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A REVIEW OF THORIUM FUEL REPROCESSING EXPERIENCE

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*Operated by Union Carbide Corporation under contract W-7405-eng-26 with the U.S. Department of Energy.

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Rapidly escalating energy demands in the United States, coupled with the current dependence on foreign sources to meet a large fraction of these demands, have become a matter of serious concern. In reacting to this condition, which is expected to continue for the foreseeable future, the nation has adopted an energy policy aimed at attacking the problem from three directions: (1) by promoting more effective use of energy and thereby reducing the overall demand; (2) by urging the shift to abundant domestic sources of energy; and (3) by intensifying the development of new sources of energy. The effect of the third thrust of the policy has been to place an increased emphasis on the use of thorium as a nuclear fuel in the studies that are now in progress.

The introduction of the thorium fuel cycle impacts the energy picture in two ways: (1) the ^{233}U-Th fuel cycle has built-in natural advantages for the control of proliferation of nuclear fuels for use as weapons, and (2) thorium is a potentially abundant source of energy.

Thorium was recognized as a potential source of fissile material in the earliest days of atomic energy. The interest in this material continued until, by the mid-1950s (Fig. 1), a pilot plant was in operation to separate kilogram quantities of ^{233}U from irradiated aluminum-clad thorium metal slugs by using the Interim-23 flowsheet (process). The program continued, resulting in the development and demonstration of the Thorex process

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Fig. 1. SUMMARY OF THORIUM-^{233}U PROCESSING IN THE UNITED STATES

SITE	DATE (YEAR)	THORIUM PROCESSED (TONS)	^{233}U RECOVERED (kg)	^{232}U CONTENT (ppm U)	FLOWSHEET EMPLOYED
	IRRADIATED FUEL PROCESSING				
ORNL	54 & 58	5	8	10–40	INTERIM 23
	55 – 58	30	47	10–40	THOREX
	TOTAL	35	55		
SRP	64–65	14	107	225	INTERIM 23
	65	9	19	38	INTERIM 23
	66, 68, 69	193	412	6–9	THOREX
	TOTAL	216	538		
HANFORD	65	4			INTERIM 23
	66	250	270	6–10	ACID THOREX
	70	400	589	6–10	ACID THOREX
	TOTAL	654	859		
NUCLEAR FUEL SERVICE (CON ED FUEL)	69	17	1019	125	INTERIM 23
	UNIRRADIATED PROCESSING				
ORNL	73, 74, 75	30	1100	10	5.0% DSBPP

for recovering both ^{233}U and thorium from the slugs. By 1964, the demand for ^{233}U to fuel experimental reactors exceeded the supply and programs were initiated in which aluminum-clad thorium oxide powder was processed in modified Purex facilities at Hanford and Savannah River to recover 1400 kg ^{233}U from 870 metric tons of thorium. The Acid Thorex process, which uses HNO_3 rather than $Al(NO_3)_2$ as the salting agent in the solvent extraction step, was developed in response to to an increasing concern about the disposal of nuclear wastes as well as the need to process stainless-steel-clad power reactor fuels.

The first use of thorium fuel for power generation occurred in the Consolidated Edison Reactor at Indian Point, New York. Seventeen tons of stainless-steel-clad thorium oxide pellet fuel from this reactor was reprocessed at the privately owned and operated Nuclear Fuel Services plant at West Valley, New York.

Other reactor programs involving thorium fuel include the Peach Bottom reactor (which was operated for 7 years with a gas-cooled thorium core), the Light Water Breeder Reactor, and the Fort St. Vrain gas-cooled reactor in Colorado. The latter two reactors are currently in operation. There are no plans at present for recovering the fuel from these reactors, even though the Peach Bottom spent fuel was sent to Italy for a reprocessing demonstration in the PCUT facility; however, the plant was never operated and the fuel is simply being held in storage.

Considerable experience was obtained in the fabrication of fuel for the LWBR core. This reactor used ^{233}U-thorium instead of ^{235}U-thorium, which has been the conventional fuel for all other reactor cores. About 1100 kg of ^{233}U was processed at ORNL to produce reactor-grade ceramic oxide in pilot-plant-size equipment. Approximately 27 metric tons of hard fabrication scrap resulting from this program was dissolved, and the ^{233}U was recovered using a solvent extraction flowsheet that features a diethylbenzene (DEB) solution of di-sec-butyl-phenylphosphonate (DSBPP) as the extractant.

Most of the development of the thorium fuel cycle in recent years has been conducted in connection with the High-Temperature Gas-Cooled Reactor (HTGR) program. The objectives of this program, however, have not included reprocessing of irradiated fuel; instead, the emphasis has been on engineering-scale demonstrations of most of the processing steps using tracer techniques. These latter studies have resulted in the development of preliminary designs and cost estimates of a large-scale demonstration facility.

Only limited effort has been expended on thorium reprocessing outside the United States until recently; however, Germany is currently developing a fully integrated thorium fuel cycle. A 300-MW(e) reactor and a semi-industrial facility to reprocess its fuel are scheduled for completion in 1978.

