

FOR REPRODUCTION

URANIUM DIOXIDE NUCLEAR FUEL ELEMENT PRODUCTION
TECHNIQUES AND EVALUATION OF THE RELATED STUDIES
IN TURKEY

by
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APPROVAL OF READERS

This is to certify that I have read and approved the thesis entitled "URANIUM DIOXIDE NUCLEAR FUEL ELEMENT PRODUCTION TECHNIQUES AND EVALUATION OF THE RELATED STUDIES IN TURKEY" , submitted by Berrin Erbay in partial fulfillment of the requirements for the degree of Master of Science, Department of Nuclear Engineering, Boğaziçi University.

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ABSTRACT

The procedure for UO_2 nuclear fuel element production involves a number of steps each of which belongs to an independent field of specialization. Therefore the diverse fields of study pertinent to fuel element production have been searched and a coherent picture of the processes involved has been presented.

Since it is highly probable that Turkey will make use of nuclear energy to alleviate its future energy shortage, Uranium reserves and activities related to the nuclear fuel element production in Turkey have been investigated and documented.

Considering the nuclear future on a national scale, present studies in Turkey relating to nuclear fuel element production have been evaluated and some recommendations have been made for the direction of future activities in this field.

ÖZET

Su soğutmalı reaktörlerde kullanılan UO_2 nükleer yakıt elemanlarının üretimi bir çok safhadan oluşmaktadır. Bu tez çalışmasında, herbiri bağımsız ihtisas konularının bir parçası olan bütün adımlar araştırılmış ve bir bütün teşkil etmek üzere derlenmiştir.

Türkiye'nin ,gelecekteki enerji açığı problemini hafifletmek için nükleer enerjiyi kullanması kuvvetle muhtemel olduğu için, Türkiyedeki Uranyum rezervleri ve nükleer yakıt elemanı üretimiyile ilgili çalışmalar araştırılmış ve biraraya getirilmiştir.

Ulusal çapta nükleer geleceği gözönünde bulundurarak, Türkiye'de nükleer yakıt üretimi ile ilgili var olan çalışmalar değerlendirilmiş ve bazı önerilerde bulunulmuştur.

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Chapter 1

1. INTRODUCTION

Uranium dioxide is the most common fuel material used in water reactors. In comparison to other fuel types Uranium dioxide has striking advantages such as high radiation and dimensional stability, chemical compatibility with cladding materials and coolants and high melting point. Uranium dioxide as a nuclear fuel can be either granular or in bulk form.

Fuel element production technology is composed of a number of steps starting with Uranium exploration studies and ending with fabrication. Each step belongs to a field specialization; For example, exploration studies are under the control of geophysicists and geologists, ore excavation belongs to the realm of mining engineers, ore concentration, however, is completely a chemical engineering problem. That being the case, fuel production steps have been dealt with in separate publications. Therefore reviewing the literature and collecting the data on UO_2 fuel element production technology and presenting it as one single reference constitutes the first purpose of this study.

It is well known that one of the primary problems of the last decade as well as the present one is the energy shortage. The problem of energy shortage is especially severe in Turkey because of Turkey's lack of any appreciable petroleum reserves. The future energy shortage of Turkey can be outlined as follows (1); In 1995, the energy demand for electricity will be about 165×10^9 KWh, in the year 2000 the demand, however, will reach to a value of 250×10^9 KWh. On the other hand, it is estimated that when all known national fossil and hydraulic potential is used to generate electricity, Turkey will have an energy production potential of 150×10^9 KWh. After 1995, national conventional energy resources will obviously be insufficient. Nuclear energy seems to be the only viable option to alleviate this deficiency. Because of this Turkey has been interested in nuclear energy for over 25 years. As part of this effort there have been some studies in Turkey concerning the front end of the nuclear fuel cycle. However these studies have been carried out by different groups and organisations. To our knowledge there has not been a single reference that brings together all these studies and evaluates them. Therefore the second purpose of this study is to accomplish the task of reviewing the available literature concerning the fuel element production studies in Turkey, talk to individuals and groups working in this area and present their activities in the form of a single complete source of

reference.

Finally the third purpose of this study is to evaluate the fuel element production studies in Turkey and recommend future studies in this area.

In order to illustrate the nuclear fuel element production procedures, all steps are taken into consideration one by one in this study. After the introduction chapter, the properties of Uranium dioxide as nuclear fuel are summarized in Chapter 2. In Chapter 3, main Uranium ore deposits and minerals are mentioned. Main production procedure starts with Uranium exploration given in Chapter 4. Once the Uranium reserves are determined, the task of extraction comes next. Chapter 5 gives the information about the underground and open-pit mining techniques. When Uranium is mined, it is in the form of large lumps. In order to separate Uranium from non-uranic ones, the large lumps of rock are initially exposed to crushing and grinding. Physical concentration processes are followed by chemical ones. Concentration or milling is the subject of Chapter 6. Since the Uranium concentrate obtained at this step is far from nuclear purity, further purification must be adopted. Chapter 7 discusses the purification methods employed. Enrichment of fuel in fissile Uranium isotope and conversion to UO_2 take place before fabrication. These are dealt with in Chapters 8 and 9 respectively. In Chapter 10, all steps discussed in Chapters 4 to 9 in general are evaluated from the point of view of the fuel cycle activities conducted in Turkey. Main conclusions obtained from this study and recommendations for further work in this area are given in Chapter 11.

2. URANIUM DIOXIDE AS NUCLEAR FUEL

In nuclear reactors, unalloyed Uranium is unattractive as fuel due to its poor irradiation stability, high degree of reactivity even at room temperature, bad corrosion behaviour, poor ductility and its dimensional instability, density and other physical properties. Since unalloyed Uranium is not a well-behaved engineering metal, ceramic fuels have been preferred in most commercial power reactors.

Uranium dioxide is the most common ceramic fuel used in water reactors. UO_2 fuel was developed in 1954 and used instead of Uranium-molybdenum alloy in the first pressurized water reactor, the shipping port PWR, three years later. Granular and bulk forms of Uranium oxide such as pellets, rods, plates or blocks serve either as a convenient form of fuel or fertile material.

Ceramic fuels have demonstrated extremely high radiation and dimensional stability. Chemical compatibility of UO_2 with cladding metals and reactor coolants is very satisfactory (2). UO_2 is also quiet corrosion resistant in high-temperature degassed water.

Besides these advantages, UO_2 fuel has some disadvantages with respect to metallic Uranium fuel. The major striking disadvantages of UO_2 are low uranium density, low thermal conductivity and brittleness.

The low density of uranium atoms in UO_2 requires a larger core for a given amount of fissile species than if a rich fuel were used. Thus, the larger the reactor size for the same power level, the higher the capital cost of the reactor.

The low thermal conductivity at the beginning implies poor thermal performance. But thermal performance of a fuel element is determined by the temperature gradient as well as thermal conductivity. Poor thermal conductivity will result in the requirement of large center-line temperature of the fuel and large temperature difference between the center and the rod surface so as to get sufficient heat transfer for economic power production. Considering the fact that UO_2 can be operated even at temperatures which causes central melting, UO_2 has capacity for good thermal performance (3).

Brittleness is a common property of ceramics. At sufficiently high temperatures, however, UO_2 goes through a measurable amount of plastic deformation.

2.1. PHYSICAL PROPERTIES OF UO_2

Uranium dioxide is a dark brown or black material in powder form.

UO₂ powder has good response to some fabrication techniques. Important properties of UO₂ are summarized in table 2.1.

Table 2.1. Important Properties of UO₂ (2,4).

Property	UO ₂
Crystal structure.....	Face-centered cubic
Lattice , ^o A	5.472
X-ray density g/cm ³	10.95 + 10.97
Melting point, ^o C	2800
Thermal conductivity....	0.02_ 20 ^o C
cal.cm/ ^o C.cm ² .sec(cor-	0.008 - 1000 ^o C
rected to 100% density)	
Expansivity , ^o C ⁻¹	10.3 x 10 ⁶ (25-1000 ^o C)
Specific heat,	0.056 (25 ^o C),
(cal/g/ ^o C	0.078 (1000 ^o C).
Heat of formation,	-259,500 (25-1200 ^o C).
cal/mole	
Free energy of forma-	-246,600 (25 ^o C).
tion , cal/mole	-218,100 (727 ^o C).
	-197,700 (1227 ^o C).
Entropy, cal/mole/ ^o C ..	6.67 x 10 ⁻⁵ (1102 ^o C).
Vapor pressure ,mm Hg ..	9.66 x 10 ⁻¹ (2363 ^o C).
Tensile strength	c. 5000 p.s.i
Modulus of elasticity...	25x10 ⁶ p.s.i
Thermal n capture	0.165 cm ² /cm ³ (5)
cross section	

The crystal structure of UO₂ is the face-centered cubic fluorite (CaF₂) type. Uranium ions occupy corners and faces. The cell dimension was measured to be 5.472 ^oA. The lattice is relatively "open" and the oxygen has a negative partial molal volume. As excess oxygen is added to UO₂, the oxide volume decreases and consequently density increases.

The melting point is an important parameter for fuel elements since it is used to define the limiting power of a fuel element. The melting point of stoichiometric UO₂ is shown to be 2865 ^oC by investigators, although other investigations have found that UO₂ melts at 2800 ^oC. Much below this temperature, however, an appreciable vapour pressure is observed. During sintering, UO₂ loses weight at temperatures as low as 1400 ^oC. Sinter furnace walls are coloured besides being radioactive indicating its volatility. The volatility of UO₂ is encouraged by foreign material (i.e BeO) presence. Uranium has a num-

ber of oxidation states and while UO_2 is the stable phase above $1200^{\circ}C$, U_3O_8 has been observed on the surface of UO_2 grains. The effect of oxygen on volatility is very small. The vapour pressure of UO_2 is shown in table 2.2.

Table 2.2 The Vapour Pressure of UO_2 (4).

Temperature, $^{\circ}C$	Vapour pressure of UO_2 , p . mmHg x 10^3
1600	0.071
1750	1.7
1800	4.0
1900	18.0
2000	72.0

The thermal conductivity of UO_2 is relatively low among the crystalline oxides. The thermal conductivity of UO_2 is a function of temperatures, purity, stoichiometry, density and microstructure. It also varies under radiation. Thermal conductivity values before and after irradiation are given in figure 2.1

Determination of specific heat is useful in that it provides information for the calculation of the heat bearing capacity of a reactor core. The values shown in figure 2.2 are typical.

UO_2 has relatively high thermal expansivity in comparison with most ceramics. Between room temperature and melting point, the thermal expansion of UO_2 follows the curves given in figures 2.3 and 2.4. Thermal expansion coefficient is a function of temperature and increases slightly with increasing temperature especially near melting temperature.

UO_2 is one of the uranium-oxygen compositions. UO_2 , U_4O_9 , U_3O_7 , U_2O_5 and U_3O_8 are oxides of uranium which have already been reported. The reason for so many different compositions is easy oxidation characteristics of UO_2 in air. It has also been reported that UO_2 takes oxygen into its structure up to a composition $UO_{2.30}$ (see figure 2.5). The structures of oxide compositions are dependent on temperature; the oxide above $500^{\circ}C$ is U_3O_8 and intermediate oxide is U_3O_7 while U_3O_8 being an orthorhombic structured black powder is formed from U_3O_7 by oxidation at about $400^{\circ}C$ (7). U_3O_8 , however, begins to lose oxygen at temperatures above $550^{\circ}C$ - $600^{\circ}C$ and turns into UO_2 in between the temperatures of $1150^{\circ}C$ and $1400^{\circ}C$. At higher temperatures UO_2 presents the stable phase.

2.2 .CHEMICAL PROPERTIES OF UO₂

The most important chemical property in the fuel element is the equilibrium pressure of oxygen in the gas phase. Oxygen potential of the fuel is the measure of the existence of metal cladding oxidation. Oxidation probability increases the effective thickness of the cladding. Since the cladding is tried to be made as thin as possible so as to reduce parasitic neutron absorption and core size, using thick-wall cladding to prevent oxidation hazard will result in a negative effect on reactor economics.

An overriding advantage of UO₂ as fuel is its good compatibility with cladding and coolant materials. Both stainless-steel and zircaloy are suitable as cladding materials for UO₂ fuel.

Stainless-steel: At temperatures < 1400 °C, UO₂ does not react with stainless steel. Even at higher temperatures stainless steel is suitable as cladding material.

Zirconium-UO₂ reacts with zirconium alloys at high temperatures. A series of diffusion zones at fuel-cladding interface are observed. The thickness of diffusion zones increases with time (see figure 2.6)

Zircaloy-2 : UO₂ reacts with zircaloy-2 less rapidly than unalloyed Zr.

Aluminium : UO₂ reacts with Al. at 600 °C. The reaction is relatively slow at this temperature with UO₂ grains larger than 40 μ . Reaction products are UAl₃, UAl₄ and Al₂O₃.

Mo, Nb, Ta, Tungsten : UO₂ shows good compatibility with these up to their melting points.

Carbon : UO₂ in the powder form reacts with C at temperatures as low as 1400 °C. UC₂ or U₂C₃ are the products.

Hydrogen : UO₂ does not react with hydrogen at temperatures up to its melting point.

Silicon : In the temperature range 1900 °- 2100 °C, UO₂ reacts with silicon and forms USi₃.

Acids : UO₂ is soluble in HNO₃, not in HCl. The reaction product of UO₂ with HF is UF₄.

Bases : UO₂ does not react with NaOH solutions but is soluble in sodium peroxide forming Na₂UO₄.

Coolants : The fuel materials inside cladding are not in direct contact with reactor coolants, however, it is conceivable that during an accident fuel might come into contact with coolant. Therefore it is necessary to know the response of UO₂ to coolant materials.

Water : UO₂ does not react with H₂O at temperatures below 300 °C and no reaction is expected at higher temperatures. Sintered or

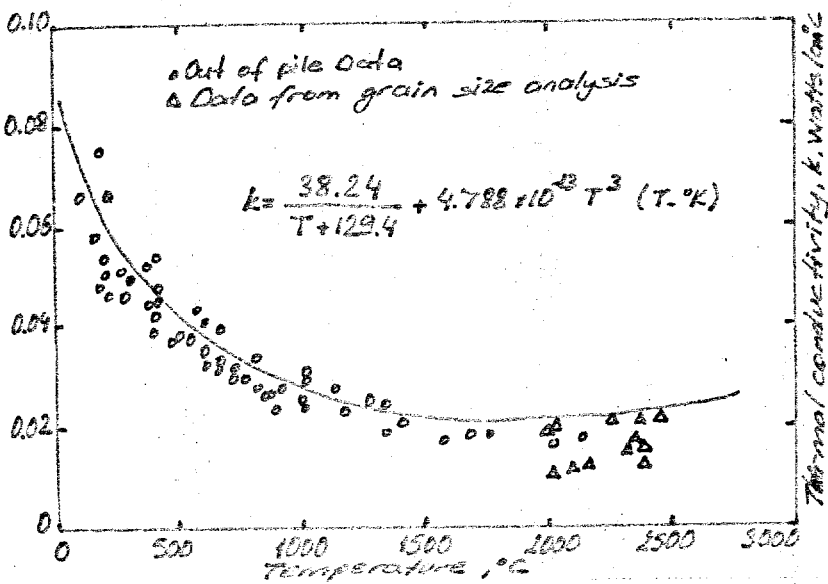


Fig. 2.1. Thermal conductivity of UO₂ (2).

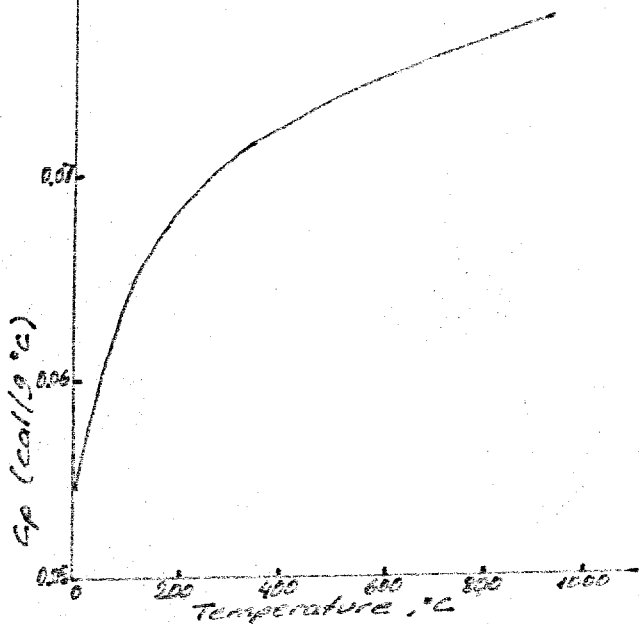


Fig. 2.2. Variation of the specific heat c_p of UO₂ with temperature (6).

