The Nuclear Fuel Cycle

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What is Nuclear Fuel Cycle?
Answer:

- The nuclear fuel cycle typically involves the following steps:
  - (1) finding and mining the uranium ore;
  - (2) refining the uranium from other elements;
  - (3) enriching the uranium-235 content to 3-5%;
  - (4) fabricating fuel elements;
  - (5) interim storage and cooling of used nuclear fuel;
  - (6) reprocessing/recycling of used nuclear fuel to recover uranium and plutonium (optional);
  - (7) fabricating recycle fuel for added energy production (optional);
  - (8) cooling of spent fuel or reprocessing waste, and its eventual transport to a repository for disposal in secure long-term storage.

http://encyclopedia2.thefreedictionary.com/Nuclear+fuel+cycle
1-Finding and mining the uranium ore
Uranium Ores

• Uranium exists in the terrestrial crust with a concentration of 3 to 4 ppm (3 to 4 g/ton).

• There is also a very small concentration amount of Uranium in the ocean: 2 to 3 ppb (2 to 3 mg/m³).

• 2 ways for prospecting uranium:
  - Direct Methods
  - Indirect Methods
Direct Methods

- Geochemical prospecting
- Radiometric prospecting
- Study of the emission of gas
- Neutrons irradiation
Indirect methods

- These methods are especially used for the determination of the location of uranium ores in deep geological formation
  - Measure of the variations of the terrestrial gravity field
  - Measure of the terrestrial magnetic field
  - Measure of the rocks and soils resistivity
  - Seismic measures

These techniques are also used for other metals prospecting
Uranium ores

- The notion of exploitation of a site depends on:
  - the uranium price on the stock market,
  - the concentration of Uranium in the ore, and
  - the total estimated mass of uranium in the site
- In average, the extracted minerals called rich minerals have a concentration of uranium of 1000 ppm to 5000 ppm (1 to 5 kg of U/ton)
- The poor minerals have a concentration of uranium between 200 ppm to 1000 ppm
- while the sterile rocks have a concentration of uranium < 200 ppm
Uranium Production

Production of $\text{U}_3\text{O}_8$, total world, in tons = 59,640 which meets 76% of demand for power generation.

PRODUCTION FROM MINES (Tons U)

<table>
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<th>Country</th>
<th>2007</th>
<th>2008</th>
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<tr>
<td>South Africa</td>
<td>739</td>
<td>655</td>
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63% of the World’s production

http://www.world-nuclear.org/info/inf23.html
Scarcity of Uranium

- Present projection of U availability is 60 to 270 years, with the second figure implying a much higher U price.
- Recycling and Transmutation provide a new technology to the nuclear fuel cycle, based on FNR and recycling of Actinides that will make the presently identified uranium resources worth 2,500 years.

Yellow cake

UF$_4$, green solid, not very soluble

Crystallized UF$_6$, colorless solid, Gas at 56°C, very reactive with water
Uranium minerals

- Numerous uranium minerals, more than 150 species. They can be separated in different classes;

- Reduced species (contain U(IV))
  - Oxides: Pitchblende or uraninite
    \[ [U(IV)_{(1-x)}U(VI)_x]O_{2+x} \]
  - Silicates: Coffinite
    \[ [U(SiO_4)_{(1-x)}(OH)_{4x} ] \]

- Oxidized species (contain U(VI))
• Oxidized species (contain U(VI))
  - Phosphates: autunite \([Ca(UO_2)_2(PO_4)_2\cdot10\text{to}12H_2O]\)
  - torbernite \([Cu(UO_2)_2(PO_4)_2\cdot12H_2O]\)

- Oxides: Parapitchblende
  \((UO_3 \text{ with } UO_2 \text{ in small quantity})\)

  Gummite \((UO_3, \text{ n } H_2O)\)
Mining Methods

• Mining methods have been changing. In 1990, 55% of world production came from underground mines, but this shrunk dramatically to 1999, with 33% then.

• In situ leach (ISL) mining has been steadily increasing its share of the total.

• In 2009 production was as follows:
  - conventional underground & open pit: 57%
  - in situ leach (ISL) 36%
  - by-product 7%
Coring provides valuable radiological data on the state of the deposit's radiometric equilibrium. It also provides information on the host formation's hydrological characteristics in the form of porosity and permeability data. Core samples can also be tested metallurgically to determine amenability to milling.
Open Pit Mining
The Sweetwater Pit and mine Site

- No uranium open pit mines are currently operating in Wyoming due to market conditions.
- This aerial photograph of the Sweetwater Pit was taken on September 25, 1980. The lower portion of the photograph shows haul trucks. The overburden pile is shown in the center of the photograph. The photograph shows the overburden pile and haulage roads typical of an open pit uranium mine.
Mining and Milling U

- Conventional mines have a mill where the ore is crushed, ground and then leached with sulfuric acid to dissolve the uranium oxides.

- At the mill of a conventional mine, or the treatment plant of an ISL operation, the uranium then separated by ion exchange before being dried and packed, usually as $U_3O_8$. Some mills and ISL operations use carbonate leaching instead of sulfuric acid, depending on the orebody.
1- Crushing and Grinding

- Use of hydrometallurgical techniques which need that uranium is in solution.
- To obtain a high solubilization yield of U, it is necessary to break and crush the minerals.
- The crushing give rocks with dimension of 15 mm.
- The grinding gives grains of 0.45 mm diameter.
- These operations need heavy equipments that require high quantity of energy, for this reason, this technique is used only for rich uranium ores.
Treatment of rich uranium ores (1000 to 5000 ppm U/ton) (2)