The Interim-23 flowsheet (Fig. 2), referred to earlier, uses dilute tributyl phosphate (TBP) to extract the ^{233}U from the dissolved, irradiated aluminum-clad thorium slugs. Thorium, which remains with the fission products, is discharged to the waste stream. The ^{233}U may be concentrated and further purified by ion exchange techniques. This was the flowsheet used to process the Consolidated Edison core. Although this process was a technical success, NFS officials have termed it a "financial disaster."

The Thorex process (Fig. 3) was developed to recover both the thorium and the ^{233}U. This process uses a feed solution from which all of the free

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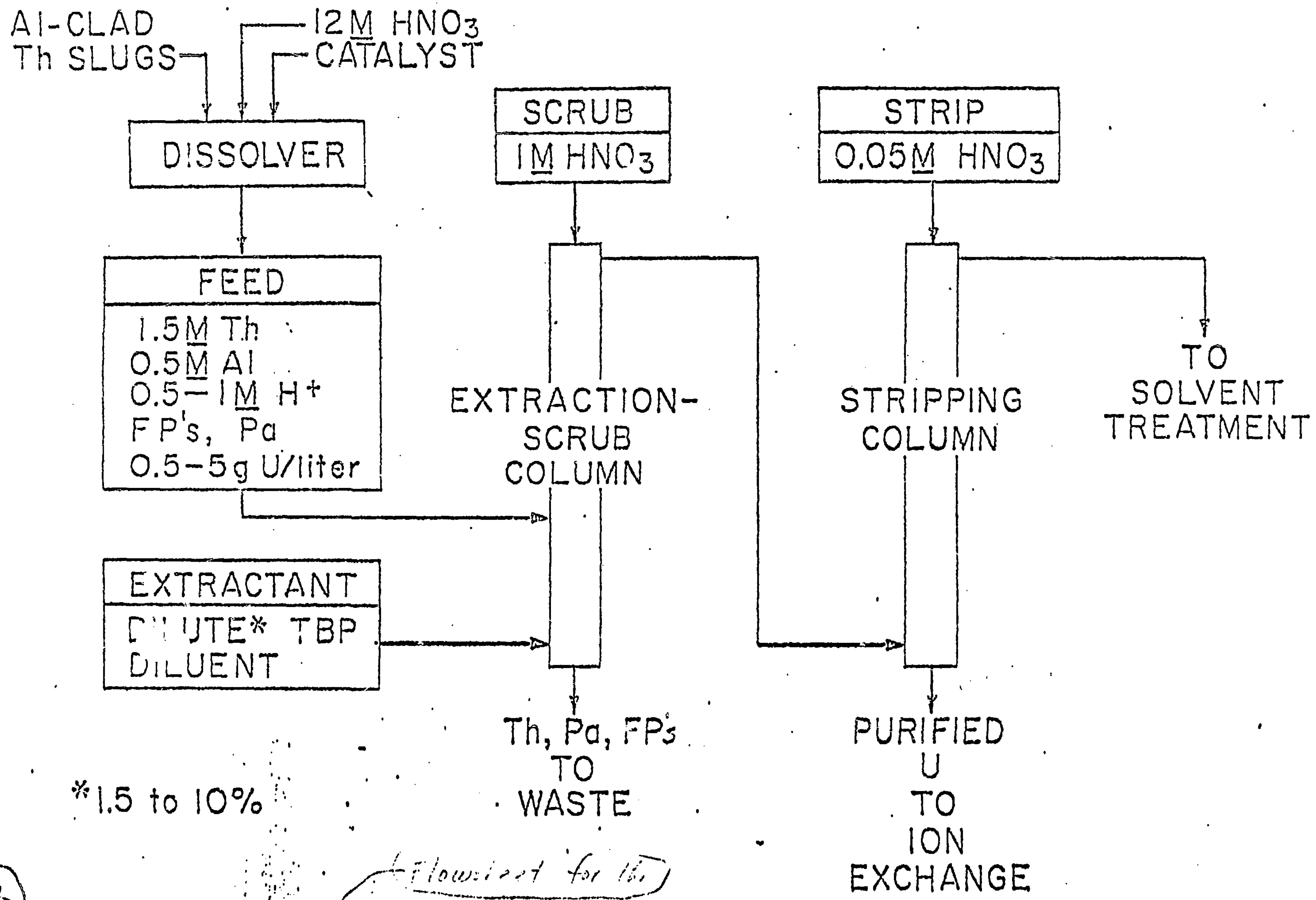

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Fig. 2 Flowsheet for the INTERIM 23 PROCESS: SEPARATION AND RECOVERY OF ^{233}U FROM IRRADIATED THORIUM.