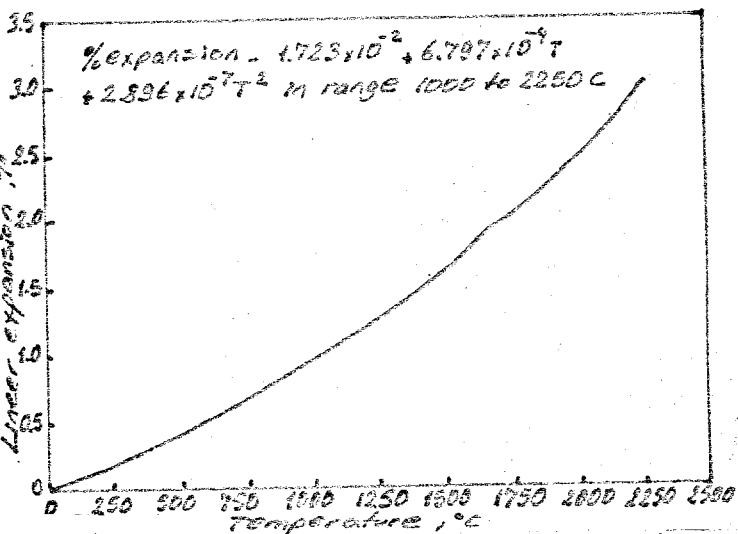


Fig. 2.3. Linear thermal expansion v.s temperature (2).

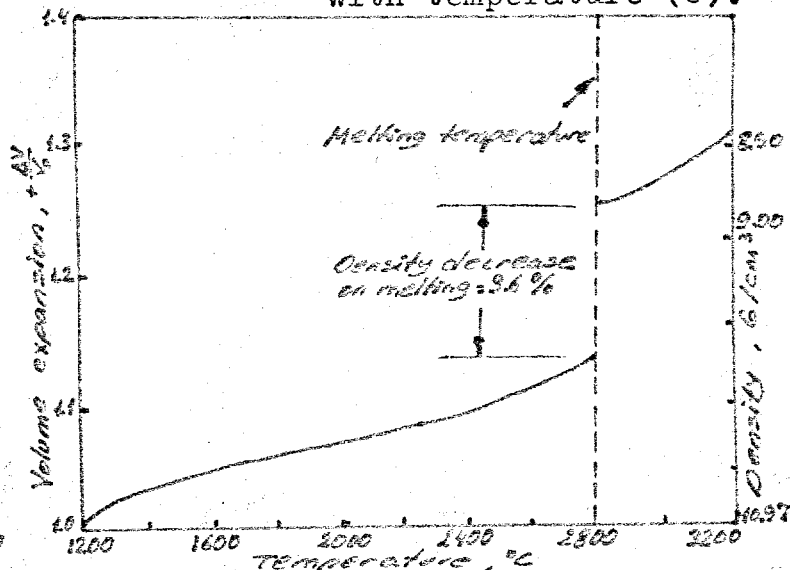


Fig. 2.4. Thermal expansion of UO₂ (2).

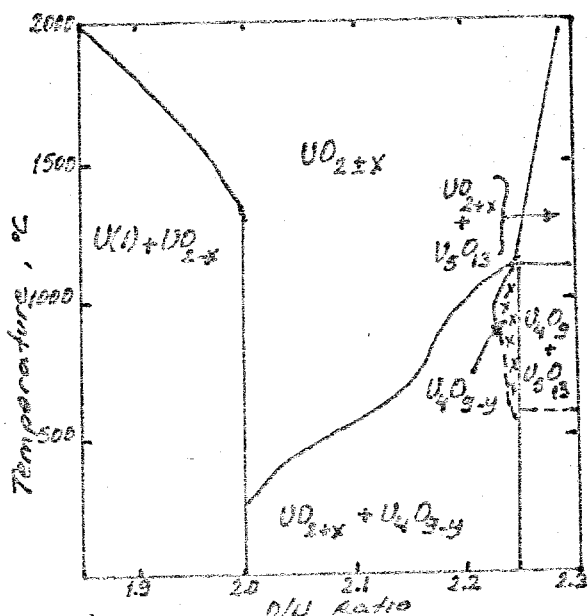


Fig. 2.5. Oxygen-Uranium phase equilibrium system (3).

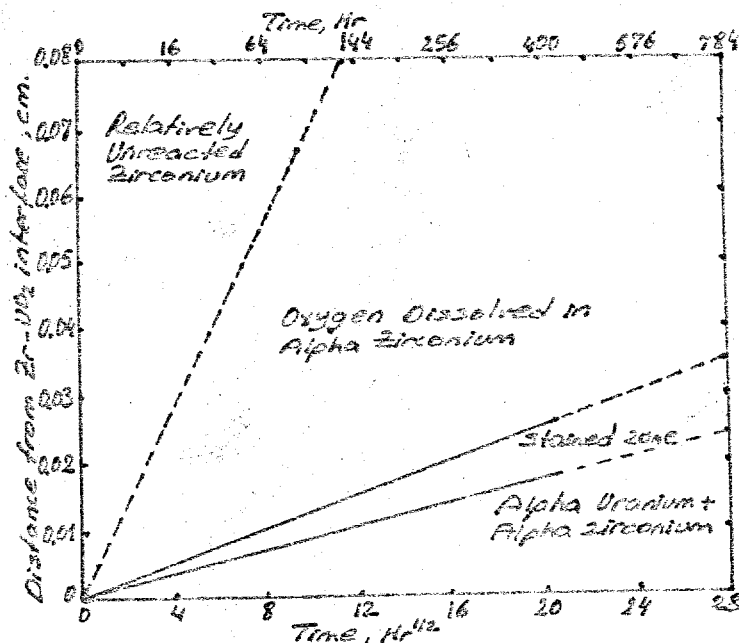


Fig. 2.6. Zone thicknesses in Zirconium measured from the Zr-UO₂ interface for the reaction at 1600 °F (2).

cold pressed UO_2 pellets in degassed water (neutral or at high P.H) shows extreme stability.

Gaseous coolants : He is most common gaseous coolant. UO_2 shows good compatibility with He similar to nitrogen. UO_2 , on the other hand, picks up oxygen from CO_2 .

Liquid metal coolants : UO_2 in sintered form does not react with liquid metals.

Organic coolants : UO_2 is compatible with organic materials.

2.3. THERMODYNAMIC PROPERTIES OF UO_2

Uranium dioxide at ordinary temperatures in air is thermodynamically stable. Thermodynamic properties of uranium oxides are given in table 2.3. Partial molal entropy and enthalpy of oxygen in uranium dioxide and temperature dependence of enthalpy are given in figures 2.7, 2.8, 2.9 respectively.

Table 2.3 Thermodynamic Properties of UO_2 (4)

Oxide	F_{298} (Kcal)	H_{298} (Kcal)	S_{987} (Kcal)
UO	-123	-129	-21
1/2 UO_2	-123.3	-129.6	-21.2
1/8 UO_2	-100.5	-106.7	-20.8
1/3 UO_3	-91	-97.3	-20.7

2.4. MECHANICAL PROPERTIES OF UO_2

The isothermal elastic moduli of polycrystalline stoichiometric UO_2 at $25^{\circ}C$ are as follows and given in figure 2.10.

$$E = 2.19 \times 10^8 \text{ kN / m}^2 \text{ (Young's modulus)}$$

$$G = 8.14 \times 10^7 \text{ kN / m}^2 \text{ (Shear modulus)}$$

Polycrystalline UO_2 is a brittle material under normal conditions, that is, at temperatures less than about one-half the melting point and in the absence of radiation. Brittleness means little capacity for plastic deformation. In case of UO_2 , at sufficiently high temperatures measurable amounts of plastic deformation before failure occurs. It is observed from figure 2.11 that the brittle-to-ductile transition temperature happens to be at $\sim 1200^{\circ}C$. The temperature range between $1200-1400^{\circ}C$ is the region of semibrittle behaviour and at temperatures above $1400^{\circ}C$ UO_2 experiences considerable ductility.

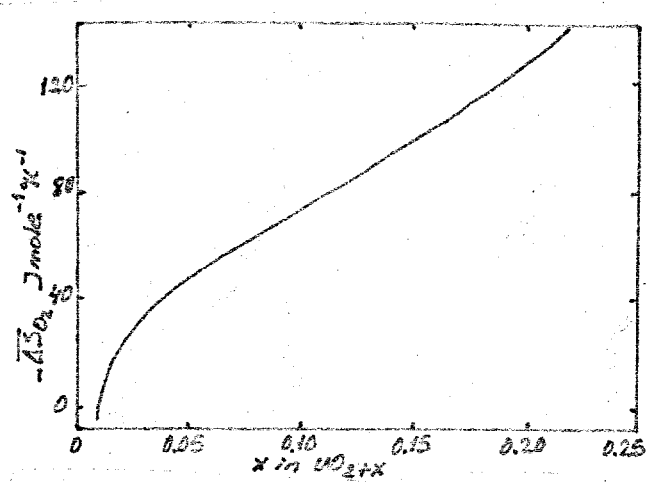


Fig.2.7. Partial molar entropy of oxygen in $UO_2 + x$ (3).

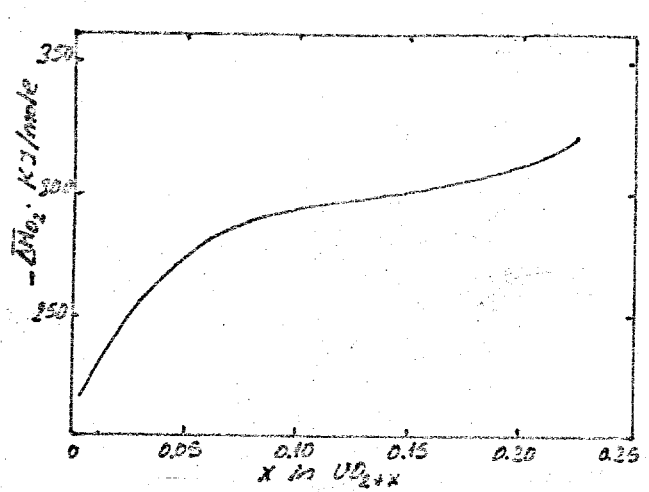


Fig.2.8. Partial molar enthalpy of oxygen in $UO_2 + x$ (3).

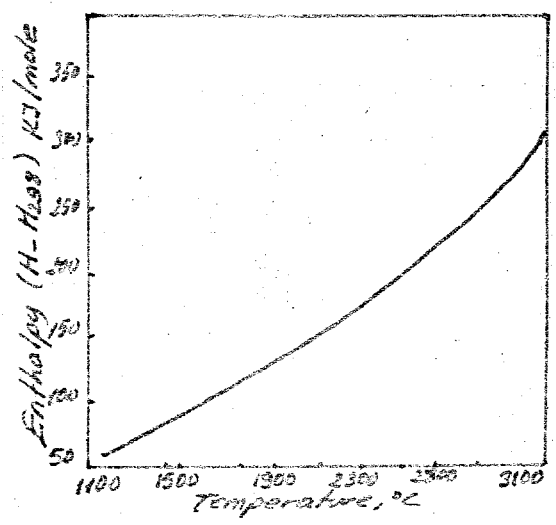


Fig.2.9 Enthalpy- Temperature data for stoichiometric UO_2 (4).

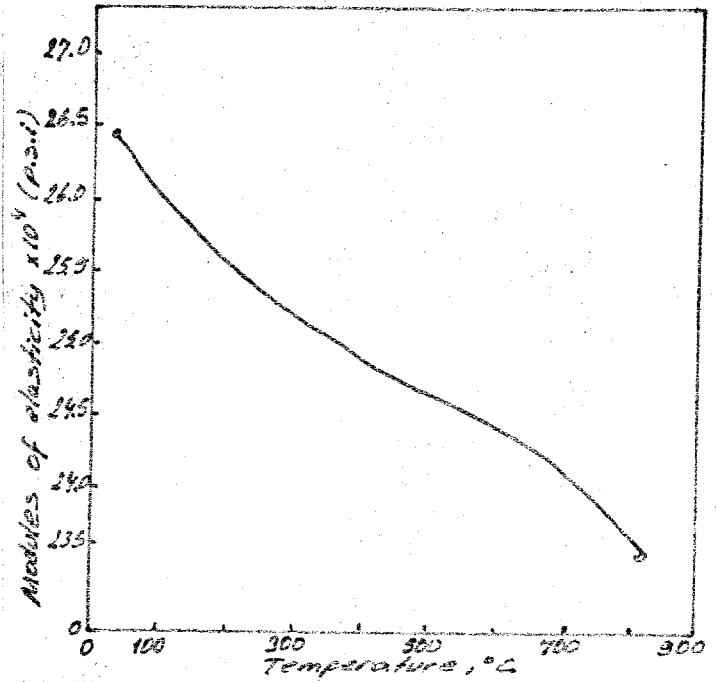


Fig.2.10. Modulus of elasticity of sintered UO_2 (6).

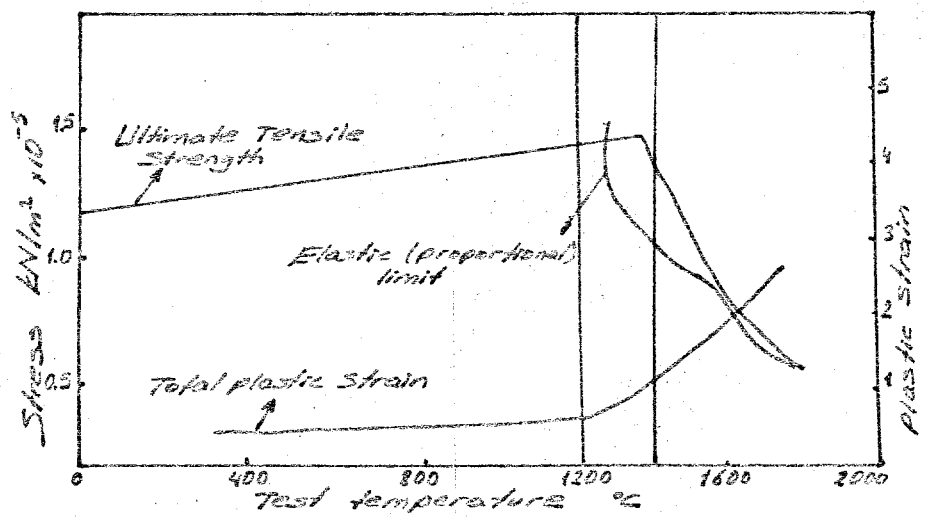


Fig.2.11. Fracture and flow characteristics of UO_2 as a function of temperature, ultimate tensile stress, elastic limit, and total plastic strain (3).

Chapter 3

3. URANIUM ORES AND DEPOSITS

3.1. URANIUM IN THE EARTH'S CRUST

The earth's crust contains about 3×10^{-4} % of uranium(8)(2-4 ppm) (9). High grade deposits of uranium are scarce (6). Uranium is usually found in conjunction with other commercially valuable minerals.

The uranium content in igneous rocks changes according to the SiO_2 content while the mean uranium content in sedimentary rocks is about $1.3-3.1 \times 10^{-4}$ %. Uranium occurrence in igneous rocks are in the following basic forms:

1. Uranium minerals,
2. Isomorphic conversion,
3. Cation exchange state,
4. Adsorption on the surface and along the cracks inside minerals,
5. Uranium dissolved in liquid inclusions,
6. Uranium dissolved in an intergranular liquid.

Studies made for determining the uranium content in igneous rocks are summarized in table 3.1.

Natural waters; namely ocean, lake and river waters contain uranium element at following concentrations:

Ocean waters:	0.3×10^{-6}	-10^{-5}	g/l.
Lake waters:	3×10^{-8}	-10^{-3}	g/l.
River waters:	3×10^{-8}	-10^{-4}	g/l.

Table 3.1 Mean Uranium Content in Igneous Rocks (8).

