IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

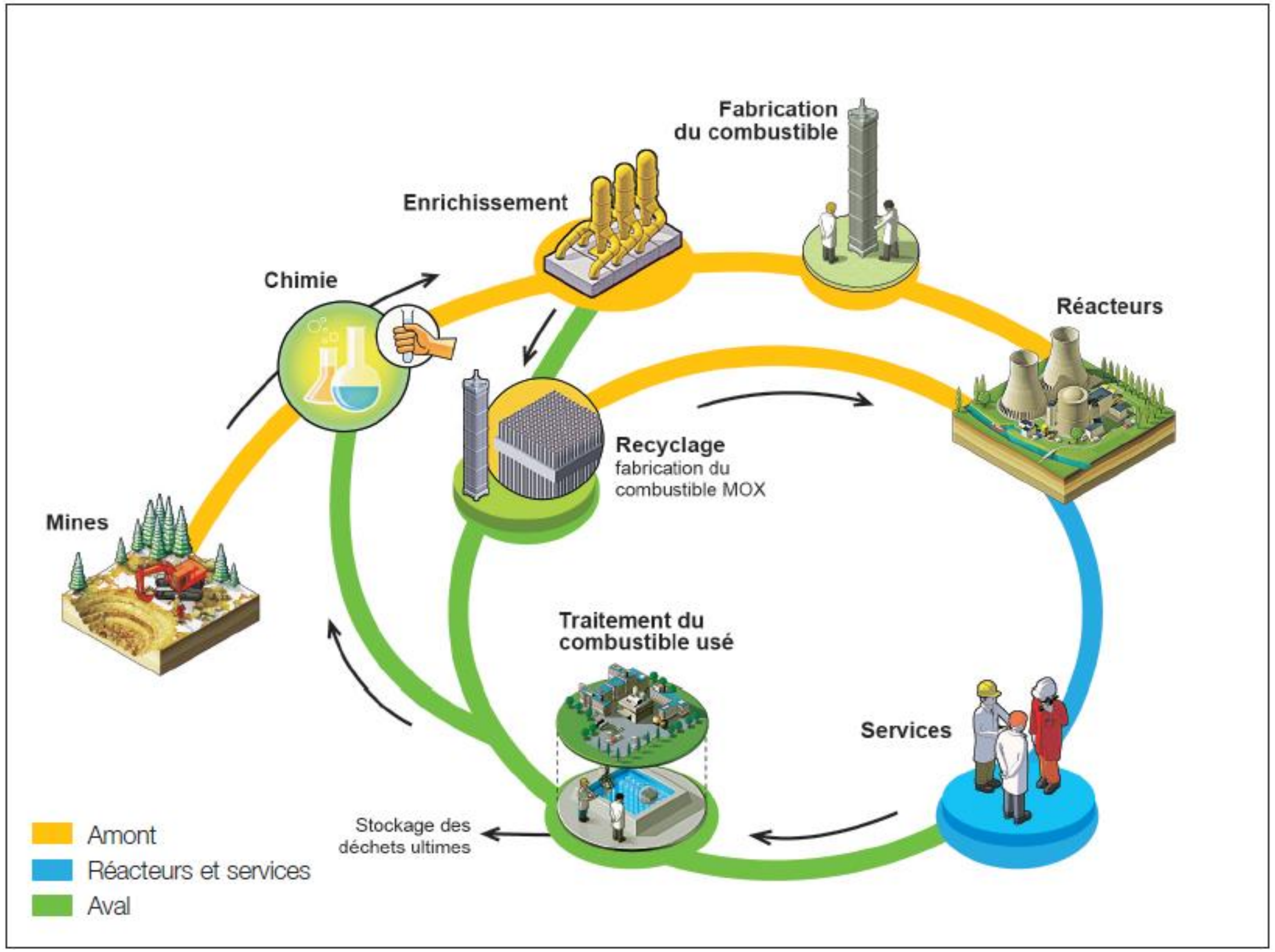
Subatech

The Nuclear Fuel Cycle and Environmental Impact

Abdesselam ABDELOUAS
Professor of Radiochemistry
SUBATECH department

Abdesselam.Abdelouas@subatech.in2p3.fr

Nuclear Fuel Cycle



IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Major steps of fuel cycle

- ✓ Uranium extraction
- ✓ Purification and uranium concentration
- ✓ Fuel fabrication and element assembly
- ✓ Fuel irradiation in reactor
- ✓ Temporary storage of irradiated fuel
- ✓ Fuel recycling
- ✓ Radioactive waste management

The 2 options of the cycle

- ✓ When the spent fuel is considered as waste, the cycle is « open ». It is the case of Sweden, Finland, Spain, and Canada.

- ✓ When the spent fuel is recycled, the cycle is closed. Plutonium and uranium are separated for reuse. It is the case of France, Japan, UK, Belgium…

Specificities of the cycle

To obtain enriched uranium 2 steps are required:

✓ Natural uranium conversion after extraction, purification/concentration. Uranium is converted into UF_4 and UF_6.

✓ Uranium enrichment in order to increase the isotope fraction of U-235 necessary for the fission reaction. UF_6 is enriched in U-235.

Uranium

Can be found in:

- ✓ Humain body
- ✓ Plants
- ✓ Animals
- ✓ Food

Use:

- ➢ Energy
- ➢ Military applications

Uranium in Earth

Natural uranium :
U-238: 99,284 % ; U-235: 0,711 % ; U-234: 0,005 %
($T_{1/2}$: 4,5 10^9 y) ; ($T_{1/2}$: 7,1 10^8 y) ; ($T_{1/2}$: 2,5 10^5 y)

Atmosphere
10^{-5} ppm

Surface water
10^{-3} ppm

Oceans
3,3 10^{-3} ppm

Lithosphere
4 ppm

Carbonates 0,1-9 ppm
Phosphates 1-350 ppm
Shales 1-13 ppm
Bauxites 3-27 ppm
Granit 4 ppm
Coal 10 000 ppm

Mantle
0,18 ppm

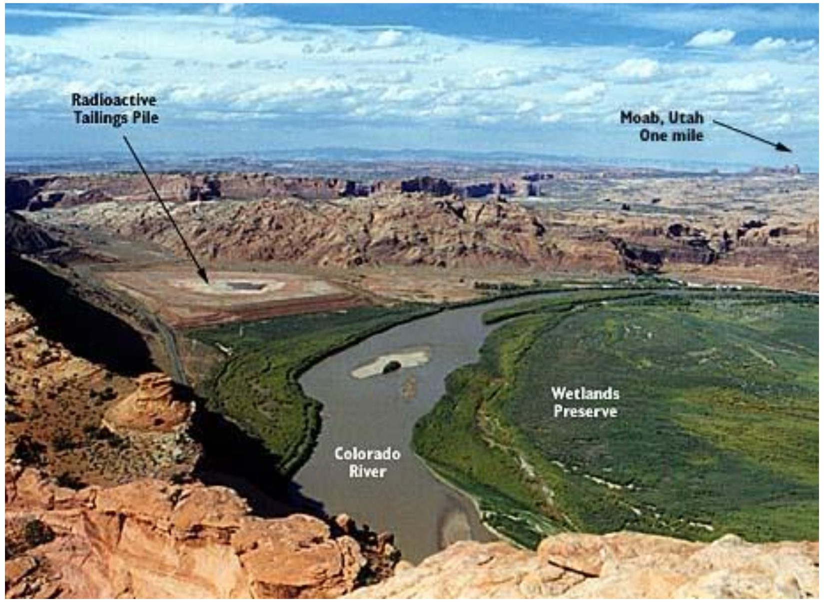
IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Distribution of uranium in environment

- Uranium natural release from uranium rocks

- Industrial release

1. Fuel cycle (mines, mill tailings, enrichment, reprocessing)
2. Weapons (bombs, shells)
3. Coal combustion
4. Use of phosphate fertilizers



Colorado uranium site

Mill tailings

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Uranium mineralogy

Autunite

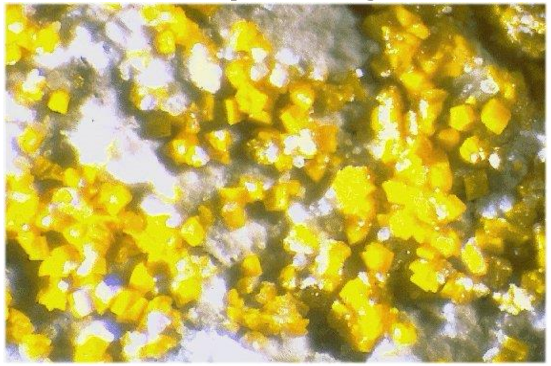
$Ca(UO_2)_2(PO_4)_2.10H_2O$

High solubility

Schoepite

$UO_3.2H_2O$

$U^{4+} = U^{6+}$ (uranyl: $U^{6+}O_2^{2+}$) $+ 2e^-$



Carnotite

$K_2(UO_2)_2(VO_4)_2.3H_2O$

Uraninite

$U^{4+}O_2$

Low solubility

Pitchblende

$U_2O_5.UO_3$ ou U_3O_8

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Uranium stocks

- ✓ Australia 667,000 tonnes – 28%

  Olympic Dam, Beverley Mine, et Honeymoon Mine (Australie)

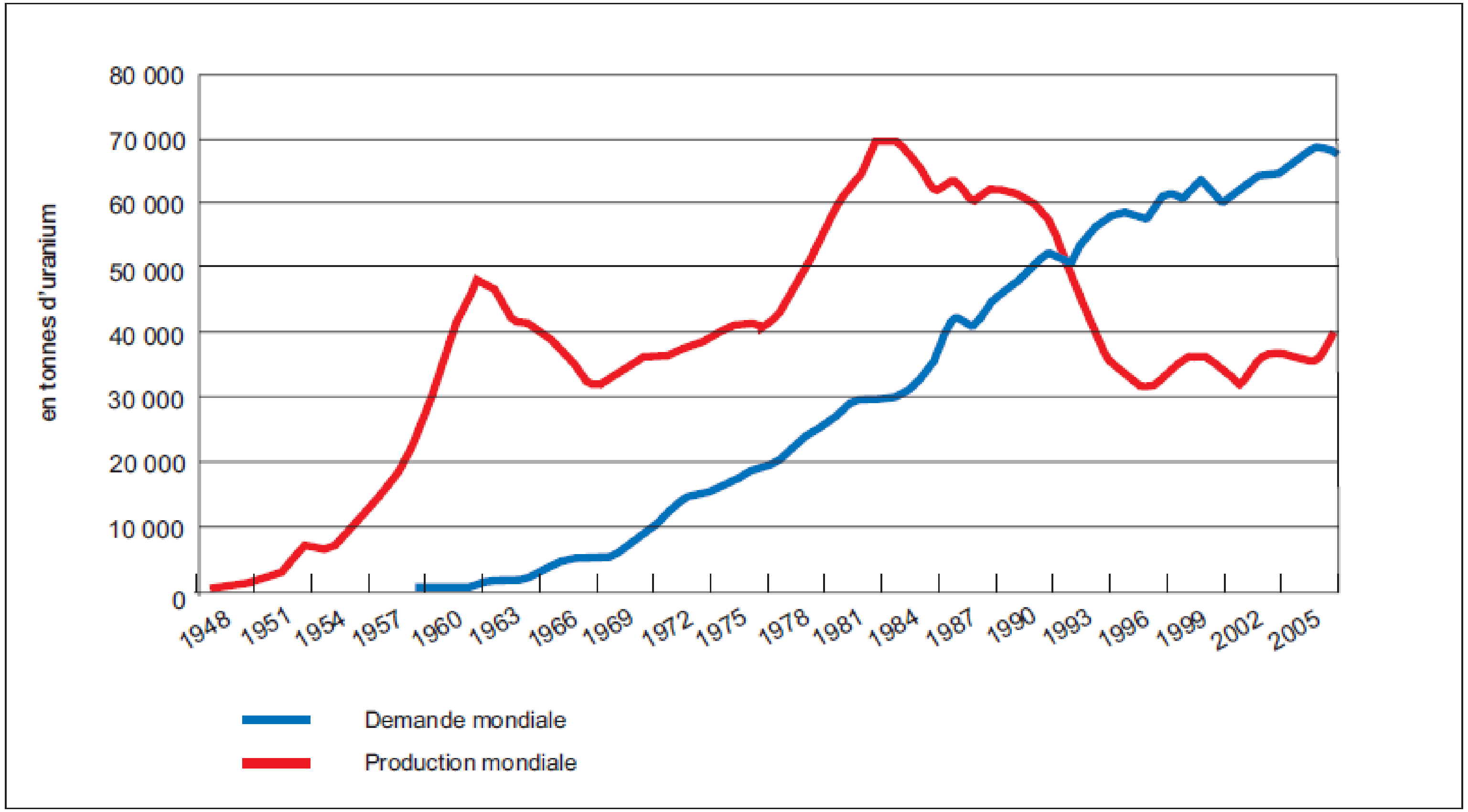
- ✓ Canada 326,000 tonnes – 14%

  Northern Territories et Ontario

- ✓ United States – 3%

  Operations à Utah, Wyoming, New Mexico, et Texas

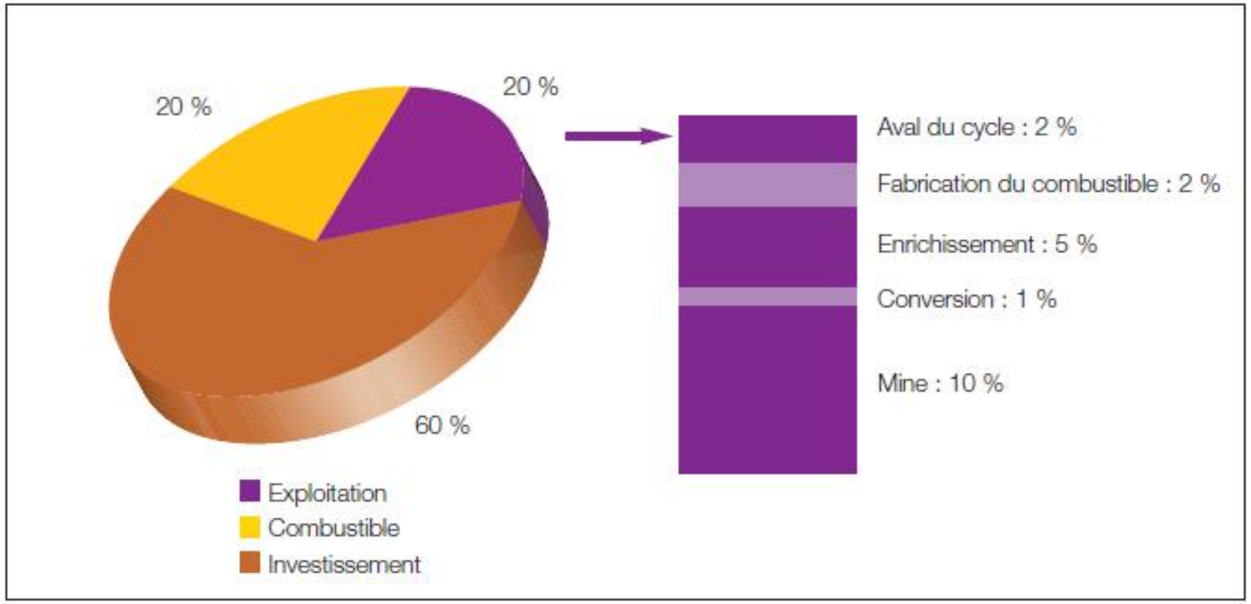
Uranium demand



World – Evolution of demand and production – after AREVA 2007.