2-SULFURIC ATTACK

• The attacking reagent will allow the solubilization almost quantitative of uranium and a minimum solubilization of the other elements present in the rocks
• This reagent needs to be cost effective
• These conditions met the requirements for using sulfuric acid (H₂SO₄) and in certain cases, aqueous solutions of sodium carbonate (Na₂CO₃).
• The amount of H₂SO₄ used to attack the minerals are between 25 kg to 100 kg/ton of minerals
2-SULFURIC ATTACK(2)

- Sulfuric acid is consumed essentially by
  - Oxides, hydroxides and sulfides: Iron
  - Silicates and/or Silico-aluminate: Alkalines
  - Silicates and/or Silico-aluminate: Alkaline earths
  - Carbonates

which are present in the minerals

In most of the minerals treated, uranium is present as U(IV), very poorly soluble in sulfuric medium

In order to solubilize U(IV) in $H_2SO_4$, one needs to add an oxidizing agent to the solution to oxidize U(IV) to U(VI)
2-SULFURIC ATTACK(3)

• Oxidizing agents to add to oxidize U(IV) to U(VI) are:
  - Sodium chlorate (\(\text{NaClO}_3\))
  - Manganese dioxide (\(\text{MnO}_2\))
  - Hydrogen peroxide (\(\text{H}_2\text{O}_2\))

• This is \(\text{NaClO}_3\) which is the most used, the consumption is generally 1 to 5 kg/ton of mineral, the decomposition reaction is

\[
\text{Na}^+, \text{ClO}_3^- \rightarrow \text{Na}^+, \text{Cl}^- + \frac{3}{2} \text{O}_2
\]

• 45% of its mass is liberated as oxygen gas
• **2-SULFURIC ATTACK(4)**
  - The sulfuric attack is performed under hot conditions (40 to 80°C) and it takes 3 to 10 hours to realize it.
  - The reaction is performed in vessel under constant agitation.
  - Depending on the vessel, the volume ratio between the solution and the minerals mass can vary. In certain cases, the volume ratio can be <1 and be close to 0.1 - 0.15 if concentrated H$_2$SO$_4$ is used.
  - The uranium solubilization yield is between 96 to 97% with an initial uranium concentration of 3000ppm to 5000 ppm in the minerals.
  - After the solubilization is performed, the separation solid-liquid takes place to extract the uranium solution. It can be done by using filters or countercurrent wash.
In Situ Leach (ISL)

- In situ leaching (ISL), also known as solution mining, or in situ recovery (ISR) in North America, involves leaving the ore where it is in the ground, and recovering the minerals from it by dissolving them and pumping the pregnant solution to the surface where the minerals can be recovered.

- Consequently there is little surface disturbance and no tailings or waste rock generated.

A solution is injected into the uranium ore deposit then pumped out. The uranium then is separated from the solution.
ISL Process

http://world-nuclear.org/info/inf27.html
Treatment of uranium solutions (1)

• The methods for concentrating and purifying uranium solutions are numerous and depend essentially on
  - the nature of the minerals that have been treated,
  - the nature and concentrations of impurities present in the minerals and
  - the companies

• These methods are based on the partition of uranium between 2 phases
  - Precipitation
  - Ion Exchange resins
  - Solvent extraction
Treatment of uranium solutions (2)

- Solvent extraction, the more common method, uses tertiary amines in an organic solvent in a continuous process.

- First the amines, $R_3N$, react with sulfuric acid:

  $$2 \text{R}_3\text{N} \text{ (org)} + \text{H}_2\text{SO}_4 \text{ (aq)} \rightarrow \text{(R}_3\text{NH})_2\text{SO}_4 \text{ (org)}$$

- Then the amine sulfate extracts the uranyl ions into the organic phase while the impurities remain in the aqueous phase. In the case of the uranyl sulfate ion, the following reactions occur:

  $$\text{(R}_3\text{NH})_2\text{SO}_4 \text{ (org)} + \text{UO}_2\text{(SO}_4\text{)}_3 \text{ (aq)} \rightarrow \text{(R}_3\text{NH})_4\text{UO}_2\text{(SO}_4\text{)}_3 \text{ (org)} + 2\text{SO}_4^{2-} \text{ (aq)}$$

- The solvents are removed by evaporating in a vacuum and ammonium diuranate, $(\text{NH}_4)_2\text{U}_2\text{O}_7$, is precipitated by adding ammonia to neutralize the solution. The diuranate is then heated to yield a purified, solid $\text{U}_3\text{O}_8$, known as yellow cake.
Yellow Cake
2- Refining the uranium from other elements
Refining the yellow cake

- At the refinery, the yellow cake is dissolved in nitric acid.
- The presence of reducing impurities in the yellow cake is translated by the formation of nitrous vapors as:

\[
\text{NO}_3^- + \text{Reducing species} \rightarrow \text{Oxidizing species} + \text{NO}_x
\]

- After attack, the insoluble species such as \(\text{SiO}_2\), \(\text{TiO}_2\) and phosphates are eliminated from the solution by filtration through a rotary filter.
- The clarified solution of uranium contains 600 to 800 g/L uranium (VI).
- The resulting solution of uranium nitrate, \(\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}\), is fed into a continuous solvent extraction process.
Liquid-liquid extraction

• This uranyl nitrate solution is then directed towards the liquid-liquid extraction cycles

• The reaction is:
\[ \text{UO}_2^{2+}, 2\text{NO}_3^- + 2\text{TBP} \xleftrightarrow{\text{ }} \text{UO}_2(\text{NO}_3)_2(\text{TBP})_2 \]

• This reaction is very selective towards uranium

• The operations are generally realized in pulsed columns

• The following figure depicts the different operations
Purification of Uranium by liquid-liquid extraction

1-Extraction Column

2-Washing Column

3-Reextraction column

4-Solvent Washing Column

5-Solvent Reconditioning Column

UO₂(NO₃)₂ Solution
To be purified

Na₂CO₃
Demineralized water

HNO₃

Storage TBP + Diluent

Pure TBP

Diluent

Effluent storage

Effluent storage

Towards Effluent reprocessing

Towards the ammonium uranate precipitation

UO₂(NO₃)₂ purified

Madic C., DEA 3R, University Paris XI, 1989
After this purification, the uranium is washed out of the diluent with dilute nitric acid and concentrated by evaporation to pure $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$.