SLIDE 2

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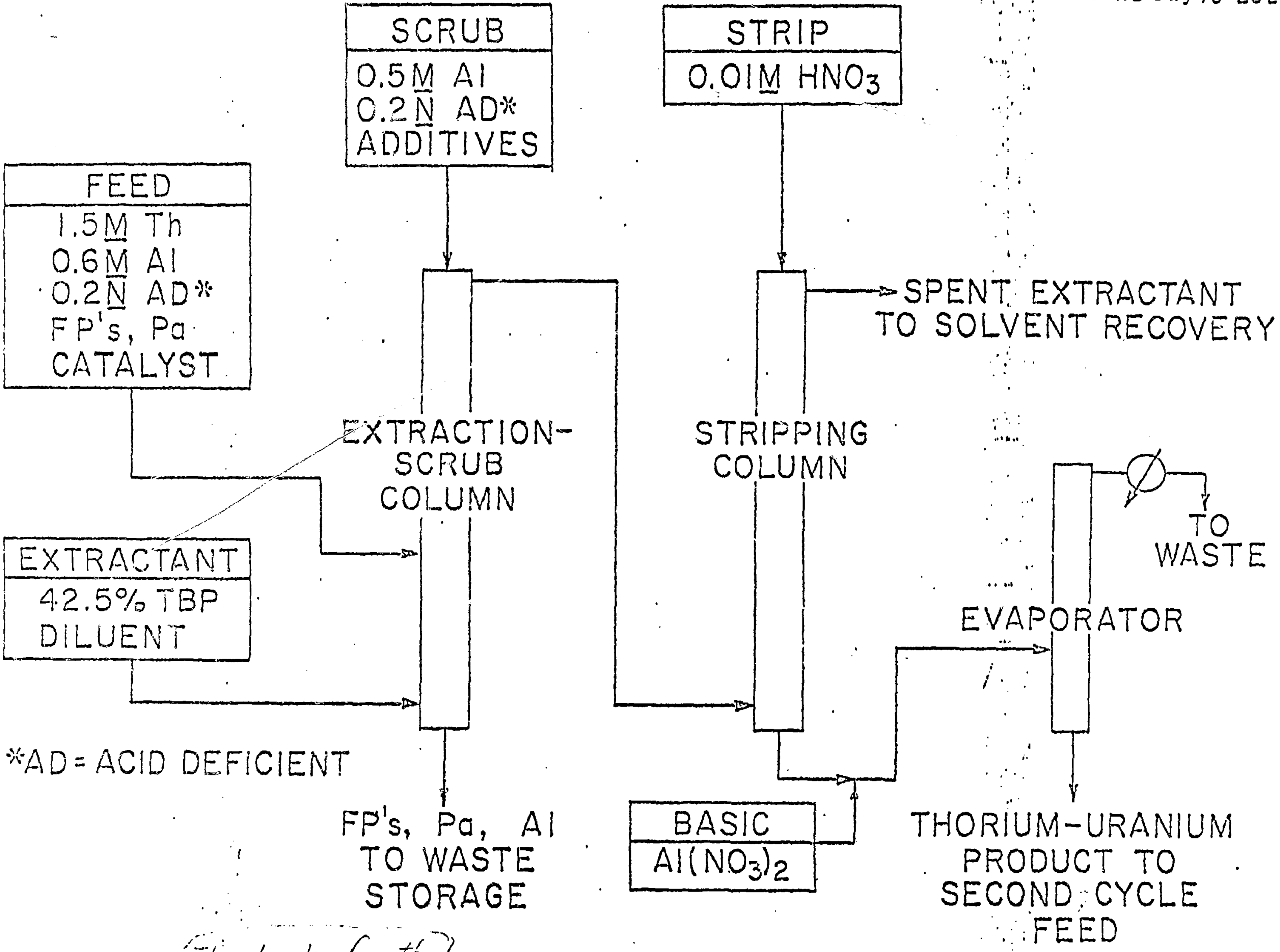

Fig. 3. Flowsheet for the THOREX PROCESS: FIRST SOLVENT-EXTRACTION CYCLE.

acid and part of the nitrate from the salts are removed by evaporating the dissolver solution to about 150°C. Both the uranium and thorium are coextracted from the "acid-deficient" feed with a 42.5% TBP solution, while the aluminum and fission products are rejected to the aqueous waste. After the thorium and uranium have been selectively stripped from the solvent, they are separated and further decontaminated in additional solvent extraction cycles. These flowsheets are satisfactory for processing aluminum-clad thorium or thorium oxide irradiated in government-owned plutonium production reactors but are not suitable for power reactor fuels which operate at higher temperatures and require stainless steel or zirconium alloy as cladding for the fuel.

The Acid Thorex process (Fig. 4) was developed initially in response to the need to recover the ThO_2-$^{235}UO_2$ core of the Consolidated Edison reactor mentioned above, but was not used. However, the head-end process that was developed later consisted in chopping the fuel element into 1- to 2-in. segments with a large shear and leaching the fuel from the segments with fluoride-catalyzed HNO_3. In the Acid Thorex process as in the Thorex process, the acid is removed from the dissolver solution to prepare an acid-deficient feed from which uranium and thorium are coextracted with about 30% TBP. Nitric acid is added below the feed point to enhance the extraction. The remainder of the flowsheet is essentially identical to the original Thorex process. Some modification of this process is being proposed for all future recovery schemes for thorium fuel in order to effectively deal with the problems stemming from the higher irradiation levels characteristic of power reactor fuels.

