

(6) Magnox Fuel Fabrication, (7) AGR Fuel Fabrication, (8) CANDU Fuel Fabrication, and (9) Reprocessing.

3. Yellowcake Production

In all cases the starting point is uranium ore. Uranium is explored for and produced much like base metals - lead, iron, zinc, copper - with a few interesting variations. In nature uranium consists of about 99.28% U^{238} , 0.711% U^{235} , and the balance other isotopes. Mined uranium ore is chemically and physically processed to produce U_3O_8 or yellowcake. Physical and chemical processing of the ore is as follows in some typical processes:

- The ore is removed from the uranium mines via a series of conveyor belts or trucks to one crushing stations. At the ore crushing stations, the ore undergoes reduction in size to prepare it for chemical processing, blending and storage.
- Uranium ore leaving the crushing station is mixed with water and ground to a size that fits through a fine mesh screen. This process produces a mud slurry of approximately 50% solid and 50% water. The ore is now ready for chemical treatment.
- The mud slurry is pumped to leaching agitators. As the slurry enters the leaching circuit, sulphuric acid (H_2SO_4) and sodium chlorate ($NaClO_3$) are added. Uranium and any other metals soluble in sulphuric acid are leached or dissolved. The sodium chlorate oxidizes the ore, which speeds up the leaching process and improves recovery.

- After approximately eight hours of leaching, heavier particles (sand) are separated from lighter particles (slime) by centrifugal force in classifier separations.
- The sand is removed from the bottom of the classifiers and the slime from the top. The sand, still in slurry form, is fed into a five stage rake classifier where it is thoroughly washed with an acid-water solution. As the sand is washed, the uranium, now in solution, is separated from individual grains of sand. At the end of the rake classifier circuit, the barren sand is pumped to the tailings disposal pond.
- The lighter component of the ore slurry (slime) is pumped to a thickener circuit. The slime goes through a six stage washing cycle to remove uranium attached to microparticles of slime. Barren slime is pumped to the tailings pond.
- As the acid-water-uranium solution leaves the thickener, it has advanced through five stages of slime washing. The solution now contains all the uranium that can be removed economically from the ore. This completes the second stage of ore processing.
- Next, the uranium solution enters the solvent extraction (SX) circuit to remove uranium from the acid-water solution which may contain traces of vanadium, iron, molybdenum, etc. As the uranium solution enters the one end of the SX circuit, barren solvent, usually tributylphosphate (TBP), is introduced at the other end. The two solutions advance countercurrent to each other and proceed through four stages of mixing and settling.

- The solvent extraction, or ion-exchange process, performs two basic functions. First, it selectively removes the uranium from the acid-water solution leaving the unwanted metals in solution. Second, the uranium is concentrated in the solvent threefold.
- The barren acid-water solution, or raffinate, free of uranium, leaves the last stage of the solvent extraction circuit and is pumped back into the thickener circuit as a washing solution or to the tailings disposal pond.
- From the SX circuit, the concentrated uranium in the solvent solution is pumped to the stripping circuit. Here the uranium is stripped from the solvent in a four-stage mixer-settler and again concentrated.
- Leaving the stripping circuit, the stripping solution, containing concentrated uranium, flows to a precipitation circuit. Here the uranium, which has been up to this point in solution, is caused to precipitate or "fall out" of solution. The addition of ammonia, air and heat in the precipitation circuit causes uranium to become insoluble in the acid strip solution. During precipitation, the uranium solution is constantly agitated to keep the solid particles of uranium in suspension.
- Leaving the precipitation circuit, the uranium is pumped to a thickener tank where the solid is allowed to settle to the bottom of the tank.

- From the bottom of the product thickener tank the precipitated uranium in the form of a slurry is pumped into a three stage drum filter circuit. Moving through the drum filter circuit, the uranium is thoroughly washed to remove any soluble salts that might be entrained in the product.
- The uranium leaves the last washing filter in the form of a filter cake. It is then dropped onto a perforated plate where a roller pushes the material through openings into spaghetti-like particles. The uranium in this form is fed to dryers.
- In the dryer, the product is dried by steam heat and readied for packaging. The final product - U_3O_8 , or yellowcake - is packaged in 55 gallon drums for shipment.