Heating (oven in a countercurrent mode with hot air $350^\circ\text{C}$) yields pure $\text{UO}_3$.

The powder $\text{UO}_3$ is orange and is then directed towards the conversion operation (conversion into $\text{UF}_4$).
3- Enriching the uranium-235 content to 3-5%
Fluorination- Conversion into UF$_4$

- The conversion from UO$_3$ to UF$_4$ is the same for the fabrication of uranium metal or uranium dioxide (for PWR reactor, UO$_2$ with enriched U).
- For the heavy water reactor such as CANDU, the fuel is made of UO$_2$ (with natural uranium), so the conversion into UF$_4$ is not necessary.
The conversion is realized in 2 steps:

- Reduction of UO$_3$ to UO$_2$
- Fluorination of UO$_2$ to UF$_4$

These 2 reactions involve gas-solid equilibrium and are particularly sensitive to the surface state and particle size analysis of the solid UO$_3$. 
Fluorination- Conversion into UF₄ (3)

**Reduction UO₃ to UO₂**

- This reaction can be done by the action of hydrogen under hot conditions:
  \[ \text{UO}_3 + \text{H}_2 \rightleftharpoons \text{UO}_2 + \text{H}_2\text{O} \]
- The reaction is exothermic with \( \Delta H = -26 \text{ kcal/mole} \).
- To moderate the exothermicity of the reaction, it is possible to generate hydrogen via the breaking of ammoniac \( \text{NH}_3 \) as:
  \[ 2\text{NH}_3 \rightarrow 3\text{H}_2 + \text{N}_2 \Delta H = +11 \text{ kcal/mole} \] (endothermic reaction)
- The global reaction is:
  \[ 3 \text{UO}_3 + 2 \text{NH}_3 \rightleftharpoons 3 \text{UO}_2 + 3 \text{H}_2\text{O} + \text{N}_2 \]
• Fluorination UO₂ to UF₄
• The conversion of UO₂ into UF₄ is realized around 350°C to 450°C by action of gaseous HF: The exothermic reaction is:

\[ \text{UO}_2 + 4 \text{HF} \rightleftharpoons \text{UF}_4 + 2 \text{H}_2\text{O} \]

\[ \Delta H = -42 \text{ kcal/mole} \]

• The reaction is not really quantitative so an excess of HF is needed to insure the maximum conversion of UO₂ into UF₄
• A competing reaction can occur in the case where impurities of UO₃ have been transferred into UO₂

\[ \text{UO}_3 + 2\text{HF} \rightleftharpoons \text{UO}_2 \text{F}_2 + \text{H}_2\text{O} \]
The production of the nuclear fuel for the PWR consists of the enrichment step realized by different methods by gaseous diffusion or by ultra-centrifugation. This is UF$_6$ which is subject to this treatment.

The UF$_6$ production is performed by fluorination: reaction of UF$_4$ (solid) and fluor (gaseous F$_2$).

Fluor being a dangerous reagent and difficult to store, it is produced on the site where UF$_6$ is produced.
Fluorination UF$_4$ to UF$_6$

• The transformation of UF$_4$ into UF$_6$ is realized by the combustion of UF$_4$ such as:
  $\text{UF}_4 + F_2 \rightleftharpoons \text{UF}_6$

• The reaction is very exothermic

• The product formed UF$_6$ is a gas.

• In the next figure, the phase diagram of UF$_6$ is presented
Phase Diagram of UF$_6$

- It is a colorless solid at the ambient temperature (for $P = 1$ atm) with a sublimation point very low (56.54°C, 760 Torrs)
- The triple point is $T = 64.052$°C, $P = 1142$ Torrs)
- The critical point is $T_c = 64.052$°C, $P_c = 3.46 \times 10^4$ Torrs
- This diagram is used to determine that for $P \leq 1142$ Torrs, only the equilibrium gas-solid is observed.
- The conversion solid-liquid, necessary for the filling of the tanks for example, can be done by heating with a few bars of pressure.

Madic C. DEA 3R, University Paris XI, 1989
Enrichment of UF₆

• Enriching uranium is difficult because the two isotopes have identical chemical properties, and are very similar in weight:
  • U-235 is only 1.26% lighter than U-238.
  • Several production techniques applied to enrichment have been used, and several are under investigation.
  • In general these methods exploit the slight differences in atomic weights of the various isotopes.
Enrichment of UF$_6$ (2)

- A feature common to all large-scale enrichment schemes is that they employ a number of identical stages which produce successively higher concentrations of U-235.
- Each stage concentrates the product of the previous step further before being sent to the next stage.
- Similarly, the tailings from each stage are returned to the previous stage for further processing.
- This sequential enriching system is called a cascade.
Enrichment of UF₆ (2) (Techniques)

- Gaseous diffusion
- Gas centrifuge
- Zippe centrifuge
- Aerodynamic processes
- Laser processes
- Chemical methods
- Plasma separation
Gaseous diffusion

• It is a technology used to produce enriched uranium by forcing gaseous UF₆ through semi-permeable membranes

• This produces a slight separation between the molecules containing U-235 and U-238. Throughout the Cold War, gaseous diffusion played a major role as a uranium enrichment technique, though it has now been almost completely replaced by newer methods.
Enrichment – Gaseous Diffusion

- **Mass Transfer Process**
  - Diffusion rate proportional to mass
    - $^{235}$U Diffuses Faster
  - Very low efficiency
    - Requires many stages
    - Cascades use 1000+ stages