Some concern has been expressed over the possibility that fissile fuels might fall into the hands of terrorists and be used to fabricate crude nuclear

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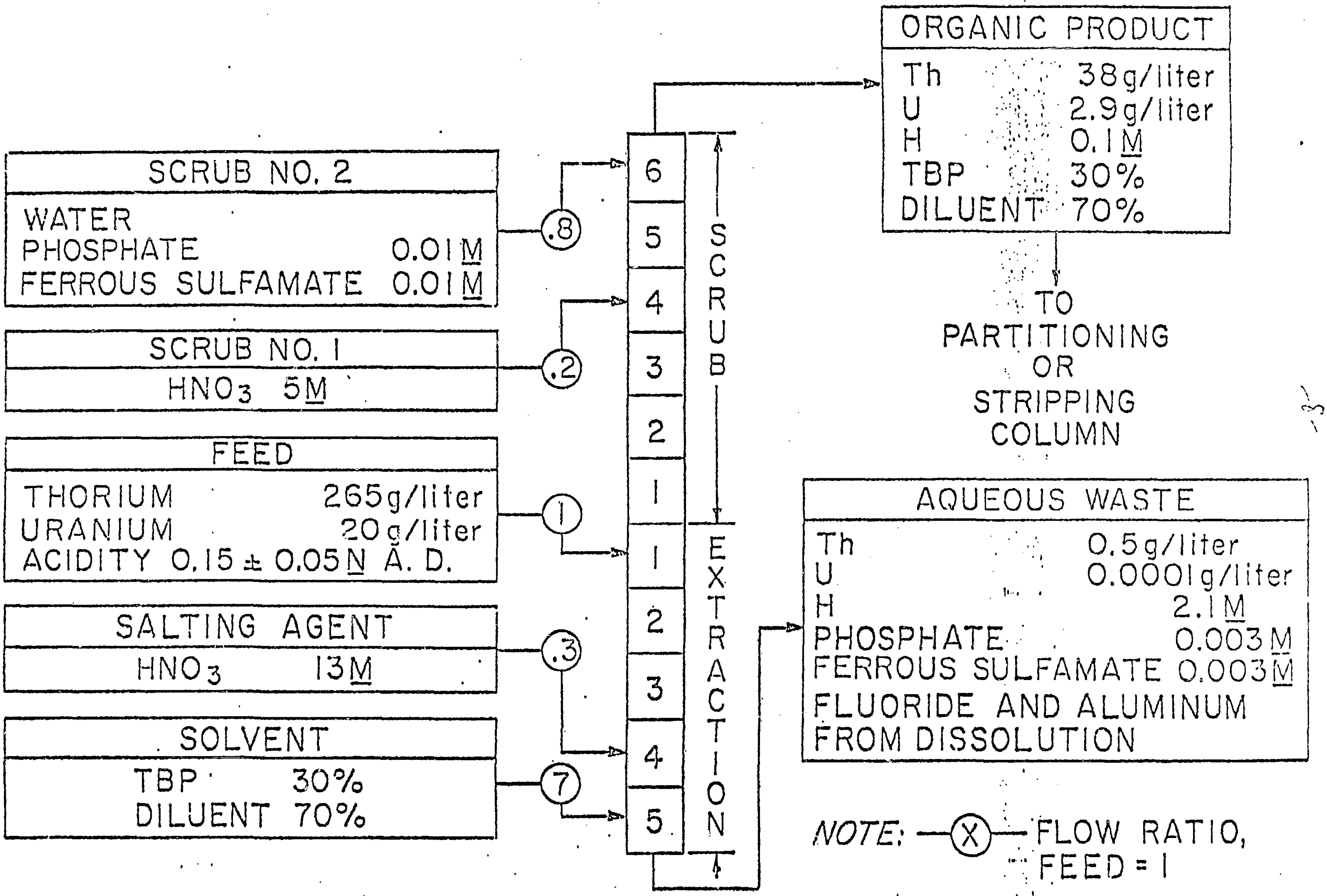

Fig.4. ACID THOREX FLOWSHEET FOR EXTRACTION OF URANIUM AND THORIUM FROM IRRADIATED THORIUM FUEL.

weapons. This concern has led to the consideration of a number of schemes to make fissile fuels unattractive and hazardous such as by adding some highly radioactive material (e.g., spiking with ^{60}Co) or by conducting the reprocessing in such a way that a significant fraction of the fission products is left in the fissile fuel product. It is of interest to note that the fuel in the thorium fuel cycle has a built-in deterrent, ^{232}U, which is formed in a side reaction from thorium during irradiation. The ^{232}U content of the ^{233}U recovered from power reactor fuel will range from 1000 to 4000 ppm, depending on the irradiation history of the fuel.

Uranium-232 is useful as a deterrent to diversion because it decays through a series of daughters to ^{208}Pb (Fig. 5). One of the intermediate short-lived daughters is $^{208}\mathrm{T}\overset{\ell}{\cancel{\mathrm{e}}}$, which decays with an intense gamma emission (2.6 MeV). This gamma radiation is very difficult to shield, rendering the ^{233}U highly detectable and extremely hazardous to personnel exposed to it (Fig. 6); for example, it is estimated that the radiation level at 1 ft from a 5-kg mass of ^{233}U from a typical thorium reactor fuel is greater than 1000 R/hr at 1 ft. Handling such material would be very difficult for potential diverters since the probability of death from a 30-min exposure is 50%. On the other hand, if a diverter was motivated by foreign nationalistic purposes, personnel exposure would be of no concern since exposure even at these levels would not result in immediate death.

