

NUCLEAR ENGINEERING FOR AN UNCERTAIN FUTURE

International Symposium on the 20th Anniversary of the
Department of Nuclear Engineering, University of Tokyo

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PLENUM PRESS, NEW YORK

The Nuclear Fuel Cycle : An Overview

Manson BENEDICT

1. Introduction

My purpose today is to give a brief overview of the technology of the nuclear fuel cycle. I shall describe briefly the processes which are now being used and shall venture some opinions about future trends.

To keep within the time allocated me and to concentrate on the fuel cycle likely to be used in most nuclear power systems, I'm limiting my talk to various forms of the uranium-plutonium fuel cycle, those which use uranium-235 or plutonium as fissile material and uranium-238 as fertile. I don't mean to suggest that fuel cycles using thorium and uranium-233 are not important, but power systems using these fuels are farther off in time and are used in fewer systems.

2. Uranium-Plutonium Fuel Cycle

Figure 1 illustrates the uranium-plutonium fuel cycle. In this figure each rectangle, numbered from 1 to 20, represents a fuel-cycle step or process; each line, lettered from A to Z, represents a material being transferred or processed. The two rectangles with heavy borders, 9 and 18, represent respectively converter and fast breeder reactors, in which electricity is generated, the objective of these fuel cycles.

Processes 1 through 10, in the first two rows, are the steps in the once-through, slightly-enriched uranium fuel cycle to which nuclear power systems in the United States have been presently limited by Presidential directive. In these steps materials handled range from uranium at A to irradiated fuel J. In countries such as France, England, and Japan, in which reprocessing is practical and recycle of plutonium to thermal reactors is considered, the fuel cycle includes steps 11 through 15 of the second and third rows and deals with additional materials L through Q, ending with high-level waste Q in permanent storage 15. For the fast breeder reactor

Massachusetts Institute of Technology, U.S.A.

18 being introduced in France and the U.S.S.R. and under consideration in England, Germany, and Japan, the fuel cycle includes process steps 16 to 20 and materials R to Z of the last row.

3. Uranium Resources and Their Energy Potential

Uranium ore A is found in almost all parts of the world and occurs in a great variety of minerals. At the present price of uranium concentrates B, around \$30 per pound of U_3O_8 or \$80 per kilogram of uranium, ore containing from 0.1 to 0.2% of uranium is of commercial grade.

The top part of Table 1 gives the OECD's¹⁾ figures for the reasonably assured uranium resources which could be produced for less than \$80/kg U and the annual uranium production in 1978 of the principal uranium-producing countries. To compare these figures with uranium requirements of nuclear power plants it may be noted that the annual uranium consumption of a one-gigawatt (1,000-megawatt) pressurized water reactor running at 70% capacity factor requires about 23.8 metric tons per year of uranium enriched to 3.3%.

To produce this in an enrichment plant rejecting depleted uranium containing 0.2% U-235 requires about 147 metric tons of natural uranium. This involves steps 1 through 10 of Figure 1. If irradiated fuel is reprocessed and the recovered uranium and plutonium are recycled to pres-

Table 1. Uranium resource and production data^{2*} (Metric tons U).

	Resources reasonably assured at cost under \$ 80/kgU	Annual production in 1978
United States	531,000	14,200
Australia	290,000	516
Union of South Africa	247,000	3,960
Canada	215,000	6,803
Niger	160,000	2,060
Namibia	117,000	2,697
France	40,000	2,183
Others*	250,000	1,491
Total, all countries*	1,890,000	33,900
Reasonably assured at cost of \$80-130/kgU	740,000	
Estimated additional at under \$130/kgU	2,500,000	
Total*	5,030,000	

* Excluding centrally managed economies.

^{2*} from OECD.¹⁾

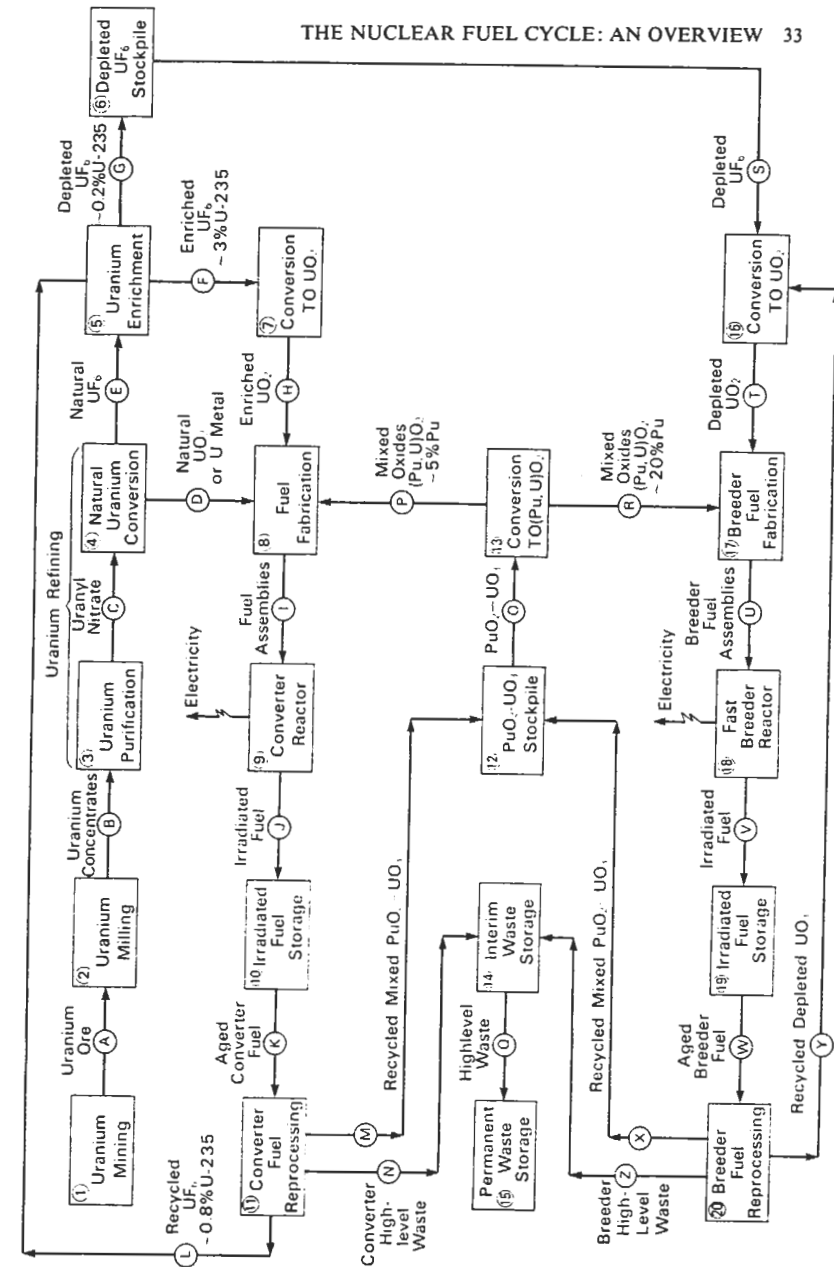


Fig. 1. Uranium-plutonium fuel cycles.

surized water reactors (steps 11 through 15 of Figure 1), the annual consumption of natural uranium is reduced to 108 metric tons, a saving of 27%.