- **Requires Gaseous product**
  - Mass Difference
    - $^{235}$UF$_6$-$^{238}$UF$_6$
    - $\Delta = 0.85\%$

- **Energy Intensive**
  - $10^7$ SWU/yr => 2700 MWe
Gaseous Diffusion Plant
(Paducah, KY)
**Gas centrifuge**

- This process uses a large number of rotating cylinders in series and parallel formations.
- This rotation creates a strong centrifugal force so that the heavier gas molecules containing U-238 move toward the outside of the cylinder and the lighter gas molecules rich in U-235 collect closer to the center.
- It requires far less energy to achieve the same separation than the older gaseous diffusion process, which it has largely replaced.
Enrichment Concentrates the Uranium Isotope
Enrichment - Gas Centrifuge

- **Mass Transfer**
  - **Centrifuge**
    - “High” G field
  - **Buoyancy**
    - $^{235}\text{UF}_6$ floats
    - $^{238}\text{UF}_6$ sinks

- **Summary**
  - **Gaseous Feed**
  - **Higher Efficiency**
    - > Gas Diffusion
    - Fewer Stages needed
  - **Less Power Intensive**
    - Minimal Pumping
    - $10^7$ SWU/yr => 109 MWe

[www.npp.hu/uran/3cent-e.htm](http://www.npp.hu/uran/3cent-e.htm)
(4) Fabricating fuel elements
Defluorination – Production of UO$_2$

- After the enrichment step, realized by gaseous diffusion or by ultracentrifugation of UF$_6$, UF$_6$ needs to be converted into UO$_2$, principal ingredient of PWR nuclear fuel.

- Two processes can be used:
  - Humid path or
  - Dry path
Defluorination – Production of $\text{UO}_2$

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  - Humid path or
  - Dry path
Humid Path

- This technique is based on the hydrolysis of UF₆ by an aqueous solution, the different steps are as follow:
  - Hydrolysis of UF₆ and ammonium uranate precipitation
    \[ 2\text{UF}_6 + 14 \text{NH}_4\text{OH} \rightarrow (\text{NH}_4)_2\text{U}_2\text{O}_7 + 12 \text{NH}_4\text{F} + 7 \text{H}_2\text{O} \]
  - Filtration of ammonium uranate
  - Pyrohydrolysis of ammonium uranate
    (performed in a turning oven, hot conditions)
    \[ 9(\text{NH}_4)_2\text{U}_2\text{O}_7 \rightarrow 6\text{U}_3\text{O}_8 + 2\text{N}_2 + 14 \text{NH}_3 + 15 \text{H}_2\text{O} \]
  - Reduction of U₃O₈ in UO₂
    \[ \text{U}_3\text{O}_8 + 2\text{H}_2 \rightarrow 3 \text{UO}_2 + 2\text{H}_2\text{O} \]
Defluorination - Production of UO$_2$ (3)

**Dry Path**

- This technique requires only gaseous or solid reagents
- Pyrohydrolysis of UF$_6$ (850°C to 900°C)
  \[ UF_6 + 2 \text{H}_2\text{O} \rightleftharpoons \text{UO}_2\text{F}_2 + 4 \text{HF} \]
- Reduction of UO$_2$F$_2$ (750°C)
  \[ \text{UO}_2\text{F}_2 + \text{H}_2 \rightleftharpoons \text{UO}_2 + 2 \text{HF} \]

These 2 operations can be done in the same oven. The produced HF can be recycled towards the F2 production unit by electrolysis.

The advantage of this technique is the absence of liquid effluents.
Nuclear Fuel Preparation-PWR

- The enriched UO$_2$ is produced as small spheres with the following dimension:
  - $H = 15$ mm
  - Diameter = 8.2 mm
  - The volumetric mass reaches 95% of the real volumetric mass of UO$_2$ approximately 10.4 g/cm$^3$
Nuclear Fuel Preparation- PWR (2)

• The fabrication of these small spheres consists in a first step in compressing under high pressure $\text{UO}_2$ powder with the addition of a small percentage of organic products.

• These organic products allow a good agglomeration of the powder.

• The raw pellets are then sintered under high temperature ($1700^\circ \text{C}$)

• Then, the pellets are placed into Zircaloy tubes that form the fuel rod
A single pellet has a diameter of 8 mm, weighs 7 to 8 grams and can produce as much energy as a ton of coal!

By producing some 200 million pellets every year, nearly 1 billion tons $CO_2$ emission is prevented into the atmosphere.
Uranium Is Encased in Solid Ceramic Pellets
Fuel Rods Filled With Pellets Are Grouped Into Fuel Assemblies
Nuclear Energy Comes From Fission

Neutrons

Uranium atom

Split atoms
Splitting Atoms Releases Neutrons, Making Heat
This process continues in a chain reaction, producing a great deal of heat. It is this process—creating heat through the splitting of atoms—that turns water to steam. The steam is moved from the reactor to turn the turbine-generator, which makes electricity. All radioactive water stays within the reactor system and is not released into the environment.
• Electrical Power: 900-1450 MW
• Moderator: H2O
• Medium: H2O (155 Bars, 300°C)
• Fuel: UO2 or MOX
• Cladding: Zircaloy (Zr, Sn, Fe, Cr)
• Fuel Assembly: Square 17*17, 264 rods
• Rod: 3.8m to 4.5 m
• Diameter: 9.5 mm
• Pellet Diameter: 8 mm, h = 13.5 mm, porosity 5%
  Extracted power = a few 100W/cm²
• Reactor: 157 fuel assemblies (>40,000 rods) annual discharge ¼ core
• 1000tons discharged annually
5- Interim storage and cooling of used nuclear fuel;
• After a certain period of irradiation time, it is necessary to take out the fuel from the reactor
• Decrease of the content of fissile material
• Progressive poisoning of the fuel
• Risk of cladding breaking
• This operation is performed before the consumption of all initial fissile material
The recycling activity answers 2 objectives:

- Recovery of the fissile material to re-use it for the fabrication of new fuel elements (example, recycling Pu via MOX fuel, recycling U for new enrichment for PWR)

- Separation of nuclear wastes (activation and fission products) as a function of their pollution in order to store and to avoid any potential danger and release towards the biosphere
Reprocessing

• The reprocessing activity answers 2 objectives:

  - Recovery of the fissile material to re-use it for the fabrication of new fuel elements (example, recycling Pu via MOX fuel, recycling U for new enrichment for PWR)

  - Separation of nuclear wastes (activation and fission products) as a function of their pollution in order to store and to avoid any potential danger and release towards the biosphere
Characteristics of fuel irradiated during 3 years in a PWR

Initial Fuel (1,000 kg)

Irradiated Fuel (1,000 kg)

Fission Products

Different Isotopes Of Pu (9 kg)

235U (33 kg)

238U (967 kg)

3 years

235U (8 kg)

238U (943 kg)

236U (4.6 kg)

237Np (0.5 kg)

244Cm (0.04 kg)

243Am (0.12 kg)
96% of a UNF Assembly is Recyclable

Composition of used light water reactor fuel

- 1 LWR fuel assembly = 500 kg uranium before irradiation in the reactor (1 tonne total weight)

Recyclable materials

Waste

After irradiation*

U 475 to 480 kg (94 to 96 %)

Pu 5 kg (1 %)

FP/MA 15 to 20 kg (3 to 5 %)

Power from 1g Pu equals power from 100g U or 1 - 2 tons oil

* Percentages may vary based on fuel burnup

Sven Bader, AREVA FS, Recycling of UNF in the US, UNLV 27 Jan 2010
Transport from Reactor to la Hague

All casks from Europe arrive by train and are transported by trucks to la Hague.
All casks from overseas are transported by boat.
Transport

- Fuel assemblies consisting of rod bundles measuring about 4 m long, holding usually 264 rods (PWR 17*17), initially containing \( \text{UO}_2 \) based on uranium enriched to about 3.5% U-235, irradiated to ~2.85*10^{12} \text{ J/kg} (33,000 \text{ MWd/t}) for PWR fuel and about 2.42*10^{12} \text{ J/kg} (28,000 \text{ MWd/t}) for BWR fuels are transported in shielded casks from the power plant site to the reprocessing plant site.
Chateau = Cask

The used fuel, fuel assemblies around 12, is transported in these containers, 300-400°C inside.
Dry unloading
Dry vs. wet unloading

The choice of unloading procedure depends on the type of container used during transportation and the characteristics of the fuel being unloaded. The dry unloading process (TO facility), which involves connecting the container to the unloading cell, only receives the MARK II, or equivalent, container families.

The wet unloading procedure (NPH facility) can receive and unload all types of container, including small packing units used to transport fuel from research reactors (HAO facility).

Whatever the unloading procedure, the fuel is placed in baskets and then transferred to inter-connecting storage pools.
The container docks

Underwater unloading
1/ Receiving and checking the container
The container arrives horizontally on a trailer. It immediately undergoes a radiological examination and its protective cover is checked before unloading. It is then tipped into a vertical position and transferred to an automatic trolley to be taken to the storage ponds.

2/ Preparing the container before unloading
This operation consists in making sure there are no ruptured fuel units (i.e. that are no longer watertight), in adjusting the depression in the container’s internal cavity, and in fitting the adapters needed for watertight docking to the interim-storage pond.

3/ Unloading the fuel
After the container has been docked and opened, the fuel is unloaded and identified automatically, unit by unit, then rinsed with water until it cools to 80°C. Once it has been ascertained that the fuel units are intact, they are placed in a basket and transferred to the storage pools.

4/ Interim-storage pond
The fuel remains in the storage pool in nine metres of water for between three and five years, during which time its radioactivity decreases. There are four metres of water between the fuel and the surface to provide biological protection. The demineralised water is constantly cooled and filtered within the same pond.

5/ Preparing the container after unloading
Sealed up again and released from the discharge cell, the empty container is sent to the preparation unit before it can depart. The docking elements are disassembled and stopper fittings put back. The internal cavity is emptied, rinsed and dried, checked for watertightness, non-contamination and irradiation, then the shock absorbent covers are replaced and the container released to collect a new load from the reactor.
Fuel assemblies are placed in a basket and then transferred to the pool.
Before recovering different materials contained in used fuel, the fuel assemblies are kept in pools for 3 years. This allows used fuel to cool before reprocessing operations begin. As an example, La Hague has 4 pools with a total capacity of 10,300 tons in operation.
6-Reprocessing/recycling of used nuclear fuel to recover uranium and plutonium
Recycling of used nuclear fuel

- The universal process used today is the PUREX Process.
- It uses a nitric dissolution of the fuels.
- A specific separation of U and Pu by extraction, using a solvent n-Tri-butylphosphate diluted in an aliphatic diluent (dodecane).
- The scheme of the PUREX Process is reproduced next slide.
FLOWSHEET

FEED SOLUTION

EXTRACTION COLUMN

EXTRACT

UO$_2$(NO$_3$)$_2$·2TBP
Pu(NO$_3$)$_4$·2TBP

SOLVENT
30% Tributyl phosphate and 70% n-dodecane (Japan)
or HPT (France)

RAFFINATE: Fission Products, An(III), Ln(III)
PUREX Process - unit operations

- Fuel decladding
- Dissolution/ feed clarification
- Separations
- Product conversion
- Waste treatment
Shearing
Dissolution
PUREX Process - unit operations