Uranium Content %				Author and date of determination of uranium content
Acid Rocks	Intermediate Rocks	Basic Rocks	Ultrabasic Rocks	
7.01×10^{-4}	5.6×10^{-4}	3×10^{-4}	6×10^{-5}	Jeffries (1936)
6×10^{-4}	—	—	—	I.O. Komlev (1938)
2.8×10^{-4}	—	3.4×10^{-5}	—	Keovil (1938)
4.01×10^{-4}	1.4×10^{-4}	1.1×10^{-4}	6×10^{-5}	Goodman and Evans (1941)
2×10^{-4}	—	2×10^{-5}	—	Hoffmann (1941 to 42)
3.9×10^{-4}	2.6×10^{-4}	—	—	Senftle and Keovil (1947)
4.3×10^{-4}	—	—	—	A.O. Vinogradov (1955)
3.4×10^{-4}	—	7×10^{-5}	—	Patterson (1955)
2.7×10^{-4}	1.8×10^{-4}	1.8×10^{-4}	—	Adams (1955)
5.7×10^{-4}	—	6×10^{-5}	—	I.O. Komlev (1956)
—	—	2.1×10^{-4}	—	—
3.5×10^{-4}	1.8×10^{-4}	5×10^{-5}	3×10^{-7}	A.P. Vinogradov (1962)
4×10^{-4}	4.6×10^{-4}	7×10^{-5}	—	Towson (1962)

Table 3.2 Main Uranium Minerals (8-10).

MINERAL	COMPOSITION	COLOUR	REMARKS
Primary minerals: Uraninite	Uranium oxide	Black (grayish, greenish, brownish)	Massive or crystalline mineral; found in veins, pegmatites and disseminated in sedimentary rocks. Uranium content is 46.5-88.2 %, cubic in system, hardness is 5.06-7.6, specific weight is 7.6-10.8
Pitchblende	Uranium oxide	Black (grayish, greenish)	Uranium content: 52.3-76.5 %. Specific weight: 4.8- 7.7 Hardness : 4.0- 6.29
Coffinite	Uranium silicate	Black	Finely disseminated in sandstone; often intimately mixed with uraninite and carbonaceous material. Uranium content is 45-67 %. Specific weight: 5.1. Hardness is 5-6 and its system is tetragonal.
Secondary minerals:			
Carnotite	Potassium Uranium Vanadate	Canary yellow	Occurs in scattered deposits forming irregular lenses in sandstone beds. Frequently associated with fossil logs and bones. Uranium content is about 51.7 %. Specific weight : 4.46 Hardness : 2 System : Rhombic
Tyuyamunitite	Calcium Uranium Vanadate	Greenish yellow	Most often formed in fractures in limestone or dolomite. Also found with carnotite. Uranium content is 44.5-52.4 % . Specific weight : 3.31-4.35 Hardness : 1-2 System : Rhombic
Brannerite	Titanate	Yellowish Green	Uranium content : 27.5-43.6 %. Specific weight : 4.5- 5.43 Hardness : 4.5- 5.5. System : Monoclinic.
Davidite	Titanate	Cinnamon	Uranium content : 27.5 -43.6 % Specific weight : 4.5 - 5.43 Hardness : 6 System : Cubic.

3.2. URANIUM MINERALS

The chief uranium pay ores occur in nature as oxide and silicate and as complex salts with potassium, phosphorus, vanadium, copper and calcium. The principal uranium minerals, their composition and properties are shown in table 3.2. As it is observed, minerals are divided into two groups, namely, primary and secondary minerals. Most important ones are uraninite, pitchblende and coffinite. The first two are uranium oxides

while the composition of coffinite is uranium silicate.

3.3. URANIUM DEPOSITS

Uranium minerals are deposited in earth's crust at different concentrations. Uranium deposits are originally divided into two classes. The first class is "Endogenous" deposits which are connected with magmatic processes. "Exogenous" class is the second and formed in connection with accumulation of deposits, metamorphism and the action of sub-surface waters. There can be some types of deposits out of these two classes. Known uranium pay deposits are divided into 14 types by D.Ya.Surazhkii (see table 3.3). The types given occupy different places according to the resources and the amount of uranium obtained in ores. The comparison of deposits is summarized in table 3.4. As can be seen from this table, gold-uranium and uranium-thorium ores in ancient conglomerates play the dominating role in western territories. Pegmatites, however, occupy the last place. Origin and formation of mineral deposits can easily be observed from fig. 3.1.

3.4. TECHNOLOGICAL GRADES OF URANIUM ORES

Technological grades of uranium ores are determined by the following criteria;

1. Uranium mineralisation: Due to its nature, uranium mineralization is explained in three classes.

- i. Primary ores which contain uranium $>75\%$ of total amount and uranium is in the form of endogenous minerals unaffected or affected by oxidation.
- ii. Secondary ores containing exogenous uranium minerals.
- iii. Mixed ores having both endogenous and exogenous uranium minerals in a mixed form. Uranium content in each mineral group is between 75-25% of total metal content.

Concentration capacity of the ore highly depends on oxidation level of the mineral. The lower the oxidation of the ores the better they undergo the concentration process.

2. Contrast : Contrast characteristic of uranium ores is determined by the degree of non-uniformity of the metal content in the mineral lump, which plays an important role in radiometric concentration.

- i. Contrasted ores having extremely low metal content and 10 times higher uranium content in the whole mined ore mass.
- ii. Slightly contrasted ores having metal content comparatively

Table.3.3. Scheme of Classification of Uranium Pay Deposits (8).

CLASS	GROUP	TYPE
A. ENDOGENOUS DEPOSITS	I. PEGMATITE AND PEGMATOIDS	1. Granite pegmatites occurring in veins or as columnar substances with uraninite and/or complex oxides of uranium, tantalum, niobium, titanium and others. 2. Pegmatoid veins with iron-and uranium titanates. 3. Zones of magnetised rocks with uranite.
	II. HYDROTHERMAL DEPOSITS	4. Uranium, uranium-nickel-cobalt-bismuth-silver, uranium-semimetal and other veins formed in open cavities. 5. Uranium, iron-uranium, copper-uranium and other lamellar deposits, formed by metasomatism of lateral rocks. 6. Uranium, uranium-molybdenum and other columnar deposits and veins formed by filling of open cavities and by metasomatism of lateral rocks.
B. EXOGENOUS DEPOSITS	III. SYNGENETIC DEPOSITS IN MARINE DEPOSITS	7. Black shales containing uranium. 8. Phosphorites containing uranium. 9. Clays containing uranium, with bone residues of fossil fish. 10. Marine sandstones containing uranium.
	IV. EPIGENETIC (INFILTRATION) DEPOSITS IN CONTINENTAL DEPOSITS	11. Uranium, copper-uranium, uranium-vanadium and other lamellar and lenticular deposits in coarse sandstones conglomerates and other rocks, chiefly of fluvial origin. 12. Lamellar uranium deposits in caustic bioliths.
	V. METAMORPHIC DEPOSITS	13. Lamellar gold-uranium and uranium thorium deposits in pre-paleozoic conglomerates.
C. EXOGENOUS DEPOSITS	VI. ANCIENT METAMORPHISED ALLUVIAL DEPOSITS	14. Lamellar gold-uranium and uranium thorium deposits in pre-paleozoic conglomerates.

more than that of group a.

iii. Slightly contrasted ores with relatively uniform metal content.

3. Size of Aggregates and Grains : Following groups are considered.

i. Coarse-grained ores: Diameter is less than 3 mm.

ii. Intermediate ores : 0.1-3.0 mm.

iii. Fine-grained ores : 0.07-0.1 mm.

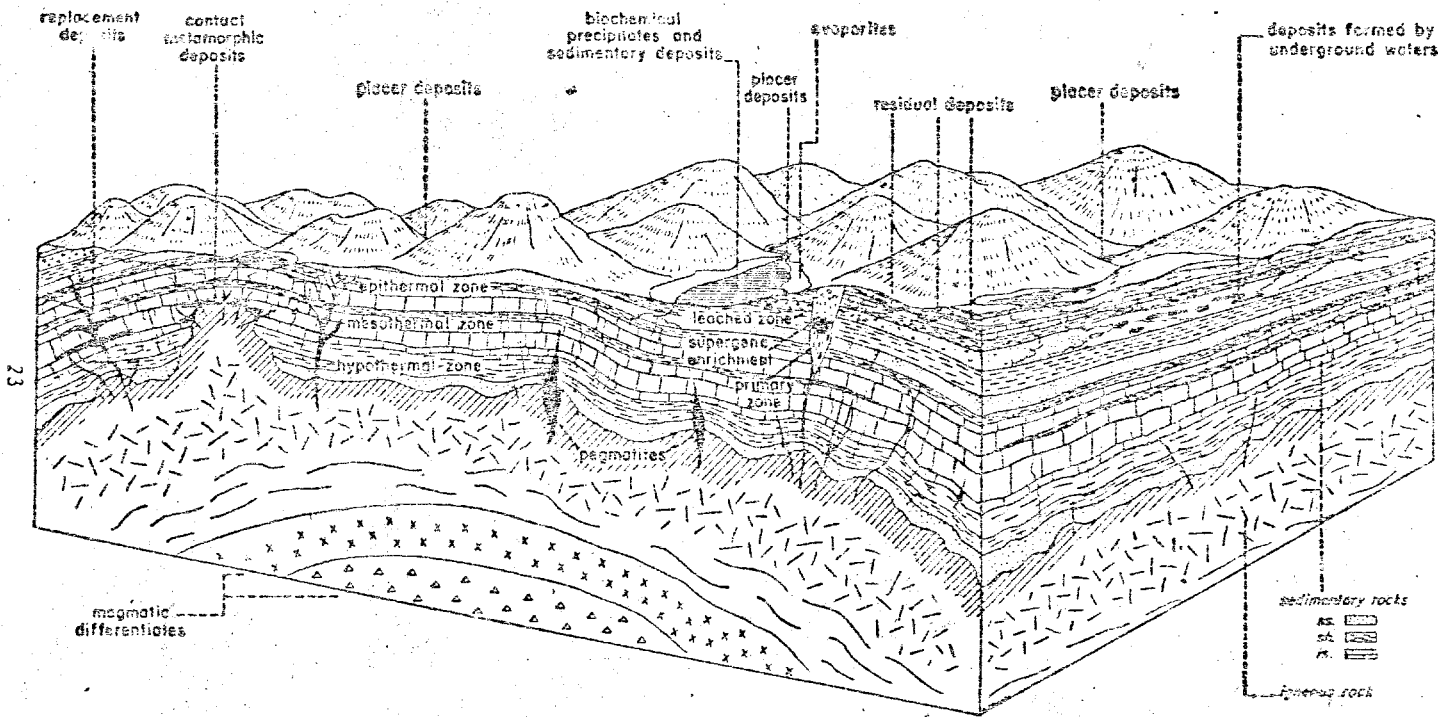


Fig.3.1. Origin and formation of mineral deposits (11).

iv. Disperse ores : 0.07 - 0.005 mm.

The degree of crushing is determined by the size of aggregates and grains of uranium minerals.

4. Chemical Composition : The methods used to separate uranium from its ores containing non-metallic constituents vary according to the type of non-metallic participants. Following groups, therefore, are mentioned.

- i. Silicate ores,
- ii. Carbonate ores,
- iii. Iron oxide ores,
- iv. Sulphide ores,
- v. Caustic biolith ores,
- vi. Phosphate ores.

5. The Content of Basic Metal: According to the content of basic metal, four grades are observed.

- i. Grade 1 ores (uranium content $> 3\%$),
- ii. Grade 2 ores (1.0-3.0 %),
- iii. Grade 3 ores (0.1-1.0 %),
- iv. Grade 4 ores (0.05-0.1%).

3.5. WORLD URANIUM RESOURCES AND PRODUCTION

The largest sources of uranium accumulate at certain regions (given in table 3.5) in the United States , Canada , South Africa , France, and Australia (12).

When the uranium resources of countries are summarized, resources are put into three groups; namely , the Reasonable Assured resources, the Estimated Additional resources and Speculative resources. The former indicates the uranium resources which are found in well known mineral resources and can be obtained by today's technology at a reasonable price. The estimated Additional resources means the uranium expected in the extension of well-explored regions due to their geological formation. The last class, however, includes uranium resources expected to be found in the world but have not been discovered yet. The table 3.6 illustrates the recent data on the Reasonably Assured and the Estimated Additional uranium resources of some countries.

The main uranium production, till the beginning of commercial nuclear power production, was made for military purposes. In 1959, a peak annual production of 34200 tU was reached while the production in 1966 was only 14700 tU. The world uranium production between 1972 and 1975 did not show reasonable increase and annual production was

Table 3.4 Some Data as to the Scale of Deposits of Different Genetic Ores (8).

Group of deposits	Maximum resources of uranium(t)		Maximum mean content (%) of uranium	Specific Weight in resources of Western countries (%)	
	In deposits	In Ore		According to uranium resources in mineral	According to uranium yield in ore
1. Pegmatites and pegmatoid veins	2,000	20	0.08	1.0	3.0
2. Hydrothermal deposits	20,000	20,000	1.50	10.0	28.0
a) Veins deposits	20,000	1,000	1.50	6.0	16.0
b) Columnar "	20,000	20,000	1.50	4.0	7.0
c) Other "	5,000	5,000	0.20	-	-
3. Remaining (Syngenetic) deposits	500,000	100,000	0.06	-	-
4. Metamorphic deposits	50,000	2,000	0.10	-	-
5. Infiltration deposits					
a) In sandstone	125,000	25,000	0.25	22.0	40.0
b) In coals	3,500	1,000	0.30	-	-
6. Ancient Conglomerates	370,000	100,000	0.08	67.0	34.0
a) Gold-uranium	370,000	100,000	0.03	35.0	16.0
b) Uranium-Thorium	350,000	100,000	0.08	32.0	18.0

reported as 19000-20000t. Since then, increase in uranium production has continued and reached ~ 36500t in 1979. On the other hand the maximum production capacities of countries (see table 3.7) deserve consideration. U.S.A, Canada, South Africa and Namibia have the largest production capabilities in 1982. In future, however, Australia and Niger show great expectations.

Table 3.5 The Largest Resources of Uranium

COUNTRY	REGION
U.S.A	Colorado, Utah, Arizona, New Mexico
Canada	Blind River, Great Bear Lake, North of Lake Alhabasca
The Rep. South Africa	Wit-Watersrand (South Transvaal, Orange Free State)
France	Central plateau (Autun, Limousin, Lascaux)
Australia	Rum Jungle, Mary Kathleen, Queensland

Table 3.6. Exploration, Production, Resources and Production Capability (13).

COUNTRY	First Exploration	First Production	Total Production to 1980	US \$80/kg Reasonably Assured 1000 tonnes U	US \$150/kg Reasonably Assured 1000 tonnes U	US \$80/kg Estimated Additional 1000 tonnes U	US \$130/kg Estimated Additional 1000 tonnes U	Attainably maximum Production capability	Year Maximum Production capability reached	QUALITATIVE POTENTIAL
Algeria	Before	1961	0	28	28	0	6			moderate/high
Argentina	1968	-	750	23	28	4	9	700	1983	high
Australia	1947	1954	9600	292	301	127	53	20000	1990	very high
Austria	-	-	0	2	2	0	0			moderate
Bolivia	late 1960's	-	0	0	0	0	<1			moderate
Botswana	late 1960's	-	0	0	0	0	0			moderate/high
Brazil	1952	1979	100	74	74	90	90	1000	1983	high/very high
Canada	1942	1938	131500	230	259	381	770	15500	1990	very high
Cen. Afr. Re.	1947	1982	0	18	18	0	0	1000	1982	moderate
Chile	1950	-	0	0	0	5	5			low
Denmark (Greenland)	1955	-	0	0	27	0	16			moderate/high
Egypt	-	-	0	0	0	0	5			-
Finland	1959	1958	<100	0	3	0	<1			moderate
France	1945	1949	29600	38	54	26	46	4500	1986	moderate/high
Gaben	1948	1969	9700	36	35	0	0	1500	1982	Moderate/high
Ger. Fed. Re.	1953	1975	200	4	5	7	8	200	1984	low
India	1953	-	0	30	30	1	24	200	1979	high
Italy	1954	1981	0	0	0	1	2	<100	1981	moderate
Japan	1954	1970	<100	8	8	0	0	<100	1979	low
Korea (Rep.)	-	-	0	0	4	0	0			low
Madagascar	1946	1955	4000	0	0	0	2			moderate
Mexico	1957	-	<100	6	6	2	2	90	1979	moderate/high
Namibia	1966	1977	9400	113	122	30	53	5000	1985	high
Niger	1954	1967	13000	157	157	53	53	12000	1986	high
Philippines	1953	-	0	<1	<1	0	0	<100	1981	low
Portugal	1945	1945	2200	7	8	3	3	300	1984	moderate
Somalia	1955	-	0	0	7	0	3			moderate
South Afr.	mid 1959's	1952	8800	242	386	54	139	10700	1986	high/very high
Spain	1952	1958	1200	10	10	9	9	1300	1985	high
Sweedn	mid 1950's	-	200	0	301	0	3	400	1983	moderate/high
Turkey	1956	-	0	2	4	0	0			moderate
Uni. Kingdom	1945	-	<100	0	0	0	7			moderate
U.S.A	1945	1942	272300	496	673	773	1158	44200	1990	very high
Yugoslavia	1965	-	0	5	7	5	20	400	1990	moderate
Zaire	1920's	1940	25600	2	2	2	2			high

Table 3.7. Attainable Production Capabilities (tonnes U) (13).