Thus, the 1,890,000 reasonably assured uranium resources of Table 1 would support $1,890,000/147 = 12,900$ gigawatt-years of electric generation without reprocessing or recycle, or $1,890,000/108 = 17,500$ gigawatt-years with reprocessing and recycle of both uranium and plutonium. A world with 500 gigawatts of nuclear capacity, if all in pressurized water reactors, would have enough reasonably assured uranium available at \$80 per kg to operate 26 years without recycle or 35 years with.

The bottom part of Table 1 shows that the same OECD report identifies 740,000 tons more of reasonably assured uranium resources available at a cost between \$80 and 130 per kg and 2.5 million tons more of estimated additional resources, for a rounded total of 5 million metric tons.

As a one-gigawatt fast breeder reactor 18, with its associated fuel cycle steps 16-20, needs only one or two tons of depleted uranium S for makeup per year, the world's present stock of over 200,000 metric tons of depleted uranium would provide fuel for at least 100,000 reactor-years of operation for one-gigawatt breeder reactors, without requiring the mining of one additional ton of uranium ore. Or, the U-238 in the 1.89 million tons of reasonably assured uranium resources, in fast breeder reactors, would provide fuel for around a million reactor-years of operation for such breeder reactors. This enormous extension of the energy obtainable from limited uranium resources is what makes successful development of the breeder reactor so important, especially for a country like Japan with little domestic uranium.

4. Uranium Minerals and Mining

The principal uranium minerals are primary minerals, usually containing tetravalent uranium such as pitchblende U_3O_8 , or secondary minerals in which all uranium is hexavalent, such as carnotite, potassium uranyl vanadate. Increasing amounts of uranium are being recovered as a byproduct of processing other minerals, notably from crude phosphoric acid obtained when phosphate rock is dissolved in sulfuric acid for fertilizer production, or from tailings from South African gold mines.

The principal methods of mining uranium are open-pit mining, underground mining, and solution mining, in which uranium is extracted by pumping a solvent, for example ammonium carbonate, down an injection well, through the mineralized zone, and up through a production well.

A unique feature of uranium mining and milling is the radioactivity of uranium ore. This is advantageous in facilitating location of economic ore deposits and in grading mined rock for uranium content. A price is

paid for the radioactivity, however, in the precautions which must be taken to ventilate uranium mines, remove dust from mines and refineries, and prevent their refuse from spreading radioactivity. The principal hazard is from radium, its daughter the gas radon, and their decay products. As these are removed during uranium refining and form only slowly in refined uranium owing to the long half-life of their parent, thorium-230, refined uranium concentrates are much less hazardous than uranium ore.

5. Uranium Milling

In milling uranium ores²⁾ no one method is universally applicable, because of the great variety of uranium minerals and host rock. Uranium minerals are not susceptible to flotation and are usually too finely divided for density separation. Consequently, uranium is usually extracted by chemical leaching. The leaching agent used depends on the nature of the uranium mineral and the host rock. When the rock is a silicate or some other material insoluble in acid, sulfuric acid leaching is preferred, because it costs less and dissolves uranium values faster than sodium carbonate. However, when the rock is limestone or other material soluble in acid, leaching with sodium or ammonium carbonate is preferred. With tetravalent uranium, an oxidant such as air or sodium chlorate must also be used.

Uranium may be recovered from leach solutions by precipitation with sodium hydroxide, by ion exchange, or by solvent extraction. Precipitation now is used only with carbonate leaching, because from acid solution too many impurities are precipitated with uranium.

Most ion-exchange processes use anion-exchange resins to effect selective separation of uranium, which forms complex sulfate or carbonate anions, from other metallic impurities, which do not. A typical anion-exchange resin for uranium extraction is a trimethylamino-substituted co-polymer of styrene and divinyl benzene (Figure 2). Types of ion-exchange equipment

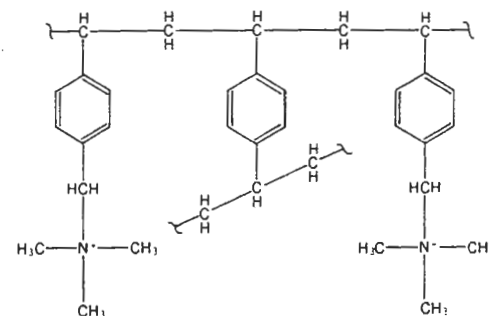


Fig. 2. Quaternary ammonium anion-exchange resin.

used include fixed-bed (in which resin is fixed in place and solutions are shifted from one contactor to another), moving bed (in which solution flow is fixed and resin is shifted from one bed to another), and continuous (in which solution and resin are alternately contacted and separated with countercurrent flow between stages).

Two highly selective classes of solvent extraction processes have been developed for recovering uranium from sulfuric acid leach liquors: the Dapex process, using di(2-ethylhexyl) phosphoric acid, and the Amex process, using trioctylamine. In both, the distribution coefficient for uranium is high, even when complexed with sulfate ion. The trioctylamine solvent is now generally preferred because it is more selective for uranium. Most new U.S. mills use this process. Uranium is stripped with concentrated sodium or ammonium chloride or sulfate.

Uranium concentrated by ion exchange or solvent extraction is precipitated, usually with ammonia as ammonium di-uranate, and constitutes the "yellow cake" of commerce.

This discussion of uranium concentration would not be complete without mentioning recovery of uranium from sea water. Although the uranium concentration is only 3.34 milligrams per cubic meter, the oceans of the world contain around 4 billion tons of uranium, which anyone with a pipe can "mine." The most promising process thus far developed for extracting this uranium selectively is ion exchange on hydrated titanium oxide. Early work in England and at Oak Ridge developed plant designs for which uranium production costs were several hundred dollars per pound. I understand that further work aimed at lowering costs is going on in Japan. Principal problems are those of handling enormous volume of sea water, preventing fouling or loss of the absorbent, and minimizing consumption of regenerant.