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

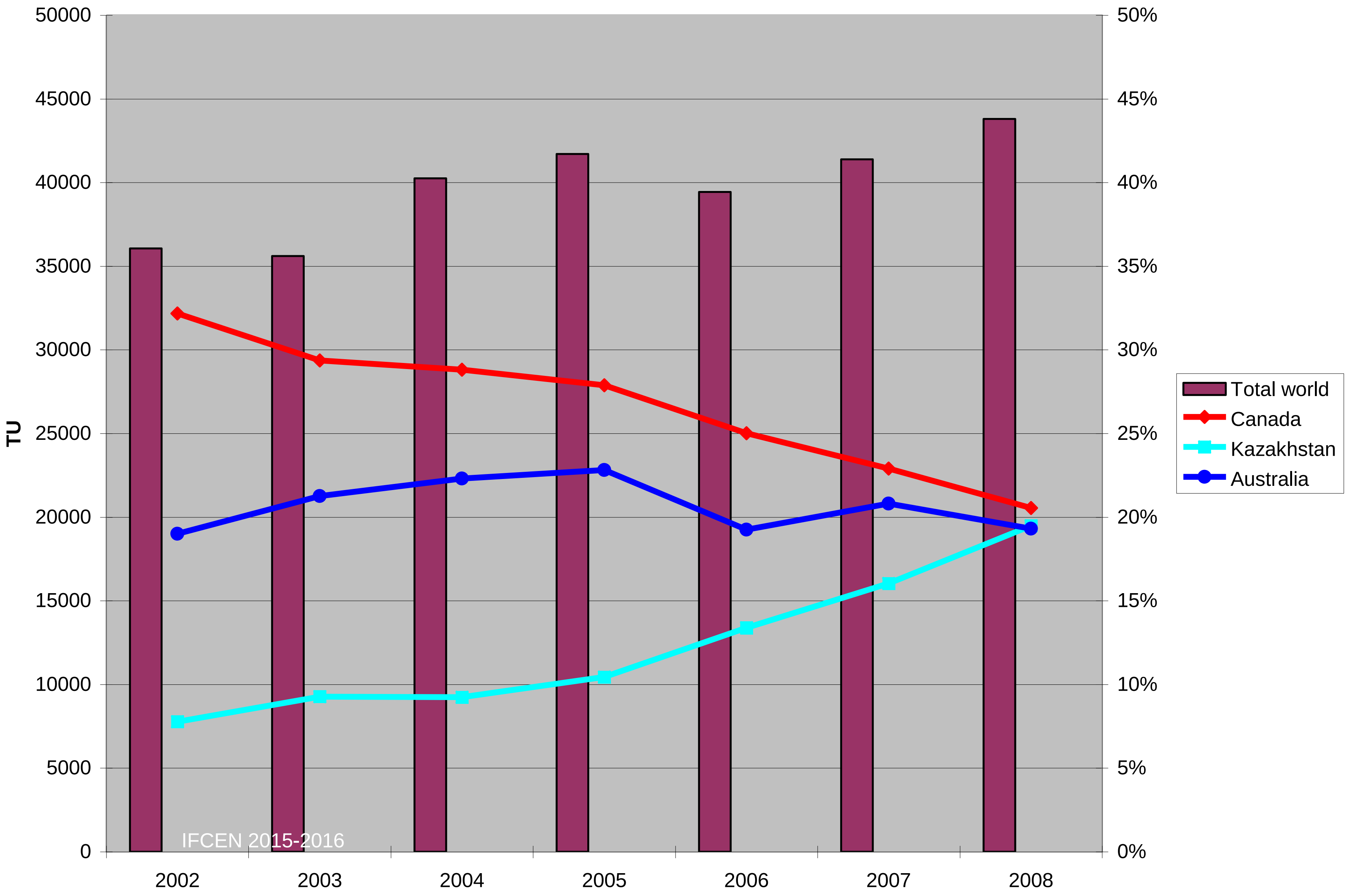
Production cost



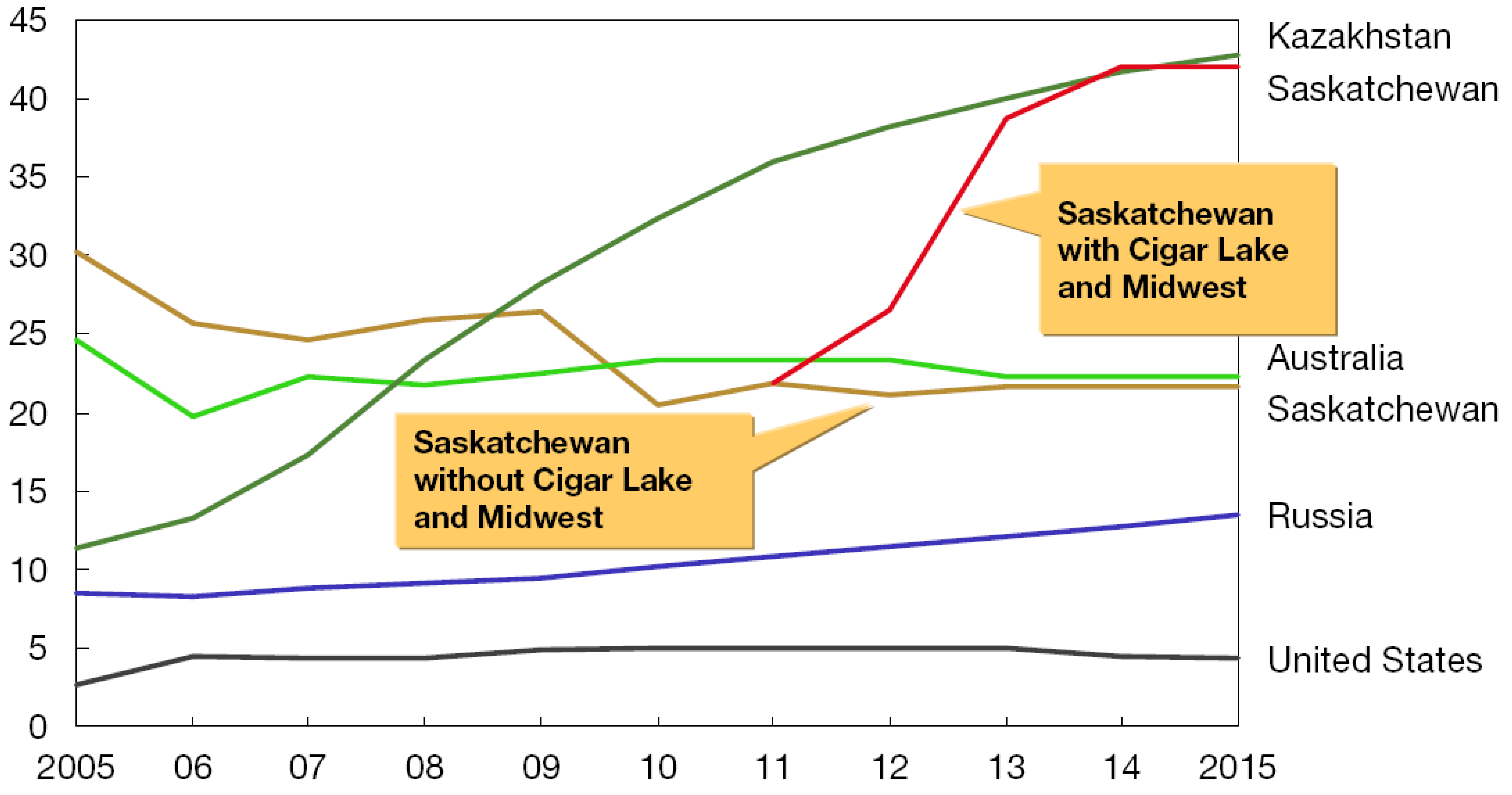
World average – production cost of nuclear electricity for PWR – after AREVA 2007.

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Uranium production

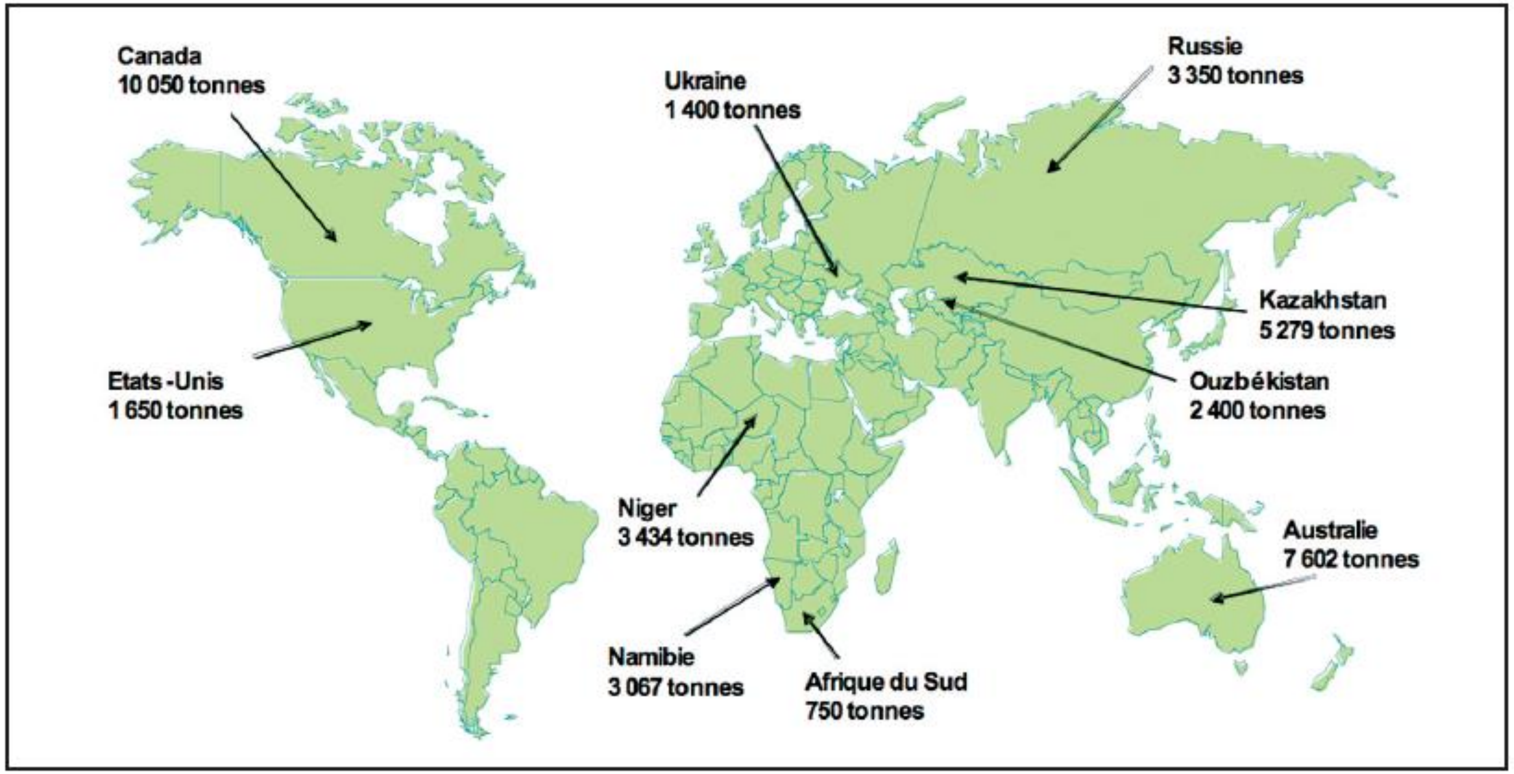


Uranium production



Source: UxC, August 2008

Uranium production



World – Main countries producing natural uranium – after AREVA 2007. In 2006: 41000 tonnes.

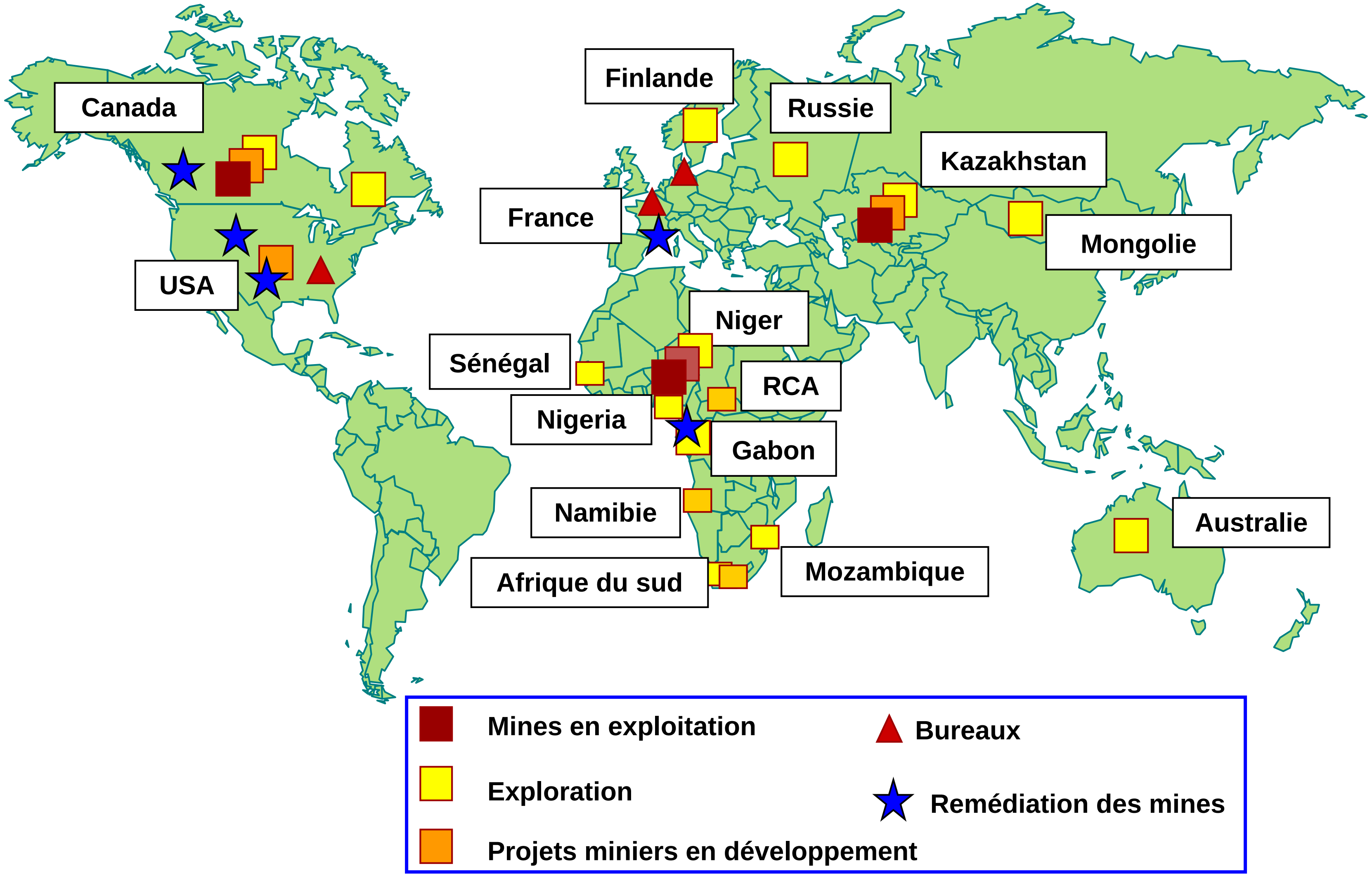
IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

ORANO in the world
Nuclear weapons recycling

- ✓ ORANO and Cameco involved in weapons recycling.
- ✓ 15,294 nuclear war heads eliminated in 2009.