COUNTRY	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990
Argentina	135	200	280	380	680	680	680	680	680	680	680	680
Australia	600	600	2300	3800	5000	6500	12000	13600	15200	16800	18400	20000
Brazil	103	510	510	810	970	970	970	970	970	970	970	970
Canada	6900	7200	9000	9900	11000	13500	14400	14500	14500	14700	15400	15500
Cent.Afr.Rep.	0	0	0	1000	1000	1000	1000	1000	1000	1000	1000	1000
France	2950	3450	3650	3870	4020	4020	4020	4520	4520	4520	4520	4520
Gabon	1000	1000	1000	1500	1500	1500	1500	1500	1500	1500	1500	1500
Germany Fed.	100	100	150	150	150	200	200	200	200	200	200	200
Germany Reb.	200	200	200	200	200	200	200	200	200	200	200	200
India	0	0	120	120	120	120	120	120	120	120	120	120
Italy	30	30	30	30	30	30	30	30	30	30	30	30
Japan	30	30	30	30	30	30	30	30	30	30	30	30
Mexico	90	170	550	550	550	550	550	550	550	550	550	550
Namibia	3700	4100	4400	4550	5000	5000	5000	5000	5000	5000	5000	5000
Niger	3350	4300	4500	4500	5800	8000	10500	12000	12000	12000	12000	12000
Philippines	38	38	76	76	76	38	0	0	0	0	0	0
Portugal	85	95	100	100	100	270	270	270	270	270	270	270
South Africa	5240	6500	7300	8600	9900	10400	10600	10700	10700	10600	10600	10400
Spain	339	678	678	678	678	678	1272	1272	1272	1272	1272	1272
Sweden	0	0	0	0	400	400	400	400	400	400	400	400
U.S.A	19000	20900	24300	27100	30900	53600	34100	35000	38400	40800	42600	44200
Yugoslavia	0	0	120	120	120	180	180	180	245	310	375	440
TOTAL (Rounded)	43900	50100	59300	68000	78200	87800	98000	102700	107800	111900	116100	119300

4. EXPLORATION

Uranium exploration, like other mineral explorations, requires money, time, and qualified personnel. An advantage for uranium exploration is the radiation property. Since uranium emits gamma radiation, it can easily be detected from a considerable distance. Using this fact, radiometric exploration techniques have been developed (14). Exploration programmes vary depending upon the differences in geological properties of the site and objectives of the programme (15). That's why there is no standard exploration procedure. However, the sequences given in table 4.1 are suggested. It can be observed from the table that uranium exploration program is carried through a combination of geologic, radiometric, geochemical, geophysical, geobotanical and engineering techniques.

4.1. RADIOMETRIC SURVEYS

Radiometric surveys are the most useful techniques. To measure specific gamma-ray activity is the working principle of radiometric surveys. Instruments mounted in aircraft and automobiles have been used to detect radioactive anomalies. In radiometric exploration studies, a marked increase in radioactivity indicates where further work should be done.

The main radiometric surveys are classified as Aerial, Surface and Subsurface surveys.

i. Aerial Radiometric Surveys :

Exploration studies of large areas are started by aerial radiometric surveys. Instruments used in airborne surveying (see Fig.4.1) must be highly sensitive gamma-ray detectors to locate anomalous concentrations of radioactivity at an air distance determined by aircraft safety. After radioactive anomalies are detected, they are recorded. Then, the information is plotted on maps. Spectral data obtained is evaluated and used for further explorations.

ii. Surface Radiometric Surveys :

Surface radiometric surveys are performed by the use of portable, hand-held or jeep-mounted radioactivity detection equipment, principally scintillometers, spectrometers and Geiger Counters. Discovery of uranium deposits depends on high gamma detection efficiencies, high count rates and low statistical fluctuations of such instruments. Scintillometers which are the most frequently used counters are installed in vehicles for measuring gamma-rays emitted by U, Th, K in rocks. The field spectrometer also permits the determination of

Table 4.1. Uranium Exploration Sequence (14)

I. Planning Stage

II. Reconnaissance Stage (Low density)

Areas of unknown potential ($> 5000 \text{ km}^2$)
 Scale of map : 1:250000 to 1:100000
 Photogeological interpretation
 Reconnaissance geology
 Radiometric survey:
 (Gross-count, γ -ray spectrometry)
 Airborne, carborne
 Geochemical survey: (0.1-1 sample/ km^2)
 Heavy mineral, lake sediment, stream
 Sediment, water

↓ → Area of no interest

III. Follow-up Stage (Intermediate density)

Areas of interest (200-2000 km^2)
 Scale of map : 1:50000 to 1:25000
 Photogeological interpretation
 Geological mapping
 Radiometric survey:
 Airborne (close-space), carborne, ground
 Geochemical survey: (2-10 samples/ km^2)
 Stream sediment, water, soil, soil-gas *
 Large-space drilling (1 hole/ 2-5 km^2)

↓ → Insignificant anomalies
 (Filed)

IV. Detailed Stage (High density)

Significant anomalies (2-20 km^2)
 Scale of map : 1:10000 to 1:1000
 Geological mapping, prospecting, trenching
 Ground radiometric survey
 Electromagnetic survey (VLF) or others
 Geochemical survey (7100 sample / km^2)
 Soil, soil-gas, rock sampling *
 Systematic drilling (1 hole / km^2) *

↓ → False anomalies (Filed)

V. Exploration Development Stage

Prospects
 Detailed mapping, trenching
 Close-grid drilling
 Mineralogical and petrographic study

↓ → Uneconomic mineral
 Occurrence (Filed)

ORE DEPOSIT

* for sandstone-type deposit

gamma radiation having the particular energy. This leads to the determination of U, Th and K concentrations. To provide rapid indication of elemental concentrations in mineral, radioisotope x-ray fluorescence analysers have also been used (16).

iii. Subsurface Radiometric Surveys :

After aerial and surface radiometric surveys if further explorations are wanted, subsurface studies are conducted. In fact, actual delineation of ore bodies is a matter of subsurface development. Subsurface radiometric techniques include gamma-ray and neutron logging of exploratory drill holes and measurements of radon content of gases issuing from soils, springs and drill holes. 50 to 80% of the total cost of an exploration programme is for drilling processes.

In borehole radiometric logging method, a gamma-ray detector is lowered into a hole, then detected anomalies are recorded rapidly. Radioisotope x-ray fluorescence borehole probes are now being developed for determining mineral concentrations at depth in an ore body. Fig. 4.2 illustrates studies in Pakistan.

The working principle of radon surveys, however, depends on detecting the radiation emitted by uranium decay products. Emanometers, in other words, radon monitors, are mostly used. These instruments detect radon, thorium and their immediate decay product concentrations. The advantage of radon survey is the capability of detecting uranium at depths of 5 to 50 metres.

4.2. GEOCHEMICAL SURVEYS

After radioactive anomalies are detected, the problem now arises as to how the hidden uranium ore deposits are to be found (17). This problem has been solved by the application of geochemical techniques.

i. Preliminary Investigations :

Preliminary investigations consider the comparison between a region with other regions having similar geological and climatic conditions. Mineralization type of the region is obtained.

ii. Low-density Sampling Surveys (scale 1:250000-1:25000) :

Taking 0.1-2 samples per km² indicates low-density surveys. This method is used to eliminate the regions which are not favourable before precise delineation.

iii. Intermediate-density Sampling Surveys (scale 1:20000-1:50000):

Taking 10-20 samples per km² indicate intermediate-density sampling surveys. Origin of surface anomalies are determined in the regions selected by the use of low-density sampling surveys. On the other hand, sediment samples of water and streams are taken. Spring waters are

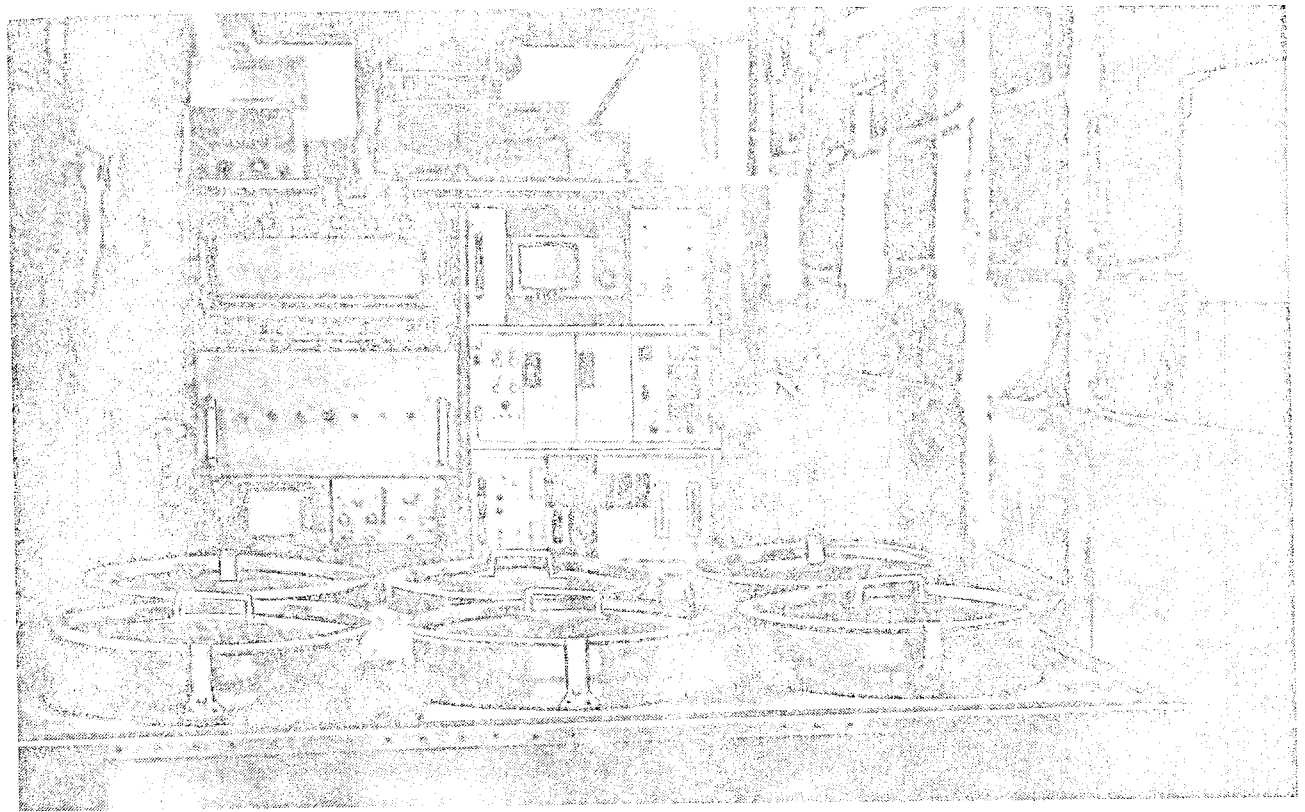
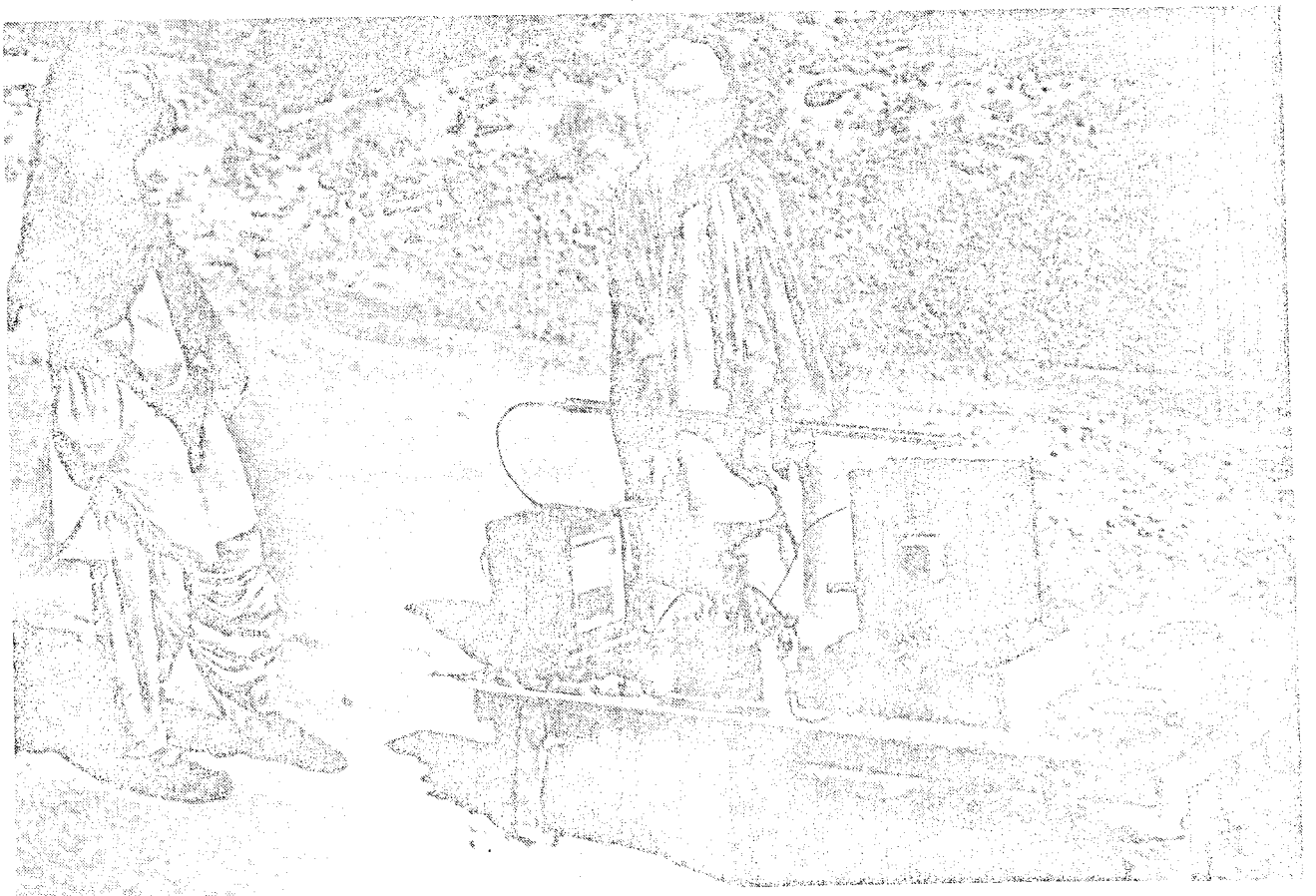


Fig. 4.1. Airborne γ -ray spectrometric system consisting of six large sodium iodide - NaI(TL)-detectors shown here in the foreground of the picture installed inside a survey aircraft, with the associated electronics behind the detectors (14).

Fig. 4.2. Borehole logging in Pakistan. The worker is standing behind the logger recording apparatus and the manual winch used to lower the probe into the hole, and is holding the probe itself in his hands (14).



sampled and geological information of anomalous zones is obtained. Then a proper method for further studies is determined in this intermediate phase.

iv. High-density Sampling Surveys (scale 1:50000-1:500) :

This is accomplished by increasing the sampling to 200 samples per km². The objective of this phase is to distinguish economic mineralization from uneconomic ones. A square sampling grid having intervals of 10m.-50m. is suitable at this phase.

4.3. OTHER TECHNIQUES

i. Geophysical Surveys :

These techniques include natural potential, seismic reflection and refraction and magnetic, electrical resistivity methods. These are used at detailed exploration phases. The working principle of surface resistivity, for instance, is transmission and distribution of electric currents in the ground. Studies of surface resistivity is used for drilling programmes. A new technique depending upon thermal anomalies of geological formations including uranium have promised great expectations (18).

ii. Remote Sensing :

Remote sensing techniques are only an indirect method for uranium exploration. These are used for obtaining geological and tectonic information on a regional scale. Multispectral reflectance data obtained from satellite or aircraft and thermal-infrared images are examples of remote sensing.

iii. Botanical Prospecting :

Botanical prospecting methods are dependent upon the accumulation and absorption of metals by plants growing over metalliferous deposits. The trunk, branches and leaves of plants are examined to get radiation trace (19).

iv. Hydrogeochemical Prospecting :

Radioactive materials brought up by water or gases are examined in hydrochemical prospecting. Underground uranium deposits can be determined by finding the spring of water or gases under consideration.