6. Uranium Purification

Uranium concentrates still are too impure for nuclear use. The standard method of purification (step 3) is to dissolve the yellow cake in nitric acid and separate it from impurities by countercurrent solvent extraction with a 30% solution of tributyl phosphate (TBP) in dodecane, from which uranyl nitrate C, is stripped with dilute nitric acid.

7. Natural Uranium Conversion

If natural uranium is to be used as reactor fuel, it must be converted (step 4) into metal or $UO_2(D)$. If it is to be enriched in uranium-235, today's enrichment processes require that it be converted into $UF_6(E)$, the most

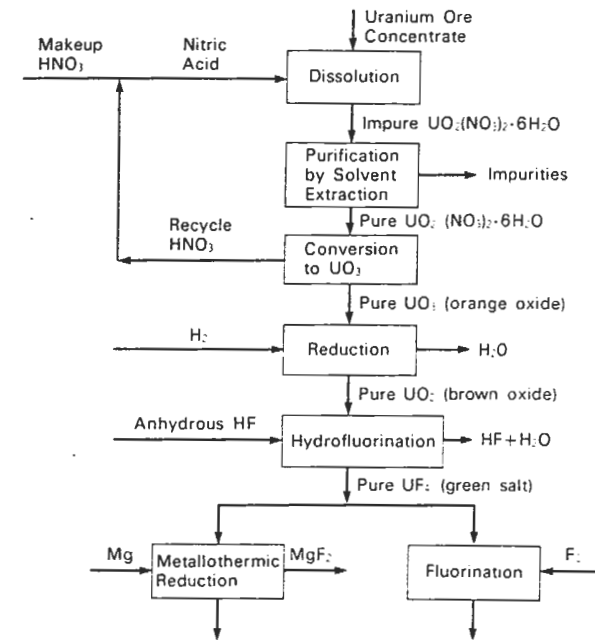
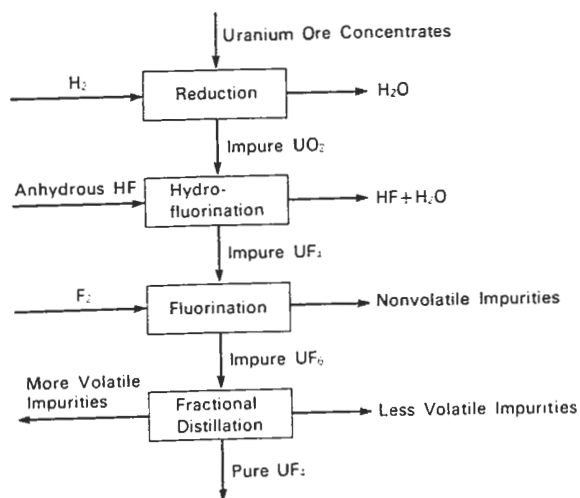


Fig. 3. Steps in conventional uranium refining processes.

stable, volatile compound of uranium. Figure 3 shows the steps in these conversion operations. Uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ is first converted to UO_3 either directly (in the United States), by heating to $400^\circ C$, or in two steps (in France) by precipitation with ammonia as the diuranate followed by decomposition with steam at $400^\circ C$. The UO_3 is next reduced to UO_2 with cracked ammonia gas at $590^\circ C$. If the UO_2 is to be converted to metal or UF_6 , it is then converted to UF_4 by reaction with anhydrous hydrogen fluoride at $500^\circ C$.

To produce metal, a mixture of UF_4 and magnesium metal in a steel vessel lined with calcium oxide is preheated to around $400^\circ C$, at which the reduction reaction takes place with sufficient heat production to melt both products, uranium metal and magnesium fluoride.

To produce UF_6 , powdered UF_4 is burned with fluorine gas in a reactor with monel walls held at $500^\circ C$. UF_6 is purified by distillation at a pressure slightly above its triple-point pressure of 1.5 atmospheres.

Fig. 4. Allied Chemical UF_6 process.

In the United States, the Allied Chemical Company produces UF_6 from ore concentrates in the different sequence of steps shown in Figure 4. Concentrates are reduced directly to impure UO_2 which is first hydrofluorinated to impure UF_4 and then fluorinated to impure UF_6 , which is finally purified by distillation. Conversion cost is around \$5/kgU.

8 Uranium Enrichment

Provision of uranium enrichment services, step 5, is one of the major technical challenges of the nuclear fuel cycle. The one-gigawatt pressurized water reactor we have been using as an example uses 23.8 metric tons per year of uranium enriched to 3.3% U-235. To produce this in a separation plant depleting U-235 to 0.2% requires the production of 194,000 separative work units per year, presently costing about \$100 per SWU, at a total annual cost of \$19.4 million dollars, about the same as the annual cost of the natural uranium from which the enriched uranium is produced.

Table 2 lists processes for enriching uranium now in use or under development.

8.1 Gaseous Diffusion

The gaseous diffusion process has produced almost all of the enriched

Table 2. Uranium enrichment processes.

Process	Status	Countries involved	Separ. factor	Energy use, kWh/SWU
Gaseous diffusion	Major industrial use	U.S.A., England, France, U.S.S.R., China	1,004	2,500
Gas centrifuge	Large pilot plants, Major industrial use in 1980s	England, Holland, W. Germany, U.S.A., Japan	1.1	135
Separation nozzle	Large pilot plant being built	W. Germany, Brazil	1,015	3,300
UCOR	Large pilot plant being built	South Africa	1,025	3,300
Chemical exchange	Pilot plant operating	France	1,002	600
Ion exchange	Lab. development	Japan		
Atomic vapor laser	Lab. development	U.S.A.	High	Low
Molecular laser	Lab. development	U.S.A.	High	Low
Plasma separation	Lab. development	U.S.A.	High	Low

uranium used for nuclear power production. Its low separation factor requires the use of 1,200 stages to enrich uranium to 3.3%. Its high energy use contributes around \$50 to the cost of a separative work unit. Nevertheless, the process is still economically competitive with other processes. Its reliability is evidenced by the 99% onstream efficiency of the diffusion plants of the U.S. Department of Energy. When the present improvement program is complete, these plants will have a capacity of 27 million SWU/yr and can thus serve 225 one-gigawatt nuclear power plants. The diffusion plant being built at Tricastin, France, owned by the international consortium Eurodif, will have a capacity of 10 million units per year in 1982. The U.S.S.R. plant is rumored to have a capacity around 10 million SWU/yr, of which 3 million is available for export. The English diffusion plant is small and is being phased out in favor of the centrifuge. Little is known about the plant in China.

