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

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Background to Uranium

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, 146 n & 92 e in U-238; 92p, 143 n & 92 e in U-235.

Background to the Nuclear Fuel Cycle

- 1939 Discovery of fission of uranium by Hahn & Strassman in Germany and extra neutrons released to give possibility of a chain reaction.
- 1939-1942 Concept of an atomic bomb developed in UK and USA and put into practice as soon as the USA joined the War after Pearl Harbour.
- 1942 Start of the Manhatten Project and the need for the nuclear fuel cycle with uranium ore processing, 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-fuelled 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 optimised 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 optimised 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

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Mining and Milling 200 te of U3O8 0.7% uranium-235



Fuel Fabrication 24te U as UF6 3% uranium-235

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Nuclear Reactor 24te U as UO2 3% uranium-235 1000 MWe / 1 year Enrichment 24te U as UF6 3% uranium-235

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Depleted U Tails 146te U as UF6 0.2% Uranium-235 to Storage

World Uranium Resources

Comparison of Uranium Resource Countries, 2007 Reasonably Assured plus Inferred Resources to US\$130/kg U at 01/01/07

Australia	1,243,000 teU	23%
Kazakstan	817,000	15
Russia	546,000	10
South Africa	435,000	8
Canada	423,000	8
USA	342,000	6
Brazil	278,000	5
Namibia	275,000	5
Niger	274,000	5
Ukraine	200,000	4
Others	636,000	11
Total	5,469,000	100

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

World Uranium Production

Comparisons of World Production, 2006			
Canada	11,630 te U ₃ O ₈	25.0%	
Australia	8,931 (10,145 te in 2007)	19.2 (23% in 2007)	
Kazahkstan	6,228	13.4	
Russia	4,009	8.6	
Namibia	3,615	7.8	
Niger	3,674	7.9	
Uzbekistan	2,667	5.7	
USA	2,000	4.3	
Others	3,657	7.9	
Total	46,411	100	
Total Based on data	46,411 from the Ux Consulting Company www.uxc.	100 com 27 Nov 2007	

World requirements for current 439 reactors totalling 370 GWe in 30 countries are about 65,000 te 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.

Occurrence in Minerals

Uranium occurs in hundreds of minerals, the best known being pitchblende, uaraninite 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, eg. 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 orebody, 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 Open Cut Mine and Uranium Processing Plant at Ranger in the Northern Territory, Australia



Aerial view of Ranger Mine and plant

The Mining and Milling Processes for Underground and Open-cut Mines

- 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 of 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 U3O8 called Uranium Ore Concentrate - UOC)
- Packaging in 44 gallon (200 litre) 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 UO2 or UF6.

The world demand for conversion services is currently equivalent to about 60,000 te UF6 for the 90% of reactors which use enriched uranium fuel.

There are five major companies which supply these services:

- * Areva, France
- * Cameco, Canada
- * Converdyn, USA
- * Springfield Fuels Ltd, UK
- * Tenex, Russia

And their capacity is expected to supply demand until about 2015.

Uranium Conversion Processes

The feed material – Uranium ore concentrates in 44 gallon/ 200 litre drums

The product – Very pure uranium dioxide (UO2) for natural U reactors or very pure U hexafluoride (UF6) 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 UF_4 fluorination stage and in an extra distillation stage if necessary The final product in both processes is very pure 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 treats solution by solvent extraction with a solvent such as tributylphosphate (TBP) in an inert diluent such as odourless 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 (UO3) which is then reduced in a mixture of hydrogen and nitrogen to uranium dioxide (UO2). 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 UO3 is heated with hydrogen fluoride in a fluidised bed to form uranium tetrafluoride (UF4) and in a second stage, the UF4 is heated with fluorine in a fluidised bed to form UF6. The product is very pure solid UF6 sublimed into special cylinders for shipment to the customer.

The Dry Conversion Process

The UOC is received in 44 gallon/200 litre steel drums. The UOC has to be pelletised suitable for chemical treatment in a series of fluidised beds. It is first analysed for sodium and if it contains above a set level it is pre-treated with a solution of ammonium sulphate, filtered, dried and then pelletised.

Stage 1 – UOC to UO2. The pelletised low-sodium UOC is heated in hydrogen/nitrogen gas to reduce it to uranium dioxide (UO2).

Stage 2 – UO2 to UF4. The UO2 pellets are heated in another fluidised bed in hydrogen fluoride gas to form uranium tetrafluoride (UF4) (green salt). This product still contains residual metallic and non-metallic impurities.

Stage 3 – The UF4 pellets are heated in another fluidised bed with fluorine gas (F2) to form the volatile uranium hexafluoride (UF6). Any impurities with involatile fluorides are removed in the residual pellets. Some impurities with volatile fluorides may be carried over with the UF6 product.

Stage 4 – If volatile impurities are detected, then the product is fractionally distilled to provide a UF6 final product meeting strict specifications.

Commercial Conversion Plants



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

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



Conversion Plant of British Nuclear Fuels, 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 53,000 te SWU/year (where SWU is a Separative Work Unit, a measure of the energy required to produce a unit (kg or te) of product at specified enrichment levels in the product and tails).

* In comparison, the current supply is about 58,000 te SWU/year, thus giving a surplus. By about 2015 this surplus is estimated to become a deficit due to the closure of old gaseous diffusion plants in the USA and France and the completion of the USA-Russian Agreement for conversion of Russian Highly Enriched Uranium from decommissioned warheads into low enriched uranium for use in civil reactors.

* The old GD plants are being replaced by new gas centrifuge plants which are very 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 optimised 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 Manhatten Project
*	Gaseous Diffusion	The first large commercial method
*	Gas Centrifugation	The most efficient current method
*	Laser Excitation	The most recent method with claims of even higher efficiency than the gas centrifuge
*	Chemical Exchange	Solvent extraction 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% to 99%.