There are a number of variations to the process for producing U_3O_8 depending upon the initial form of the ore and the location of the mill. Other processing variations are: (1) Acid-Leach/Ion Exchange (IX)/Precipitation, (2) Acid Ion Exchange (IX)/Eluex/Precipitation, (3) Acid-Leach/Resin-in-Pulp (RIP)/Precipitation, (4) Acid-Leach/Rip/Eluex/Precipitation, (5) Alkaline Leach/Caustic Precipitation, (6) Alkaline Leach/Rip/Precipitation, etc. Since these processing variations are similar to the one already described, no further information will be provided other than to recognize that they do exist.

4. UF₆ Conversion

The next step in the fuel cycle is the chemical conversion to UF_6 (LWR and AGR). The conversion of uranium concentrates to UF_6 consumes tremendous quantities of industrial chemicals. Every ton of processed uranium requires

more than a ton and a half of fluorspar, two thirds of a ton of hydrofluoric acid and almost two thirds of a ton of sulphur.

There are two processes used in the commercial production of UF_6 from U_3O_8 . These two processes are (1) the Dry Fluoride Volatility Process and the (2) Wet Solvent Extraction Process (Refining Fluorination Process). For the purpose of this section, both of these processes will be briefly described.

As we will see, the processing of uranium concentrates (U_3O_8) into uranium hexafluoride (UF_6) has two objectives - removal of impurities, and the conversion of the concentrates into a chemical form required by enrichment. The Dry Volatility Process, developed by Allied Chemical Corporation, proceeds as follows:

- The concentrates are received at the conversion plant and undergo weighing, sampling, and moisture content determination.
- Mechanically sized concentrates are placed in a chemical reactor to react with hot "cracked" ammonia to form uranium dioxide.
- The uranium dioxide (UO_2) is placed in another reactor to react with vaporized anhydrous hydrofluoric acid to form uranium tetrafluoride (UF_4), or "green salt". (At this point, the UF_4 could be drawn off and used to produce Magnox fuel after a series of purification steps.)
- The UF_4 is combined with gaseous fluorine in a fluidized bed at temperatures approaching $1000^\circ F$. The uranium is volatilized as UF_6 gas.

- The UF_6 is cooled and separated from other gaseous components, then re-vaporized and fractionally distilled to remove any remaining impurities.
- The UF_6 is fed as a liquid into carbon steel containers (cylinders) which hold up to 14 tons of product. On cooling, the UF_6 becomes a white crystalline solid. In this form the UF_6 is shipped to an enrichment facility to undergo the next step in the fuel cycle.

The classic process for ore concentrate conversion was developed by the US Atomic Energy Commission and is the refining-fluorination process. The refining step involves purification of a uranium solution by solvent extraction with tributylphosphate (TBP). There are two variations to the process requiring different equipment and operating conditions but overall the basic operations are similar. The Refining-Fluorination Process proceeds as follows:

- The first step in the process is digestion. The ore concentrate (U_3O_8) is digested with 40% nitric acid (HNO_3) in a heated tank to form a slurry.
- The aqueous slurry is fed to a series of pumper decanter contactors for extraction of uranium into a 30% TBP solution. The solvent and slurry are contacted in the pumper decanter contactors countercurrently. (The solvent flows in one end, the slurry from the other.) The ratio of the organic TBP to the aqueous solution is about 13:1. Raffinate leaves the last decanter with a uranium concentration less than 0.1 g U/l.

- After removal of traces of TBP, the raffinate is neutralized with a lime slurry which causes the residual trace uranium to precipitate and settle to the bottom of open storage ponds.
- The precipitate - uranyl nitrate ($UO_2(NO_3)_2$) - is pumped in solution through an evaporator where the solution is concentrated to the approximate composition of uranyl nitrate hexahydrate (UNH).
- The UNH is now fed into heated troughs with rounded bottoms to undergo denitration. In the denitration trough, rotating agitators keep the bed thoroughly mixed. The end result of denitration is uranium trioxide (UO_3).
- The UO_3 is now transferred into two vertical stainless steel reactors. Dissociated ammonia is fed into both reactors. The UO_3 is partially reduced in the first reactor and overflows into the second where reduction is completed and UO_2 is formed. The two stages are controlled at $1100^\circ F$.
- UO_2 from the fluidized bed reducers is screw fed into the first stage hydrofluorinator where it is contacted with HF exhaust gas from the second stage. The partially reacted solid is screw fed to the second stage where it reacts with anhydrous HF. The solid formed is uranium tetrafluoride (UF_4), or "green salt".
- The final step of the fluorination process is the reaction of UF_4 with elemental fluorine to produce UF_6 . The UF_4 and pure fluorine are introduced at the top of a vertical tower reactor. The

solid reacts with the gas almost immediately in a flame reaction having an estimated temperature of 3000°F. Essentially complete conversion of the UF_4 to UF_6 is achieved.

