

# MINING, MILLING, CONVERSION, AND ENRICHMENT OF URANIUM ORES

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## Uranium Background

### Key points over 150 years

- 1789 – Uranium discovered by Klaproth in Germany and named after the planet Uranus recently discovered by Herschel.
- 1896 – Professor Becquerel in Paris discovered radioactivity in uranium minerals and then radium discovered by Mme. Curie in Paris.
- 1910 – Dr. Soddy in Cambridge, UK, proposed “isotopes” for atoms with different atomic weights but identical chemical properties.
- 1913 – Professor Thomson at Cambridge showed neon had “isotopes” and therefore other elements were likely to have them too.
- 1932 – Dr. Chadwick at Cambridge discovered the neutron.
- 1935 – Dr. Dempster in Chicago showed uranium contained 0.7% of uranium-235 and the rest was uranium-238. Uranium structure shown to be 92 p and 146 n in U-238; 92p and 143 n in U-235.

# Background to the Nuclear Fuel Cycle

- **1939 – Discovery of fission of uranium by Hahn and Strassman in Germany and extra neutrons released to give possibility of a chain reaction.**
- **1939–1942 – Concept of an atomic bomb developed in UK, U.S., and Germany.**
- **1942 – Start of the Manhattan Project and the need for the nuclear fuel cycle with uranium ore processing, uranium enrichment, plutonium production, etc.**
- **1942 – Chemical and physical separation processes became very important for the production of large amounts of uranium-235 and plutonium.**

## The Need for Separation Processes in the Nuclear Fuel Cycle

Uranium as mined cannot be fed directly into a nuclear power station in contrast to coal, gas, or oil in a fossil-fueled power station.

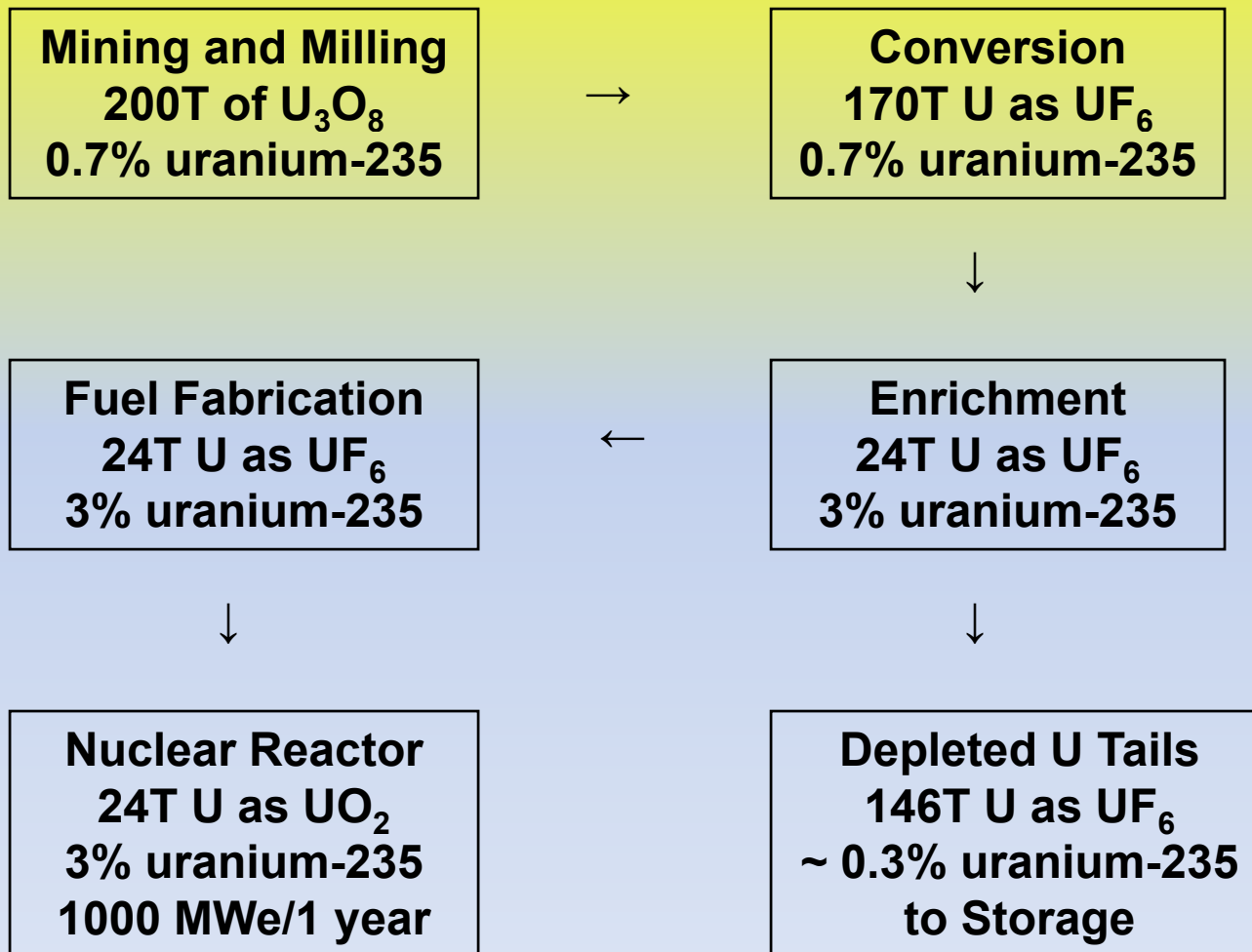
Uranium ore contains mineral and chemical impurities including radioactive daughter products of uranium. The uranium consists of 0.7% uranium-235 and 99.3% of uranium-238 isotopes.