It is apparent then that if the thorium and uranium are coprocessed (i.e., they are not separated from each other in the process), the radiation level would remain very high at all times and a much larger quantity of material would be needed to fabricate a weapon.

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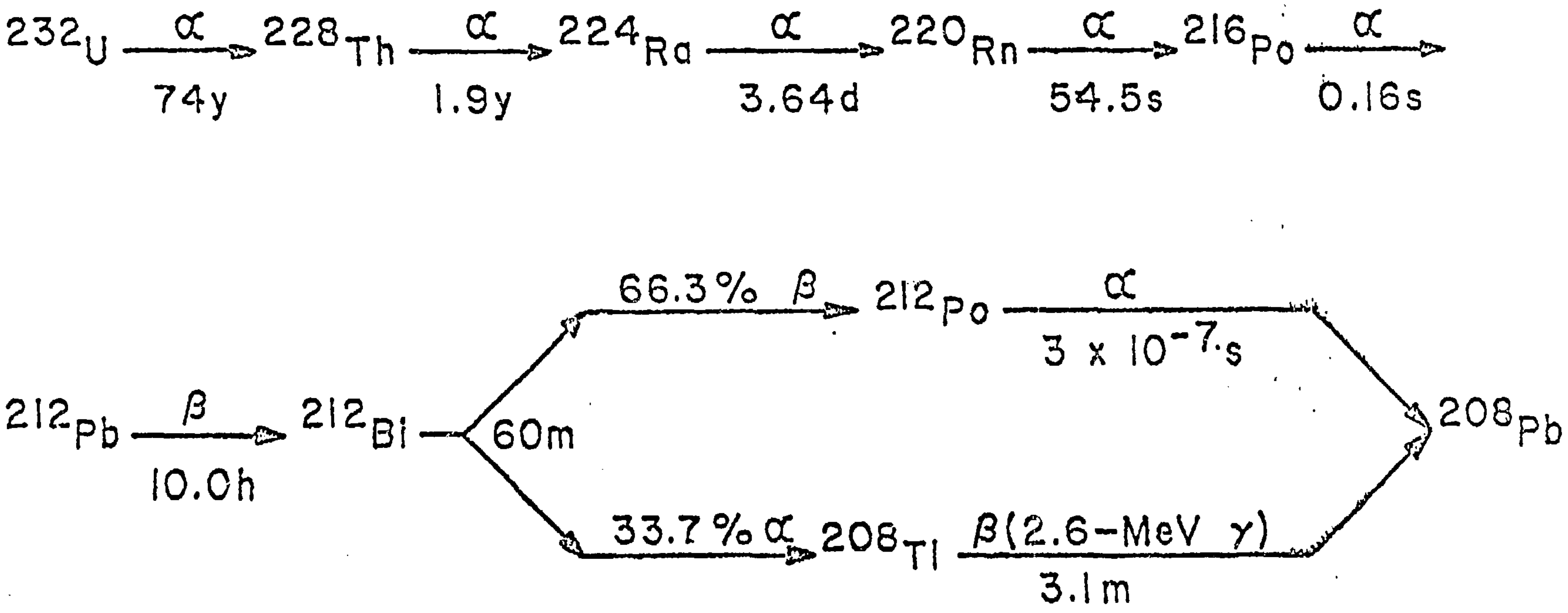

Fig. 5. Uranium-232 Decay Chain.