- The outlet gas stream, containing UF_6 , fluorine, and diluent gases is cooled to 300°F and passed through cyclone filters and a sintered Monel filter to remove entrained solids. The UF_6 is then readied for packaging.

The purity of the UF_6 produced by the refining-fluorination process is exceptional. The chemical purity of the product is consistently 99.97%, and the overall yield of the process is better than 99.5%.

5. UF_4 Conversion

The Magnox reactors require that uranium concentrates be chemically converted to uranium tetrafluoride (UF_4), or "green salt". The conversion process proceeds as follows:

- Raw material, uranium ore concentrates, are sampled and checked for purity and moisture content.
- The ore is then dissolved in nitric acid (HNO_3) to form uranyl nitrate ($UO_2(NO_3)_2$). The nitric acid serves to dissolve some of the impurities but still there are a few left in suspension.
- The mixture of uranyl nitrate, nitric acid, and impurities is then filtered to remove the undissolved impurities.
- The filtered liquid passes thru a purification circuit which separates the uranyl nitrate using a solvent extraction process (similar to those described earlier).

- The pure uranyl nitrate is then passed through evaporators to remove excess water and concentrate the liquid.
- The concentrated liquid is sprayed into a chemical reactor containing a bed of about 10 tons of uranium trioxide (UO_3) powder which is electrically heated and kept "fluidized" by a stream of compressed air drawn up into the vessel from the bottom.
- The sprayed uranyl nitrate decomposes to form more uranium trioxide (UO_3) powder. As the bed builds up, the powder overflows to a second fluidized bed reactor.
- In the second fluidized bed reactor, the UO_3 is reduced by a stream of hydrogen to uranium dioxide.
- The uranium dioxide (UO_2) passes to a third fluidized bed reactor where it is converted to uranium tetrafluoride (UF_4) by introduction of hydrofluoric acid gas. The UF_4 or "green salt" is ready for shipment to a Magnox fuel production facility.

b. The Enrichment Process

For the LWR and the AGR, enrichment in the U^{235} isotope is required. There are two major commercial methods of enrichment being used today. These processes are (1) the Gaseous Diffusion Process and (2) the Gas Centrifuge Process. There are other advanced techniques being investigated on pilot and laboratory scale that show promise commercially, but that will not be available for years. These advanced enrichment technologies involve plasma and laser applications.

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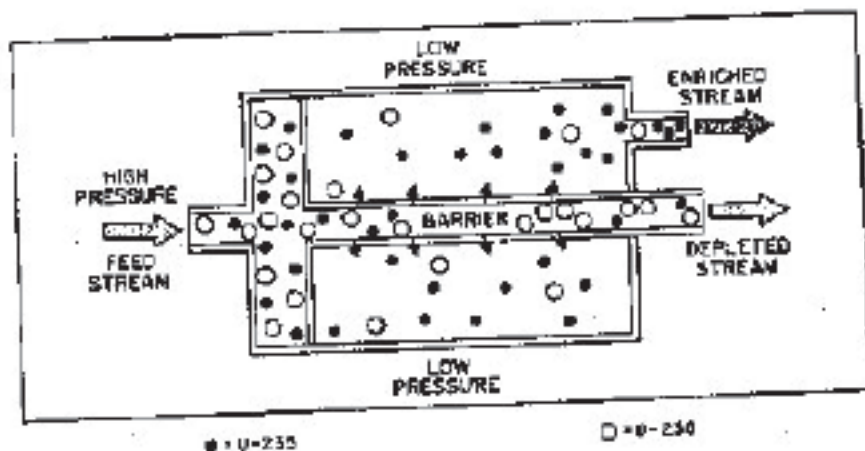
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The gaseous diffusion process involves the diffusion of isotopes of UF_6 through a porous membrane - the barrier. The diffusion process is based on the fact that when a gas passes through a membrane or port of a diameter smaller than the mean free path of the molecules in the gas then the flow is governed by Knudsen's Law. Knudsen's Law states that for a given pressure difference, diffusion is inversely proportional to the square root of the molecular weight of the gas. In the case of UF_6 , it is 1.00429. (The point of this chemical and physical law is that $U^{235}F_6$ is slightly lower in molecular weight than $U^{238}F_6$. As a result, it is the $U^{235}F_6$ molecule that selectively passes through the barrier slightly more than the $U^{238}F_6$ molecule.) This indicates that enrichment per stage is very small and a large number of stages in series is required to produce practical enrichment. For example, production of 4.0 w/o - U^{235} from natural uranium (0.711 w/o U^{235}) requires about 1500 stages.