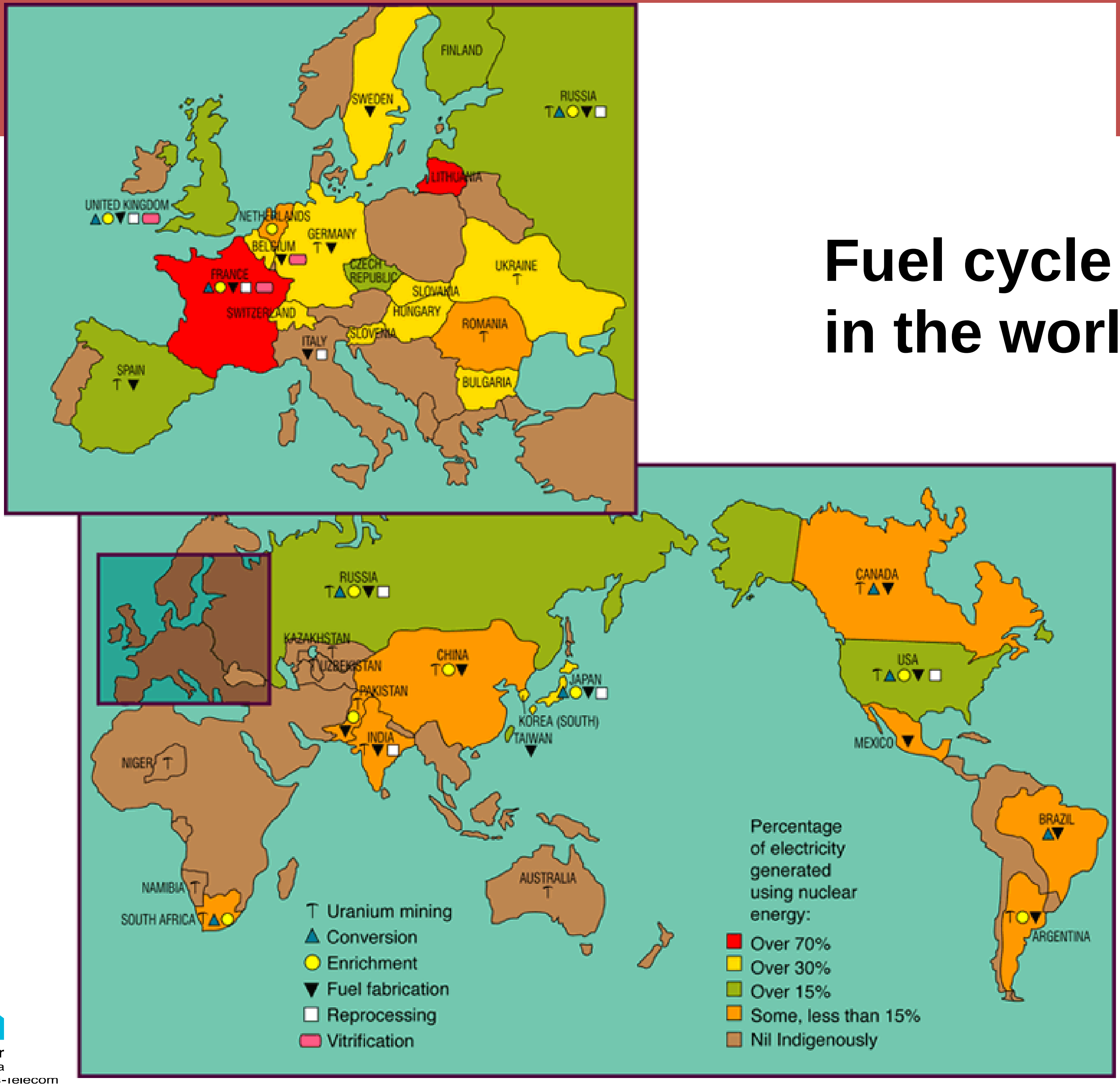
IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

ORANO in the world Uranium Exploration and Extraction



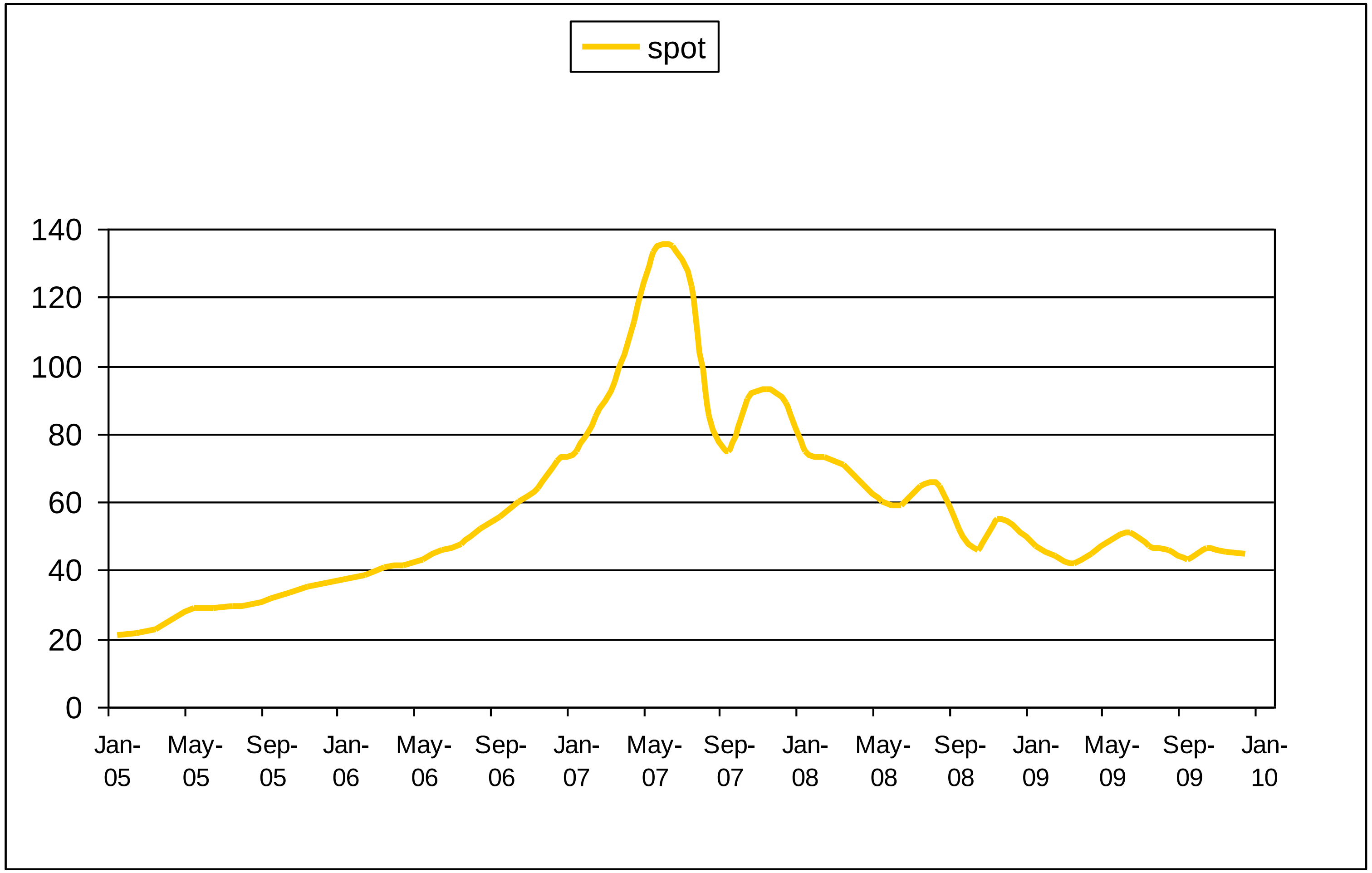
IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Fuel cycle installations in the world

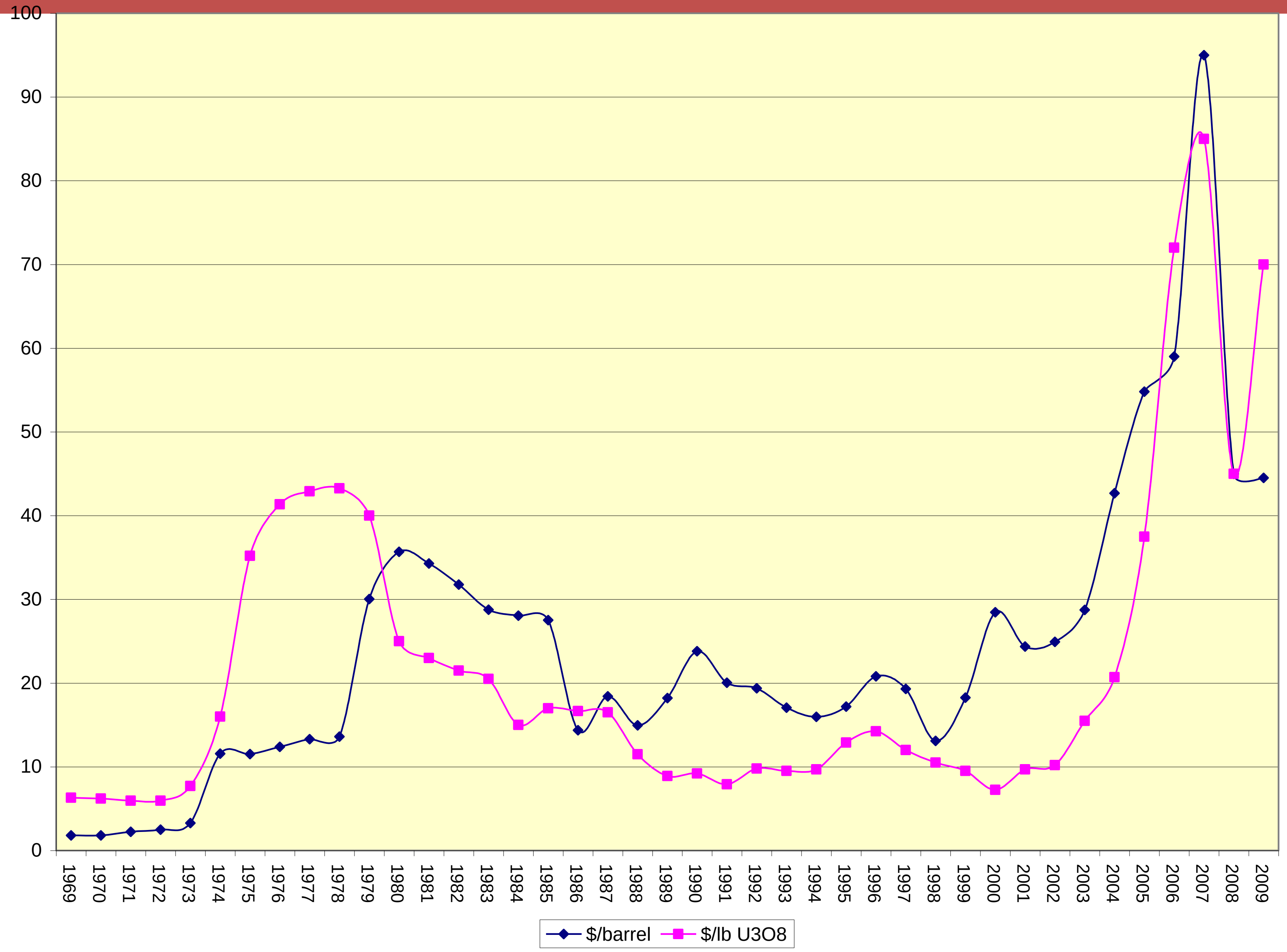


IMT Atlar
Bretagne-Pa
École Mines-Telecom

Uranium market (in $)

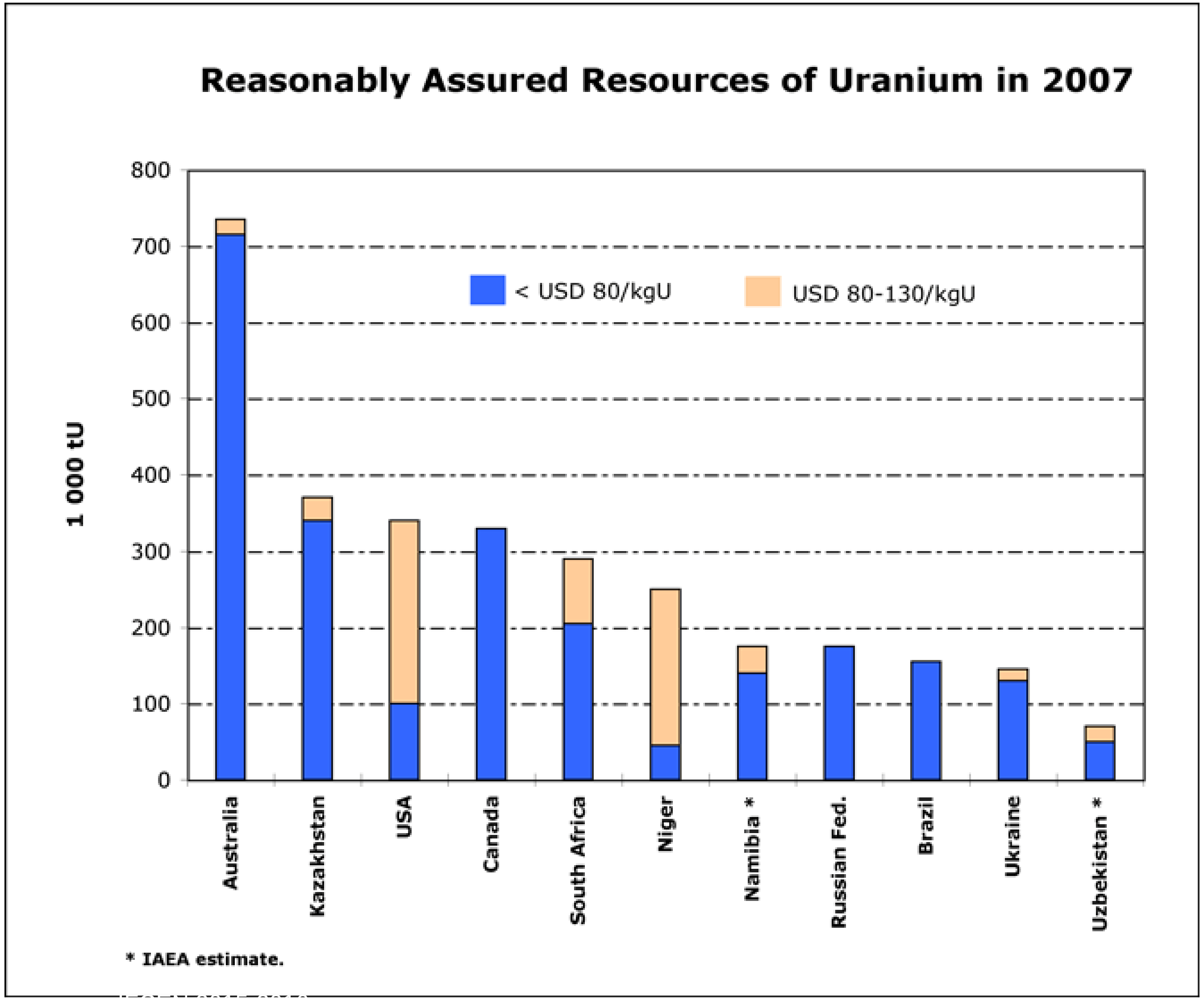


Uranium price vs. oil (in $)



IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Uranium ressources



Life Cycle of uranium mine

EXPLORATION

EXPLOITATION

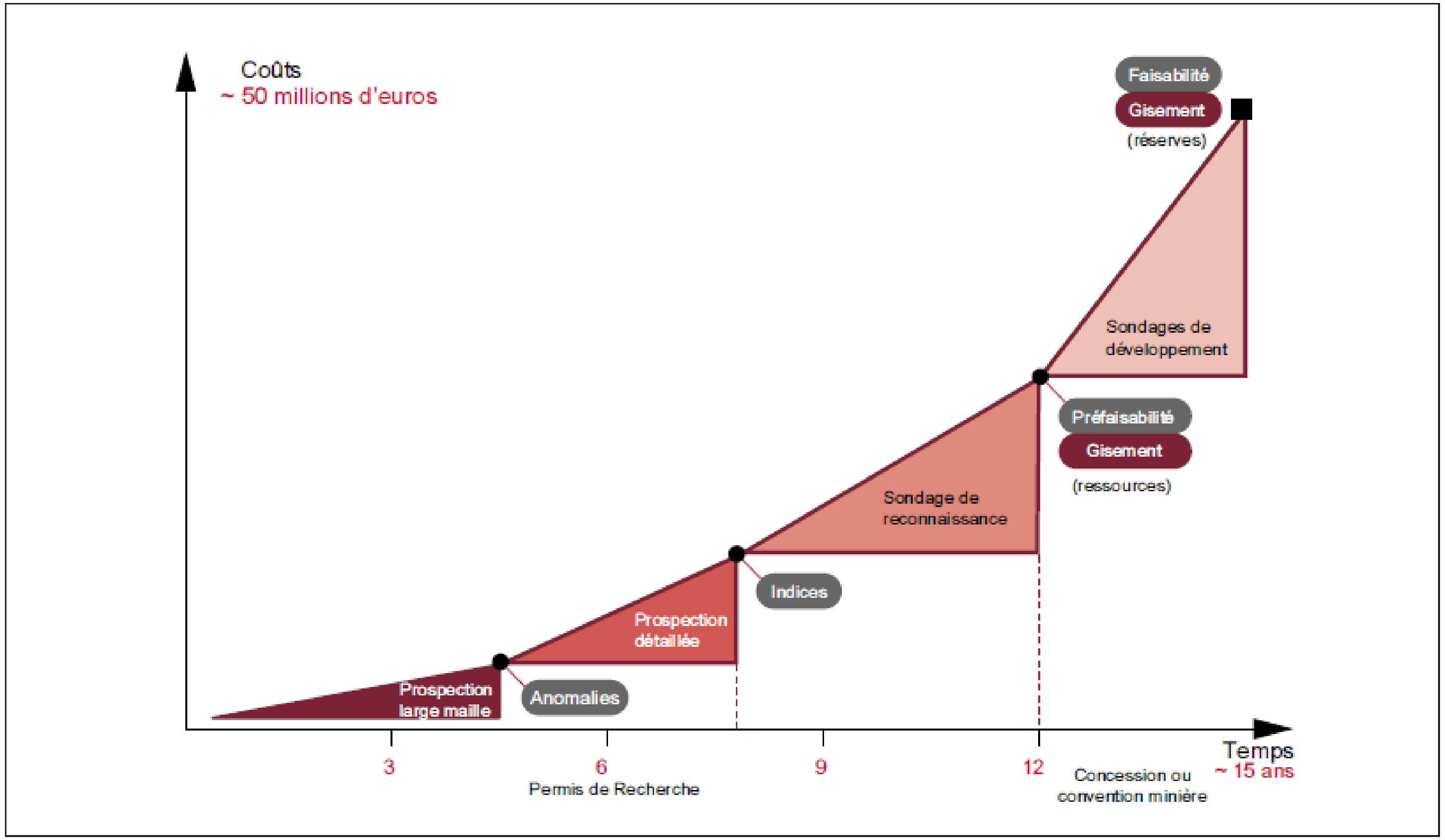
REMEDIATION

Explor – ***Dévelop*** – ***Extraction*** – ***Treatement*** – ***Remediation***

- **Exploration costs**
- **Development costs** : prefaisability, faisability, environnemental impact, ressources estimation
- *Direct Cost: man power, chemical products, materials, energy, transport*
- **Taxes, environmental costs**
- **Remediation costs**

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Mine prospection costs



Costs of mine prospection to the exploitation as a function of time – after AREVA 2007.

ORANO mining activities

ORANO activities include :

- In **Canada**, where AREVA holds shares in a few projects such as **Cigar Lake mine**.

- In **Niger**, with high prospectives in the uraniferous area of Arlit. AREVA has been granted 4 exploration permits from the government.

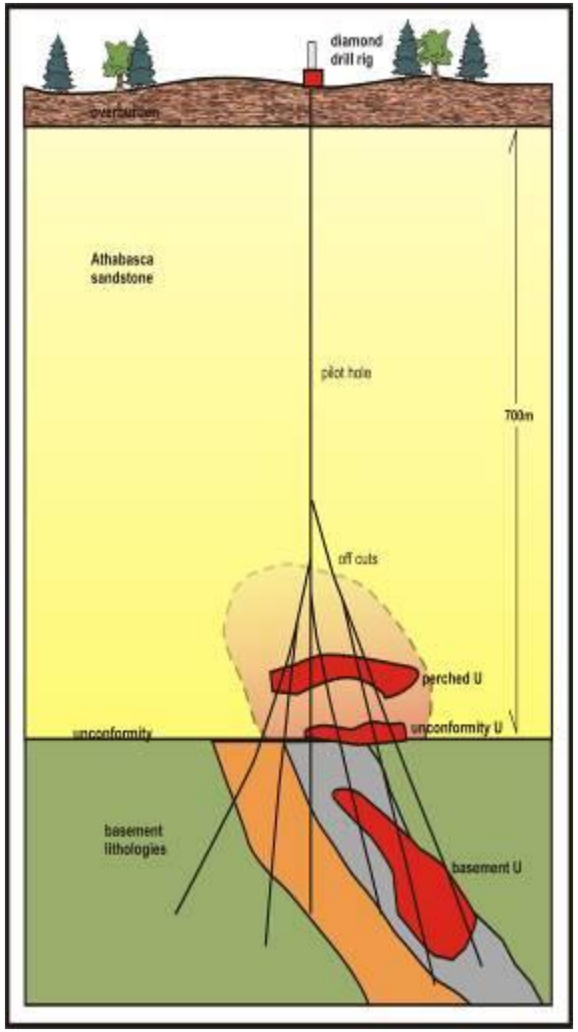
- In **Kazakhstan**, where operation of factory of **Muyunkum and Tortkuduk** started in2006 and 2007 and exploration continues to discover new uranium depoists.

Drilling in Imouraren site in Niger

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

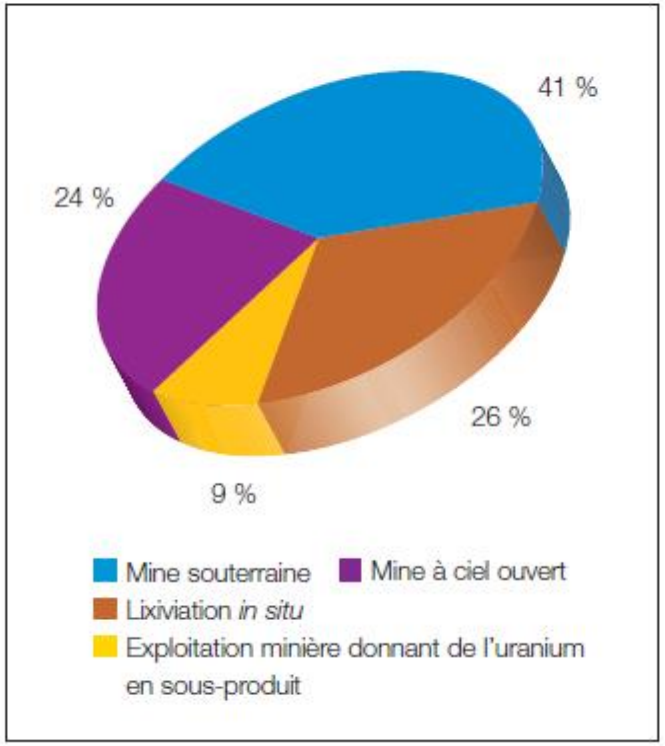
Uranium exploration

A new drilling technique developed ORANO



IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Origin of natural uranium



Underground mine

Surface mine
(Open pit mine)

In situ leaching

Surface mines

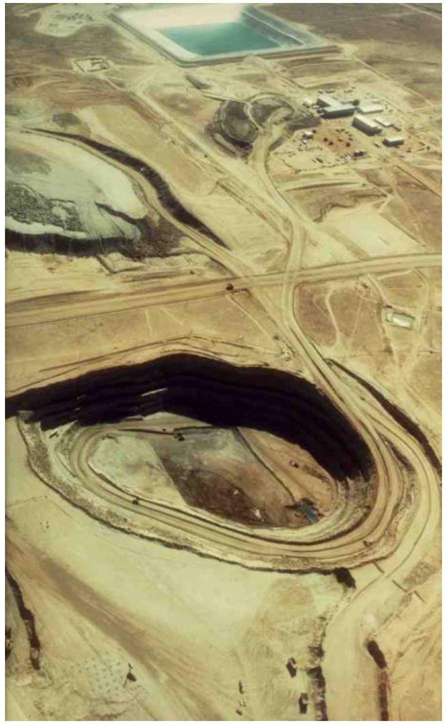
Surface mines require:

- ✓ Surveillance and environmental impact evaluation
- ✓ Extraction of important volume of rock
- ✓ Uranium is extracted and transported for treatment

↓

Impact environnemental important

Surface Mines



Important environmental disturbance

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Underground mines

- ✓ If the ore is deep for surface exploitation it can be exploited underground,
- ✓ Tunnel digging and ore excavation.
- ✓ Then, the uranium is transported for treatment

↓

Less waste compared to surface mining.

Underground mines

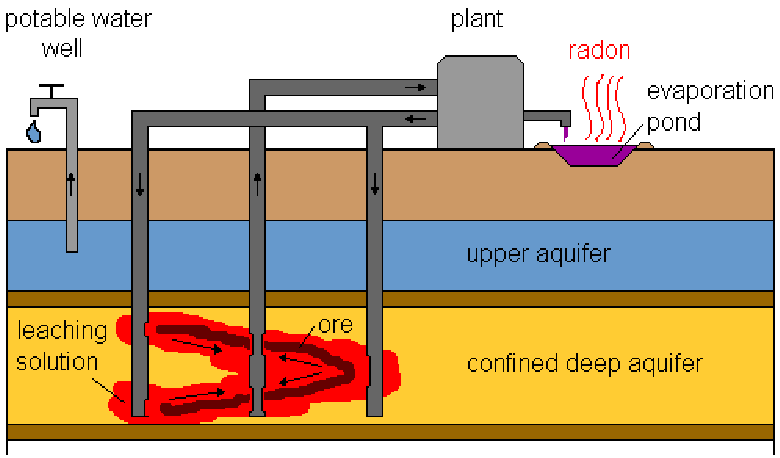
Uranium ore extraction in Jouac (Haute-Vienne), the last mine in France, which stopped in June 2001.

Australia

In-situ leaching

- ✓ More and more used because of the low environmental impact.
- ✓ The low cost permits the exploitation of less concentrated ore.
- ✓ It is possible in permeable rocks (sandstone).

In-situ leaching



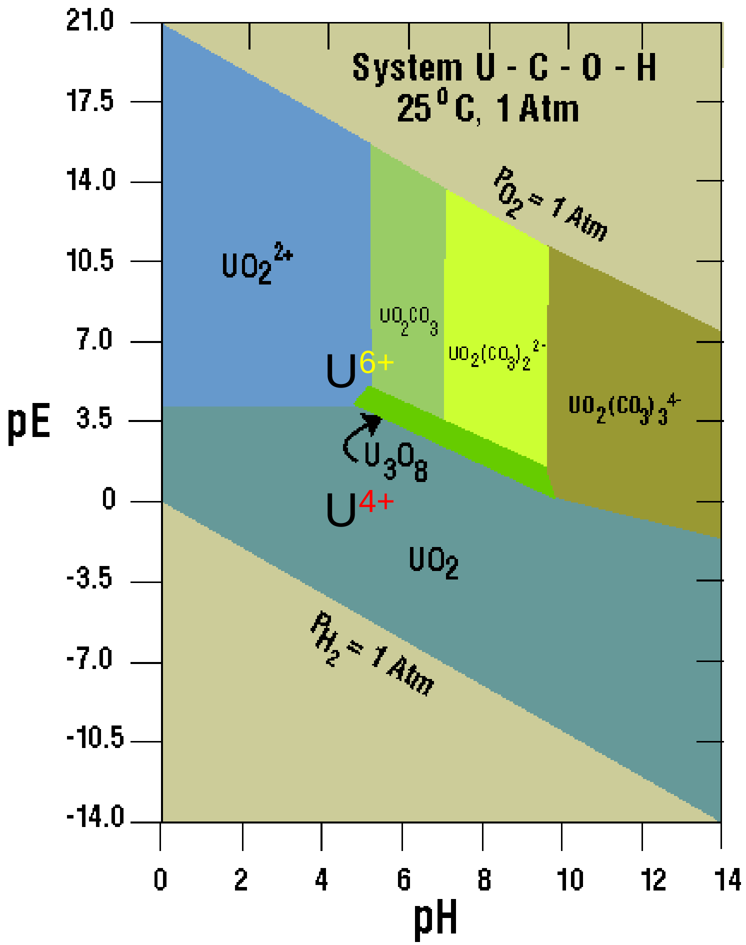
- ✓ The oxidized ore is dissolved in situ
- ✓ The production wells pump the uranium to the surface
- ✓ The uranium is extracted from the solution, which will be reused.
- ✓ The uranium liquor is precipitated to form the yellow cake.