• Dissolution/ feed clarification
  - Nitric acid dissolves UO₂ pellet from cladding hull, forming UO₂(NO₃)₂ in solution
  - Dissolver product contains approx. 300 g/l uranium
  - Releases radioactive off-gas (iodine, krypton, xenon, carbon-14, small amounts of tritium)
  - Undissolved solids are removed by centrifugation before transfer to extraction process
  - The solution is adjusted to 4 M HNO₃ before entering the extraction unit
Extraction Cycle

- The nitric acid dissolution solution of the irradiated fuel contains the totality of uranium and plutonium as nitrate complexes ($\text{UO}_2^{2+}, 2\text{NO}_3^-$) and ($\text{Pu}^{4+}, 4\text{NO}_3^-$) and the fission products.
- The extractant chosen, tri-butyl phosphate (TBP) is diluted to 30% by volume in an aliphatic hydrocarbon, n-dodecane, HPT or a petroleum cut.
- TBP presents a great affinity towards U(VI) and Pu(IV).
- Its affinity towards the FP and other metals is low, which brings a very selective extraction of U (VI) and Pu(IV)
PUREX process - Basic principles

1) Mix Phases
2) Allow to Settle

\[
\text{UO}_2^{2+} + 2\text{NO}_3^- + 2\text{TBP} \rightleftharpoons \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}
\]

\[
\text{Pu}^{4+} + 4\text{NO}_3^- + 2\text{TBP} \rightleftharpoons \text{Pu(NO}_3)_4 \cdot 2\text{TBP}
\]
1st extraction cycle

Feed: Aqueous Solution + Solvent

Mixing: U+Pu+PF*

Settling: U+Pu + Solvent
PUREX process chemistry

Early actinides have multiple oxidation states available in aqueous solution. The PUREX process makes use of this to separate U and Pu from fission products.
The PUREX solvent is typically 30 vol% TBP in a hydrocarbon diluent (dodecane or kerosene).

The extracting power of TBP is derived mainly from its phosphoryl oxygen atom coordinating to metal ions:

TBP is classed as a neutral extractant i.e. it will only extract electroneutral complexes into the organic phase e.g.

\[
\begin{align*}
\text{AnO}_2^{2+} + 2\text{NO}_3^- + 2\text{TBP} & \rightleftharpoons \text{AnO}_2(\text{NO}_3)_2 \bullet 2\text{TBP} \\
\text{An}^{4+} + 4\text{NO}_3^- + 2\text{TBP} & \rightleftharpoons \text{An}(\text{NO}_3)_4 \bullet 2\text{TBP}
\end{align*}
\]
Representation of the extracted $\text{UO}_2^{2+}$ complex with TBP

$$(\text{UO}_2^{2+}, 2\text{NO}_3^-) + 2\text{TBP} \iff \text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$$
PUREX Process- Basic principles

Extraction

Scrubbing

Stripping

Organic Solvent

Separates metal to be recovered
Removes impurities from metal
Recovers product in solution
• During the contact between the organic phase and the aqueous phase, the 2 following reactions take place

\[
(UO_{2}^{2+}, 2NO_3^{-}) + 2TBP \leftrightarrow UO_2(NO_3)_2(TBP)_2
\]

\[
(Pu^{4+}, 4NO_3^{-}) + 2TBP \leftrightarrow Pu(NO_3)_4(TBP)_2
\]

• The reactions are strongly displaced towards right (extraction) if \([NO_3^-]\) is high and towards the left (reextraction) if \([NO_3^-]\) is low

• The choice of HNO\(_3\) allows to predict the direction of the solutes (U(VI) and Pu(IV)) transfer
Solution $U + Pu + FP$

$HNO_3$

$H_2O$

Solvent Wash

Extraction $U + Pu$

$U + Pu$

Reextraction $U + Pu$

Solvent Treatment

$UO_2(NO_3)_2(TBP)_2$

$Pu(NO_3)_4(TBP)_2$

ORGANIC PHASE

AQUEOUS PHASE

3M $HNO_3$

SCRUB = WASH $H_2O$

AQUEOUS PHASE AFTER WASH

$UO_2(NO_3)_2$

$Pu(NO_3)_4$

1st EXTRACTION CYCLE
The 1st decontamination cycle (U + Pu) is presented on the next slide.

The aqueous flow (U + Pu + FP) is contacted with the organic phase in a pulsed column, countercurrent flow.

The first stage is hence a co-decontamination stage during which the U and Pu are removed from most of the FP.

The organic phase charged in U and Pu is then washed by a nitric acid solution in order to scrub from the organic phase the small quantities of FP that was entrained with U and Pu into the organic phase.
After this first extraction column, most of the PF are separated from U and Pu and exit as raffinate.

- U and Pu exit the column as organic phase
- The organic phase is stripped of U and Pu, and the solvent can be recycled after treatment, to eliminate the degradation products $H_2MBP$ (monobutyl phosphate) and $HDBP$ (dibutyl phosphate), formed by the hydrolysis and radiolysis of TBP.
- U and Pu prepurified exit the second column in the aqueous solution.
$UO_2(NO_3)_2$

$Pu(NO_3)_4$

$UO_2(NO_3)_2(TBP)_2$

$Pu(NO_3)_4(TBP)_2$
How to separate U(VI)\textsubscript{org} from Pu(IV)\textsubscript{org}?