While a nuclear power station can be built using natural uranium in the fuel, the majority of nuclear power stations have been optimized to use uranium enriched from about 3–5% in the uranium-235 isotope.

Therefore, a number of chemical and physical separation processes are required to convert uranium ore into optimized nuclear fuel elements through the stages of mining, milling, conversion, and enrichment.

**These form the “FRONT END” of the nuclear fuel cycle.**

## The Front End Stages in the Enriched Uranium Fuel Cycle



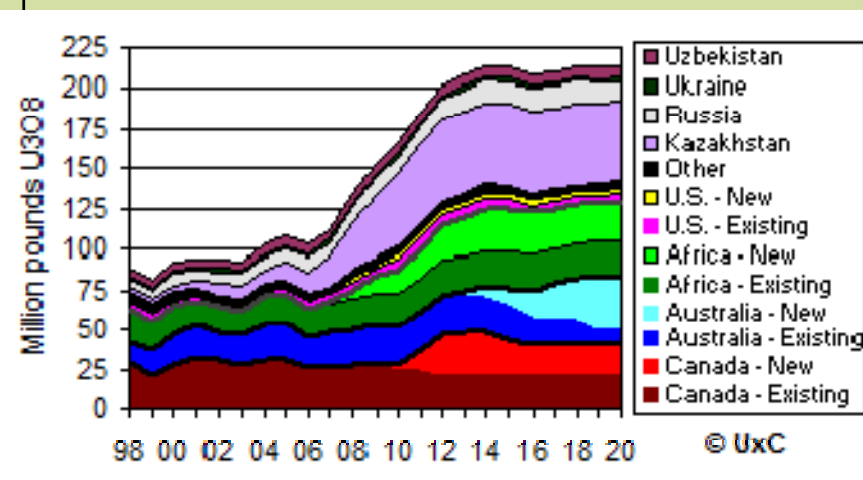
## World Uranium Resources and Production

### Comparison of Uranium Resource Countries 2007

Reasonably Assured plus Inferred Resources  
to US\$130/kg U at 01/01/07

Australia	1,243,000T U	23%
Kazakhstan	817,000	15
Russia	546,000	10
South Africa	435,000	8
Canada	423,000	8
United States	342,000	6
Brazil	278,000	5
Namibia	275,000	5
Niger	274,000	5
Ukraine	200,000	4
Others	636,000	11
<b>Total</b>	<b>5,469,000</b>	<b>100</b>

Based on data from the NEA/IAEA "Uranium 2007 Resources, Production & Demand"



Based on data from the Ux  
Consulting Company,  
[www.uxc.com](http://www.uxc.com)

World requirements for current 439 reactors totaling 370 GWe in 30 countries are about 65,000T U per year. Known low-cost resources will last over 80 years even with once-through use. Recycling U and Pu will extend this time.