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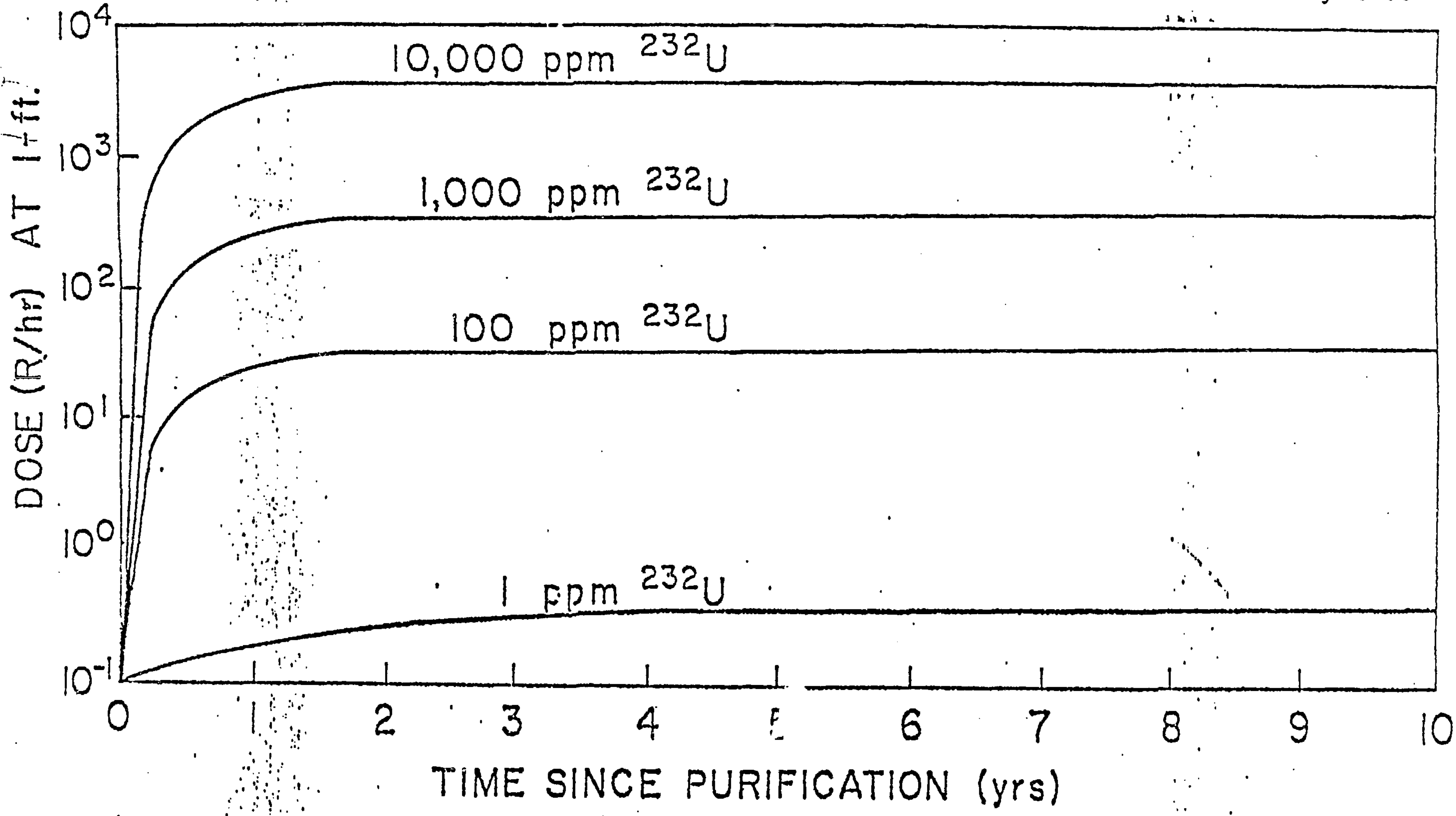

Fig. 6. THE ^{232}U CONTAMINANT IN THE ^{233}U GIVES IT UNIQUE RADIOACTIVE PROPERTIES.

Dose levels from ^{233}U as a Function of the Amount of ^{232}U contaminant present.

If one chooses to follow this route, the conversion and ~~fuel~~ fabrication of the thorium fuel must be conducted in remotely operated and maintained equipment; thus there would be less incentive to obtain high decontamination from fission products in reprocessing spent fuel. As already pointed out, the extracted fission products would increase the gamma radiation level of the products, thereby decreasing the attractiveness of the product for diversion. If desired, the conditions can be chosen so as to give a low-decontamination flowsheet in which fractions of the ruthenium and zirconium accompany the fuel products through the various processing steps. The penalty resulting from selecting to recover a fuel product of this type is illustrated in Fig. 7, which shows that fuel fabrication costs increase drastically as the radiation level increases.

Another alternative is to decrease the attractiveness of the fissile ^{233}U product by diluting (denaturing) it with ^{238}U, which is not fissile. In this case, the flowsheet shown in Fig. 8 would be used to process the spent fuel where conditions are adjusted in the solvent extraction system to recover three products: a uranium stream (^{233}U-^{238}U), a thorium stream, and a plutonium-thorium stream. The fissile fraction of each of these streams is low, making it an unattractive source of nuclear weapons material. The development of this alternative, including the fuel fabrication and spent fuel processing process, represents one of the greatest technical challenges facing nuclear technologists today when compared to other diversion-resistant schemes.

The development effort associated with the thorium fuel cycle has not equaled that expended on the uranium cycle. As already mentioned, several