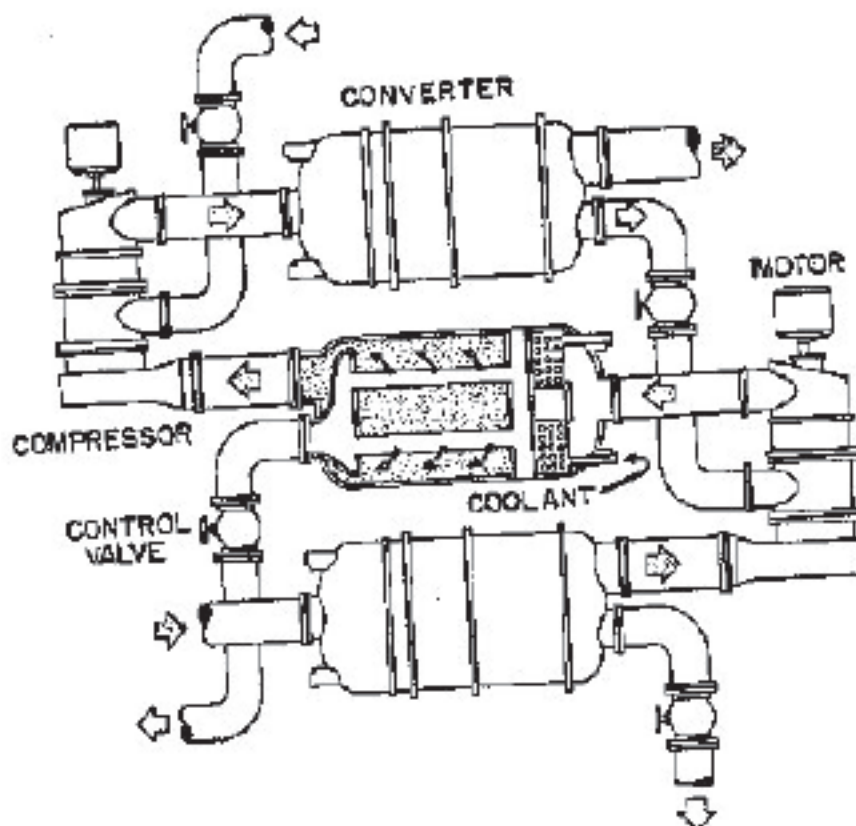
The gaseous diffusion process proceeds as follows:

- UF_6 is introduced at high pressure inside a barrier tube. About half of the gas diffuses through the barrier and is fed to the next higher stage. The reject, or undiffused stream, is recycled to the next lower stage. (Figure V-5).

A typical arrangement of gaseous diffusion equipment in a series of stages is shown in Figure V-6. The UF_6 gas is moved by axial flow compressors in the larger stages. These compressors are driven by electric motors, some as large as 2000 HP. A cooler is provided to remove the heat of compression at each stage.



Gaseous Diffusion Stage
Figure V-5



Series of Stages and Equipment

Figure V-6

The barrier tubes are contained in large cylindrical vessels called converters. To provide proper flow balance of the stream, a control valve is used in the reject stream outlet from the converter. The enriched stream from the bottom stage enters the central compressor and after being partially compressed is mixed with the depleted stream from the top stage. After further compression, the gas is then fed to the converter in the center. Groups of such stages are combined to make up operating units which, in turn, make up the diffusion cascade.