# Uranium Abundance, Occurrence, and Commercial Deposits

## Abundance

The average concentration of uranium in the earth's crust is 2–4 ppm. Uranium is 4 times more abundant than silver and more abundant than antimony, tin, cadmium, and mercury. It is also present in seawater.

## Occurrence in Minerals

Uranium occurs in hundreds of minerals, the best known being pitchblende, uraninite, and autunite. It also occurs in many phosphate deposits and monazite sands in which it is associated with rare earths.

## Commercial Deposits

The most important commercial uranium deposits have been found in veins in granitic rocks, adsorbed on sand grains in sandstone deposits, and in porphyry deposits such as the large deposit at Olympic Dam in South Australia where it is associated with copper and gold.

## Methods of Uranium Ore Mining

**There are four basic methods of obtaining uranium from ores and materials:**

- \* Underground mining**
- \* Open cut mining**
- \* In-situ leaching**
- \* Recovery from mining of other materials, e.g., phosphate rock, mineral sands, coal ash, etc.**



## Methods of Mining and How to Choose

- \* **Underground Mining** – Vertical shafts or inclined access tunnels depending on depth of deposit found by exploratory drilling. Then tunnels used to follow veins.
- \* **Open-cut Mining** – Excavation of a large amount of overburden to reach the ore body found by exploratory drilling. The pit is usually terraced.
- \* **In-situ Mining** – A large number of vertical bore holes to introduce a leaching solution and to extract it from a shallow deposit between impermeable layers (clays).
- \* **The Choice** – An analysis of the depth of overburden, the depth of the ore body, the grade of the ore, the inclination of the ore body to the surface, and many other factors is required to decide which method (underground, open cut, or in-situ leaching) is the most economic.

# Examples of Three Types of Mining in Australia



*Aerial view Olympic Dam plant.*

The Underground Mine and Copper, Gold, and Uranium Processing Plants at Olympic Dam, South Australia



The Uranium In-situ Leaching Plant at Honeymoon, South Australia



*Aerial view of Ranger Mine and plant*

The Open Cut Mine and Uranium Processing Plant at Ranger in the Northern Territory, Australia

# The Mining and Milling Process

- **Delivery of Ore to Processing Plant (Mill)** by trucks and/or conveyors
- **Primary and Secondary Crushing** to provide a fine powder
- **Leaching of Uranium** from solid by acid or alkali (depending on type of host rock and the uranium minerals) – this separates U from many insoluble impurities
- **Filtration and Clarification** of liquor containing U and other elements with the solids being sent to a tailings pond for storage
- **Precipitation** of U, usually as ammonium diuranate which separates U from some impurity elements which remain in solution
- **Drying and Calcination** at several hundred degrees C to form yellowcake (nominally  $U_3O_8$  called Uranium Ore Concentrate [UOC])
- **Packaging** in 200-liter steel drums for delivery to customer

# Uranium Conversion – World Demand and Supply

**Conversion Services** are required to purify uranium ore concentrates and to provide a suitable product to make fuel elements for nuclear reactors using natural uranium or enriched uranium fuel. The product is either very pure  $\text{UO}_2$  or  $\text{UF}_6$ .

The world demand for conversion services is currently equivalent to about 60,000T  $\text{UF}_6$  for the 90% of reactors that use enriched uranium fuel.

There are five major companies that supply these services:

- \* Areva, France
- \* Cameco, Canada
- \* Converdyn, U.S.
- \* Springfield Fuels Ltd, UK
- \* Tenex, Russia

# Uranium Conversion Processes

**The feed material** – Uranium ore concentrates in 200-liter drums

**The product** – Very pure uranium dioxide ( $\text{UO}_2$ ) for natural U reactors or very pure U hexafluoride ( $\text{UF}_6$ ) for enriched U reactors

**The objective of conversion** – To separate impurities from UOC and produce very high purity products to tight specifications

**Processes** – There are two basic processes for conversion:  
**wet and dry**

The main difference between the wet and dry processes is the way impurities are removed from the UOC. In the wet process, they are removed in the second stage of solvent extraction, and only very pure intermediate products are processed through the later stages. In the dry process, the impurities in the UOC are removed mainly in the final  $\text{UF}_4$  fluorination stage and in an extra distillation stage if necessary. The final product in both processes is very pure  $\text{UF}_6$  contained in cylinders suitable for storage or transport to the enrichment plant specified by the customer.