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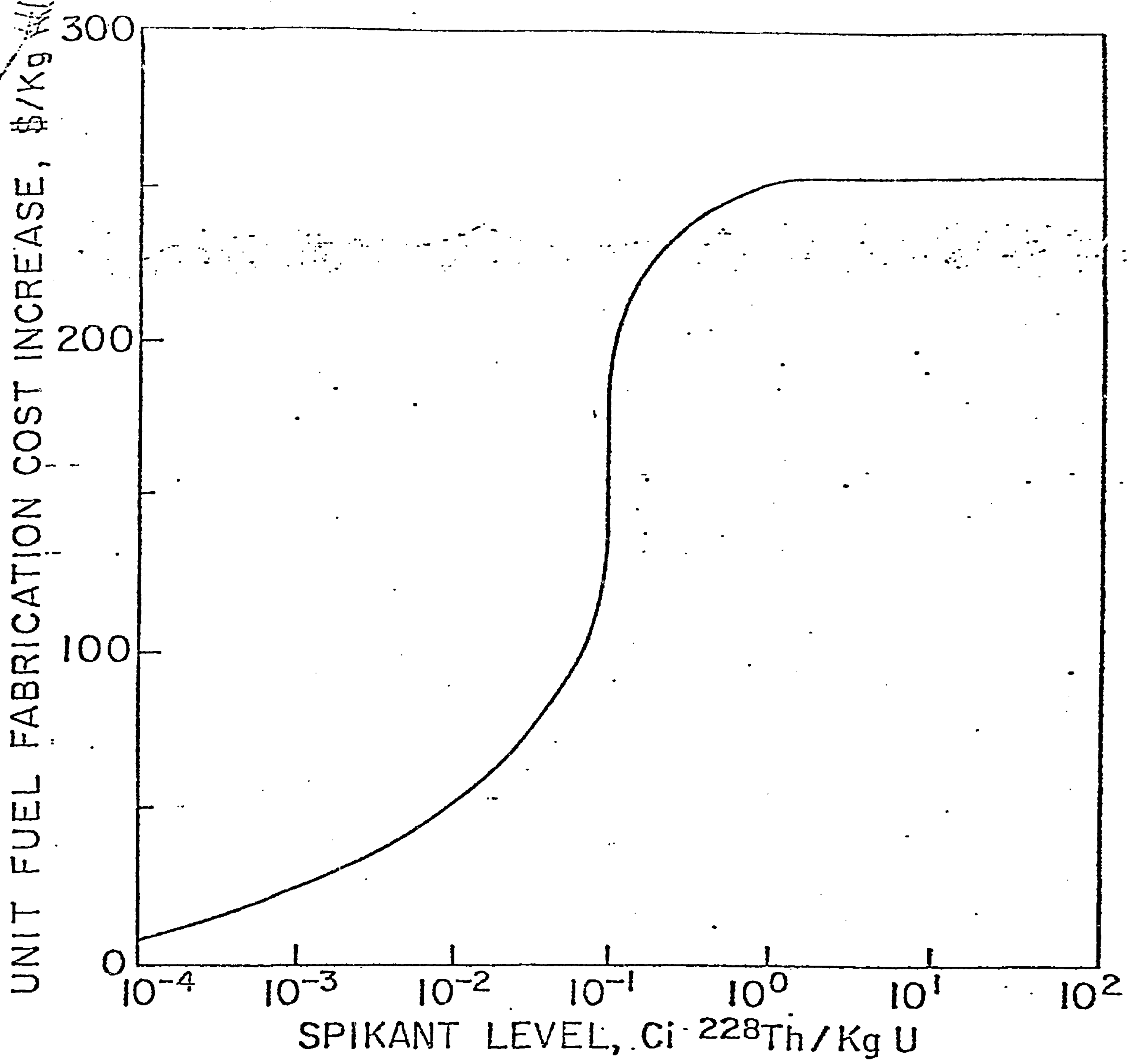

Fig. 7. EFFECT OF SPIKING LEVEL ON INCREMENTAL FUEL FABRICATION COST.

Ref. *"The spiking of special nuclear materials as a safeguards measure"* —BNL

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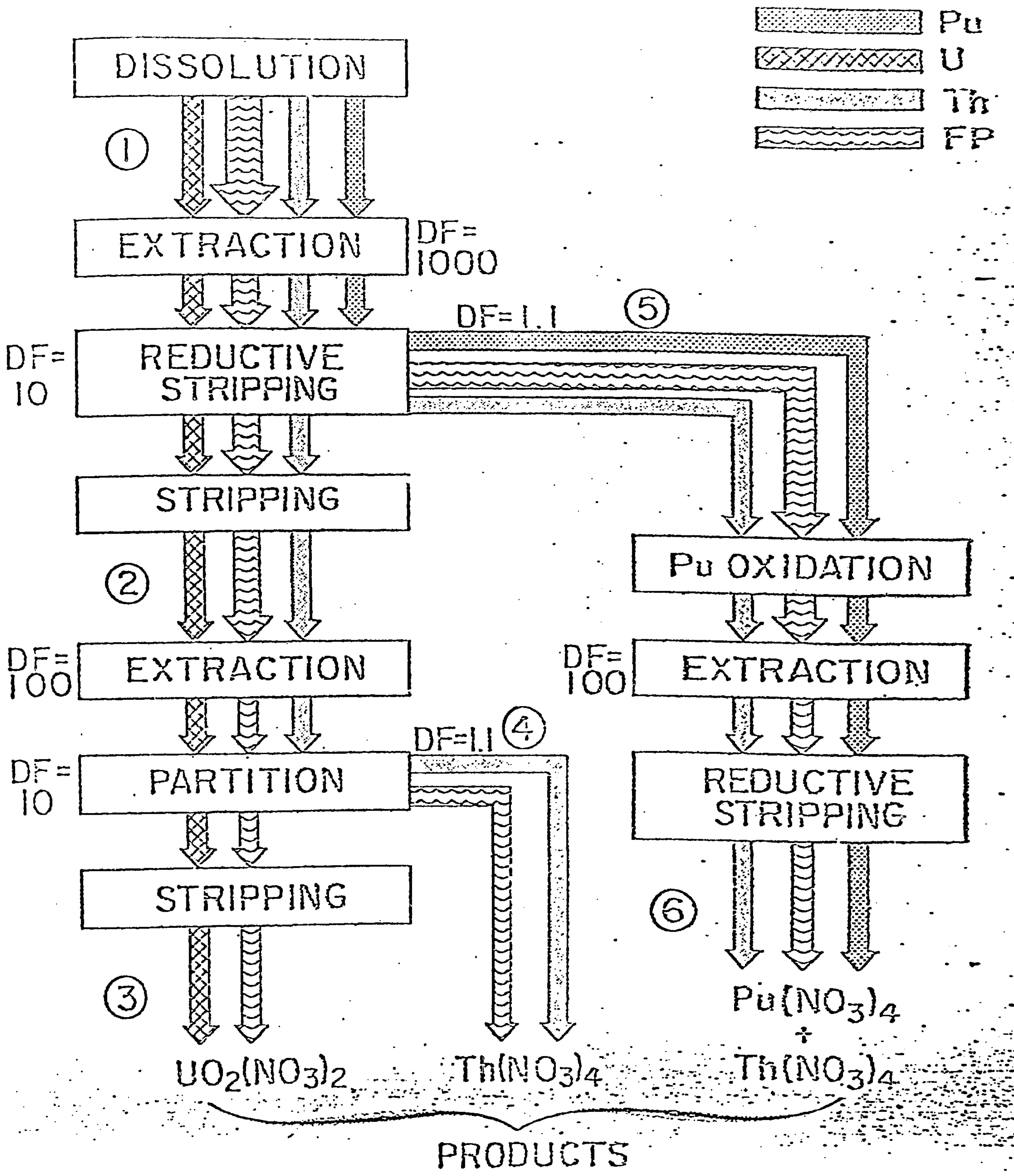