In-situ leaching

Surface treatment of uranium ore

Uranium chemistry

- U(VI) in oxic environment ; highly soluble
- U(IV) in reducing environment; insoluble phases
- Speciation in solution: Eh-pH, U-concentration, complexants (carbonate, sulfate, phosphate, organic ligands)



$U^{4+}O_2 + 1/2O^0_2 \rightarrow U^{6+}O_3$ (oxidation)

$CaCO_3 + H^+ = HCO_3^- + Ca^{2+}$

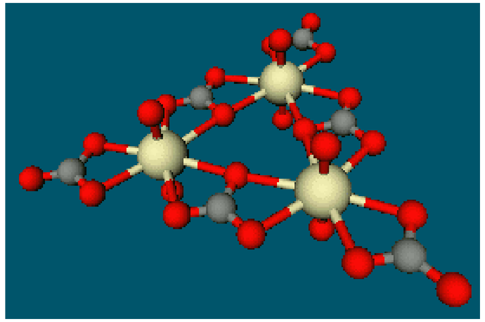
$1/2O_2 + 2e- = O^{2-}$ (oxidizing conditions)

$H_2 = 2H^+ + 2e-$ (reducing conditions)

$U^{6+}O_3 + 3H_2SO_4 = 4H^+ + H_2O + UO_2(SO_4)_3^{4-}$

(Dissolution)

$U^{6+}O_3 + 2Na_2CO_3 + 2H^+ = 4Na^+ + H_2O + UO_2(CO_3)_2^{2-}$



$(UO_2)_3(CO_3)_6^{6-}$

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Uranium ore

Crushing and milling

Pulp

Chemical treatment

Acidic ore (containing SiO_2)
by H_2SO_4 + $NaClO_3$

$UO_2(SO_4)_3^{4-}$

Basic ore (containing $CaCO_3$)
by Na_2CO_3 + $NaHCO_3$

$UO_2(CO_3)_2^{2-}$

Residues separation and purification by extraction

Uranium liquor

Precipitation & filtration + drying

by NH_4OH

$(NH_4)_2U_2O_7$

Uranate

or by $Mg(OH)_2$

MgU_2O_7

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Ore treatments

The choice of sulfuric acid coupled with sodium chlorate:

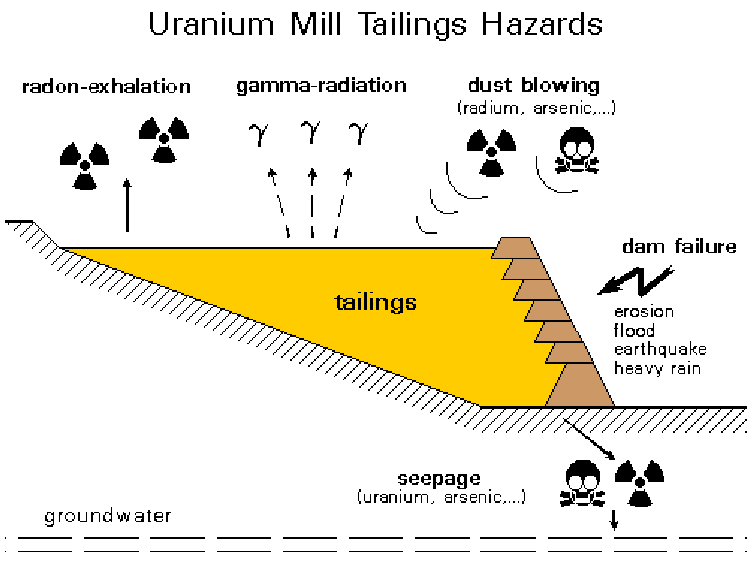
- Dissolve uranium without attacking the rest of the rock.
- Less expensive and less corrosive with respect materials.
- Sodium chlorate is a strong oxidant.

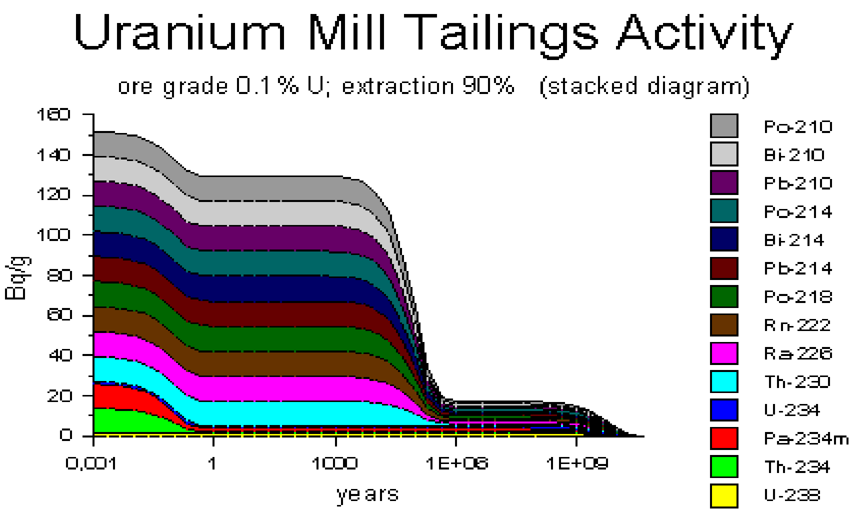
Sodium carbonate coupled with oxygen for a carbonate-rich ore:

- A difficult process because of high pressure and temperature.

Mill tailings

- ➢The recoverable fraction is about 1%, the rest is waste.
- ➢ The large volume to be hundled creates environmental problems.
- ➢ Oxidation and leaching of tailings cause groundwater contamination.

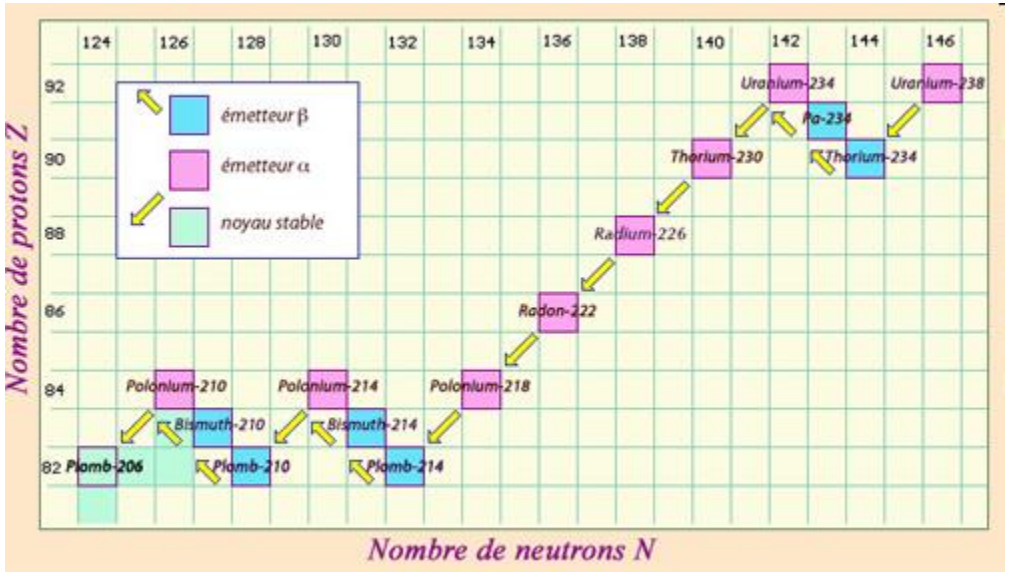




IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Mill tailings

- ✓ Contamination
  - ➢ Acid drainage water
  - ➢ $Radium^{226}$ and $Radon^{222}$
  - ➢ U and other metals
- ✓ Remediation



IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Mill tailings

Mill tailings leaching leads to dissolution of toxic metals originally present in ore: molybdenum, vanadium, selenium, iron, lead, arsenic…

The result of ore treatment is a sludge containing solid and liquid with U-decay products, traces of U and other heavy metals.

At the end of U extraction process, mill tailings contain about 85% of original radioactivity.

Acid drainage waters

Acid drainage waters are produced by chemical and microbiological mill tailings containing sulfides.

FeS_2 (Pyrite)+ $7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+$

$2Fe^{2+} + 1/2O_2 + 2H^+$ ***Thiobacillus*** $2Fe^{3+} + H_2O$

$14Fe^{3+} + FeS_2 + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$

The acidic waters leach heavy metals through infiltration in soils, surface and groundwaters waters. These waters are toxic to organisms and plants.

Radium (Ra^{226}) and Radon (Rn^{222})

Radium and radon are toxic.

Radium is an alpha emitter ($T_{1/2}$=1602 a), which could substitute calcium in the human bone.

Radon is a radioactive gas ($T_{1/2}$=3,8 j), which could cause lung cancer.

Other metals release

The reduced U^{4+} can oxidize to highly soluble U^{6+}, in the presence of oxygen:

$UO_2 + 2H^+ \ 1/2O_2 = UO_2^{2+} + H_2O$

The pH drop to 2 contribute to solubilization of Th, V, As, Sb, Ce…

In addition, Th ($T_{1/2}$=77.000 a) is highly toxic to liver.

Acid drainage waters

To reduce the quantity of acidic waters sulfide minerals can be removed by techniques such as flotation (remove 90-95%of sulfides). Also, addition of minerals such as calcium carbonate helps to neutralize excess of acidity.

$CaCO_3$ + H^+ = Ca^{++} + HCO_3^- (Buffering effect with regards H^+)

FeS_2+ 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ (Acidification)

Mill tailings can be stored in artificial lakes to minimize the access of oxygen and maintain anoxic conditions.

Social impact

- Uranium mining can cause conflict. In Niger, an Orano base was attacked by dissatisfied Tuareg rebels. At the same time, Orano was accused by the Nigerian government of supporting Tuareg militia groups to deter competitors. Social conflict due to uranium mining can also be caused by the unequal distribution of mining profits and revenue.

- Water shortages. Uranium mining and milling needs the input of large quantities of fresh water.

Strong threat to the environment

June 29 2010. Radioactive acid-mine sludge pours into Crocodile-Limpopo river system at its source above the Hartbeespoort dam. The Environment and Conservation Association on the East Rand in South Africa has lodged a law-suit against its Minister of Water Affairs and its President Jacob Zuma for ignoring the requirements of the Water Act as well as the Constitution regarding the dangerous mine-sludge pollution of the the Hartbeespoort Dam at the source of the Crocodile/Limpopo river system.

$Fe^{3+} + 3OH^{-} = Fe(OH)_3$

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Drainage treatment technology categories

Neutralization	Metals Removal	Desalination	Specific target pollutant treatment
Lime/Limestone process ($CaCO_3$)	Precipitation / Hydroxide	Biological sulfate removal	Cyanide removal: - chemical oxidation - biological oxidation - complexation
Sodium based alkali's (NaOH, Na_2CO_3)	Precipitation / Carbonates	Precipitation processes such as ettringite	Radioactive nuclides: - precipitation - ion-exchange
Ammonia (NH_3)	Precipitation / Sulfides	Membrane-based processes	Arsenic removal: - oxidation/reduction - precipitation - adsorption
Biological sulfate reduction	Wetlands, Oxidation ponds	Ion-exchange processes (Resins)	Molybdenum removal: - iron adsorption
Wetlands, anoxic drains	Other technologies	Wetlands, passive treatment process	Other technologies
Other technologies			

$$Th^{4+}(aq) + 4OH^{-} = Th(OH)_4 \text{ (solide)}$$
$$Pb^{2+}(aq) + S^{2-} = PbS \text{ (solide)}$$

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Re-vegetation

Replanting and re-building the soil of mined-out land

- Establishing long-term plant communities requires forethought as to appropriate species for the climate, size of stock required, and impact of replanted vegetation on local fauna;

- The motivations behind re-vegetation are diverse, but it is usually **erosion** prevention that is the primary reason;

- Re-vegetation helps prevent soil erosion, enhances the ability of the soil to absorb more water in significant rain events, and in conjunction reduces **turbidity** dramatically in adjoining bodies of water;

- Re-vegetation also aids protection of engineered grades and other earthworks;

- Re-vegetation is often used to join up patches of natural habitat that have been lost, and can be a very important tool in places where much of the natural vegetation has been cleared.

Re-vegetation

Environmental monitors inspect revegetated growth on a rehabilitated site near Venetia mine, South Africa

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

A new life for ancient sites

The écarpière site, Vandée (France)

Before remediation

After remediation

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Conversion

Uranium grains UF_4 (blue) and UF_6 (transparent). After ORANO. UF_6 becomes gaseous à 60°C.

Conversion (dry process)

- Transformation of uranium oxide to UF_4

UO_2 + 4HF → UF_4 + H_2O (HF: Fluorhydric Acid)

- Transformation of UF_4 en UF_6 (dry process)

U_3O_8 → reduction NH_3 or H_2 → UO_2

UO_2 → hydrofluoration HF → UF_4

UF_4 → fluoration F_2 → UF_6 impur.

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Conversion (Humid process)

- Transformation of UF_4 to UF_6 (Humid process)

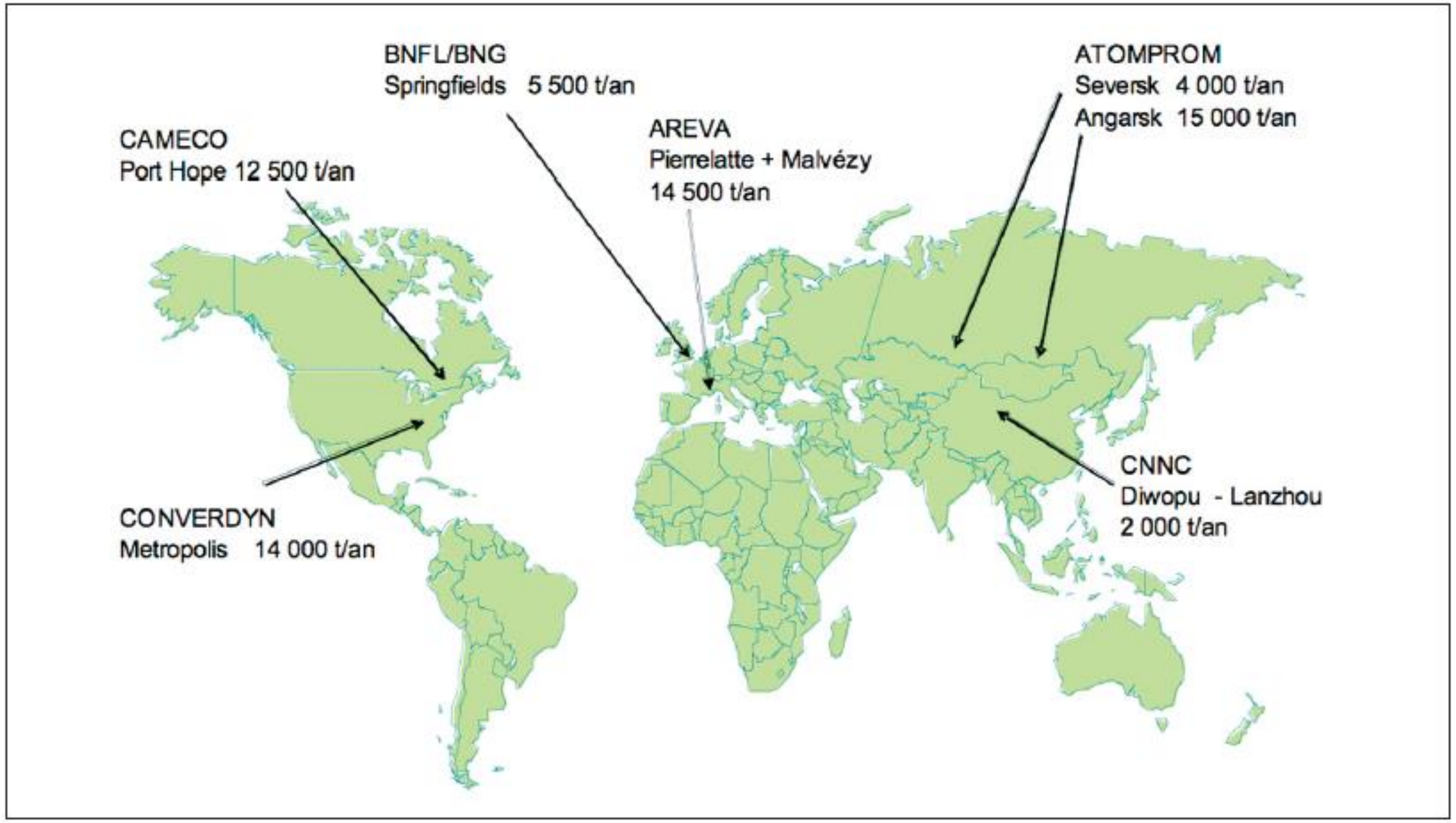
Concentrates → dissolution HNO_3 → $UO_2(NO_3)_2$ impure

Nitrate impur → extraction TBP → $UO_2(NO_3)_2$ purified

Nitrate pure → reduction NH_3 et H_2 → UO_2

Work under negative pressure to prevent from fluorine and UF_6 leakage.