Figure 5 is a schematic diagram of three stages of a U.S. gaseous diffusion plant. Each stage consists of a converter, which is fitted with thousands of tubes of porous diffusion barrier, a compressor to pump the process gas, UF_6 , between stages, and a cooler to remove the heat of compression. When UF_6 flows through the barrier tubes, the U-235 to U-238 ratio is increased by about 0.4%. Figure 6 shows the equipment for the larger stages of a U.S. diffusion plant. The large tanks are the converters, with compressors and coolers at the rear. This stage has a capacity of about 5,000 SWU/yr. Figure 7 is an aerial view of one of the three U.S. diffusion plants, this one at Portsmouth, Ohio.

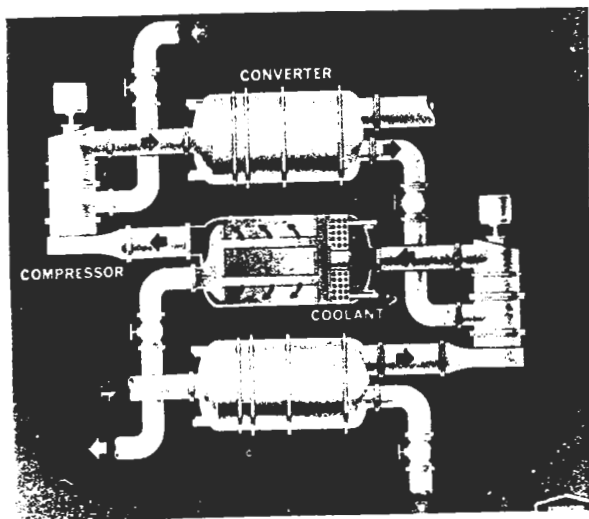


Fig. 5. Arrangement of gaseous diffusion stages.
(Photo courtesy of U.S. Energy Research and Development Administration)

8.2 Gas Centrifuge

The gas centrifuge has been chosen by the British-Dutch-German Urenco-Centec organization as the process for its enrichment plants. At present, two plants, each producing 200,000 SWU/yr are operating, one in England, the other in Holland. By the early 1980s these plants will have a capacity of 2 million SWUs per year, with the possibility of expansion to 10 million. The U.S. is building a 2.2 million SWU/yr plant, with the possibility of expansion to 8.8 million. This process has also been chosen for use in Japan, with a projected capacity of 250,000 SWU/yr by 1985 and one to two million by 1990.

Figure 8 is a schematic diagram of a gas centrifuge. It consists of a rotor made of material with high strength-to-density ratio, such as aluminum alloy, rotating inside of an evacuated casing. UF_6 gas in the rotor is subjected to centrifugal acceleration thousands of times greater than gravity. This causes the U-235 to U-238 abundance ratio at the axis to be as much as 10% higher than at the rotor wall. A system of scoops and baffles induces longitudinal counterflow (down at the wall, up near the center in this figure), thus making the abundance ratio at the top as much as twice that



Fig. 6. View of converters and compressor.
(Photo courtesy of U.S. Energy Research and Development Administration)

at the bottom, in a centrifuge of sufficient length. A set of three concentric, stationary tubes at the axis provides means for admitting feed UF_6 to the midplane and withdrawing light fraction from the top and heavy fraction from the bottom. The high enrichment, however, is coupled with slow circulation rate and low separative capacity. Urenco machines are rumored to have a capacity of around 5 SWUs per year, Japanese machines 10, and the longer U.S. machines perhaps ten times as high, but still small compared with a gaseous diffusion stage. Thus, tens or hundreds of thousands of machines are needed for a full-scale enrichment plant.

Some of the many centrifuges in the Urenco pilot plant at Almelo, Holland, are shown in Figure 9. Figure 10 is a similar photo of a U.S. Department of Energy centrifuge pilot plant.

Because separation in a centrifuge is a thermodynamically reversible process, energy consumption is much less than in irreversible gaseous diffusion. Most of the energy is used to overcome mechanical friction and viscous losses in UF_6 . In U.S. centrifuge plants the energy consumption per separative work unit is only about 5% that of gaseous diffusion. However, the capital cost of the centrifuge plant is higher. At today's

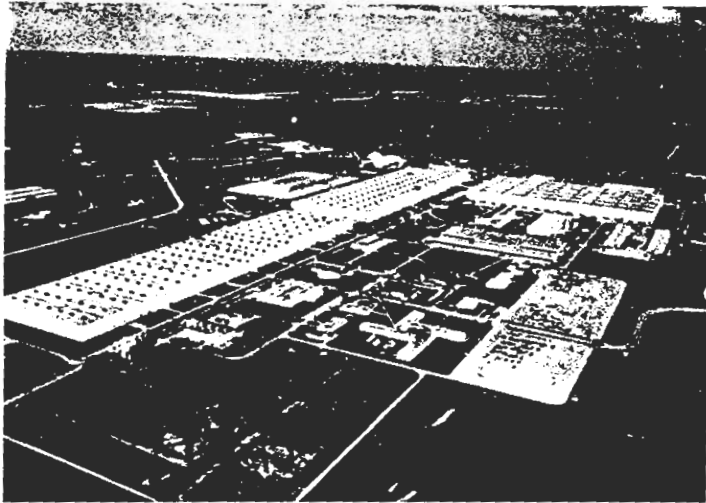


Fig. 7. Gaseous diffusion plant at Portsmouth, Ohio.

(Photo courtesy of U.S. Energy Research and Development Administration)

price for electricity the cost of separative work from the two processes is about the same, \$100/SWU.

8.3 Separation Nozzle Process

A German engineer, Dr. E. W. Becker, has developed the so-called separation nozzle process for separating uranium isotopes. The separating element for this process consists of a long semicircular groove about a tenth of a millimeter in radius, shown in transverse section in Figure 11. Feed gas, a mixture of 5% UF_6 and 95% hydrogen, flows from a pressure of about one atmosphere into a low-pressure region through a curved slit with first a convergent, then a divergent cross-section. This accelerates the gas to supersonic speed, and the curved groove downstream of the slit produces a high centrifugal acceleration. This sets up an isotopic enrichment gradient, with gas farther from the wall enriched in U-235. A knife-edge downstream from the slit divides the stream, with the more deflected portion enriched in U-235. A separation factor around 1.015 is obtained. Although this is much higher than in gaseous diffusion, the dilution of UF_6 with 19 times its volume of hydrogen gives the nozzle process about the same specific energy consumption as gaseous diffusion.