Flowsheet No. 5: Thorex with Plutonium Recovery.

Scan 8

large campaigns have been completed to recover ^{233}U from irradiated thorium. All were conducted in existing Purex equipment, which is designed for optimum effectiveness in uranium fuel reprocessing but is not suitable for thorium fuel reprocessing. More importantly, none of the thorium fuel that was processed in these campaigns had been irradiated to the burnups that are typical of fuels from power reactors. However, there are enough similarities between the solvent extraction processes for thorium and uranium that much of the uranium reprocessing development is applicable for thorium recovery also. Several steps in the reprocessing of the thorium will need considerable additional development for application in a commercial operation. One important area is in the head-end preparation of a nitrate solution of the Zircaloy-clad ThO_2 fuel as a preparatory step for solvent extraction. As indicated above, the dissolution of thoria is accomplished with fluoride-catalyzed HNO_3. This dissolver solution will also attack the Zircaloy cladding. Since zirconium in solution forms strong complexes with the fluoride, it is possible that thoria cannot be completely leached from the cladding by this system. If this should prove to be the case, then some method (either mechanical or chemical) will have to be developed to declad the thoria fuel prior to its dissolution with HNO_3-F.

Another area which requires considerable development is that of fuel fabrication. Although a full core of ThO_2-$^{233}UO_2$ for the LWBR has been fabricated, the ^{232}U content of the uranium was less than 10 ppm and remotely operated facilities with heavy shielding were not required. A remotely operated commercial fuel fabrication facility has yet to be developed and demonstrated.

It is estimated that development of the thorium fuel cycle to the demonstration scale would require about $950 million and ~~require~~ [illegible] 20 to 25 years of effort as compared with $560 million and 5 years for the uranium-plutonium system. In either case, the time is limited by the development of fuel fabrication techniques and the qualification of the fuel for reactor use. Development of the fuel cycle using coprocessing or low-decontamination systems would cost about 10% more but would require no additional time.

As you can see, recycle processes for thorium-based reactor fuel have undergone extensive development. More than 920 metric tons of irradiated thorium have been processed to recover 2500 kg of uranium. Four American reactors have been loaded with thorium fuels, and the core from one of these has been reprocessed in a commercial plant. The thorium fuel cycle shares the same limitations of the uranium cycle in that the products from the fuel reprocessing plant have not been refabricated into fuel elements and recycled to a reactor; nor has a process been developed for the ultimate disposal of the radioactive wastes. It is estimated that development of the thorium back cycle would require about $300 million more to develop than the uranium-plutonium cycle, largely because of the uncertainty of dissolution procedures and conversion and refabrication of reconstituted fuel by remote means.

In summary, it is seen that:

1. Experience in the reprocessing of irradiated thorium materials is limited.
2. Plants that have processed thorium-based fuels were not optimized for the operations.

3. Previous demonstrations of several viable flowsheets provide a sound technological base for the development of optimum reprocessing methods and facilities.
4. In addition to the resource benefit by using thorium, recent nonproliferation thrusts have rejuvenated an interest in thorium reprocessing.
5. Extensive radiation is generated as the result of ^{232}U-contamination produced in the ^{233}U, resulting in the remote operation and fabrication operations and increased fuel cycle costs.
6. Development of the denatured thorium flowsheet, which is currently of interest because of nonproliferation concerns, represents a difficult technological challenge.