A calutron is a form of mass spectrometer like that developed by Aston in the UK in 1919, used by Dempster in the USA 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 Manhatten Project after 1942. *Cal U* recognised the University of California and *tron* is from cyclo-tron.

In a calutron a small amount of uranium chloride is bombarded with high energy electrons to produce charged uranium ions in a vacuum chamber. The ions are accelerated in a semi-circle 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 Manhatten 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 travelling in a semi-circle as a production machine. He estimated that 10 calutrons could produce about 4 gm 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 Laboratory. 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 and with copper being in short supply the government released 14,700 tons of pure silver to make the wire. A total of 200 gm 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 the1950s 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 Manhatten Project started in 1942 after the USA entered the Second World War after Pearl Harbour. The Project decided to study not only 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 though the pores than uranium-238 hex molecules. The process has to be repeated a large number of times. And uses a lot of energy.



The very simple principle

The First Large Gaseous Diffusion Plant – K-25



The K-25 plant was built at Oak Ridge, Tennessee, from 1943 -1945 at a cost of \$512M with a nearby town initially planned to be 11,000 but developed quickly to 50,000 by 1944 to staff the GD plant, the Calutron plant and other plants. 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 square feet (609,000 m2). It provided medium enriched UF6 to the calutrons for final enrichment to 99%.

Further Development of Gaseous Diffusion

US Developments – After the war, larger amounts of high and low enriched uranium were required for the US 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.



French GD Plant, Tricastin.



Size of GD columns at Tricastin

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 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 centre, 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 and much higher than the 1.0003 in a diffusion plant, a large number of stages are needed in a cascade to obtain 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 34,000 te SWU per year, which is 68% of the current demand of 50,000 te 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 USA for Urenco, Areva and the USEC. Total capacity is planned to be 15,000 te SWU per year. Two of these will replace old GD plants.

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 which were irradiated by one or more types of laser. The two best known processes in the 1970s & 1980s were AVLIS (Atomic Vapour 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) being developed in the USA by GE-Hitachi.

Principle – Uranium-235 and uranium-238 have spectra in the IR, visible and UV regions that are slightly different. Irradiation 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 USA, none of the variants were brought to a commercial scale and were abandoned. The only on-going research is on the SILEX process by GE-Hitachi in the USA. This uses UF6 as the feed material and coupled lasers to selectively excite the uranium-235 molecules. No details.

Enrichment for U and Other Isotopes by Other Methods

Other Methods for Uranium - Other methods than Calutrons, GD and GC have been tried. The only two to have been taken to pilot plant scale are chemical methods using solvent extraction in France and ion exchange in Japan. The separation factors were very low, comparable to GD with 1.003 and much lower than GC.

Deuterium/Heavy Water – Deuterium is an isotope of hydrogen with a mass of 2 and heavy water has the formula D2O and is comparable to H2O. Heavy water is important for some types of nuclear reactors which use natural uranium fuel and in some research reactors. The reason is that D2O 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).

Occurrence of D – Deuterium occurs naturally in water and is present mainly as the HDO molecule with abundance of 1 in 3,200. The D2O molecule is present only as 1 in 41 million. HDO/D2O can be separated from H2O by distillation, electrolysis and by various chemical exchange reactions, but a lot of energy is required.

Separation/Enrichment of Deuterium/Heavy Water

Commercial Production – The first commercial plant was built in Norway in 1934 with a capacity of 12 te per year. This was remarkable given that D was only discovered by Urey in 1931 !!

Canada built a plant in Trail, British Columbia, in 1943 as part of its contribution to the Manhatten Project. In 1953, the USA began using heavy water in nuclear reactors for production of plutonium and tritium (hydrogen-3) at the Savannah River site in S. Carolina. Canada built a second plant at Trail and then a third plant in 1979, the Bruce Heavy Water Plant in Ontario with four nuclear power plants to provide the energy and another four NPPs to supply the Ontario grid. This was the largest plant in the world with a capacity of 700 te per year using the GS Process.

The US developed the chemical exchange process known as the Girdler Sulphide (GS) Process and this soon replaced distillation and electrolysis for the large scale production of heavy water, although distillation was still used to make 99.75% product.

Principle of the GS Process – Isotopic exchange between hydrogen sulphide (H2S) and water (H2O) in hot (120-140oC) and cold (30-40oC) towers. D in H2S migrates into H2O in the cold section and D migrates from H2O to H2S in the hot section. Many stages are needed and a lot of energy. One te D2O needed 340,000 te water feed.

Nuclear Fuel Fabrication

The providers of UOC, conversion services and enrichment services deliver relatively standardised products to customer's specifications. Highly purified products of natural and enriched uranium hexafluoride do not need any further purification or separation processes before being made into uranium dioxide in fuel elements. Nuclear fuel fabricators produce highly engineered fuel assemblies made to detailed specifications set by the customer. There are 20 major fuel fabrication plants in the world and capacity is sufficient to meet demand until at least 2020.



Four types of fuel assemblies from two manufacturers

Conclusions

- 1. The main stages in the front end of the nuclear fuel cycle are mining and milling to provide UOC, conversion to UF6 or UO2, enrichment of UF6 and fuel fabrication.
- 2. 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.
- 3. Physical processes are then used to enrich the uranium in the uranium-235 isotope to produce an optimised product for use in the majority of NPPs. The most widely used methods were calutrons, gaseous diffusion and now gas centrifugation. Laser excitation is a promising method but no commercial process has yet been developed.
- 4. Physical and chemical processes are used in the production of heavy water for use in some NPPs and research reactors.

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







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