Conversion



World – Production capacities of major factories of uranium conversion to UF_6 in 2007. After ORANO.

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Enrichment

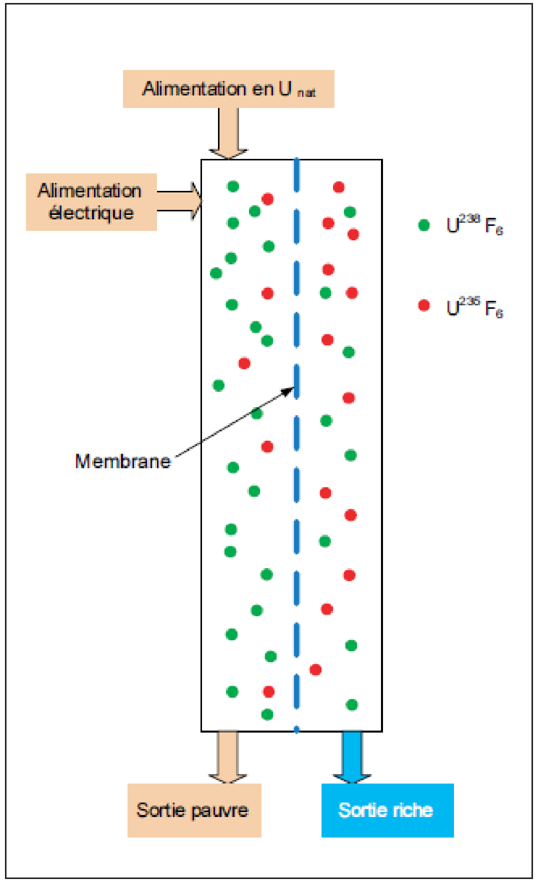


Schéma d'un diffuseur.

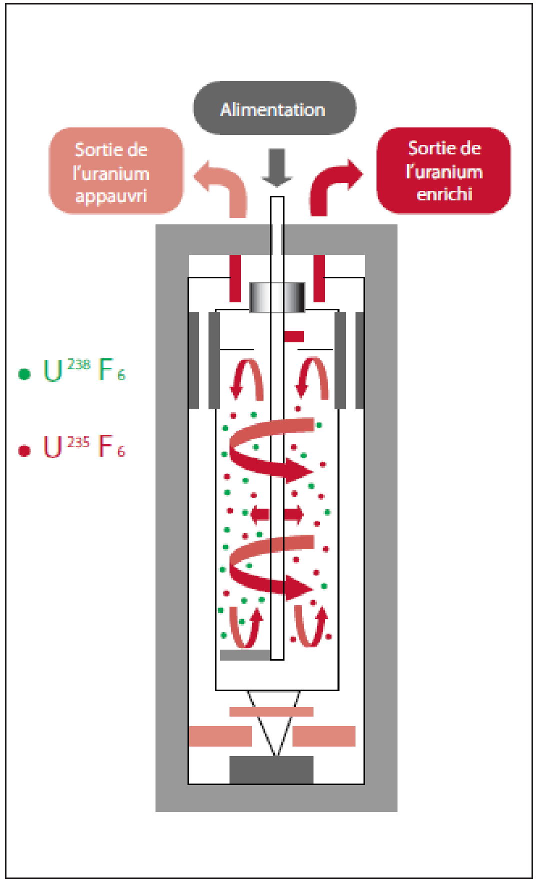


Schéma d'une centrifugeuse.

Uranium enrichissement : U-235/U238 from de 0,7% à 3-5%. After ORANO.

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Diffusion

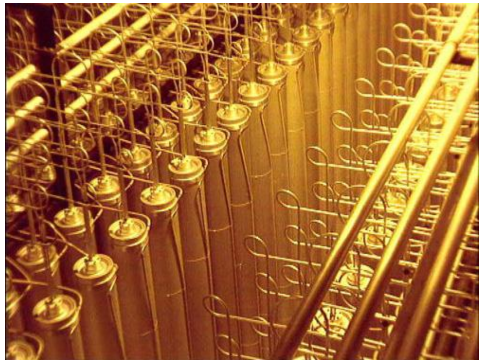
This technology has been used in **Georges Besse** factory **d'EURODIFe**and by **USEC** USA.

U-235 is lighter than U-238 and diffuses faster through the porous membranes under pressure. The cycle is reproduced up to 1400 times to obtain enrichment of about 3-5%.

Georges Besse factory (Eurodif)

Centrifugation

During centrifugation U-238 is concentrated toward the wall and U-235 remains in the middle of the vessel. Centrifugation is less expensive than diffusion.



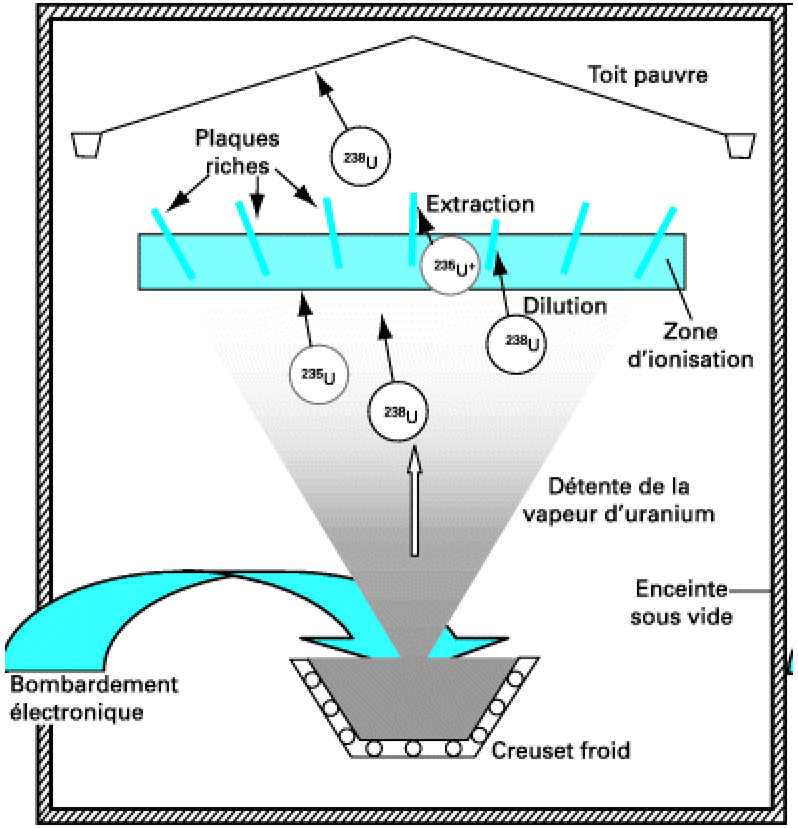
Centrifugation

Advantages of centrifugation (Georges Besse II) :

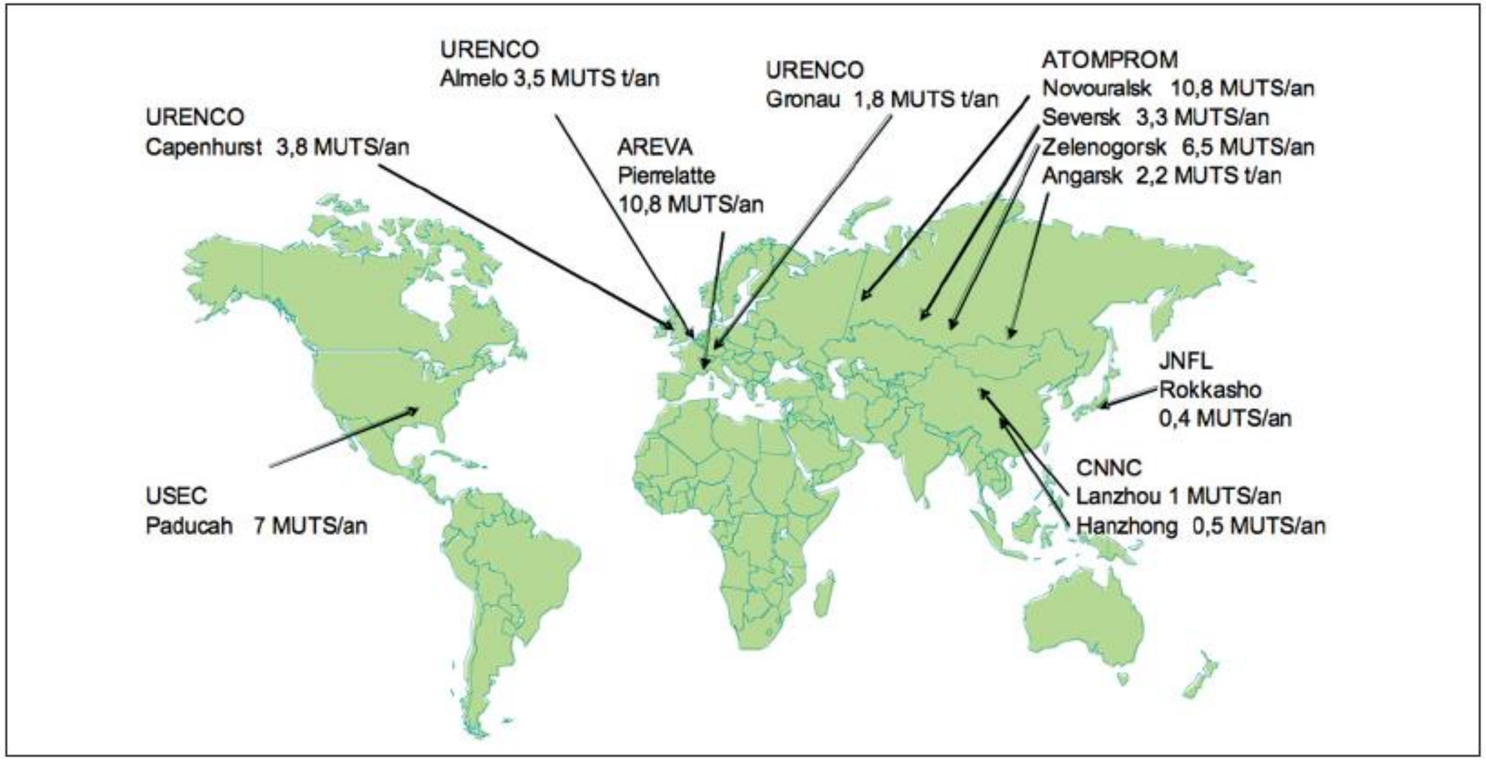
✓ consumes less electricity than diffusion,
✓ does not require for cooling,
✓ works under atmospheric pressure and involves small amount of simultaneous use of matter (10 tons) than diffusion (3000 tons), which insures high safety standards,
✓ less visual impact than diffusion.

Laser separation

Consists of selective excitation of U-235 using a laser beam. The ionized U-235 is then collected in a negatively charged plate.

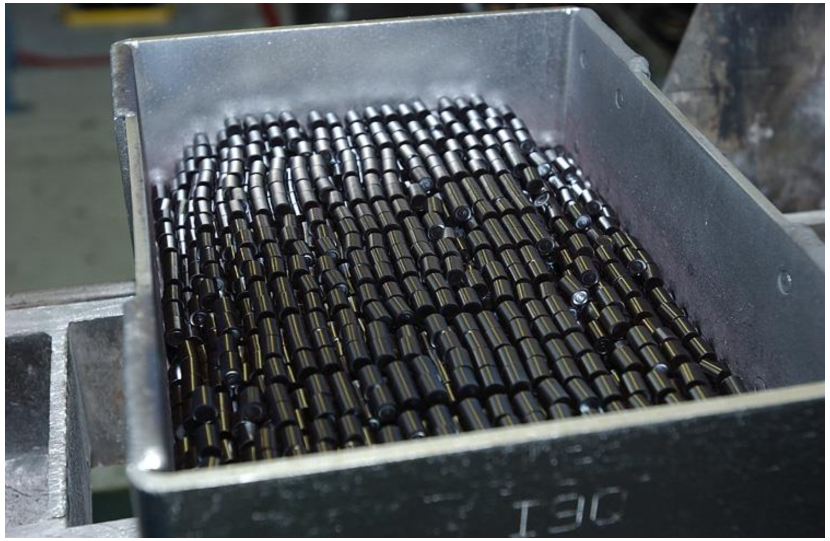


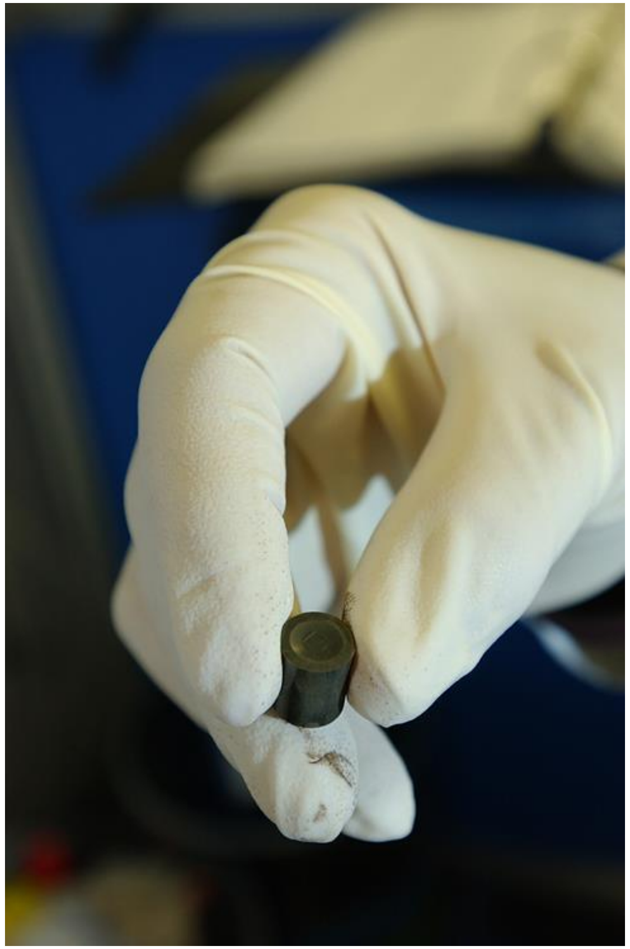
Uranium enrichment



World – Production capacities of the major uranium enrichment factories in 2007. After ORANO.