## The Wet Conversion Process

UOC is dissolved in nitric acid and then treated by solvent extraction with a solvent such as tributylphosphate (TBP) in an inert diluent such as odorless kerosene (OK) in mixer settlers. Uranium is extracted preferentially to impurities and then removed from the TBP/OK by washing with water and precipitated with an ammonia solution to give a very pure ammonium diuranate. This is dried and calcined at a few hundred degrees C to give an intermediate product ( $\text{UO}_3$ ), which is then reduced in a mixture of hydrogen and nitrogen to uranium dioxide ( $\text{UO}_2$ ). This is the product shipped in drums to a fuel fabrication plant if a customer wants **natural uranium fuel**.

If the customer wants **enriched uranium fuel**, the intermediate product is converted to uranium hexafluoride in a two-stage process. In the first stage, the  $\text{UO}_2$  is heated with hydrogen fluoride in a fluidized bed to form uranium tetrafluoride ( $\text{UF}_4$ ). In a second stage, the  $\text{UF}_4$  is heated with fluorine in a fluidized bed to form  $\text{UF}_6$ . The product is very pure solid  $\text{UF}_6$  sublimed into special cylinders for shipment to the customer.

# The Dry Conversion Process

The UOC is received in 200-liter steel drums. The UOC has to be pelletized suitable for chemical treatment in a series of fluidized beds. It is first analyzed for sodium, and, if it contains above a set level, it is pretreated with a solution of ammonium sulphate, filtered, dried, and then pelletized.

**Stage 1** – The pelletized low-sodium UOC is heated in  $H_2/N_2$  gas to reduce it to uranium dioxide ( $UO_2$ ).

**Stage 2** – The  $UO_2$  pellets are heated in another fluidized bed in hydrogen fluoride (HF) gas to form uranium tetrafluoride ( $UF_4$ ) (green salt). This product still contains residual metallic and nonmetallic impurities.

**Stage 3** – The  $UF_4$  pellets are heated in another fluidized bed with fluorine gas ( $F_2$ ) to form volatile uranium hexafluoride ( $UF_6$ ). Any impurities with nonvolatile fluorides are removed in the residual pellets. Some impurities with volatile fluorides may be carried over with the  $UF_6$  product.

**Stage 4** – If volatile impurities are detected, then the product is fractionally distilled to provide a  $UF_6$  final product meeting strict specifications.

# Commercial Conversion Plants

**Converdyn Conversion Plant,  
Metropolis, Illinois, USA, which  
uses the Dry Process**



*FIG. 14: ALLIED CHEMICALS CORPORATION URANIUM HEXAFLUORIDE PLANT  
(foreground)*

**British Nuclear Fuels  
Conversion Plant,  
Springfields, UK, which uses  
the Wet Process**



## Uranium Enrichment – Demand and Supply

- The demand for enrichment for the majority of the world's 439 reactors of 370 GWe is about 53M SWU/year (where SWU is a Separative Work Unit, a measure of the energy required to produce a kilogram of product at specified enrichment levels in the product and tails).
- In comparison, the current supply is about 58M SWU/year, thus giving a surplus. Supply will be decreased due to the closure of old gaseous diffusion (GD) plants in the U.S. and France and the completion of the U.S.-Russian Agreement for conversion of Russian Highly Enriched Uranium from decommissioned warheads into low enriched uranium for use in civil reactors. Supply will be increased due to the completion of new enrichment plants.
- The old GD plants are being replaced by new gas centrifuge (GC) plants which are much more energy efficient and can be built in modules as demand increases. For example, the energy use for one SWU in a GC plant is only 50 KWh compared with 2,500 KWh in an old GD plant.

# Uranium Enrichment Methods

The basic objective is to increase the percentage of uranium-235 from its level of 0.7% in natural uranium to about 3–5% in optimized nuclear fuel with the rejected “depleted uranium” or “tails” being in the range 0.2–0.3%.