Chapter 5

5. MINING

5.1. MINING TECHNIQUES

Mining is the process of getting the ores or mineral mixtures from earth's crust by sequences of operations. By considering the ore depth, deposit size, ore grade, ground conditions, surface topography etc., optimum mining system for a certain deposit is determined.

The size of uranium ore deposits indicates the ore production per day which varies from less than 50 tons to 40000^{*} tons. Uranium is produced either by underground or open-pit operations. Figure 5.1 and 5.2 illustrates the Osamu Utsumi Open-pit uranium mine in Brazil and an underground uranium mine in the Vendée region of France, respectively. Some underground mines are at depths of 1000m. and even deeper whereas some are less than 30m. below the ground. Conversely, while some underground mines are 30m. below the surface, some open-pit mines operate at a depth of 150m.. Figure 5.3 can give an idea about a deep open-pit mine.

Underground methods are applied to the large ore bodies which are worked from vertical or inclined shafts and result in high grade ore production (20). By open-pit mining in importance recently, the grade of the ore, however, can be controlled by selective mining and blending. Since the uranium ores occur in a different geological type of setting, every type of mining technique has been used. Let us look at some of the uranium mining techniques used in the U.S.A and Canada.

In the United States, the mining industry centers are placed in Colorado, Utah, New Mexico, Wyoming and Arizona and there are more than 500 individual mines (19). Table 5.1 summarizes the deposits in the United States. For the first type of deposits, room-and-pillar, long wall-retreat and panel mining techniques are employed. Figure 5.4 illustrates the long-wall-retreat mining method. The shallow carnotite deposits are operated more conveniently by adits driven on the ore horizon.

In Canada three types of mining methods are used. These are open-pit, underground mining with track haulage and trackless mining. The open-pit method is only employed in Gunnar mine (see Fig.5.5.). Here the ore is blasted out of the pit-wall and taken out of the pit up a spiral roadway (22). In the Blind River region in Canada tracked and trackless underground mining methods are applied. Trackless transport is used where the ore beds are inclined at less than 20°; tracked transport for greater inclinations (22).

*At Rossing open-pit mine in Namibia (20)

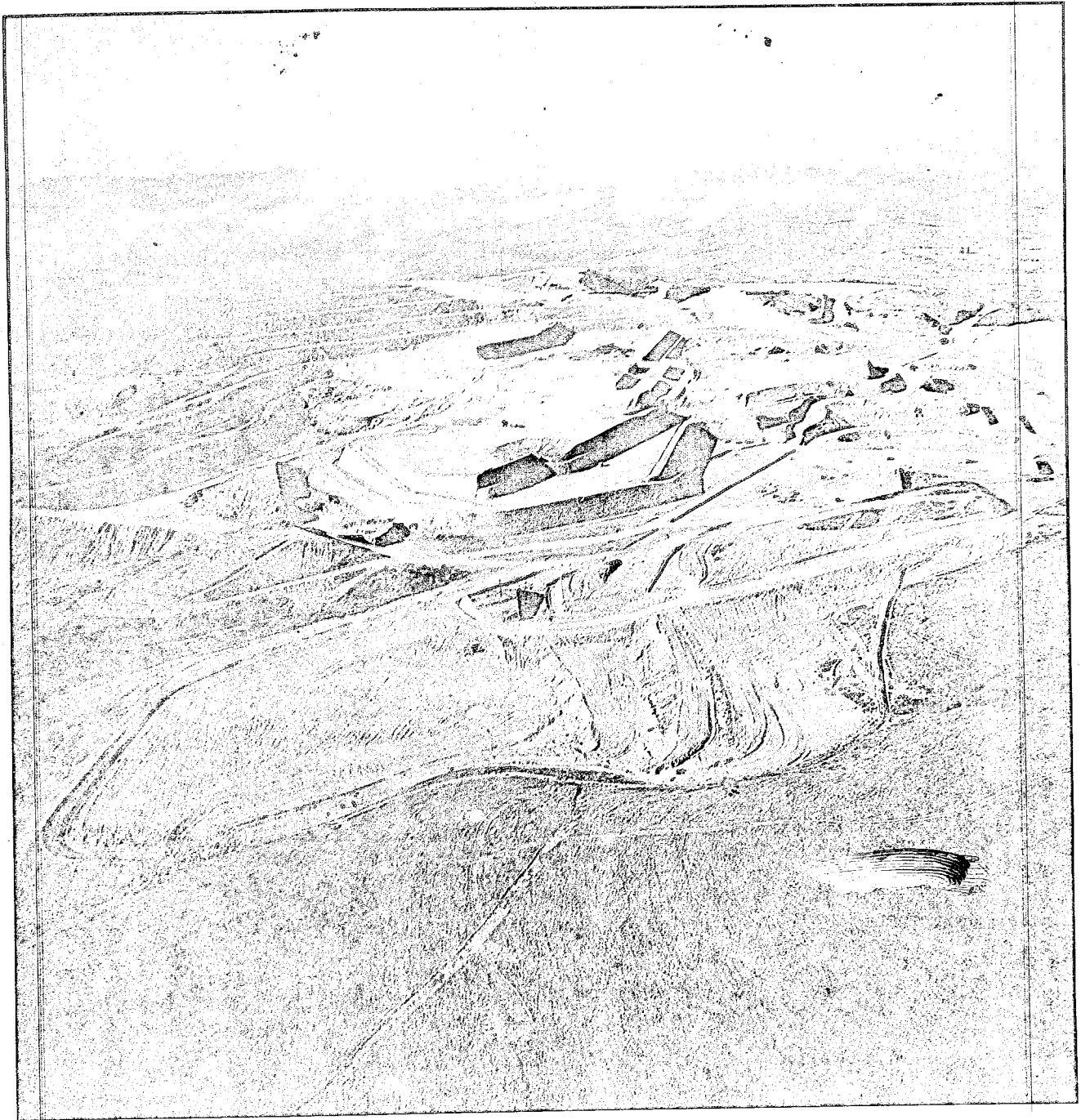


Fig.5.1. The Ossaçu Ubraudi uranium mine in Brazil (21).

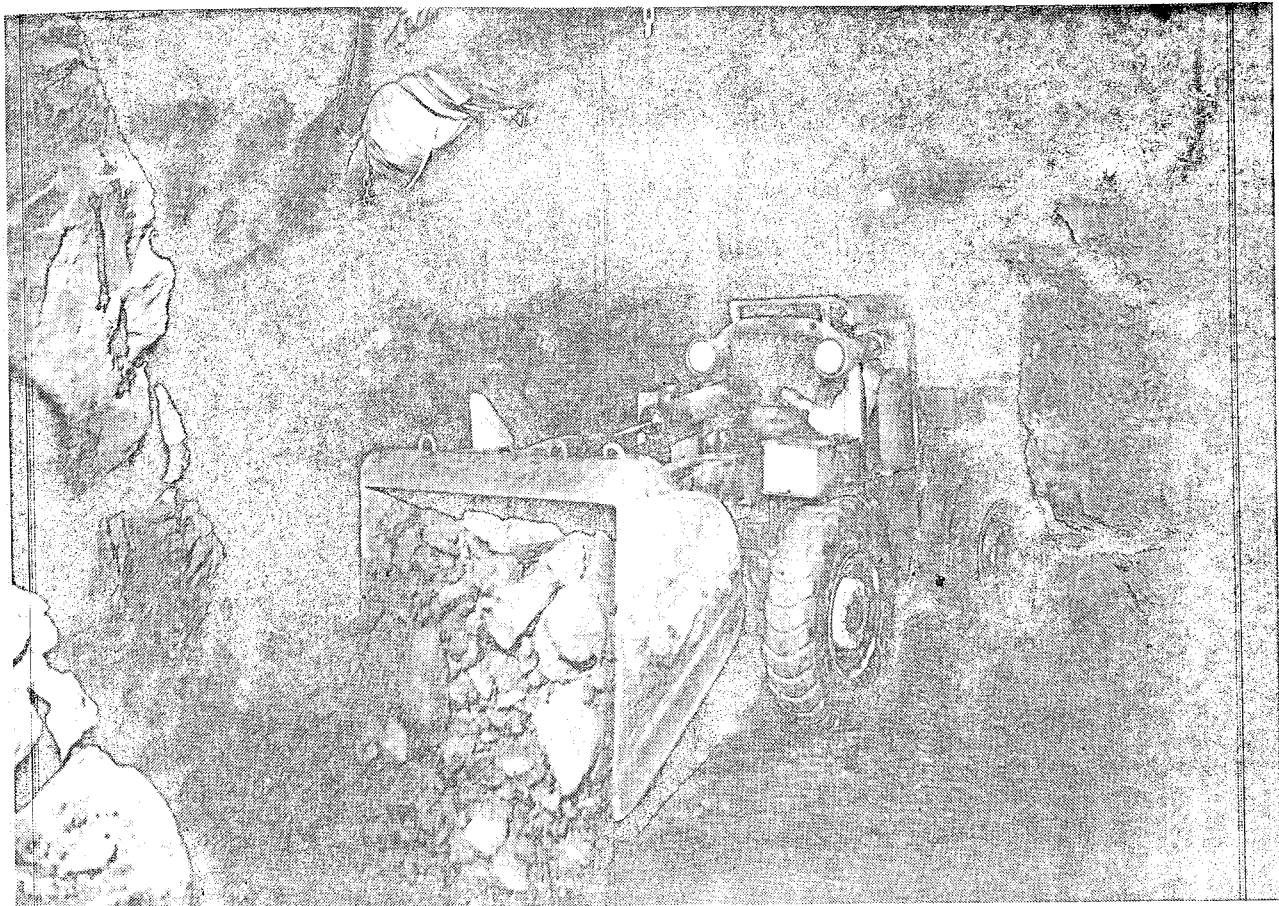


Fig.5.2. Inside an underground uranium mine in the Vendée region of France (21).

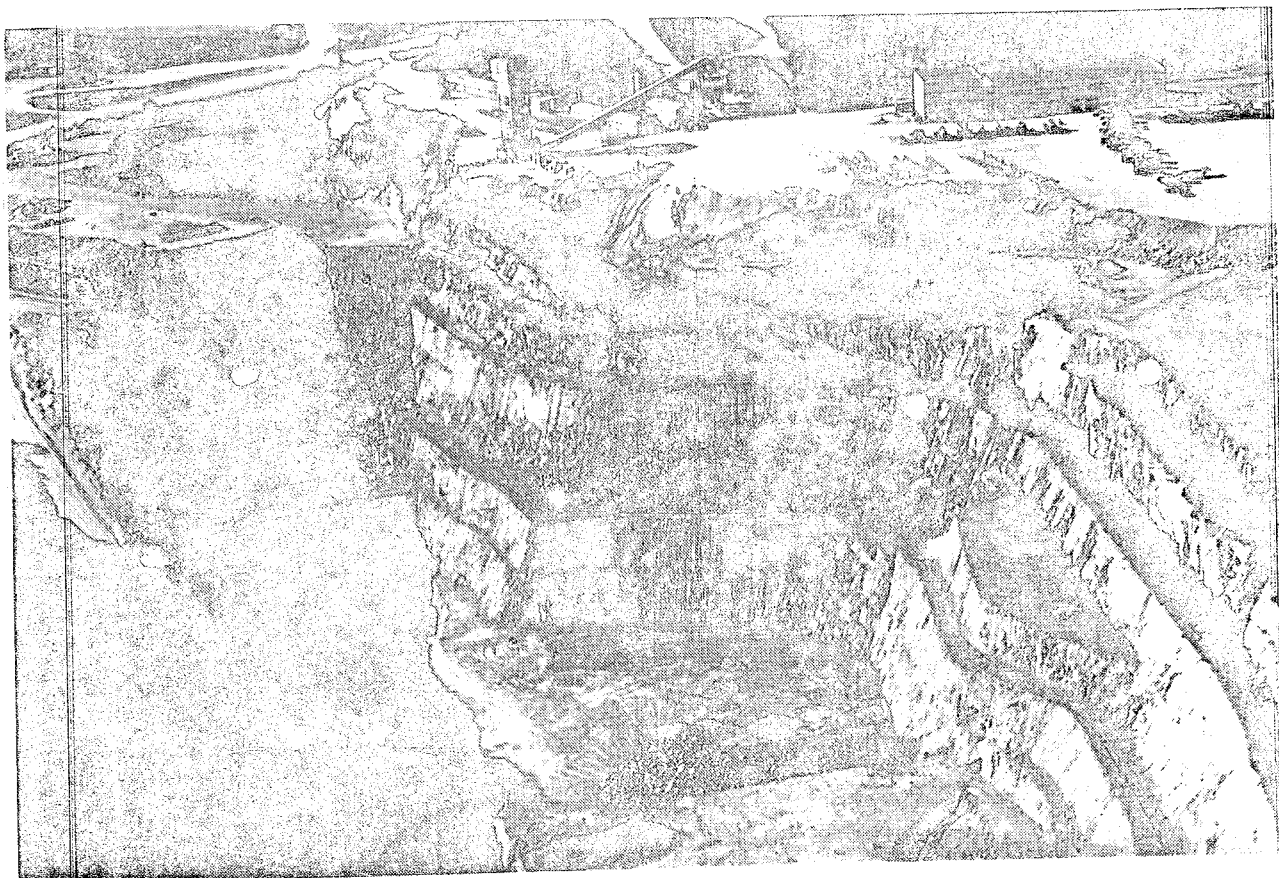


Fig.5.3. An open-pit uranium mine in the Vendée region of France (21).

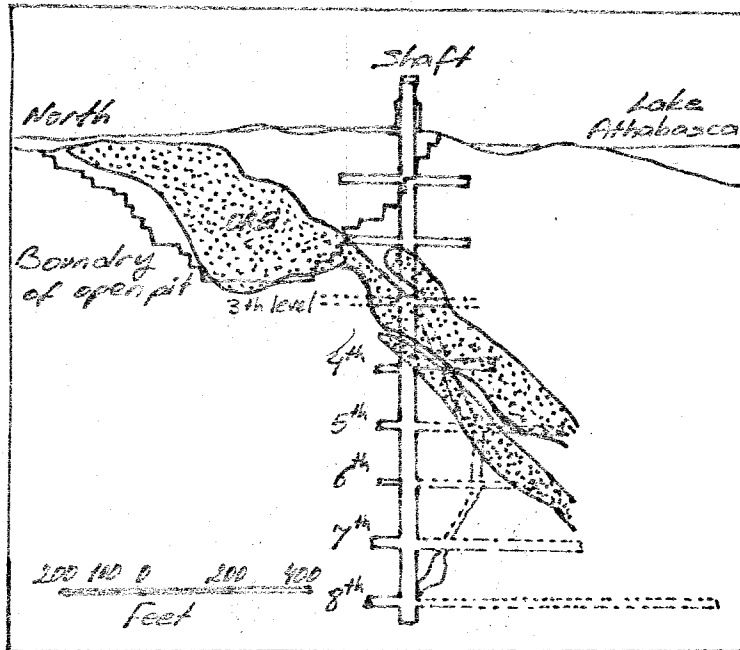


Fig.5.5. Generalized longitudinal section along axis of the Gunnar ore body, looking East(22).

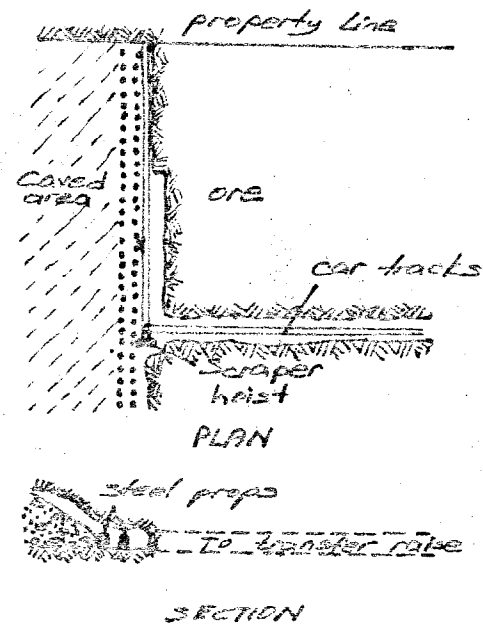


Fig.5.4. Longwall-retreat mining method, Radon Mine (22).

