d. Gradual warming-up and melting of the glass-mass at 1100-1150⁰C.**
- e. Periodical drainage of the molten glass-mass into the steel containers.**
- f. Interim storage and ultimate disposal of the steel HLW containers.**

The alternative technology presumes the HLW implantation into the mineral-like SYNROC-materials.

The term **SYNROC** (Synthetic Rocks) means the **artificial rock-like material**.

It was hoped that the **SYNROC-materials** would be characterized by **the same properties** (primarily, long-term stability) as their **natural analogues**.

Main stages of the SYNROC-technology

- 1. Mixing of the evaporated HLW** with predecessors of the SYNROC-materials (refractory oxides of titanium, calcium and some other metals).
- 2. Calcination** at 700⁰C.
- 3. Hot pressing** of the SYNROC pellets.
- 4. Filling up the steel containers** with the SYNROC pellets, interim storage and ultimate disposal of the HLW containers.

Ultimate disposal of the HLW containers in geological repositories

Geological formation is a suitable place of ultimate RAW disposal only if the formation meets the following requirements:

Geographical features of the place

1. Far distance from the **densely populated areas**.
2. **Low seismicity and low probability of earthquakes**.
3. The geological stratum must **not enter the earth surface**.
4. Far distance from the level of **ground waters**.

Physical properties of the formation

1. Good **heat conductivity**.
2. Good **mechanical strength**.
3. Good **plasticity**.
4. Good **chemical stability**.
5. Good **retentivity of radioisotopes**.

Three geological formations

are being estimated now as the most promising candidates:

1. **Salt mines.**
2. **Sedimentary clayish formations.**
3. **Rocky formations.**

There is no obvious leader among them.

All the candidates have their own **advantages and drawbacks.**

Salt mines

Advantages

1. **Far distance from the level of ground waters.**
2. **Good plasticity.**
3. **High heat conductivity.**

Drawbacks

1. **Solubility** by light water.
2. Potential **usefulness** for industrial applications.
3. **Radiolysis** with intense release of harmful gases (chlorine, for instance).

Sedimentary clayish formations

Advantages

1. **Full water impermeability.**
2. **Good plasticity.**
3. **High retentivity of radioactive FP (except of ^{99}Tc and ^{129}I).**

Drawbacks

1. **Low retentivity of ^{99}Tc and ^{129}I , radioisotopes with high migration ability.**
2. **Low heat conductivity.**
3. **Proximity to the earth surface.**

Rocky formations

Advantages

1. **High water impermeability.**
2. **Good mechanical strength.**
3. **Chemical stability.**

Drawback

1. **Low plasticity, inclination for cracking.**

The RAW disposal **projects under development now** are oriented towards the **rocky formations** as ultimate RAW repositories.

Treatment of liquid middle-level (MLW) and low-level (LLW) radioactive wastes

Main stages:

- 1. Removal of solid particles** (adsorption, precipitation, filtration).
- 2. Ion-exchange purification** of the clarified solutions.
- 3. Evaporation** up to the dry sediment.
- 4. Immobilization by bituminization or cementation.**
- 5. Placement of the solidified RAW** into the steel containers.
- 6. Interim storage and ultimate disposal** of the steel containers.

Advantages of bitumen

Low leaching rate by light water.

- 1. Suitability for immobilization** of any chemical forms.
- 2. Good radiation resistance.**

Drawbacks

Inflammability (by-product of natural oil reprocessing),
softening under warming-up.

**Alternative option for the RAW bituminization is a cementation,
i.e. the RAW implantation into the concrete blocks**

Advantages

1. **Low cost and simplicity** of the cementation process.
2. **Good radiation resistance.**
3. **High heat conductivity.**
4. Concrete is not an **inflammable** material and shows **no softening** under warming-up.

However, concrete is very **sensitive to the water leaching.**

**Comparative data
on the water leaching rate**

1. Glass - $10^{-8} \div 10^{-7}$ g/(cm² · day).
2. SYNROC - $10^{-6} \div 10^{-5}$ g/(cm² · day).
3. Bitumen - $10^{-6} \div 10^{-4}$ g/(cm² · day).
4. Concrete - $10^{-3} \div 10^{-2}$ g/(cm² · day).