- **Calutrons – One of the first methods in the Manhattan Project**
- **Gaseous Diffusion – The first large commercial-scale method**
- **Gas Centrifugation – The most efficient current method**
- **Aerodynamic – Nozzle or vortex tube (the “stationary centrifuge”)**
- **Laser Excitation – The most recent method with claims of even higher efficiency than the gas centrifuge**
- **Chemical Exchange and Ion Exchange processes taken to pilot plant scale but not commercial scale**

# The History of Calutrons

**Brief review of the calutron because of its historic significance as the first large scale method of enriching uranium from 0.7%–99%.**

**A calutron is a form of mass spectrometer like that developed by Aston in the UK in 1919, used by Dempster in the U.S. in 1935 to show uranium had two main isotopes of mass 235 and 238. It is also like the cyclotron developed by Lawrence at Berkeley in the 1930s and adapted by him in the Manhattan Project after 1942. *Cal U* recognized the University of California and *tron* is from cyclo-tron.**

**In a calutron, a small amount of uranium tetrachloride is bombarded with high-energy electrons to produce charged uranium ions in a vacuum chamber. The ions are accelerated in a semicircle through a strong magnetic field and ions of different mass are separated by a small amount and can be collected in separate receivers. The energy efficiency is very low.**

## The Development of the Calutron in the Manhattan Project

The Cyclotron – Lawrence developed a 37-inch (94 cm) diameter cyclotron in Berkeley in the late 1930s and used it to prove uranium ions could be separated in the laboratory.

The Alpha Calutron – After 1942, Lawrence developed a 184-inch (467 cm) magnet with the ions traveling in a semicircle as a production machine. He estimated that ten calutrons could produce about 4 g of uranium-235 each day. This was called the **Alpha Calutron**.

The Project needed larger amounts faster, so a giant magnet (24 times larger) was designed and built at the Oak Ridge facilities. This was surrounded by giant vacuum tanks with the whole machine being 122 feet (36 m) long, 77 feet (23 m) wide, and 15 feet (4.5 m) high. The magnet needed a huge amount of wire; with copper being in short supply, the government released 14,700T of pure silver to make the wire. A total of 200 g of 12% uranium-235 was made by 1944. This was not enough, so production was stepped up and a second stage of machine was developed to enrich the 12% product to 99% for the bomb specification. This was known as the **Beta Calutron**. A total of 22,000 persons were involved.

## The Calutron Preserved

Most of the calutrons were decommissioned in the 1950s as the gaseous diffusion process overtook them, but several were retained and produced a wide range of stable and radioactive isotopes of many elements for use in medicine and in research. One complete Beta Calutron was preserved.

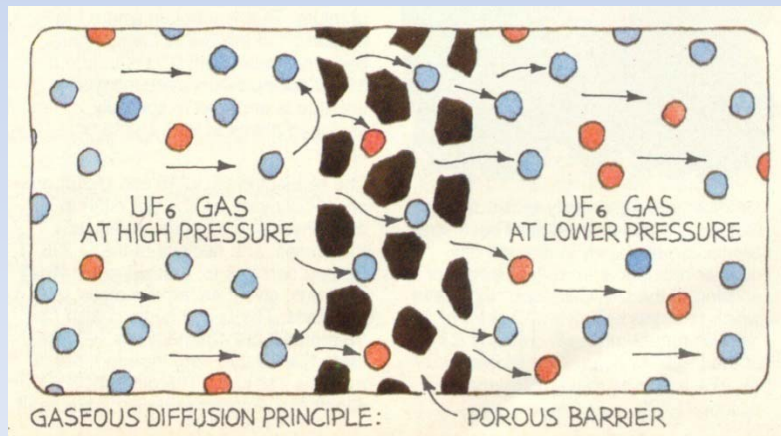


A Beta Calutron preserved at the Y-12 National Security Complex in Oak Ridge and first shown to the public in 2005.