To discuss enrichment services, it is necessary to understand the concept of separative work. This concept provides a universal method for defining quantitatively in terms of a single measurement unit the enrichment services being performed.

Separative work is best understood in terms of the "separative potential" $\{ \phi \}$ - a quantity associated with a unit mass of material at a given enrichment or concentration $\{ C \}$.

$$\phi = (2C-1) \log_e \left(\frac{C}{1-C} \right) + AC + B$$

(A & B are constants)

Passage through a separation barrier produces two fractions, an enriched product of concentration C_p and mass M_p and a depleted (waste) fraction characterized by C_w and M_w . Since the conservation of total mass and U^{235} mass is required, the following equations apply.

$$M_p + M_w = M$$

$$M_p C_p + M_w C_w = M C$$

The total separation potential times mass, however, is increased by an amount S which we term SEPARATIVE WORK.

$$S = M_{\text{pop}} + M_{\text{r}\phi\text{w}} - M_{\phi}$$

Thus, as evidenced by the above equation, a specific enrichment task can be described in terms of the quantity of material fed and the quantity withdrawn from the cascade as product and tails and the U^{235} isotope content of each of these three streams.

In essence, separative work is the work or energy required to carry out this separation of feed into product and tails. The units of separative work are Metric Tons Separative Work Units (MTSWU). This is not a mass unit but simply the units that result from the derivation of the separative work equation.

The degree of depletion of U^{235} in the tails stream is significant in determining the amount of separative work required to accomplish the production of a stated amount of enriched product. It also has an important bearing on the amount of UF_6 required (and consequently the U_3O_8 required). With a higher tails assay, less separative work is required but more feed is required to produce specific (enriched) product. Thus, there is a trade-off between the use of feed and the use of separative work in producing enriched material.

Centrifuge technology basically involves a cylinder containing the UF_6 gas rotating at a high rate of speed. The UF_6 gas within the cylinder has the same rotational speed as the cylinder. This rotational speed imposes a cen-

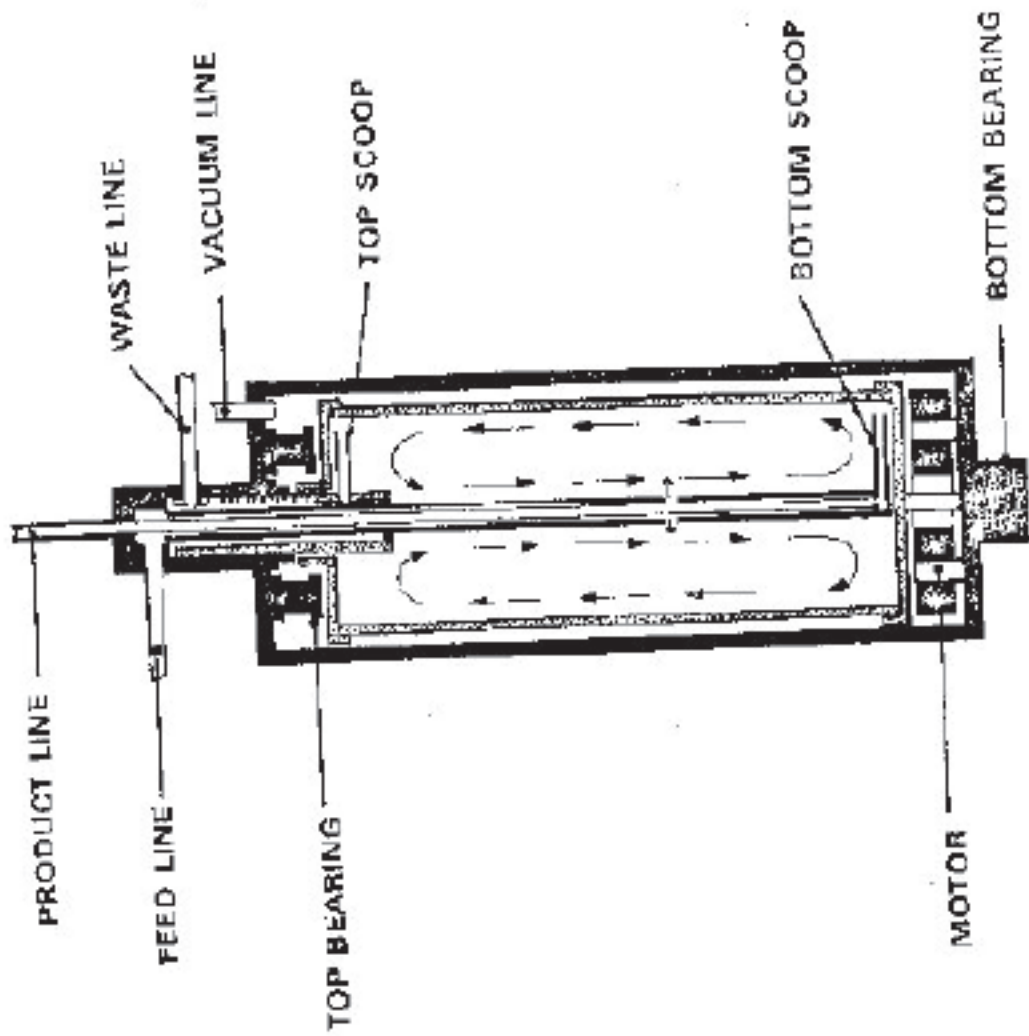
trifugal force on the UF_6 molecules ($U^{235}F_6$ and $U^{238}F_6$) which modifies the density distribution resulting from random kinetic motion. The resulting density distribution for a gas of molecular weight M is:

$$\rho(r) = \rho(0) \exp\left(\frac{M\omega^2 r^2}{2RT}\right)$$

where $\rho(r)$ is the density at radius r and ω the angular velocity of rotation. The key feature of this formula is that the molecular weight M appears in it. Thus, if two molecular species are present in the gas ($U^{235}F_6$ and $U^{238}F_6$), the concentration of one in relation to the other is different at the center from the rim of the cylinder.

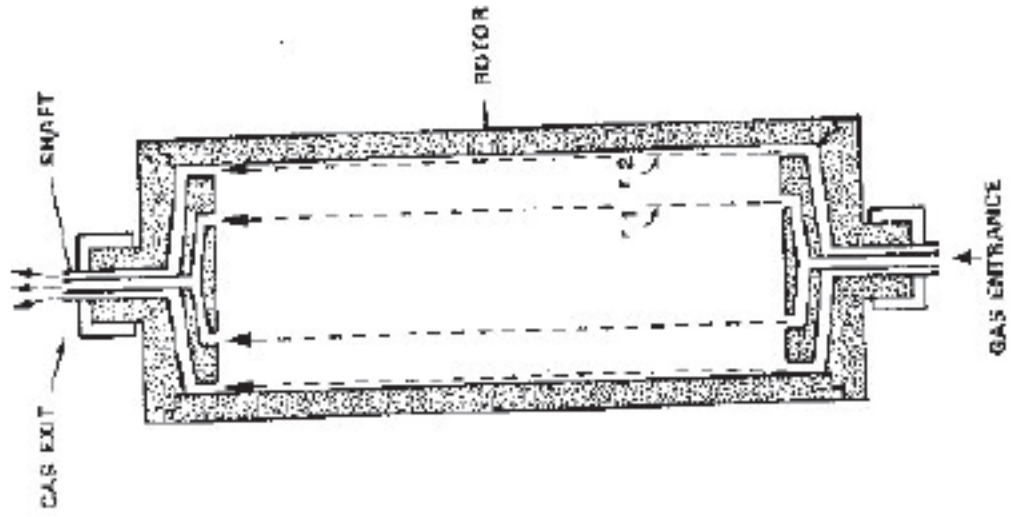
In the early stages of development the simplest techniques were used to design a functioning centrifuge. The result of this early work was the Concurrent Centrifuge (Figure V-7). In this scheme, the gas (UF_6) flows in one end and takes up the rotational speed by collisions with the walls of the centrifuge. By the time the gas reaches the other end of the cylinder, the equilibrium radial density distribution should be set up making it relatively simple to draw off the heavy ($U^{238}F_6$) and light ($U^{235}F_6$) fractions.

From this early work, countercurrent centrifuges were designed offering better performance. Most of today's large scale centrifuge facilities utilize countercurrent machines (Figure V-7). In the countercurrent arrangement, the fed UF_6 is passed through an annular space and emerges into the center of the rotor. Pitot tubes, or 'scoops', are used to extract the gas from the top and bottom of the rotor which will be depleted and enriched, respectively, in the light isotope.