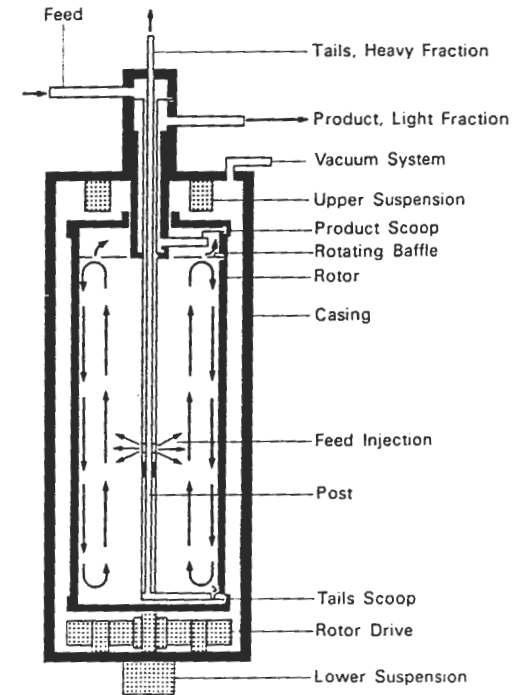


Fig. 8. Countercurrent gas centrifuge with internal circulation.

This process is used in a 180,000 SWU/yr pilot plant being built in Brazil.

8.4 South African Process

The UCOR process being developed by the Uranium Enrichment Corporation of South Africa bears some resemblance to the separation nozzle process, in that the separating element is characterized as a fixed-wall centrifuge, and the process fluid is a mixture of hydrogen and UF_6 . However, there must be substantial differences, as the UCOR process operates at pressures of several atmospheres, only one-twentieth of the feed gas to a stage is taken for the enriched fraction, and the separation factor is higher. Energy consumption is about the same. Details of the separating element have not been described. At last word, a large pilot plant using this process was being built in South Africa.

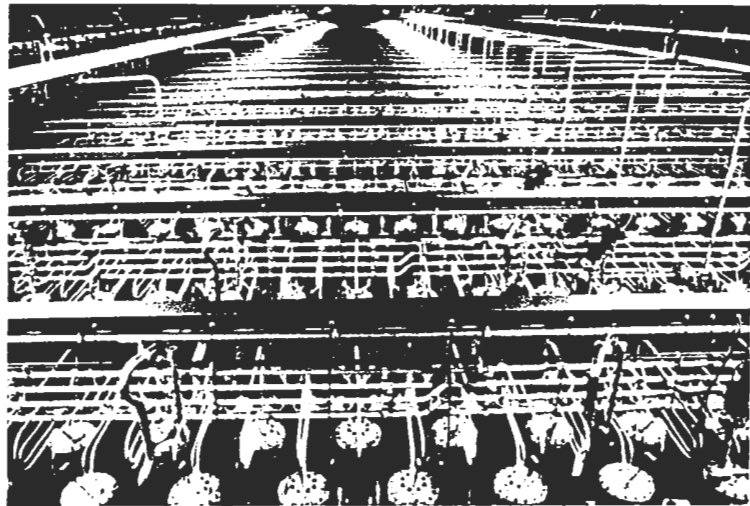


Fig. 9. Urenco-Centec pilot plant of German centrifuge machines at Almelo, Netherlands. (Photo courtesy of Urenco Limited)

8.5 French Chemex Process

A promising new process for enriching uranium has been under development in France for over ten years, but few details have been disclosed. A recent paper by Dr. Coates stated that the process involves chemical exchange between unspecified uranium compounds in two immiscible liquid phases, one organic, the other aqueous.²¹ Refluxing means were not disclosed. The separation factor exceeded 1,002. Contactors were pulse columns 1m in diameter by 20 m high. Power consumption would be under 600kWh/SWU. Cost would be competitive with other processes. The long equilibrium time of 15 months to make 3% enriched uranium is seen as an advantage because it precludes practical use of the process to make highly enriched uranium.

8.6 Advanced Processes

The U.S. Department of Energy has under development three advanced isotope separation processes: the Atomic Vapor Laser Isotope Separation Process (AVLIS), the Molecular Laser Isotope Separation Process (MLIS), and the Plasma Separation Process. None has yet reached the pilot plant

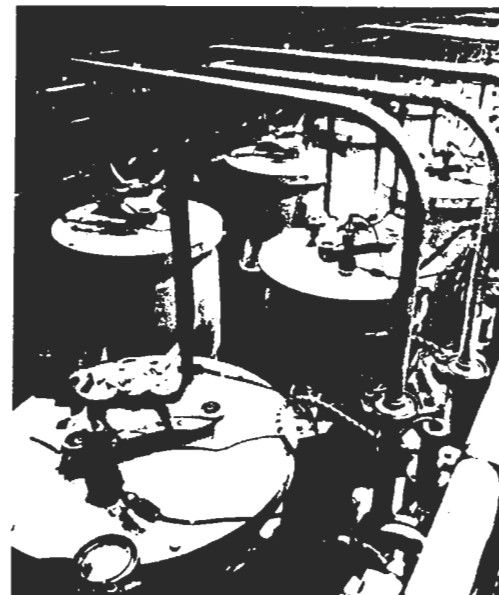


Fig. 10. U.S. gas centrifuge pilot plant. (Photo courtesy of U.S. Energy Research and Development Administration)

stage, but all are judged possible competitors for the gas centrifuge, certainly with higher separation factors and likely with lower costs.