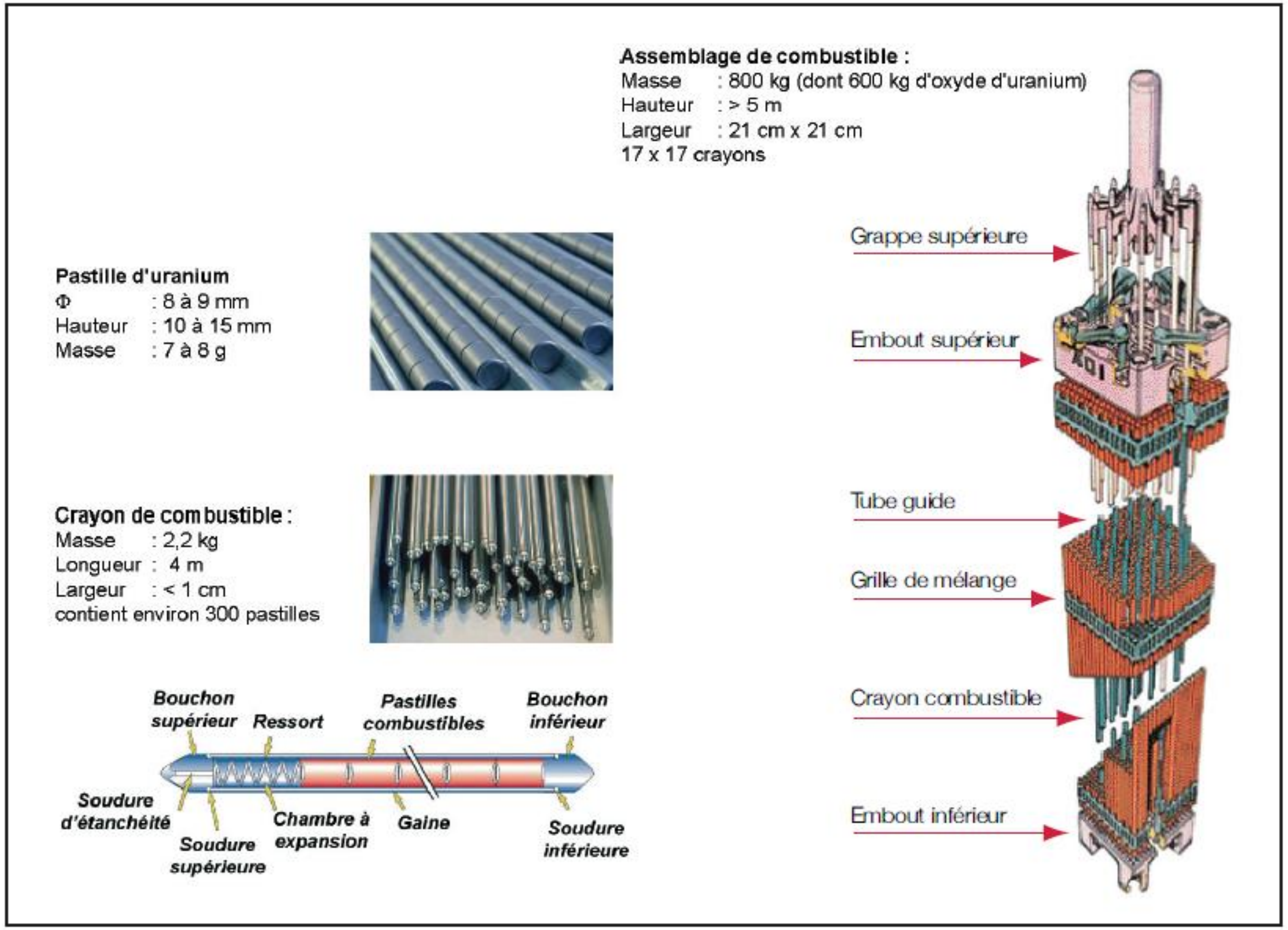
The nuclear fuel





Uranium oxide pellets prepared at high temperature in Melox factory at Marcoule (Gard)

The nuclear fuel

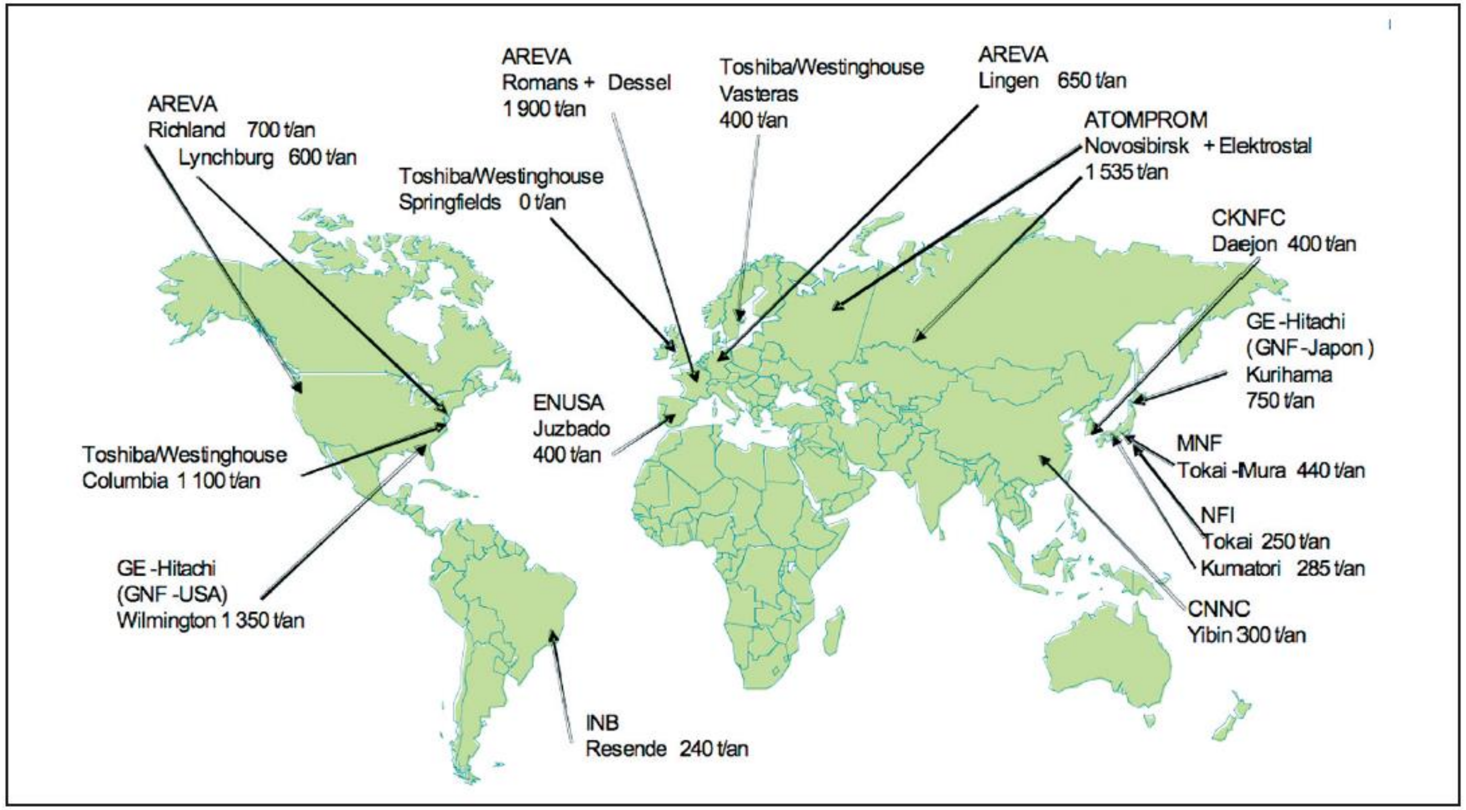


The nuclear fuel

Nom des usines	Types de réacteurs auxquels sont destinés les combustibles fabriqués
Romans (France) ; **Dessel** (Belgique) ; **Lynchburg** (USA) ; Columbia (USA) ; Resende (Brésil) ; Kumatori (Japon)	REP
Richland (USA) ; Wilmington (USA) ; Kurihama (Japon) ; Juzbado (Espagne)	REB
Lingen (Allemagne) ; Springfields (UK) ; Vasteras (Suède) ; Tokai-Mura (Japon)	REP/REB
Novosibirsk (Russie) ; Elektrostal (Russie)	VVER
Yibin (Chine) ; Daejon (Corée)	REP/VVER

The major UO_2fuel fabrication factory in the world

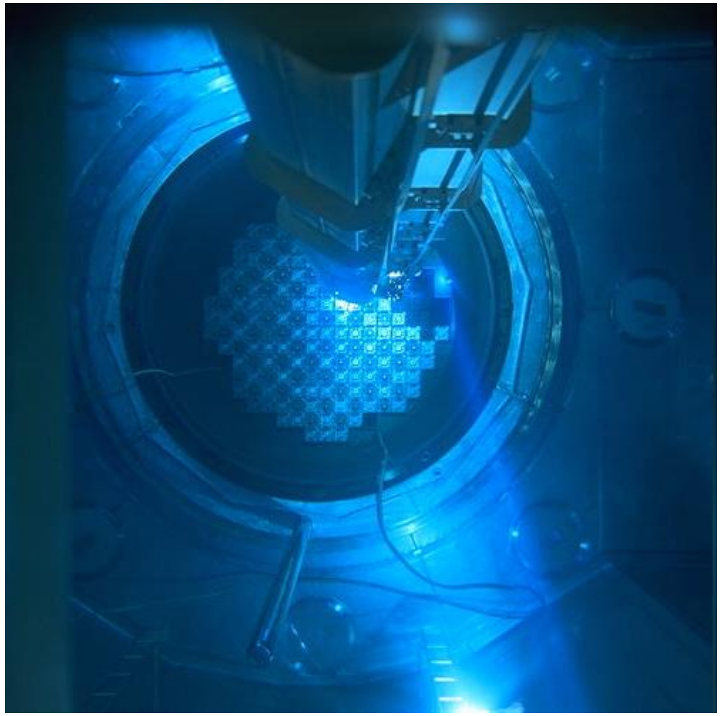
The nuclear fuel



Monde – UO_2 production capacity of the major factories for light water reactors in 2007

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Reactor core



Reactor core during fuel load at Civaux, in Poitou-Charentes.
Load is operated under water

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Fuel temporary storage

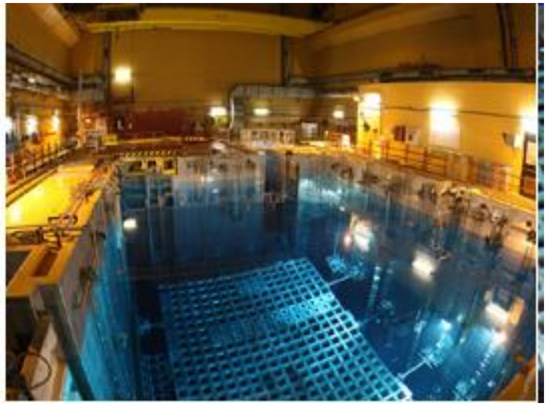
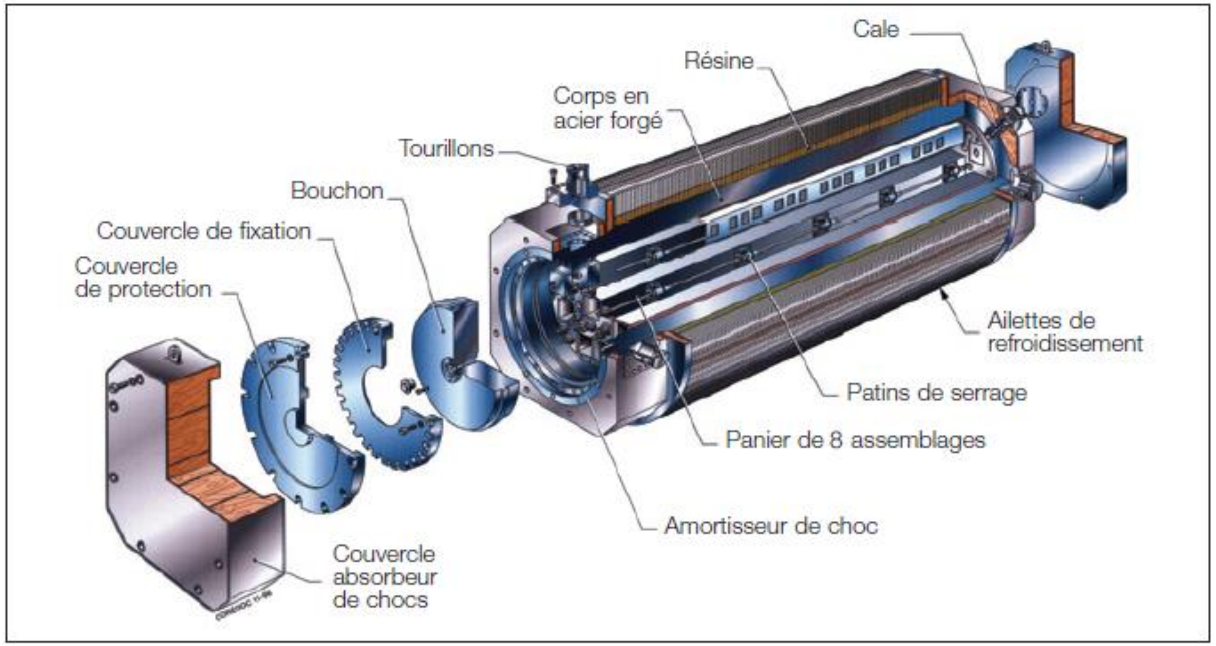


Photo 1 © La médiathèque EDF / Claude Cieutat
Fuel element in the reactor pool – NPP Civaux (Vienne)

Photo 2 © La médiathèque EDF / Franck Oddoux
Fuel element in the reactor pool – NPP Saint-Alban (Isère)

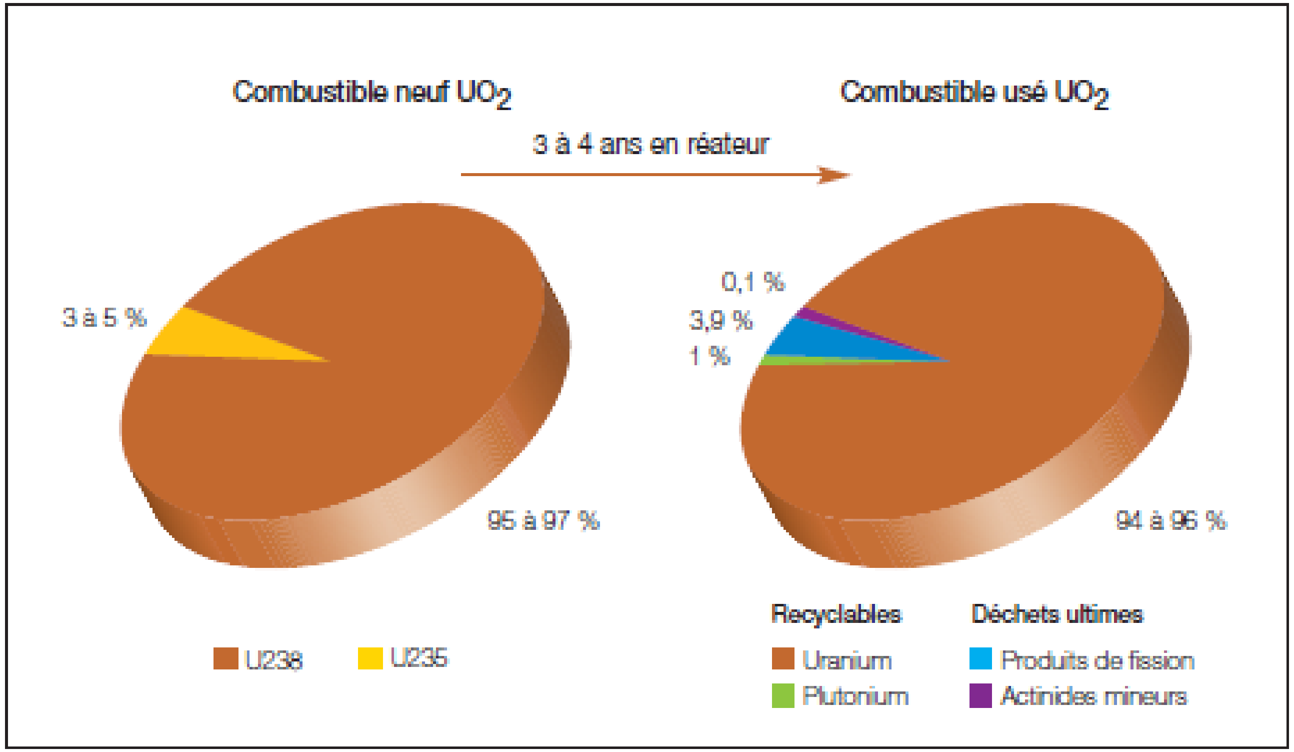
Spent fuel



Spent fuel transport container. After ORANO.