# The Gaseous Diffusion Method

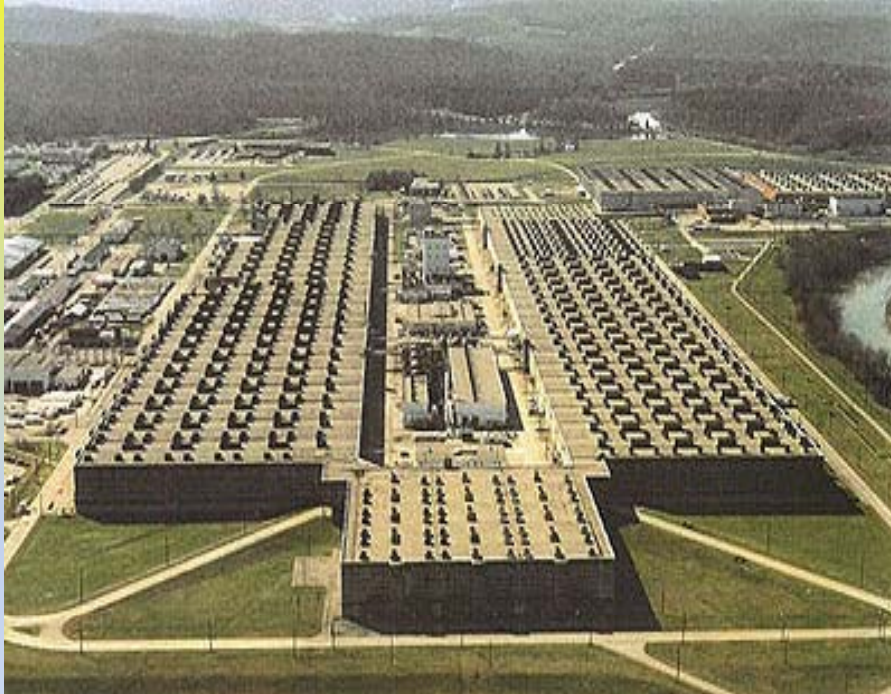
**History – Professor Peierls and Dr. Frisch at Birmingham University, UK, made a detailed theoretical study of enrichment methods in 1940. They recommended gaseous diffusion as the best large scale method. The Manhattan Project started in 1942 after the U.S. entered the Second World War after Pearl Harbor. The Project decided to not only study gaseous diffusion but also the electromagnetic method (calutron) and gas centrifugation as three of the best methods.**

**Principle – Gaseous uranium hexafluoride is forced under pressure to migrate through a porous material. Uranium-235 hex molecules travel slightly faster through the pores than uranium-238 hex molecules. The process has to be repeated a large number of times. It uses a lot of energy.**



**A very simple principle**

## The First Large Gaseous Diffusion Plant — K-25



The K-25 plant was built at Oak Ridge, TN, from 1943–1945 at a cost of \$512M. The plant was the largest building in the world in 1945 being half a mile (800 m) long, 1,000 ft (300 m) wide, and covering 2 M ft<sup>2</sup> (609,000 m<sup>2</sup>). It provided medium enriched UF<sub>6</sub> to the calutrons for final enrichment to high assay.

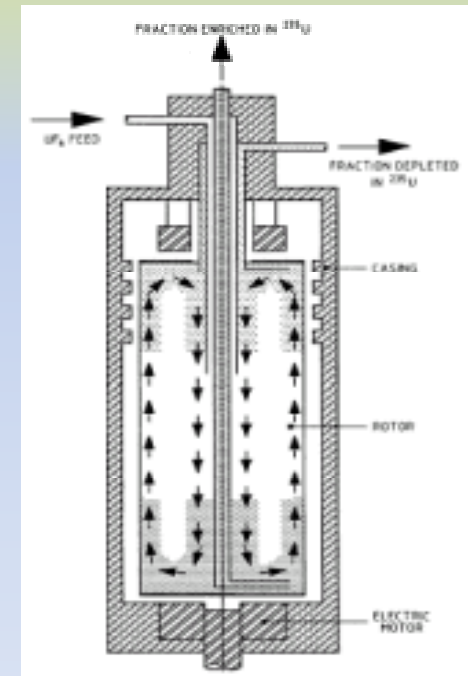
**U.S. Developments –** After the war, larger amounts of high and low enriched uranium were required for the U.S. weapons and naval programs and the world's developing commercial nuclear power programs. The GD method replaced the calutrons for the large scale production of nuclear power fuel.

Other countries soon developed their own enrichment plants, large and small. For example, UK, Russia, France, and China.