Glass and SYNROC-materials are used for the HLW immobilization while **bitumen and concrete** are used for the MLW and LLW immobilization.

Treatment of gaseous RAW

Main components of gaseous RAW

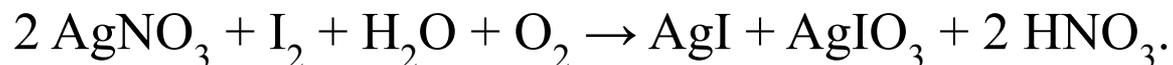
1. Noble gas ^{85}Kr (half-life $T_{1/2} = 10.7$ years).
2. Iodine isotope ^{129}I (half-life $T_{1/2} = 1.6 \cdot 10^7$ years).
3. Radiocarbon ^{14}C (half-life $T_{1/2} = 5730$ years).
4. Tritium ^3H (half-life $T_{1/2} = 12.3$ years).

Treatment of ^{85}Kr consists in **cryogenic adsorption**

by activated charcoal, molecular sieves and liquid fluorocarbons.

Treatment of ^{129}I

1. Absorption by alkaline or acidic solutions with production of solid insoluble compound HI_2O_8 .
2. Chemisorption in the filters impregnated with silver nitrate:



Gaseous I_2 is converted into solid silver iodide and silver iodate.

Treatment of gaseous RAW

Treatment of ^{14}C

Radiocarbon is a product of $^{14}\text{N}(\text{n},\text{p})^{14}\text{C}$ reaction.

Nitrogen is an impurity in coolant and structural materials.

Till now, no effective technology for capture radiocarbon oxides has been developed yet.

Some liquid fluorocarbons demonstrated efficient absorption of ^{14}C within low temperature range (from -40°C up to $+4^{\circ}\text{C}$)

Treatment of tritium ^3H

Tritium is a product of neutron reactions with hydrogen in coolant and lithium in structural materials as an impurity.

1. During SNF voloxidation, humid air can bind tritium into tritium water T_2O for further treatment as a component of liquid RAW.
2. Light-water washing-out of organic fraction after the solvent-extraction.
3. Chemisorption of tritium water by zeolite (porous mineral).

Treatment of solid RAW

Main components of solid RAW

1. Details of nuclear equipment, structural materials, rubbish, work clothes, etc.
2. Ion-exchange resins and filters.
3. Metal claddings of fuel rods.
4. Deposits on inner surfaces of technological equipment (pipes, vessels, etc).

Methods for treatment of solid RAW

(the first two categories)

1. **Reduction of RAW volume:**
 - a. **Incineration** with up to 100-fold reduction of RAW volume.
 - b. **Pressing** with up to 10-fold reduction of RAW volume.
2. **Placement of the treated RAW into the steel containers, interim storage and ultimate disposal.**

Treatment of fuel claddings

1. **Chemical treatment by hydrofluoric acid HF** at 600°C . The treatment results in the formation of superficial friable films on the cladding surface.
2. **Dissolution and removal of the films** by alkaline or acidic solutions.
3. **Melting of fuel claddings** into metal ingots in electrical furnaces.
4. **Placement of the metal ingots into the steel containers, interim storage and ultimate disposal.**

Treatment of inner radioactive deposits

The radioactive **deposits on inner surfaces** of technological equipment can be formed by the following processes:

1. **Sorption** from the SNF solutions.
2. **Gradual saturation** of the deposits with radioisotopes.
3. **Gradual hardening of the deposits** under rigid radiation, thermal, physical and chemical conditions of the SNF reprocessing.

Main decontamination technology – the RAW desorption

Desorption of radioactive deposits converts the solid RAW into liquid form.

The **multi-stage washing-out process** is performed:

1. At first, low concentrated **solution of nitric acid HNO_3** is used **to dissolve and remove the SNF residuals.**
2. **Multiple alternation** of the wall treatment by liquid desorbing solutions is used to weaken, dissolve and remove the deposits.
 - Washing-out by **alkaline solutions (chemical dissociation and loosening of the deposits).**
 - Washing-out by **acidic solutions (dissolution and removal of the friable deposits).**

Multiple alternation of the washing-out procedures
can completely clean the inner surfaces from radioactive deposits.

THANK YOU FOR ATTENTION!