Table 5.1. Principle Categories of Uranium Deposits in U.S (19,22)

URANIUM DEPOSITS	
CATEGORY	SITE
1. Extensive deep-regular	Big Indian Wash (Utah) West Water canyon sandstones of the Grants-Ambrossia Lake districts (New Mexico)
2. Shallow-irregular	Salt Wash Formation (Colorado) White Canyon (Utah)
3. Extensive-Shallow (open-pit mined)	Gas Hills (Wyoming) Grants (New Mexico) Cameron Area (Arizona)

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5.2. RADIOLOGICAL SAFETY IN URANIUM MINES

Mining began in the Erz mountains of Saxony in the fifteenth century (23). Copper, iron and silver were the first mined minerals. In the later part of the century, pitchblende mining were began. As early as 1879 Härtling and Hesse published their first paper as a result of their pathologic-histological studies on 20 deceased miners (24). Far more than 50% of all cases showed malignant changes of the respiratory tract, called by the authors "lymphosarcomata" ; later on they were correctly diagnosed by Arnstein (1913) as "primary carcinomata of the lung" (24). Many investigations and reports followed this study. As a result, official authorities were interested in solving this problem and started intensified investigations in this field.

In early times, the actual reasons for miner's deaths were unknown, because the miner's relatives mostly refused autopsy. Then, it was first observed that special health hazard were associated with uranium mining (25).

The external radiation hazard and chemical toxicity are the types of uranium hazards.

Uranium emits alpha and gamma radiations and its principal radioactive decay products listed in table 5.2 emit alpha, beta and gamma radiations. Alpha, beta and gamma radiations present a considerable health hazard. They cause tissue damage by ionization within the body. Since the alpha particles cause large number of ionizations per unit length of path, alpha emitters cause the greatest inhalation hazard. The radiological hazards in the uranium mines are due to radon and short-lived radon decay products ; namely Po-218, Pb-214, Bi-214 and Po-214 and also due to the long-lived U-238 and U-235 's decay products ; namely, U-234, Th-230, Ra-226 and Po-210. Radon, Rn-222, has a half-life of 3.82 days and is an inert gas which can easily pass into and out of lungs with minimal uptake by the respiratory system. Radon daughters are solid and travel on dust particles in the air. Significant radon concentrations occur near ore storage bins and crushing and grinding circuits. Since radium, Ra-226, having a half-life of 1.6×10^3 years is the precursor of radon, if it is removed from uranium, the gamma radiation is prevented. It has to be added that radium is much serious hazard in uranium extraction as not only is its activity high but it tends to become fixed in the bones, replacing calcium, and the maximum permitted level is only $3 \times 10^{-11} \mu\text{ccm}^{-3}$ equivalent to only $3 \times 10^{-5} \mu\text{gm}^{-3}$ (27). The recommended maximum permitted concentrations of radon is $3 \times 10^{-8} \mu\text{cm}^{-3}$ in air (27). According to International Commission on Radiological Protection (ICRP) the dose limitation is

Table 5.2. Principal Radioactive Decay Products of Natural Uranium (26).

Nuclide	Historical name	Half-life	Radiation	Atom ratio, ppb in natural U
Part A. From U ²³⁸				
⁹² U ²³⁸	Uranium I	4.49 × 10 ⁹ years	α	9.328 × 10 ⁸
⁹⁰ Th ²³⁴	UX ₁	24.10 days	β, γ	0.0146
⁹¹ Pa ²³⁴	UX ₂	1.175 min	β, γ	4.94 × 10 ⁻⁷
⁹² U ²³⁴	Uranium II	2.48 × 10 ⁴ years	α, (γ)	5.48 × 10 ⁴
⁹⁰ Th ²³⁰	Thorium	8.0 × 10 ⁴ years	α, γ	1.77 × 10 ⁴
⁸⁸ Ra ²²⁶	Radium	1622 years	α, γ	359
⁸⁶ Rn ²²²	Radon	3.825 days	α	2.32 × 10 ⁻³
⁸⁴ Po ²¹⁸	Radium A	3.05 min	α	1.28 × 10 ⁻⁶
⁸² Pb ²¹⁴	Radium B	26.8 min	β, γ	1.13 × 10 ⁻⁵
⁸³ Bi ²¹⁴	Radium C	19.7 min	β, γ	8.28 × 10 ⁻⁶
⁸⁴ Po ²¹⁴	Radium C'	1.637 × 10 ⁻⁴ sec	α	1.15 × 10 ⁻⁸
⁸² Pb ²¹⁰	Radium D	22 years	β, γ	4.86
⁸³ Bi ²¹⁰	Radium E	5.02 days	β	3.04 × 10 ⁻³
⁸⁴ Po ²¹⁰	Polonium	138.3 days	α	0.0838
⁸² Pb ²⁰⁶	Radium	Stable		

Part B. From U ²³⁵				
⁹² U ²³⁵	Actinouranium	7.13 × 10 ⁸ years	α, γ	7.15 × 10 ⁶
⁹⁰ Th ²³¹	Uranium Y	25.64 hr	β, γ	2.94 × 10 ⁻⁵
⁹¹ Pa ²³¹	Protoactinium	3.43 × 10 ⁴ years	α, γ	344
⁸⁹ Ac ²²⁷	Actinium	22.0 years	(α), β, (γ)	0.221
⁹⁰ Th ²²⁷	Radioactinium	18.6 days	α, γ	5.11 × 10 ⁻⁴
⁸⁹ Ra ²²⁶	Actinium X	11.2 days	α, γ	3.08 × 10 ⁻⁴
⁸⁶ Rn ²¹⁹	Actinon	3.92 sec	α, γ	1.25 × 10 ⁻⁹
⁸⁴ Po ²¹⁵	Actinium A	1.82 × 10 ⁻³ sec	α	5.82 × 10 ⁻¹³
⁸² Pb ²¹¹	Actinium B	36.1 min	β, γ	6.89 × 10 ⁻⁷
⁸³ Bi ²¹¹	Actinium C	2.16 min	α, γ	4.12 × 10 ⁻⁸
⁸¹ Tl ²⁰⁷	Actinium C'	4.79 min	β, (γ)	9.14 × 10 ⁻⁸
⁸² Pb ²⁰⁷	Actinium D	Stable		

is determined by considering the exposure to external radiation, to radon daughters and to ore dust. Following combination formula has been obtained by ICRP :

$$\frac{H_E}{50\text{mSv}} + \frac{E_{\text{RnD}}}{0.02 \text{ J}} + \frac{E_{\text{OD}}}{1.3 \text{ Bq/h/l}} \leq 1 \quad (28)$$

where H_E: Exposure to external radiation, expressed in effective dose equivalent (mSv) (1 mSv=0.1rem).

E_{RnD}: Exposure to radon daughters, expressed in joules (potential energy released by the inhaled radioactive elements).

E_{OD}: Exposure to ore dust (other than radon daughters), expressed in Becquerel-hour per litre.

The denominators are the corresponding annual limits.

The chemical toxicity of uranium in soluble form is concentrated in the kidney which sustain the most serious damage. The toxicity of insoluble uranium is less hazardous since it leaves the blood rapidly and excreted in the urine.

For the safety of workers in uranium mines, ventilation of the contaminated air by powerful fans is the primary precaution (29). The mechanical ventilation system is composed of primary and auxiliary ventilation. The primary mechanical ventilation used for diluting the radon and its daughter concentrations in the mine air moves the diluted air out of the mine by means of large fans located at the surface. Auxilliary systems distribute air from the main air courses to locations underground by means of small fans and flexible ducts (28). Fig. 5.6 illustrates a polyethylene duct used for ventilation in Canadian uranium mines. Since radon is soluble in water, water must be prevented from entering into the working areas.

Personal hygiene, respiratory protection and periodic medical examinations should be required of all personnel in contact with uranium concentrates.

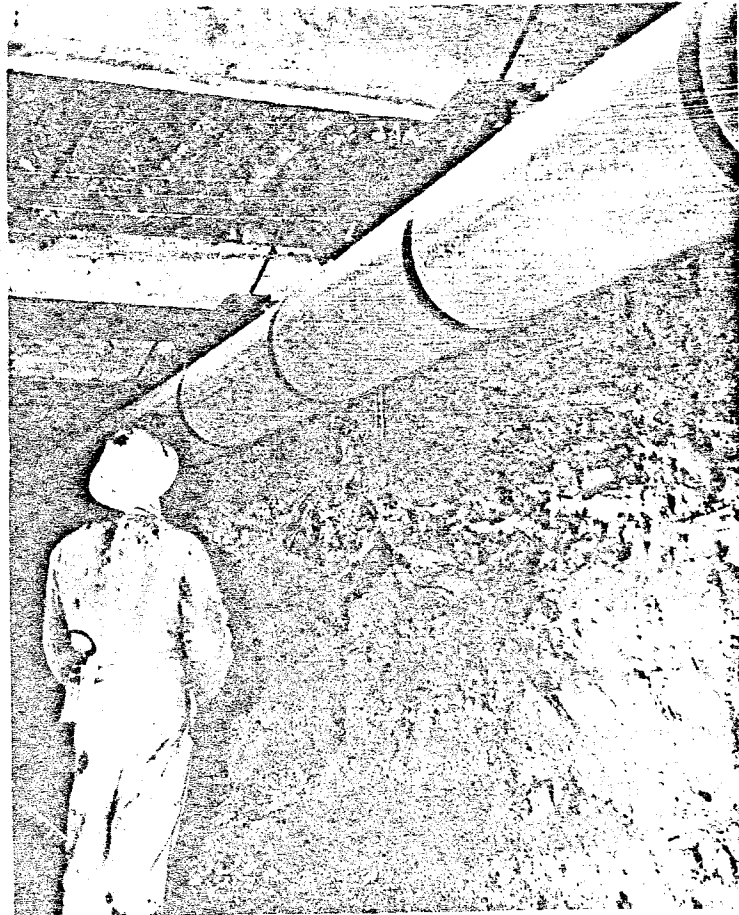


Fig.5.6. 20.in 10m polyethylene duct used for ventilation of developed headings (30).

6. MILLING

In general, when a metal is mined as an ore or mineral mixture, undesired waste minerals are also found as mixed and interground with the valuable ore. The process defined as separating a metal-liferous mineral from gangue is called "CONCENTRATION" or "MILLING".

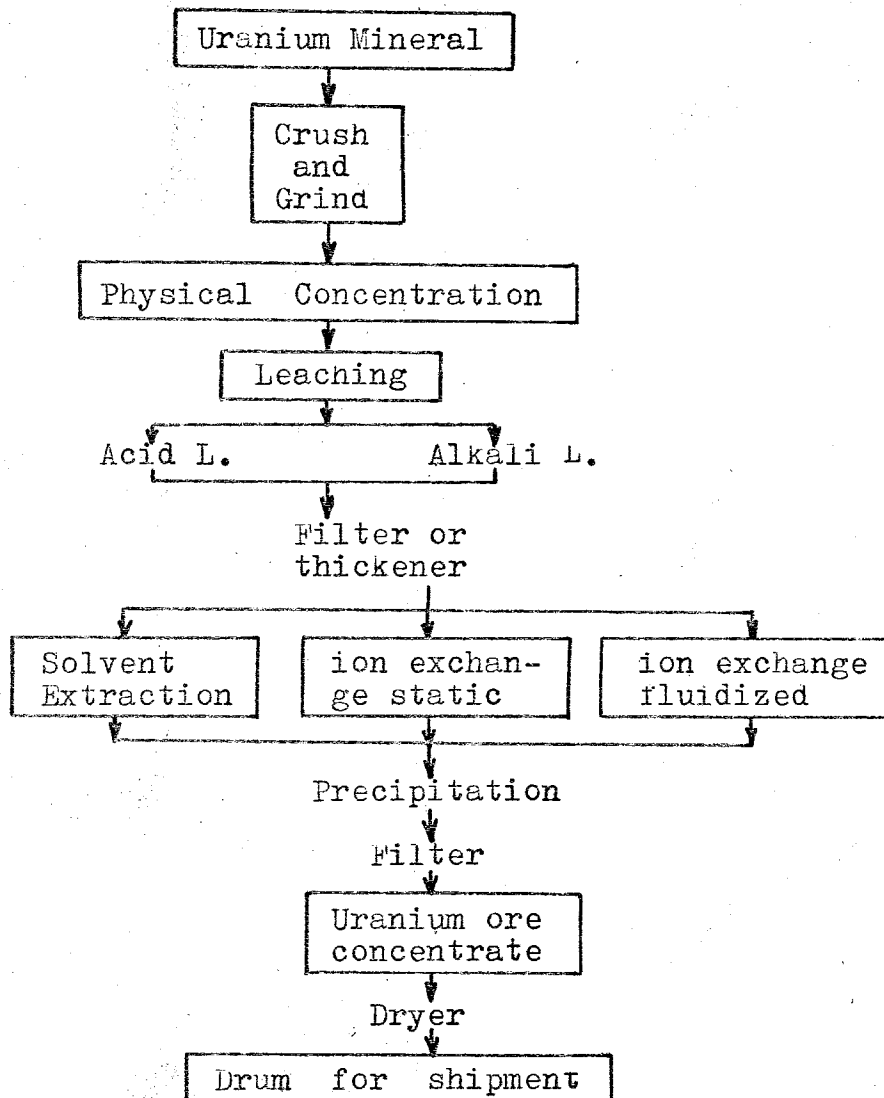


Fig.6.1. Uranium milling steps (31).

Uranium milling process starts from ore excavation and goes up to purification stage. Figure 6.1. summarizes the milling steps. Different processes used for the same purpose are observed in each step. A uranium milling plant chooses one path among these processes (e.g. see fig. 6.2). Table.6.1 shows the relative importance of the different processes used in uranium ore processing.

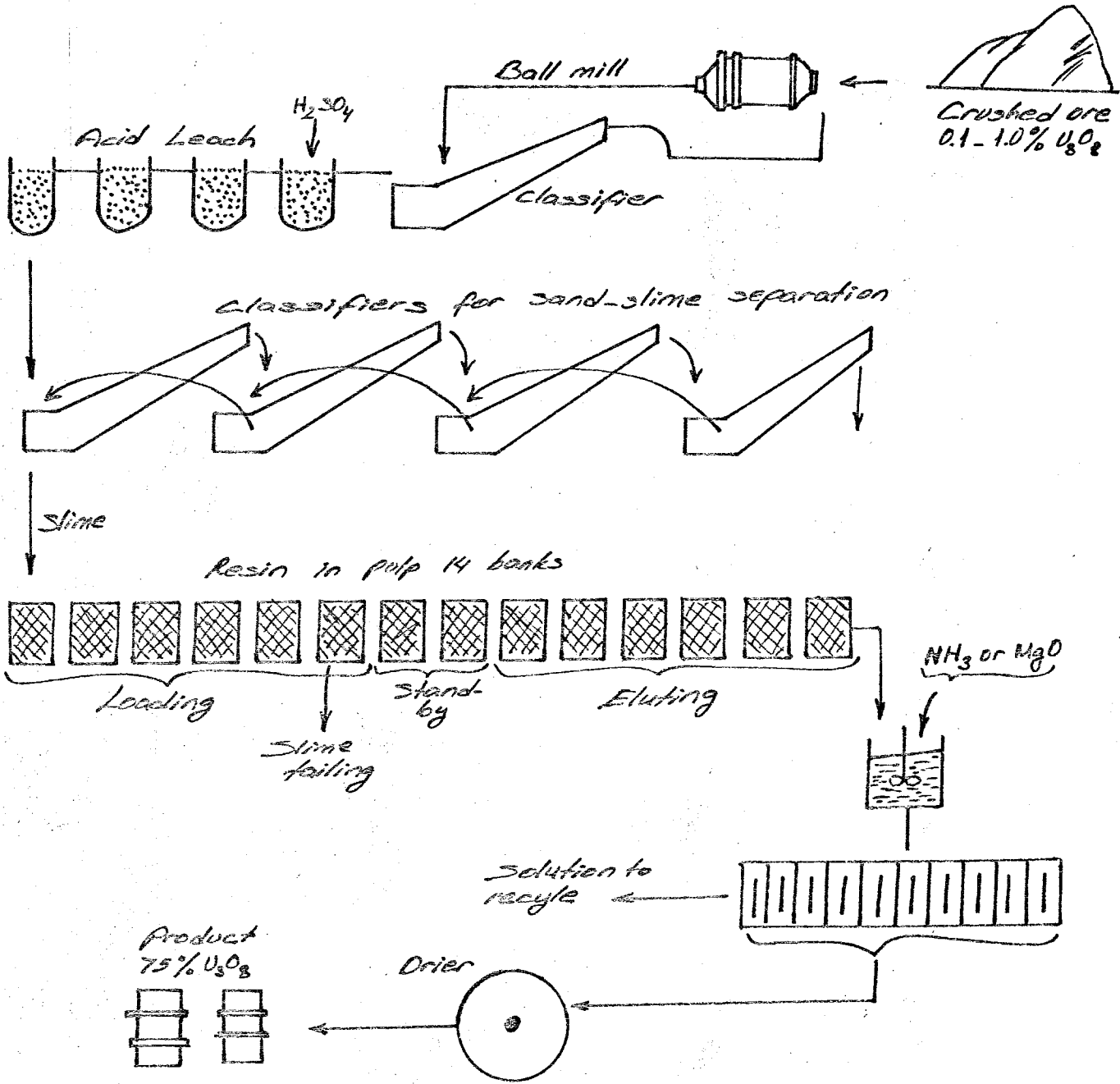


Fig.6.2. Simplified diagram of Uranium milling (10).