Countercurrent Centrifuge

Figure Y-7



Concurrent Centrifuge

The ratio of the U^{235} concentration between product and waste is given theoretically by:

$$\frac{C_p}{C_w} = \exp\left(\frac{K_1 L \Delta M v^2}{d RT}\right)$$

where L and d are the rotor length and diameter, v the peripheral velocity, K_1 a factor depending on throughput. At maximum separative work output, the ratio C_p/C_w is about half its maximum value.

The maximum separative work output is given by:

$$S = \left(\frac{K_2 \rho D \Delta M v^2}{2RT}\right)^2 \frac{\pi L}{2}$$

where ρ and D are the density and diffusion coefficient in the gas, and K_2 is a design constant. Note that the longer the centrifuge the more output, that for a given wall speed, rotor radius is immaterial, and finally and most importantly that on this simple theory, separative work output depends on the fourth power of wall speed. In reality, separative work output deviates significantly from its fourth power dependence on velocity but is still a very important factor.

So much for the physics of centrifuges. For practical outputs and enrichments they have to be operated in cascades, just as do diffusion plant stages. Some simplification results from the fact that the output of a centrifuge is measured in kilograms of separative work per annum, rather than metric tons per annum from a large diffusion plant stage. Thus, whilst diffusion plant stages of several different sizes have to be designed and

installed, the optimum shaping of a centrifuge cascade can be achieved cheaply and simply by employing centrifuges of a single size and connecting them in a series arrangement.

Leap-frogging technology, we come to advanced isotope (enrichment) separation techniques. There are three advanced enrichment processes being investigated. These processes are the Plasma Separation Process (PSP), the Molecular Laser Isotope Separation (MLIS) Process, and the Atomic Vapor Laser Isotope Separation (AVLIS) Process. All of the processes work on physical principles which give rise to greater isotopic selectivity than either gaseous diffusion or gaseous centrifuge.

To start with, the PSP takes advantage of the difference in the gyrating frequency of different mass ions in a magnetic field. The fact that moving charged particles are deflected by a magnetic field is an old physical fact. This process exploits that fact. By applying an electromagnetic field whose frequency equals the frequency of the U^{235} ion, it is possible to accelerate the U^{235} ion over U^{238} which is not in resonance with the field. In this manner, the resonant U^{235} ion gains energy and increases its orbit size. As the U^{235} ion is heated it moves towards a collector array. The higher energy U^{235} ion has a larger probability of being collected as product than the lower energy U^{238} . At present, there are several areas requiring further resolution.

The next two processes are Laser Isotope Separation (LIS) processes. These processes also take advantage of different resonances in U^{235} and U^{238} , but these resonances are internal. Because these internal resonances

(energy states) correspond to different degrees of internal energy, the resonant electromagnetic frequencies are considerably higher than that of PSP. In the case of a molecule, the internal vibrational and rotational levels of the molecule correspond to radiation in the infrared portion of the spectrum. For atoms, the electronic energy states correspond to radiation in the visible portion of the spectrum. Thus, these processes use lasers as their radiation source.

The Molecular Laser Isotope Separation (MLIS) Process involves the following. UF_6 gas is expanded through a nozzle along with an inert buffer gas. The established supersonic flow lowers the internal temperature of the molecule. This increases the spectral resolution (clarity) of the vibrational bands, and separates the U^{235} and U^{238} resonances to the point where a precisely tuned infrared laser can preferentially excite or heat the U^{235} . This increased heating makes it possible for a second laser (high power ultraviolet laser) to preferentially dissociate the $U^{235}F_6$ into $UF_5 + F$. The new molecule UF_5 has a lower vapor pressure than UF_6 and can be made to condense on an appropriate collector.

The approaches to Atomic Vapor Laser Isotope Separation (AVLIS) utilize the reasonably large separation between the absorption bands of U^{235} and U^{238} . Using tunable dye lasers operating on excited levels of the atom, sufficient energy can be imparted to preferentially ionize only the U^{235} . Once the U^{235} is ionized (charged), one can use electric and/or magnetic fields to extract the ions onto a collector.

To conclude, while conceptually these advanced isotope separation processes appear to be relatively simple, the development beyond scientific feasibility are far more complicated and years away.