• We need to strip Pu(IV) from the organic phase?
• Does Pu(IV) wants to go back to the aqueous phase? No
• So we are going to reduce Pu(IV) to Pu(III) by using a reducer and in the same time we are changing the acidity in the aqueous phase

\[ Pu(NO_3)_4(TBP)_2 \]

1) Change nitric acid concentration from 3M to 0.5M
   Disturb the complex
2) Add to the aqueous phase a reducer to reduce Pu(IV) to Pu(III)
3) Pu(III) will migrate to the aqueous phase

\[ Pu(NO_3)_3 \]

AS A RESULT we have U(VI) still in the organic phase and Pu(III) in the aqueous phase
Reducer for Pu

Several Pu reducer can be used

- Ferrous sulfamate (Fe^{2+}, 2NH_2, SO_3^-)
  \[ \text{Pu}^{4+} + \text{Fe}^{2+} \rightleftharpoons \text{Pu}^{3+} + \text{Fe}^{3+} \]

- Uranium (IV)*
  \[ 2\text{Pu}^{4+} + \text{U}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons 2\text{Pu}^{3+} + \text{UO}_2^{2+} + 4\text{H}^+ \]

- Hydroxylamine nitrate (NH_3OH^+, NO_3^-)*
  \[ 2\text{Pu}^{4+} + 8\text{NO}_3^- + \text{NH}_3\text{OH}^+, \text{NO}_3^- \rightleftharpoons 2\text{Pu}^{3+} + \frac{1}{2}\text{N}_2\text{O} + \frac{1}{2}\text{H}_2\text{O} + 3\text{H}^+ + 9\text{NO}_3^- \]

(*: the most used)
The second step consists in separating U/Pu realized by liquid-liquid extraction (see next figure).

- It exploits the different redox properties of U and Pu.
- In the first extraction column, the co-extraction U(VI)/Pu(IV) is again performed.
- After washing, the organic phase loaded in U(VI)/Pu(IV) is injected into the second column where it is contacted with an aqueous solution containing a specific Pu reducer.
- U/Pu splitting takes place by reductive stripping of the plutonium.
- Indeed, Pu(IV) is reduced to Pu(III) and migrates into the aqueous phase, the organic phase containing U(VI) is treated by water (countercurrent) to realize the extraction of U(VI) into the aqueous phase.
- From this step, U and Pu will go in separated purification cycles (2 more cycles)
7- Fabricating recycle fuel for added energy production
Plutonium

- Plutonium is precipitated from the purified aqueous solution by addition of oxalic acid

\[
Pu^{4+} + 2H_2C_2O_4 \xrightleftharpoons{H_2O} Pu(C_2O_4)_2 - 6H_2O + 4H^+
\]

- The plutonium oxalate, after filtration is calcinated at 450°C, which gives PuO₂

\[
Pu(C_2O_4)_2 \cdot 6H_2O \xrightarrow{450°C} PuO_2 + 6H_2O + 4CO_2
\]
Final conditioning for Pu - MOX Fuel

Plutonium(2)

• The plutonium recycle strategy currently adopted by many countries consists in the preparation of mixed fuels (U, Pu)O$_2$ (~7% Pu) called MOX for LWR reactors.

• A plant is built in France, MELOX, with a production capacity of 100 tons of heavy metal per year.

• A plant is being constructed in USA (August 2007), the MFFF facility, Savannah River Site.
Uranium Recycling

- A purified uranyl nitrate solution is concentrated by distillation and the concentrated solutions (U > 400 to 500 g/L) are essentially stored waiting to be reused.
- A fraction can be recycled though but requires a new enrichment phase.
Average time operations for a PWR cycle at the equilibrium

- Pu U- recycling waste
- Reprocessing of the irradiated fuel: 24 months
- Pu Extraction: 2 months
- Reprocessing: 9 months
- Conversion: 4 months
- Enrichment: 6 months
- New Fuel Elaboration: (21.5 months)
- Fabrication: 7 months
- Storage: 4.5 months
- Reactor Loading: (21.5 months)

Reactor stays in the reactor over a period of 36 months
8 - Cooling of used nuclear fuel or reprocessing waste, and its eventual transport to a repository for disposal in secure long-term storage.
Treatment of Liquid waste
## Nuclear Waste Classification

<table>
<thead>
<tr>
<th>IAEA</th>
<th>FRANCE</th>
<th>FINLAND</th>
</tr>
</thead>
<tbody>
<tr>
<td>HLW/Used Fuel</td>
<td>HLW</td>
<td>HLW/Used Fuel</td>
</tr>
<tr>
<td>ILW</td>
<td>ILW (LL)</td>
<td>Operating Waste ILW</td>
</tr>
<tr>
<td></td>
<td>ILW(SL)</td>
<td></td>
</tr>
<tr>
<td>LLW</td>
<td>LLW</td>
<td>Operating Waste (LLW)</td>
</tr>
<tr>
<td>Exempt Waste(VLLW)</td>
<td>VLLW</td>
<td>Decommissioning waste (Nuclear reactor)</td>
</tr>
</tbody>
</table>
Organic solvent recycling
Industrial method for organic solvent recycling

- 1- Solvent wash with sodium carbonate and caustic soda
- 2- Distillation
- 3- residue mineralized.

The basic effluents generated by the alkaline wash are concentrated by distillation and stored.

These flows can be sent toward the high activity effluents and vitrified, mixed with FPs.

- Pay attention to Na+ ions because of a glass specification to respect (related to long term glass behavior) (Viscosity lower and corrosion faster)

- Since La Hague design, successful targeted efforts to reduce Na in the effluents.

- Those treatment are continuous at La Hague, thanks to diluent wash
- ==> solvent quality is always kept at the top, no batch operation of solvent renewal, like in older plants
High Level Waste
Vitrification
Vitrification

• The final storage of FP cannot be conceived without introducing first these FPs into a solid matrix which possesses the best warranty for a long and sustainable stability over the time and the best confining coefficient values of the radioactive material towards leaching of water.