Table 6.1. Data as to the Processing of Uranium Ores in Western Countries (8).

Characteristic	Country						Total
	U.S.A †	Canada	S. Africa	Australia	France	Others	
Number of plants	25	19	17	5	4	10(?)	80
Quantity of ore processed, 1000 tonnes	7000	13,700	22,100	456	1110	680	45,646
Mean U content, %	0.22	0.097	0.06	0.10	0.10	0.23	0.085
Mean U recovery, %	92	90	80	90	90	90	89
Number of works per process	8	3	9	1	2	3	26
Mechanical concentration ‡ Comprising:							
Gravitation	1	1	—	1	1	2	6
Flotation	1	3	39	1	2	1	17
Selective Crushing	6	—	—	—	—	—	6
Acid Leaching	20	18	17	4	4	5	68
Carbonate Leaching	8	1	—	—	—	1	10
Counter-flow decantation	13	2	—	3	2	2	22
Filtration	9	17	17	1	2	2	48
Absorption	11	17	17	3	2	4	54
Comprising:							
From solutions	3	17	17	3	2	4	46
From pulp	8	—	—	—	—	—	8
Extraction	12	2	—	1	1	1	17
Chemical precipitation	10	1	—	—	—	—	13

† Many plants have two sections (for silica and carbonate ores) and of the same time use different processes (in parallel or occasionally successively).

‡ Excluding radiometric concentration which is usually carried out at the mines.

6.1 ORE DRESSING

Ore dressing is the first stage of uranium milling that is a uranium concentration process. The essential operation in the uranium ore dressing includes physical separation of uranium mineral from the undesired non uranic ores(32). Mineral dressing operations generally do not involve changes in the physical or chemical identities of the minerals separated. Reducing the bulk of material which will pass to chemical treatment and the recovery of other ore constituents are the main aspects of mineral dressing.

The methods used for the uranium concentration and extraction from inert gangue vary with the grade of the ore. The separation of the high-grade minerals is easy since they can be hand picked or sorted by radioactive detection. For this purpose picker belt is a much more elaborate way. In this method, while ore pieces travel on a conveyor belt, an available Geiger or Scintillation counter operates a kicker mechanism and then the kicker mechanism pushes the piece aside into a bin. The low grade i.e poorer minerals are found as dispersed in rock. The poorer minerals contain mainly non-uranic ores and other metals. These kinds of minerals are not amenable to radioactivity sorting method. Therefore the low grade ores are crushed and ground to small pieces to get a good response for further separation processes.

6.1.1. CRUSHING

The ore is extracted at the mines as large lumps of rock. Ore lumps are treated in a sifter. Then the larger lumps of rock remain on the sifter. The sizes of lumps remaining on the sifter have to be reduced so as to separate the desired mineral easily. Obtaining the finest size product from the crude through successive reduction steps is a matter of crushing. I crushing operation, a mechanical force is applied to large size particles in order to break them apart. Typical pressure breakers include jaw, gyratory, cone, gyrosphere crushers and roller mills.

The crushing and sampling processes are done in a plant which is not approached during operation. Crushing machines, sizing apparatus, storage, feeding-transport means, sampling-control devices are present in the plant in a suitable manner. All these are designed in such a way that excavated rocks happen to be products at determined sizes, rates and time. Due to radium and argon, ventilation of the plant is also important and requires using powerful fans.

Elements of a crushing flowsheet can be given as follows:

i. RECEIVING UNIT :

The function of receiving unit starts after ores are excavated as large lumps of rock and ends by putting the lumps into the primary crusher. All transfer means are included in the receiving unit. Excavated material from the mining site is transferred by means of cars, trucks or ships in containers. There is a storage ahead of primary crushing designed to prevent the flow interrupting. For operating the crusher efficiently some means of regulating the flow to the machine are required. A feeder with push-bottoms start-stop control under the supervision of the primary crusher tender can be used for feeding purpose.

ii. PRIMARY CRUSHING UNIT :

Primary crushing unit is composed of a single crushing machine. Jaw and gyratory crushers for hard rocks and single roll crusher for softer rocks are used. Crusher having large receiving opening is preferred to take any lump easily.

iii. SECONDARY CRUSHING UNIT :

Secondary crushing unit comprises an integrated combination of crushing machines, screening, distributing, storage, feeding, separating and transporting means. Cone type crushers for hard rocks and hammer mills for soft rocks are used. Feeding uniformity is essential. Use of a bin results in uniform maximum loading of the secondary crushers. A sizing guard on the product is used if the secondary crushing unit is also the final unit. Screening is done by vibrating screens in the concentrating mill either to guard the product or for scalping. Extraneous wastes have to be removed. For instance, magnets are used to remove iron pieces if present. Crushed rocks are transported throughout a crushing plant by belt conveyors.

iv. FINE CRUSHING UNIT :

Fine crushing unit presents a number of problems more complicated than the initial units. Here the crushing machines have lower capacity, are more sensitive to size, mineralogical character, moisture and feed rate variations. Storage in the form of surge bins is offered to ensure constant feed rates. The product is guarded more frequently. Crusher type is chosen according to the maximum size of product and tonnage. Screening is always done by vibrating screens.

v. STORAGE :

Storage of crushing-plant product is the link between the crushing plant and the following stage. By the way the storage acts as

a surge bin to deliver as a uniform 24-hr flow to the mill and a mixing device for averaging the mineralogical character of different mined feeds. The storage also serves as a distributor to grinding units.

6.1.2 SCREENING

Sizing is a physical separation process in which a mixture of grains, having different sizes is divided into groups of the same size. Passing under-sized particles through the apertures and rejecting the oversized particle is the fundamental function of screening. The particles are brought to the openings for screening. In practice, particles to be sized are crowded. They arrive at the apertures at considerable velocity and in a direction nearly parallel to the screen plane.

6.1.3. GRINDING

The product in the crushing plant is so coarse that chemical treatment of the ore requires much time and acid. The product has to be ground into a powder. Powdering or pulverizing by the use of pressure and abrasion is called "Grinding".

Materials are ground either wet or dry. Physical characteristics, corrosive effect, tendency to pack or stick in the grinding zone, shape, size, range, relative economic efficiency of the operation, climatic conditions, availability of water supply, nuisance and safety factors are the primary factors determining the wet or dry grinding.

Grinding is done mostly by rod mills and ball mills. Ball mills are especially used for wet grinding and work with a combination of a classifier within a closed cycle. Rod mills ensure the finest and uniform grinding and are included in a closed cycle with a rake or spiral classifier. Classifiers remove the finer material and pass it on to the next stage but coarser material is returned. Grinding is classified according to maximum grain size, namely coarse, intermediate and fine grinding.

the uranium ores are usually ground to 0.30-1mm before acid leaching and to 0.15-0.20mm before carbonate leaching(8).

6.1.4 CLASSIFICATION

Classification also called sorting is a process in which a mass of grains having mixed sizes and different specific gravities is allowed to settle through a fluid. The fluid which may be in motion

or at rest could be a fluid such as water or a gas like air. In ore dressing, wet classification is used to separate sands, long range sands containing grains of either different specific gravities or those with same specific gravities into a number of short range grades. In a mill, classification's aim is to utilize one or both of the above product characteristics.

According to flow direction, there are two kinds of classifiers; namely, horizontal-current classifiers and vertical-current classifiers. The latter is also known as hydraulic classifiers.

6.1.5 GRAVITY CONCENTRATION

A method of separating grains of minerals having different specific gravities is gravity concentration. Only the richest pitchblende ores are susceptible to concentration by gravity methods (26). In gravity concentration process, the response of grains of different specific gravities to the gravity and one or more other forces are taken into consideration. The other force is usually the resistance to downward penetration offered by either a gas or liquid or a particulate solid. The fluid properties utilized are viscosity and density while the forces are buoyancy and upward pulse. In other gravity processes the moving fluid impulse is applied to the vertical action line of gravity and the friction between grains. In all gravity processes, a sizing element works in a closed cycle to separate different sized particles. Specific gravities of the minerals, viscosity and plasticity of the separating medium, and mechanical methods available are the important criteria for deciding the kind of separation.

6.1.6 FLOTATION

Flotation method among other physical concentration methods seems to be more applicable and promising for uranium preconcentration. In the ore preparation, flotation is used to separate some minerals within the ore from others by the use of surface tension property. Minerals heavier than water surface due to this property. Surface tension depends on wettability since wettable grains can not float. When air is blown into a pulp, i.e. a mixture of fine ground ore with water, some mineral grains hang on to the air bubbles and rise up while the others do not show the same trend. A mineralized foam happens on the surface. Using some chemical agents, surface tension of minerals could be controlled. Each mineral has a certain

grain size at which it can be floated. Grain sizes of minerals for flotation are required to be smaller than 100-150 microns.

6.2. LEACHING

Physical separation of the uranium mineral from its ores is followed by chemical separation processes. These make the uranium concentration more of a chemical engineering problem.

In general, the first step in chemical concentration is to dissolve uranium out of its ores by chemicals, which is known as "LEACHING" (33). Leaching could be acid leach or alkaline leach according to leaching reagents used. Leaching could also be agitation leach or percolation leach according to the method used for contacting the solid material with leach solution. Leaching is mainly a diffusion process. It is proportional to dissolution rate, reagent concentration, temperature, solid surface area and the rate of diffusion from liquid into solid surface.

6.2.1. ACID LEACHING

Many uranium minerals, especially high silica ores are dissolved out of their ores through acid leaching. The most widely used acid is sulphuric acid H_2SO_4 at atmospheric pressure and room temperature. Sulphuric acid among other acids is cheaper, less corrosive and easily available. It reacts with uranium bearing ore and yields uranyl sulfate (UO_2SO_4) or complex uranyl sulfate anions $[UO_2(SO_4)_3]^{-4}$

Hexavalent uranium, i.e. U(VI) is more readily soluble in acid and alkaline solutions than tetravalent uranium. Admitting this fact, ores with tetravalent uranium need to be treated with an oxidizing agent so as to obtain hexavalent uranium. Oxidants used in acid leaching could be manganese dioxide, sodium chlorate, nitric acid and the agitation air. Iron, on the other hand, is used as a catalyzer. Temperature, acid strength and fine grinding increase the amount of uranium dissolved and the rate of dissolution. If the amount of acid-consuming compounds in the original ore is decreased and the pH of the leaching solution provided is greater than 1.8, the consumption of the leaching acid may be reduced. When ion exchange or solvent extraction is preferred for further processes, leaching acid can be reused. Acid leaching process is carried out in stainless steel or rubber lined vessels. Figure 6.3 shows a typical scheme of acid leaching ores at Canadian plants.

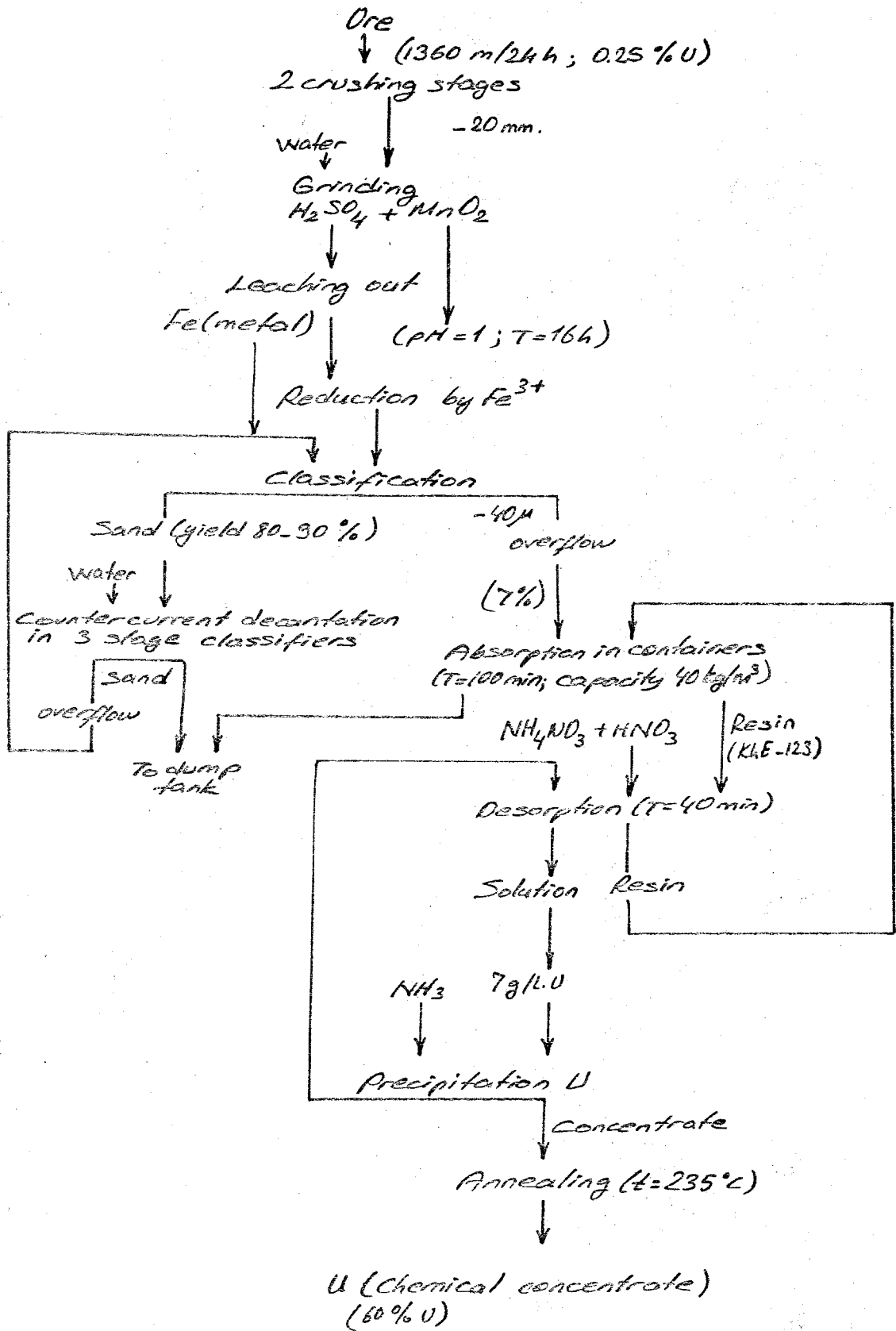


Fig.6.3 Typical flowsheet of acid leaching of uranium with Absorption extraction from solutions (Quirke, Nordic and others, Canada (8).

6.2.2 ALKALINE LEACHING

Acid consuming uranium ores, especially high carbonaceous ores are processed through alkaline leaching (34). The leaching agent is, a mixture of sodium carbonate Na_2CO_3 and sodium bicarbonate NaHCO_3 . These are effective at 70° - 90° under 100 psi pressure. Reaction results in the formation of soluble uranium carbonate anion $\text{UO}_3(\text{CO}_3)_3^{-4}$. KMnO_4 or air in conjunction with copper ammonium ion $\text{Cu}(\text{NH}_3)_4^{2+}$ is used as an oxidant. To prevent the precipitation of uranium as diuranate, bicarbonate is added.

Alkaline leaching has more selective solvent ability for uranium than the acid reagents. But yields with alkaline leach are lower than acid one.

Alkaline leaching process is carried out in mild steel equipment which is cheaper.