The AVLIS process has been under development by Lawrence Livermore Laboratory and Jersey-Nuclear Avco-Isotopes, Inc. Figure 12 shows a form of the process proposed by the latter. Uranium metal in a water-cooled crucible is struck by a focused sheet of electrons, which heat a line of metal to 3,000 K. Uranium vapor atoms diverge radially upward from the line source and flow between cooled product-collector plates so oriented that uranium metal atoms move past them. The space between the plates is illuminated by a pulsed laser whose light is at a frequency in the visible tuned to excite U-235 atoms but not U-238. A following pulse of ultraviolet light from a second laser imparts sufficient energy to the excited U-235 atoms to ionize them, while leaving U-238 un-ionized. A magnetic field perpendicular to the plane of the figure deflects the ionized uranium atoms into the collector plates. The principal problems of this process are de-

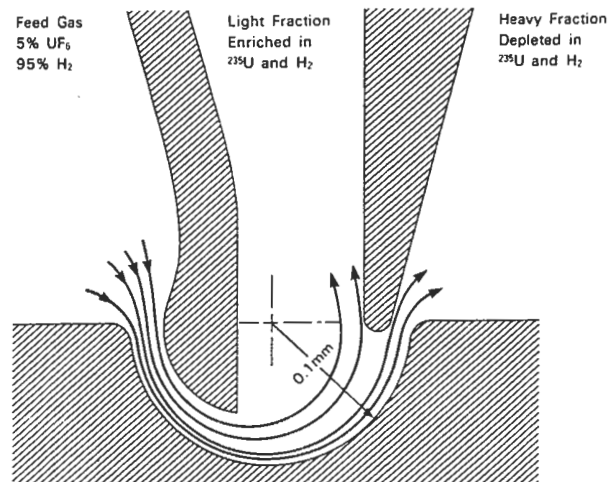


Fig. 11. Cross-section of slit used in separation nozzle process.

velopment of lasers of the requisite energy, repetition rate, and endurance, and handling uranium metal at high temperatures.

The Molecular Laser Isotope Separation Process, under development at Los Alamos, uses UF_6 vapor as working fluid. To obtain sufficiently selective absorption by $^{235}UF_6$, it is necessary to cool the vapor to around 75K to bring most of the UF_6 into its lowest vibrational state. Since the vapor pressure of UF_6 is effectively zero at this temperature, this calls for special measures to delay condensation till after light is absorbed. The proposal is to circulate a mixture of UF_6 and hydrogen through a hypersonic nozzle to obtain the desired low temperature after expansion. Before the UF_6 has time to nucleate and condense, the mixture is irradiated, first with a pulse of infrared light from a laser tuned to excite $^{235}UF_6$ but not $^{238}UF_6$, then with other light sources of sufficient energy to dissociate excited $^{235}UF_6$ while leaving $^{238}UF_6$ undissociated. The lower-fluoride dissociation product of $^{235}UF_6$ can then be separated from undissociated $^{238}UF_6$ by conventional means. The difficulties of this process are again the need to develop special lasers plus the problems of working at low temperature and high gas velocities.

Time does not permit discussion of the other processes listed in Table 1.

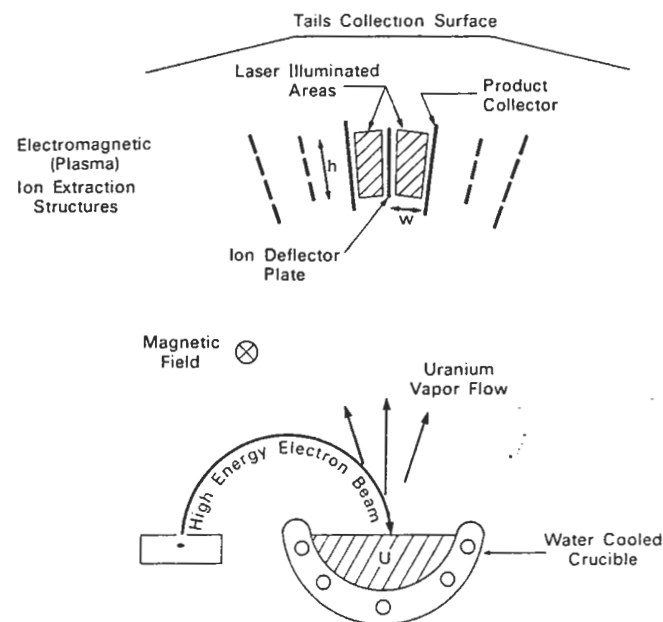


Fig. 12. Uranium metal vapor laser isotope separation process.

9. Conversion of UF_6 to UO_2

Since all enriched uranium now produced is in the form of UF_6 , it is necessary to convert this to UO_2 (step 7) before it can be used as reactor fuel. One conversion method is to reduce UF_6 to UF_4 in the gas phase with hydrogen, after which the UF_4 is converted to UO_2 by reaction with steam at 650°C.

10. Fuel Fabrication

To fabricate fuel for PWRs (step 8), the process used at the Springfields Works of British Nuclear Fuels Limited³¹ is representative and will be described briefly. UO_2 powder is milled with an organic solvent and binder. The slurry is spray-dried under conditions that produce particles of the desired size and density. Particles are formed into pellets in a hydraulic press. Binder is volatilized in a furnace at 800°C, and pellets are sintered

in a hydrogen atmosphere at 1,650° C. Pellets are finished to dimensions in a centerless grinder.

To make fuel pins, pellets are stacked in stainless-steel or zircaloy tubing, to which end caps are fitted. Sufficient space is left to accommodate fission product gases. The assembled pin is filled with helium, after which the end caps are seal-welded. Welds are proved tight by mass spectrometer leak testing.

To make fuel assemblies, the pins are fastened together with spacers, end-fittings, or both, designed to maintain the correct alignment and clearance under reactor operating conditions.

Fabrication costs in the United States are around \$100 per kg U.

11. Irradiation in Converter Reactor (Step 9)

In pressurized water reactors today fuel typically sustains a burn-up of 30,000 megawatt-days per ton and remains in the reactor for about three years. The uranium-235 content of fuel then is around 0.8%, and the fuel contains around 0.9% plutonium and 3.5% fission products.

12. Irradiated Fuel Storage (Step 10)

After this burn-up, irradiated fuel no longer contributes effectively to the nuclear chain reaction and is discharged to water-cooled storage basins lined with stainless steel. The fuel is intensely radioactive and generates considerable heat, though at a declining rate. Heat production rate per ton of fuel is around 20 kW after 150 days and 10 kW after a year. Continuity of reliable cooling is essential. The water is kept clean by filtration and ion exchange and is monitored for radioactivity. If an assembly leaking fission products is detected, it is encased in a leak-tight overpack. The foregoing is the procedure adopted in the United States for storing spent fuel until decisions are made regarding more permanent arrangements.