# The Gas Centrifugation Method

**GD Replaced by GC – The main reason GD plants were replaced with GC plants starting in the early 1970s was that the GD method required a huge amount of energy, about 2,500 kWh per SWU, whereas GC plants needed less than 50 kWh per SWU. Also, GC plants could be built in modules; GD plants could not.**

**The Principle – Uranium hexafluoride gas is introduced into a cylinder spinning at very high speed in a partial vacuum. The heavier U-238 molecules move towards the outside whereas the lighter U-235 molecules move towards the center. A counter-current flow is developed, and the slightly enriched product is extracted by scoops at the bottom while the depleted stream is extracted by scoops at the top. Even though the separation factor is about 1.1 (much higher than the 1.0003 in a diffusion plant), a large number of machines are needed to obtain usable quantities of 3–5% enriched product.**



**Schematic Diagram of Zippe Centrifuge**



# Gas Centrifuge Enrichment Plants

**Gas Centrifuge Plants – Commercial GC plants are currently operating in five countries: Germany, Netherlands, UK (the three countries in the Urenco Company), Russia, and Japan. Their total capacity is about 34M SWU per year, which is 68% of the current demand of 50M SWU per year.**



Cascade hall at Urenco Plant, Capenhurst, UK



Installation of centrifuges in USEC Plant

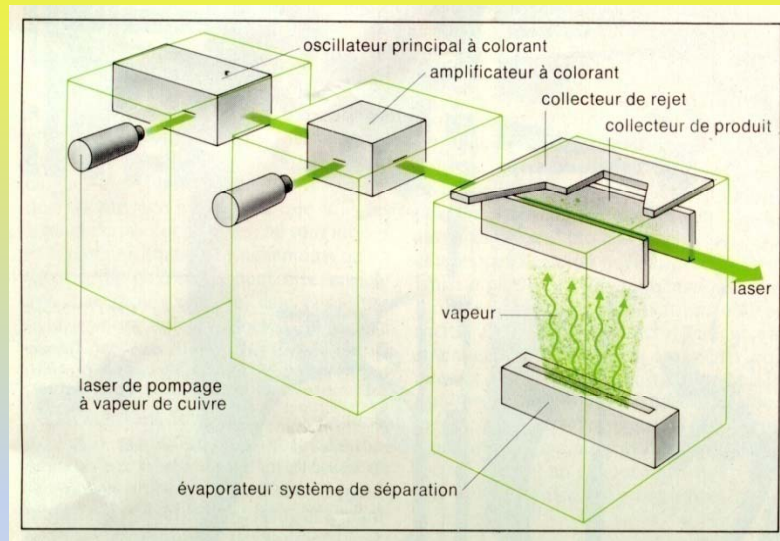
**Four new commercial GC plants are under construction: one in France and three in the U.S. for Urenco, Areva, and USEC. Total capacity is planned to be 15M SWU per year. Two of these will replace old GD plants. Pilot plants are being operated in Brazil and Iran.**

## Enrichment by Laser Excitation

**Background** – Two main types of laser excitation were studied in the 1970s in several countries as alternatives to gaseous diffusion and gas centrifugation. These methods used either atomic or molecular species of uranium illuminated by one or more types of laser. The two best known processes in the 1970s and 1980s were AVLIS (Atomic Vapor Laser Isotope Separation), also named SILVA in France, and MLIS (Molecular Laser Isotope Separation). The most recent process is called SILEX (Separation of Isotopes by Laser Excitation), currently being developed in the U.S. by GE-Hitachi.

**Principle** – Uranium-235 and uranium-238 atoms have spectra in the infrared, visible, and ultraviolet regions that are slightly different. Illumination of a mixture of species with lasers of selected frequencies can selectively excite one of the two species and enable them to be separated by chemical or physical methods.

# Enrichment by Laser Excitation



Schematic view of the SILVA (AVLIS) process studied in France in the 1980s

**No Success – Despite several billion dollars of R&D funding being spent on AVLIS and MLIS, mainly in the U.S., none of the variants were brought to a commercial scale and were abandoned. The only ongoing research is on the SILEX process by GE-Hitachi in the U.S. This uses  $UF_6$  as the feed material and coupled lasers to selectively excite the uranium-235 molecules. The details are proprietary.**

# Enrichment for U and Other Isotopes by Other Methods

**Other Methods for Uranium** – Other methods than Calutrons, GD, and GC have been tried. Two that have been taken to pilot plant scale are chemical methods using solvent extraction in France and ion exchange in Japan. The separation factors are very low, comparable to GD with 1.003 and much lower than GC. South Africa produced HEU using an aerodynamic method prior to signing the Nuclear Nonproliferation Treaty and terminating their program.