• The technique used in France and in other countries is vitrification of FP.
HLW is vitrified

Two-step calciner / hot crucible vitrification process
Operations of vitrification

- Final evaporation of the concentrated and formation of solid nitrates
- Calcination of nitrates and formation of the corresponding oxides
- Vitrification of the oxides by heating after introduction of the glass frit
- Pouring of active glass in steel containers
- Welding of the lid
- Decontamination of containers by high pressure water
- Transport and storage of glass blocks in aerated wells
Temporary Storage of Vitrified Wastes

- Vitrified wastes are poured into stainless steel containers, each holding 150 L.
- Each workshop (R7 and T7) can treat 60 L/h of wastes and produce 600 containers or (240 t or 90 m³ of glass) per year.
- R7 can store 4,500 containers and T7, 3600 containers.
- E-EV-SE, a modular extension of T7, can store 4000 containers without increasing its present capacity.
- Areva plans to construct an extension of E-EV-SE for 2012. The new hall will have space for 4212 containers. Construction began in October 2009.
- At the end of 2007, a total of 9,088 containers representing a volume of 1,488 m³ of vitrified waste were stored at La Hague.
- The strong thermal emission of these wastes necessitates intermediate storage of at least thirty years before definitive storage.

http://www.francenuc.org/en_sites/Inorm_hague2_e.htm
Vitrified waste forms are stored at the site in France

Marcoule

La Hague
Vitrified waste in France

• End waste from French used fuel is temporarily stored in a specific hall where it is monitored.
• This waste should be finally disposed of in a geological formation (clay) ~2025.
• This end waste represents 20 grams per year per French inhabitant which is the same weight of a tow Euro coin.
Treatment of Solid Wastes

- Compaction
- Incineration
- Melting
- Chemical, thermochemical, biochemical decomposition
Treatment of ILW and LLW

• Besides the organic effluents generated in a recycling facility, aqueous effluents with medium or low activity are generated.
• These effluents are issued from:
  - Fuel Storage pools
  - Analytical Labs
  - Decontaminations activities
• Treatment is by evaporation and concentration.

• Concentrates are sent to the concentration unit of higher activity, up to vitrification, final distillates are sent and released to the sea. An intermediate stream is decontaminated nitric acid, recycled in the facility.
Conditioning LLW - Cementation

- The most commonly used process for LLW is cementation, which entails incorporating waste in a hydraulic binder-based material composed of calcium aluminates and silicates.

- Many advantages:
  - Good mechanical strength,
  - Easy to use
  - Inexpensive additives can be added to adapt its chemical properties to the waste to be conditioned
  - Cement matrix acts as a diffusion barrier and provides sorption and reaction sites
  - Suitable for sludges, liquors, emulsified organic liquids and dry solids
  - Alkaline chemistry which ensures low solubility for many key radionuclides

Resistance to waste-induced damage does not exceed a few thousand years.
Cladding waste is compacted

- Compressing solids into containers or boxes to reduce the volumes
- Different types of compactors: Compressive forces between 100 and 500 kN
- Volume reduction factor 2-5
Compaction at La Hague

- Prior to 1995, the hulls and end pieces coming from PWR fuel reprocessed in UP3 and UP2-800 were cemented and then stored.
- Pieces of Cladding (Hulls) and end pieces from nuclear used fuel shearing are compacted by means of a press with a 2,500 tons capacity
- Volume reduced: 1/5 of initial volume
Compacted Waste at la Hague

- The compacted waste is in the form of disks and is stored in CSD-C canisters (universal canisters) identical in shape and size to canisters for vitrified waste.
- The compact hulls, end pieces and technological waste necessitate deep underground disposal (Bures ~ 2025)

http://www.francenuc.org/en_sites/lnorm_hague2_e.htm
Waste distribution by volume and activity, projection until 2020

<table>
<thead>
<tr>
<th>Type</th>
<th>vol%</th>
<th>Activity</th>
<th>Cumulative volume (m³) until 2020</th>
</tr>
</thead>
<tbody>
<tr>
<td>LLW</td>
<td>95%</td>
<td>&lt;0.1%</td>
<td>1 200 000</td>
</tr>
<tr>
<td>ILW</td>
<td>4%</td>
<td>3%</td>
<td>55 000</td>
</tr>
<tr>
<td>HLW</td>
<td>0.3%</td>
<td>97%</td>
<td>3 600</td>
</tr>
</tbody>
</table>

A definitive industrial management route already exists for more than 90% of the total waste volume produced.
Some numbers

• A typical 1000 MWe light water reactor will generate (directly and indirectly)
• 200–350 m³ low- and intermediate-level waste per year.
• It will also discharge about 20 m³ (27 tonnes) of used fuel per year, which corresponds to a 75 m³ disposal volume following encapsulation if it is treated as waste.

• Where that used fuel is reprocessed, only 3 m³ of vitrified waste (glass) is produced, which is equivalent to a 28 m³ disposal volume following placement in a disposal canister.

• In OECD countries, some 150 millions m³ of toxic wastes (density of 2) are produced each year, but conditioned radioactives wastes amount to only 0.081 millions m³ per year.
Waste volumes conditioned in UP3
(high level long-lived waste after packaging)

Percent of Pu in final waste (compared with initial Pu content in fuel assembly)

<table>
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<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>m³/tU</td>
<td>0.1%</td>
<td>0.1%</td>
<td>0.1%</td>
<td>100%</td>
</tr>
</tbody>
</table>

- Bitumen
- Glass
- Compacted hulls, end-fittings and technological waste
- Cement-solidified hulls and end-fittings
- Conditioned spent fuel

AREVA, Tom Coleman, ANS Regional Presentation, Idaho Falls, 2007
National policies on used nuclear fuel

Courtesy AREVA
The US faces a choice today:

- Should we continue down the same path with once through fuel cycle which has been the option for the last 30 years with a repository-only solution,

- Or should we take the path of our allies and adopt reprocessing

- Or should we lead nuclear innovation with full recycling?

E. Loewen, Testimony before the subcommittee on energy and Water Development 28 APR 2010
“The best solution for a country depends on its plans for the future use of nuclear energy and the present and future fuel cycle technologies”