13. Reprocessing

In other countries, where the fuel value of the uranium and plutonium in spent fuel is given more weight and where greater urgency is felt for packaging its radioactivity in a form more suitable for permanent storage, irradiated fuel K, aged for from a half-year to one or more years, is reprocessed, step 11. The principal reprocessing plants now operating are those at Marcoule and La Hague in France, Windscale in England, and Tokai-Mura in Japan, of which Figure 13 is a photograph. A plant to reprocess



Fig. 13. PNC reprocessing plant at Tokai Works, Japan.

5 tons of irradiated uranium per day was designed and nearly completed at Barnwell, South Carolina, in the United States, but its operation has been indefinitely deferred by Presidential directive. All these plants use the Purex process, with minor variations.

The principal steps in the Purex process are shown in Figure 14. The first step is to prepare fuel for dissolution, by cutting open the cladding. This is usually done by shearing the fuel bundle into short lengths, after removing external hardware. During decladding, radioactive xenon and krypton fission products are evolved and removed by off-gas treatment, step 16. Fuel is then dissolved in hot nitric acid (step 2) while the cladding hulls remain unattacked. Gases evolved in this step include oxides of nitrogen and fission product iodine. These are scrubbed with water to remove nitrogen oxides as nitric acid (step 15), and then also routed to off-gas treatment.

In feed preparation, step 3, the dissolver solution is diluted to bring its pH to 2.5 and plutonium is converted into its most extractable, tetravalent form by addition of NO_2 .

In primary decontamination, step 4, uranium and plutonium are separated from over 99% of the fission products by solvent extraction with

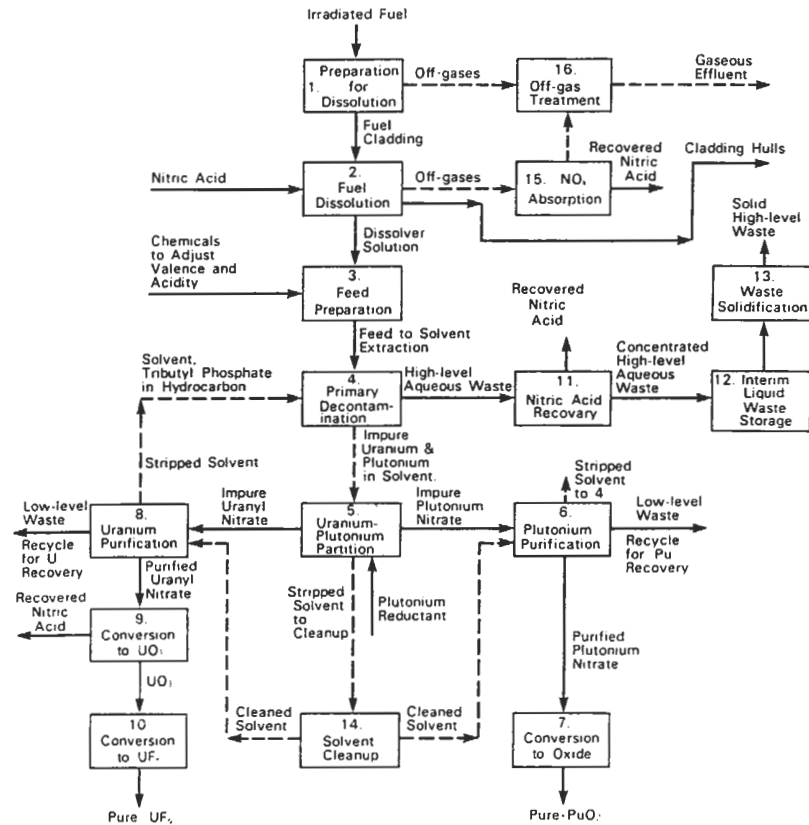


Fig. 14. Principal steps in purex process.

30 volume percent tributyl phosphate (TBP) in a paraffinic diluent. In partition, step 5, plutonium is separated from uranium by reducing plutonium to the organic-insoluble trivalent state with a reductant strong enough to reduce plutonium but not so strong as also to reduce uranium. Hydroxylamine or tetravalent uranium are preferred.

Additional cycles of solvent extraction with TBP are used to purify plutonium, step 6, and uranium, step 8. Purified plutonium nitrate is converted to oxide, step 7, either by precipitation as oxalate followed by ignition, or direct ignition. Purified uranyl nitrate is ignited to UO₃, step 9. High level wastes are concentrated by evaporation, step 11. Nitric acid recovered from these steps is recycled to the dissolver. TBP solvent, which

is gradually hydrolyzed and degraded by radiation and contaminated by some fission products, is cleaned in step 14 by washing with sodium or ammonium carbonate and then recycled. Low-level wastes from steps 6 and 8 are processed for further recovery of plutonium and uranium, then concentrated for recovery of water and nitric acid.

Because of these recycle operations, nitric acid consumption is minimized and the volume of water to be discharged is reduced to an amount which can be evaporated into the effluent ventilating air flowing up the plant stack.

In off-gas treatment, step 16, iodine may be retained by adsorption on silver-coated zeolites. Processes are being developed for removing krypton and xenon by either cryogenic distillation or absorption in refrigerated fluorocarbon. The voloxidation process is being developed for converting tritium in irradiated fuel into tritiated water in off-gases from step 1, and then absorbing the water. When these processes are fully operational, the only major radioactive wastes from a reprocessing plant should be cladding hulls and concentrated, high-level aqueous waste.

To deter misuse of plutonium, current thinking favors modifying the standard Purex process just described so that plutonium is never fully separated from uranium in the partition step and is produced mixed with uranium at a concentration no higher than needed for subsequent fuel recycle, around 5% when recycled (M,O,P, in Figure 1) in thermal reactors or 20% in fast breeder reactors (X,O,R). The Civex Process, proposed in 1978⁴⁾ is one such process.

14. Fast Breeder Fuel Cycles

The fast breeder reactor 18 (Figure 1) uses two types of fuel. The core is fueled with a mixture of 20% plutonium dioxide and 80% depleted uranium dioxide R, and the blanket uses depleted uranium dioxide T. Fuel assemblies in the core are required to sustain a burn-up of from 60,000 to 100,000 megawatt-days per ton. Hence irradiated fuel V from the core contains a higher concentration of fission products and is more radioactive than irradiated fuel J discharged from converter reactors. Irradiated fuel from the blanket contains few fission products but sufficient plutonium to provide the net breeding gain which is the objective of the fast breeder reactor. After storage, step 19, to permit fission products in core fuel to decay partially, aged core and blanket fuel W, in proportion as discharged from the reactor, is reprocessed, step 20, for recovery of uranium and plutonium X and separation of high-level waste Z.