**Deuterium/Heavy Water** – Deuterium is an isotope of hydrogen with a mass of 2. Heavy water has the formula  $D_2O$  and is comparable to  $H_2O$ . It is important for some types of nuclear reactors which use natural uranium fuel as well as in some research reactors. The reason is that  $D_2O$  is a good moderator to slow neutrons so that they can fission uranium-235 more efficiently. The best example is the type of reactor developed in Canada known as the CANDU (Canadian Deuterium Uranium) Reactor.

**Occurrence of D** – Deuterium occurs naturally in water and is present mainly as the HDO molecule with abundance of 1 in 3,200. The  $D_2O$  molecule is present only as 1 in 41 million. HDO/ $D_2O$  can be separated from  $H_2O$  by distillation, electrolysis, and by various chemical exchange reactions, but a lot of energy is required.

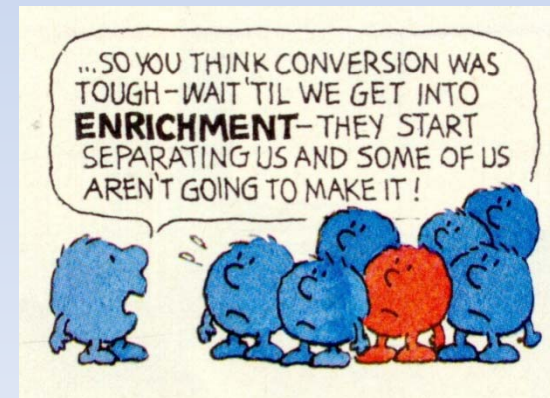
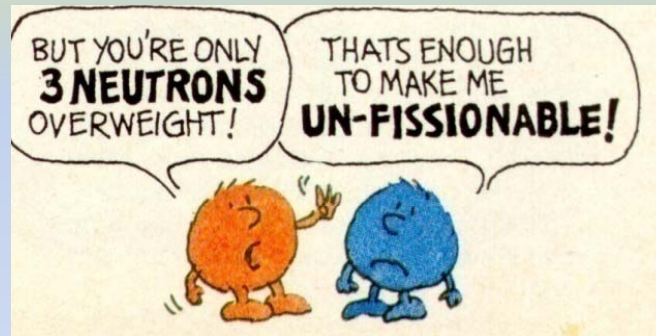
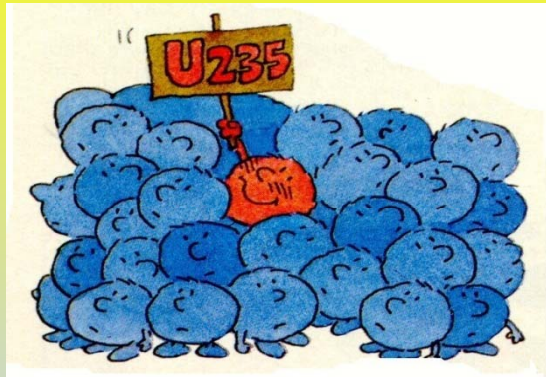
## Summary

The main stages in the front end of the nuclear fuel cycle are mining and milling to provide UOC, conversion to  $\text{UF}_6$  or  $\text{UO}_2$ , enrichment of  $\text{UF}_6$ , and fuel fabrication.

Both chemical and physical separation processes are used in these stages. The main objectives in the mining and milling of uranium ores are to separate uranium from the many mineral and chemical impurities in the ore and from the radioactive daughter products of uranium.

Physical processes are then used to enrich the uranium in the uranium-235 isotope to produce an optimized product for use in the majority of nuclear power plants. The most widely used method was gaseous diffusion but is now gas centrifugation. Laser excitation is a promising method, but no commercial process has been developed yet.

# Finally – The Cartoonists’ View of Separations in the Nuclear Fuel Cycle



With thanks to the Australian Uranium Association (formerly the Uranium Information Centre), Melbourne, Australia