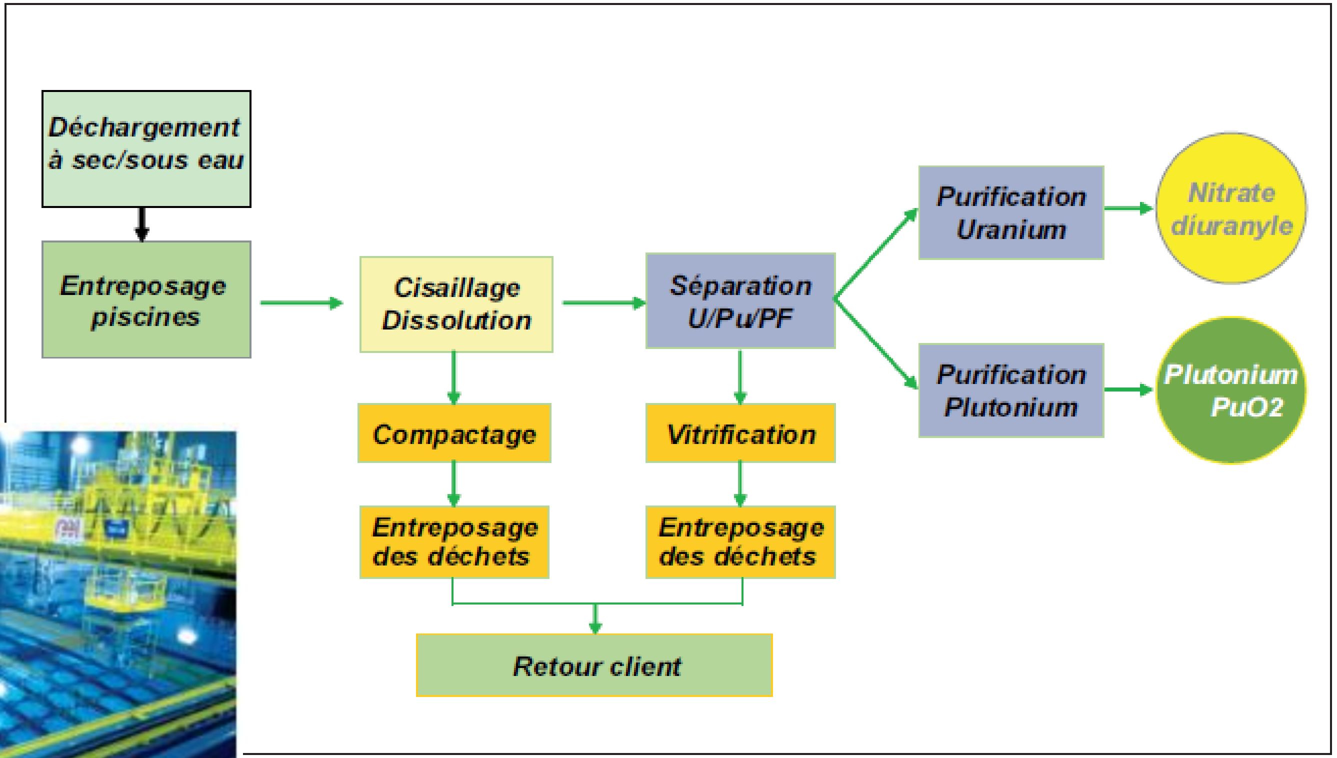
IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

Spent fuel



Fission Products: ceasium 137, strontium 90….
Minor Actinides: neptunium 237, americium 241 et 143, curium 244 et 245….
Plutonium: 239 et 241 (fissiles)….

Spent fuel recycling



Storage pool for spent fuel. ORANO-La Hague

Spent fuel recycling

Spent fuel recycling at La Hague is based on the PUREX process (Plutonium Uranium Refining by Extraction). This process has been developed in the USA in 1940s to extract plutonium for bombs, in particular Pu-239.

The used fuel contains some isotopes that could be recycled, especially uranium (94 % à 95 %) and plutonium (1%). The remaining 4% consist of fission products and minor actinides.

Spent fuel recycling

The recycling of spent fuel **last for about 10 years**. It starts from the removal of spent fuel from the reactor.

The spent fuel recycling consists of :

✓ **separation** by a mechanical and chemical processes the recyclable matter from the waste (FP and MA),

✓ **conditioning** of uranium and plutonium,

✓ **conditioning** of radioactive waste and technological waste.

The separated uranium called “retreatment uranium” is concentrated in the form of liquid nitrate for future reuse.

Plutonium is transformed into Pu-oxide (PuO_2) powder to make **MOX** fuel (mixture of UO_2 and PuO_2).

MOX is also produced from nuclear weapon dismantlement.

Acid dissolution

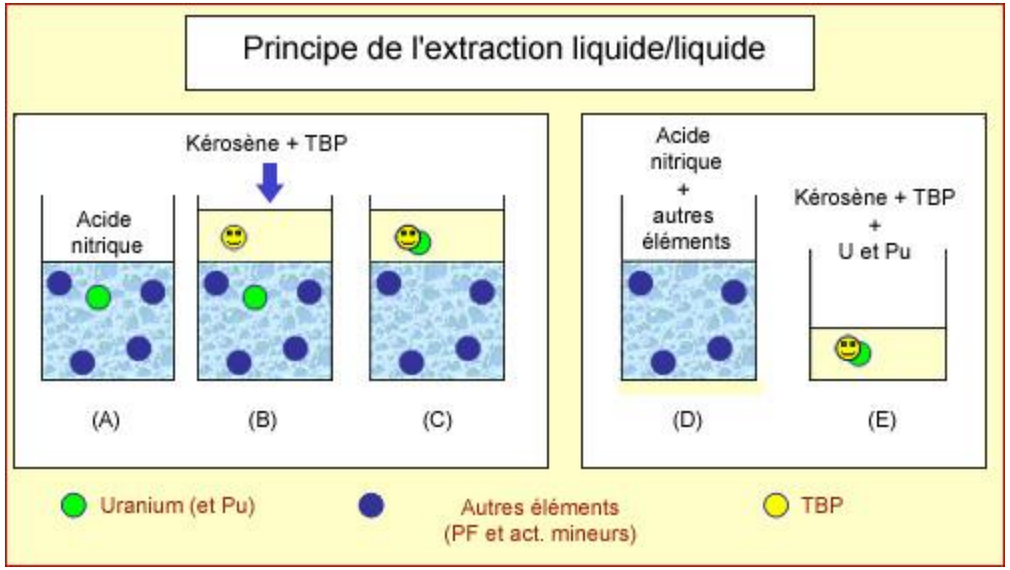
The fuel rods are cut and fuel oxide is dissolved in hot nitric acid, about 40 kg of fuel are dissolved in 600 liters of HNO_3. The resulting solution contains several chemical elements, fission products, uranium and plutonium.

$UO_2 + 8/3HNO_3 = UO_2(NO_3)_2 + 2/3NO + 4/3H_2O$ (pour [HON3] < 2M)

$PuO_2 + 4HNO_3 = Pu(NO_3)_4 + 2H_2O$

We add then a mixture of kerosene and TriButylPhosphate (TBP). TBP retains (complexes) U and Pu in acidic media. After mixing U and Pu are extracted in the organic phase.

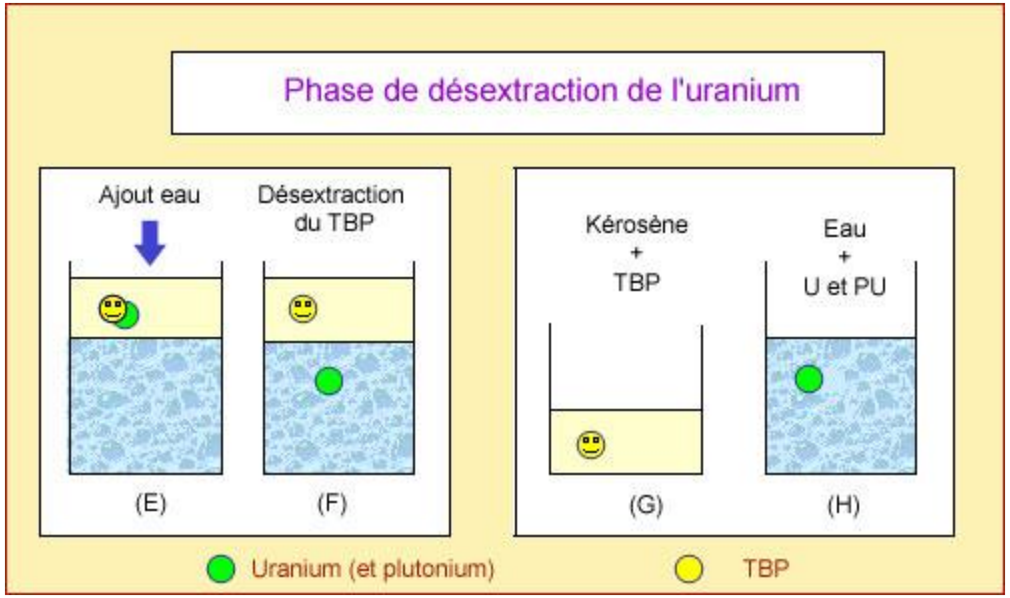
Extraction phase



U and Pu are extracted by TBP in acidic solution

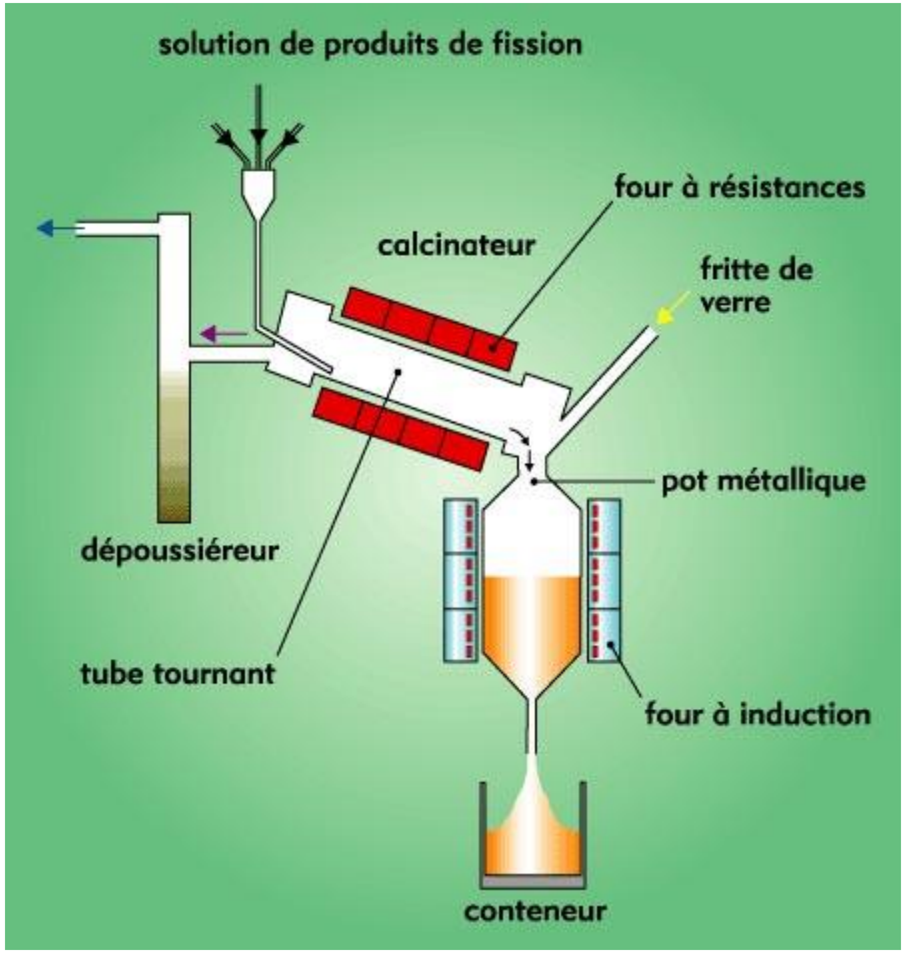
Aqueous phase (other elements) and organic phase (U and Pu) are separated

De-extraction phase



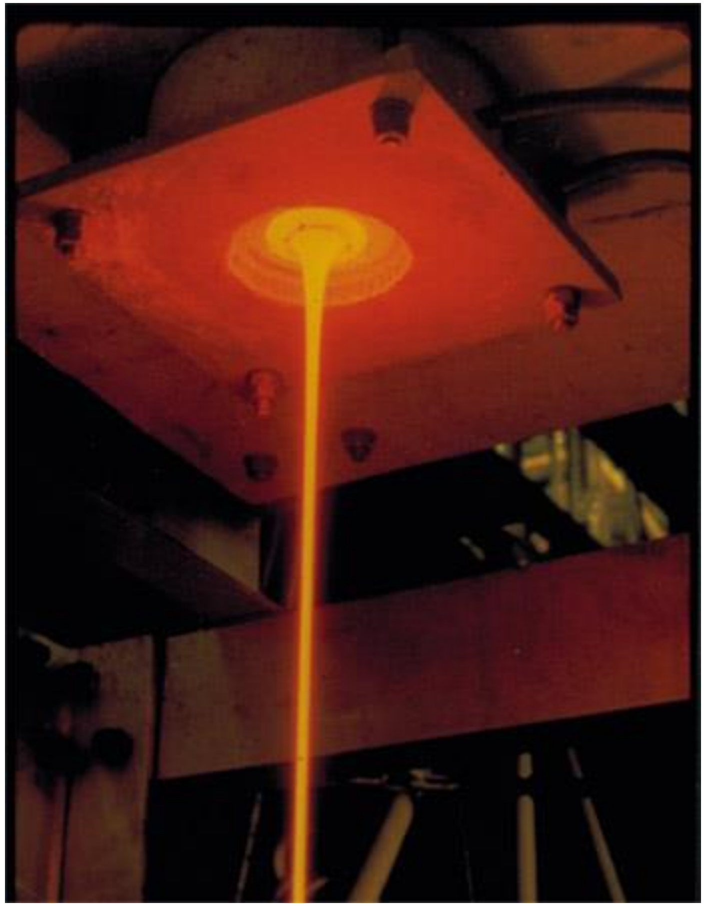
U and Pu are released in water from organic phase. Several cycles can be repeated for total extraction.

FP + MA Vitrification



The vitrification process

FP + MA Vitrification



The French nuclear waste glass R7T7

FP + MA Vitrification

Acid solution are calcinated.

The radioactive calcine containing FP and MA are mixed with glass powder and melted in a crucible at 1100°C. The melt is placed in stainless steel containers in La Hague facility.

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom

FP + MA Vitrification

Conteneur

Acier inoxydable
hauteur 1 m 338
Diamètre 43 cm
Masse 92,5 kg

Colis

Verre borosilicate
volume 175 litres
masse déchets 400 kg
produits radioactifs 11 kg

A CDS-V vitrified package

Thank you

IMT Atlantique
Bretagne-Pays de la Loire
École Mines-Télécom