Breeder fuel reprocessing will use the Purex process, modified as necessary by the higher concentration of fission products. It will probably be

necessary to use two cycles of decontamination before separating uranium and plutonium, with the first cycle removing most of the radioactivity in contactors with short residence time, to reduce solvent degradation.

15. Waste Processing

Wastes from breeder reactors Z and converter reactors N are generally similar and will be discussed together.

When first discharged from a reprocessing plant, high-level wastes are best stored in liquid form to facilitate cooling. Preferred storage conditions are: stainless steel tanks surrounded by a secondary leakage barrier, nitric acid content between 2 and 4 molar, and temperature below 60°C, to reduce corrosion. Reliable, redundant cooling systems and a spare tank to which wastes could be transferred if another tank leaks are absolutely essential.

After the wastes have decayed such that the rate of heat generation is below a few kilowatts per ton, in from 5 to 10 years they can be adequately cooled in solid form and should be converted to a water-insoluble solid. Of the numerous solid waste forms on which work has been done, borosilicate glass is the form favored in most countries. Extensive pilot-plant work on this waste form has been done in the United States, Japan, England, Germany, and France, and a full-scale glass production plant is operating in France.

Conversion of liquid wastes to glass involves three steps: removal of water, calcination of nitrates to oxides, and conversion of oxides to glass. These steps may be carried out either in sequence or concurrently. They may be carried out continuously or batch-wise.

The French AVM process shown schematically in Figure 15 is a continuous process for converting waste sequentially, first to calcine and then to glass.⁵⁷ Liquid waste is fed to the top end of an inclined, slowly rotating, heated tube. The waste is dried in the upper half and calcined in the lower half, heated to 400°C. Calcine and glass-making solids (frit) are fed to a ceramic melting crucible heated to 1,150°C by induction heaters. Molten glass builds up in the crucible for 8 hours and then is cast into a stainless-steel waste storage canister. The canister is then disconnected, cooled, and welded shut. This process has been operated on an industrial scale at Marcoule since 1977.

A different type of glass-making furnace, which has produced up to 20 kg of glass per hour at the U.S. Pacific Northwest Laboratory, is shown in Figure 16⁶¹. This may be fed with frit and calcine, as in this figure, or directly with frit and liquid waste. The melter is a ceramic-lined cavity in which the glass is heated by electric current passing between immersed electrodes.

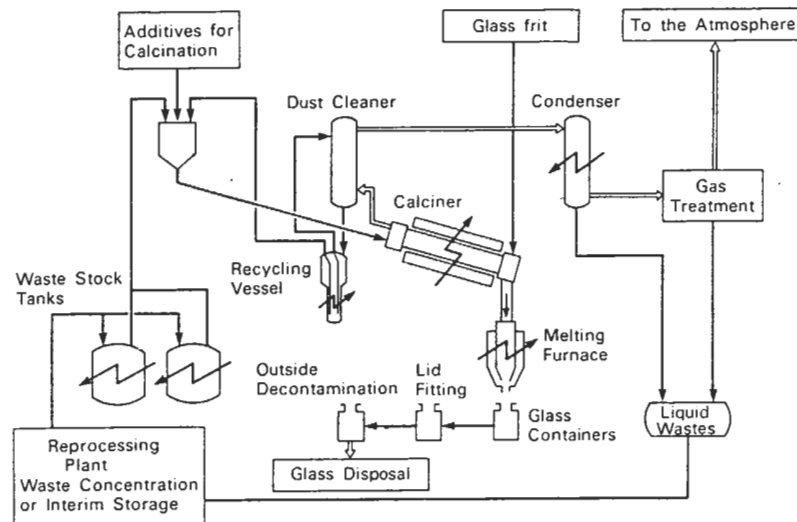


Fig. 15. The continuous process employed in the Marcoule vitrification plant (AVM Process).

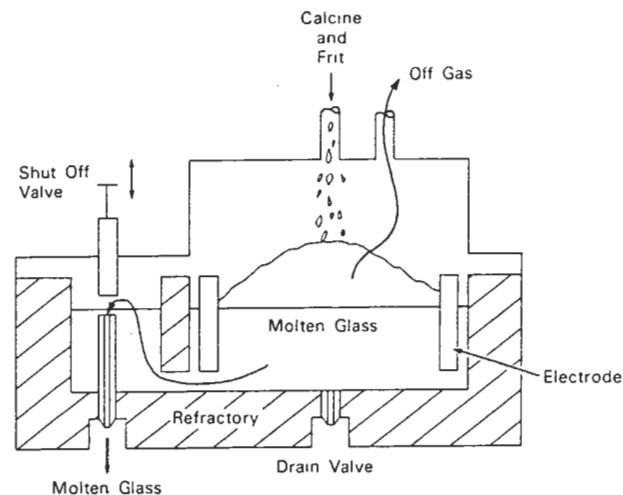


Fig. 16. Joule-heated ceramic melter.

Molten glass overflows continuously through a valve and bottom-discharge port. I will show an example of borosilicate glass made by duPont in a somewhat similar process.

16. Waste Storage

The final step in managing radioactive waste is provision of safe, long-term storage. The prime requirement here is prevention of escape of wastes into air or water contacting humans. Safe interim storage can be provided in monitored water-cooled basins, as practiced in France, or air-cooled vaults, as at the U.S. Idaho Laboratory.

For permanent storage a procedure not requiring continuous surveillance is preferred. Irrecoverable storage in stable geologic formations, 500 to 1,000 meters underground, through which groundwater can be shown not to circulate, is the storage mode now favored. Bedded salt deposits have been identified as a suitable waste repository in West Germany and are being considered in the U.S. Advantages of salt are its high thermal conductivity, its plasticity at depth, which guarantees that fissures will be self-sealing, and the absence of circulating groundwater assured by the stable existence of the salt beds for millions of years.

Granite, favored in Sweden and Canada, is another suitable geologic formation, when demonstrably free of circulating groundwater.

To provide additional assurance against escape of radioactivity from wastes in underground storage, stainless steel waste canisters can be provided with an even more corrosion-resistant overpack. Titanium has been considered in the United States and copper in Sweden.

With all these precautions, inadvertent migration of radioactivity from an underground repository can assuredly be prevented.

17. Conclusion

In this overlong talk, I have been able only to outline the several process steps of the nuclear fuel cycle. I'll be glad to give more details by answering questions. I'd like to leave the impression that fuel cycle technology is quite well established and that the processes are feasible, economic, and safe.

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