6.2.3 AGITATION AND PERCOLATION LEACHING

In the agitation leaching, whole amount of solid materials is suspended in a liquid. Agitation leach is applied on finely ground pulps coming from wetgrinding. It is suitable for continuous processing but liquid-solid separation has to be incorporated.

In the percolation leaching, the lixivants are percolated through a fixed ore bed. The percolation leach is effective for coarser solid feed and delivers a filtered pregnant solution.

It should be noted that agitation and percolation leaches present different features. Comparison of these two methods is shown in table 6.2.

Agitation and percolation leaches are mostly used in combination with each other. That being the case, coarse ground ores respond to percolation leach while finely ground ores to agitation leach. Therefore, this results in no loss of uranium in leach solutions.

Table 6.2 Comparison of Agitation and Percolation Leaches(9)

	Agitation	Percolation
Capital cost	high	low
Grinding cost	high	low
Water consumption	high	low
Reagent consumption	low	high
Pregnant solution grade	low	high
Retention time	short	long

6.3 URANIUM EXTRACTION FROM LEACH SOLUTIONS

Beside non-uranic ions, the leach liquor obtained includes relatively large and small solid particles. The large solid particles have good response to filtration while smaller particles are first treated by a flocculating agent and then filtered (35). To provide the removal of solid residue, conventional rotary filtration or thickening equipment is used.

Three different processes, however, are used for removing the uranium ions from the leach liquor. These are; namely precipitation, ion exchange and solvent extraction.

6.3.1 PRECIPITATION

The direct precipitation of uranium in leach liquors was the earliest method used. Today, however, it is not used very often. The precipitation method is mostly used for alkali carbonate leach liquors rather than acid ones. Acid leach liquors are initially processed by ion exchange or solvent extraction and then reacted with NaOH, NH_3 , or MgO to precipitate diuranate.

Uranium in the alkali carbonate leach liquors precipitates at a certain pH value in the form of phosphates, oxides, arsenates, etc. The pH of the solution in phosphate precipitation, for instance, is between 0.9-0.2 (9). Leach solutions containing uranium at high concentrations could also be treated with hydrogen peroxide so that uranium precipitates as $\text{UO}_4 \cdot 2\text{H}_2\text{O}$.

To obtain a pure precipitate, leach solution must have a slime content as low as possible since impurities tend to precipitate together.

6.3.2 ION EXCHANGE

The process of ion exchange coming into common use is used for the adsorption of uranium from leach solutions by resins. Generally in an ion exchange process, ions attached to the functional groups of the resin are replaced by other ions from the leach solution.

Resins could be either cation exchange resins or anion exchange resins. The anion exchange resins contain $-\text{NH}_2$, $=\text{NH}$ or $\equiv\text{N}$ groups while cationities contain $-\text{OH}$, $-\text{COOH}$, $-\text{SO}_3\text{H}$ groups. The ion exchange (adsorption) capacity, chemical stability and the stability of compounds which are formed by the ions absorbed by the resin are important characteristics of ion exchange resins.

The ion exchange process is extensively used with acid leach liquors. Alkaline leach liquors, however, have little application at present although the use with alkaline leach liquors is perfectly

feasible.

Different types of anion and cation exchange resins are used for uranium absorption from sulphate solutions (SG-1 carboxyl cationite, AN-2F anionite, EDE -10P anionite, etc). The pH value and non-uranic ions have an important effect on the absorption capacity of resin. The presence of phosphates, arsenates, fluorides, and oxalates can lead to a considerable decrease in absorption capacity(8). Copper, divalent iron, aluminum and manganese are absorbed in smaller quantities than uranium. Certain materials within leach liquors such as cobalt-cyanite, molybdenum, titanium, and thiocyanate poison the resin by blockage of the functional groups.

The ion exchange process is performed in two ways. The resin particles either form a static bed through which leach liquor flows or resin in pulp process (RIP) is used. In the RIP process, resin beads are filled into a number of perforated cubes and then these cubes are immersed in a leach liquor tank. During this time cubes are oscillated and resin beads adsorb uranium.

Uranium has to be desorbed from the resin used. To provide uranium desorption, the resin is regenerated by acids such as sulphuric, nitric, or hydrochloric. Then uranium is precipitated by ammonia or alkali.

6.3.3. SOLVENT EXTRACTION

The solvent extraction is an important method applied to leach liquors to separate uranium. The solvent extraction is also used for separating Zr from Hf, Th from rare earths, U, Pu and fission products from spent fuel (36). The working principle of the solvent extraction method lies in the fact that the constituents of a solution are not soluble in the same organic solvent. That is, one or more of the constituents of a solution are soluble in an organic solvent whereas others are not. The organic solvents used are immiscible with water and the solution, to be extracted.(37). In the solvent extraction process, the organic solvent comes into contact with aqueous solution and the constituents of aqueous solution begin to change their phases from aqueous to organic phase. Solvent extraction, therefore is a diffusion and is characterized by distribution coefficient D as

$$D = \frac{\text{Concentration of component in organic phase}}{\text{Concentration of component in aqueous phase}} = \frac{y}{x}$$

Temperature, the nature of the solvent, and the composition of the aqueous and organic phases affect the distribution coefficient.

Observing a single solvent-extraction stage, given in figure 6.4.a, the material balance on the extractable component is written as follows :

$$Fz = Fx + Ey$$

where F & E are flow rates of aqueous feed and organic solvent, respectively.

Using $D = y/x$, y could be written as

$$y = \frac{Dz}{1 + ED/F}$$

Then, fraction extracted, ρ will be

$$\rho = \frac{Ey}{Fz} = \frac{DE/F}{1 + DE/F}$$

From this equality, the ratio of solvent (E) to feed (F) required is found to be

$$\frac{E}{F} = \frac{\rho}{D(1-\rho)}$$

One can see that, an infinite amount of solvent (E) is needed for complete extraction of the desired component. Infinite amount of solvent has no meaning in practice. Complete extraction with a finite amount of solvent could be expected by the use of multistage counter current cascade (Fig. 6.4.b). In the multistage extraction Extract (Organic) plays the role of Solvent (Organic) and Residue (Aqueous) plays the role of Feed (Aqueous) for the next-coming stages. The whole system is mentioned under the name of Extraction section. Since the organic and aqueous phases flow in the opposite directions, the term counter current is used.

The solvent finally obtained from the extracting section contains both the organic solvent and the desired component. The component is re-extracted from organic phase into aqueous phase in order to leave the organic solvent alone for, re-use. This process is carried out in another section called "Stripping Section". Figure. 6.5 illustrates such solvent extraction flow sheet with re-cycle of solvent. During the extraction of desired component, some undesired species also succeed in passing to organic phase. In order to get rid of the undesired components, a new section which will be called "Scrubbing Section" is required. In case of uranium, undesired components are neutron-absorbing impurities. Scrubbing section

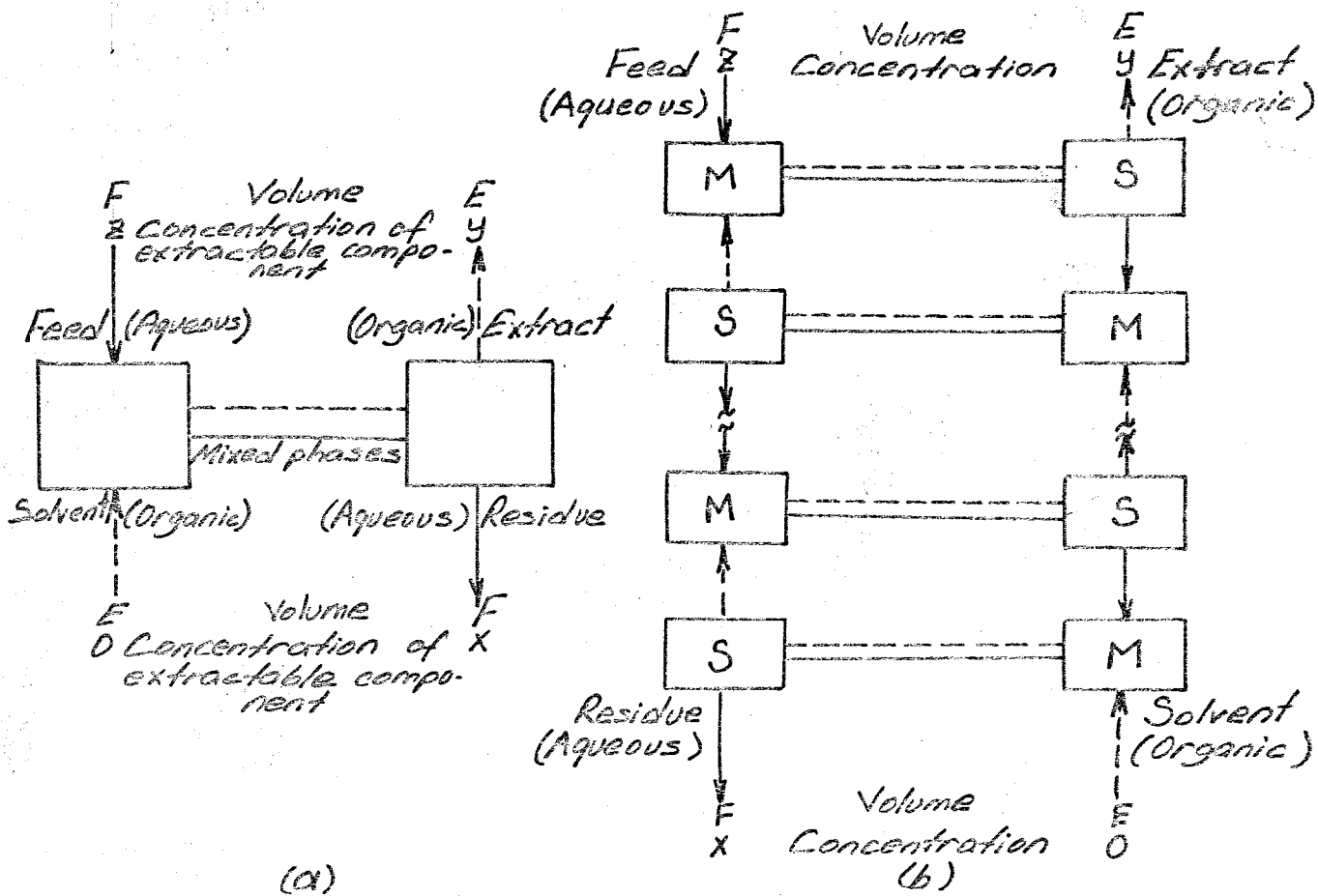


Fig.6.4-a) Single solvent extraction stage , b) Multistage counter current solvent extraction M,mixer; S, settler.(26).

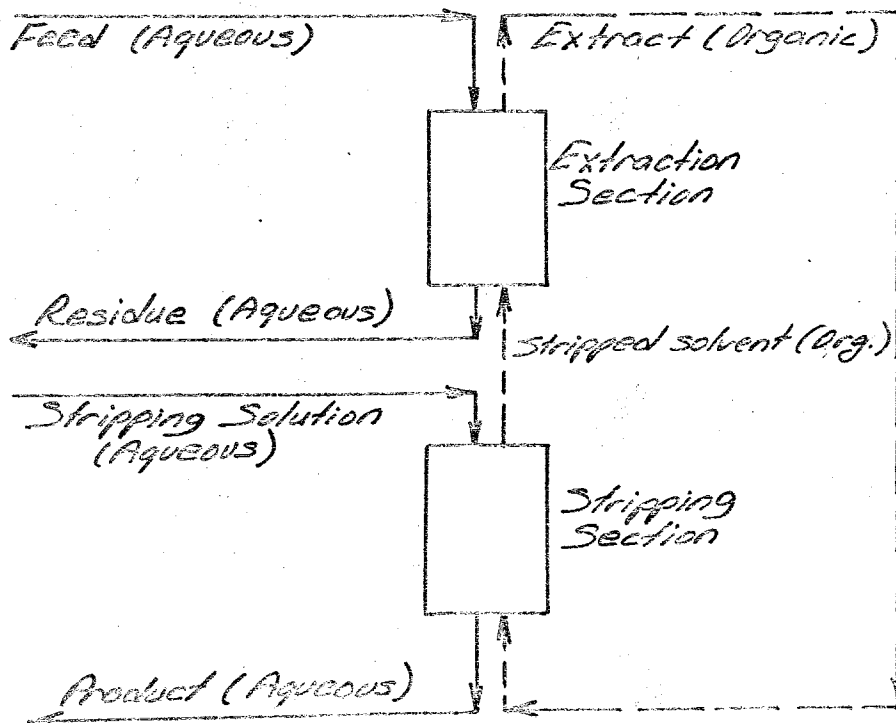


Fig.6.5. Solvent-extraction flow sheet with recycle of solvent (26).

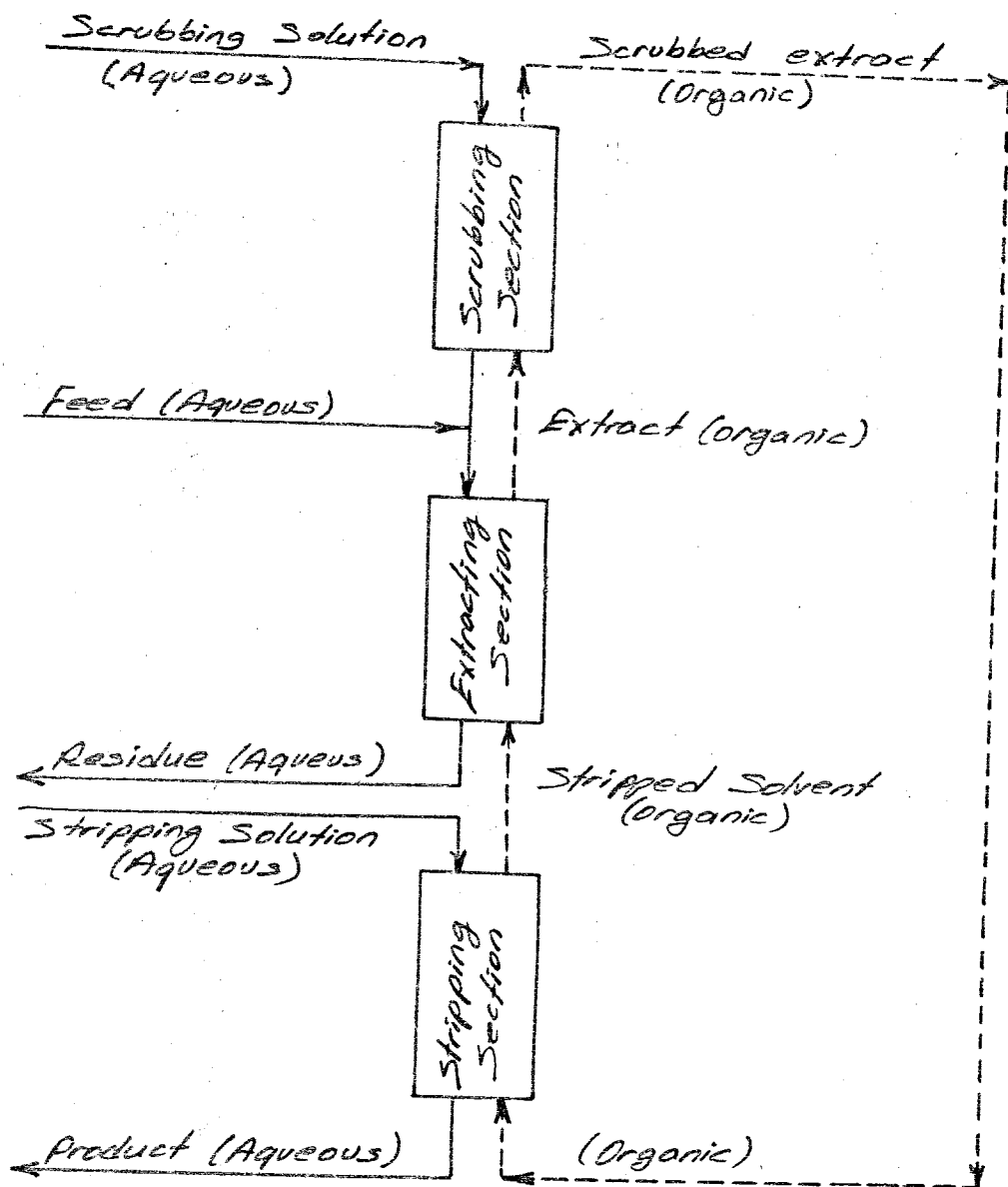


Fig.6.6 Flowsheet for fractional extraction of two extractable components (26).

enables the separation of more than one extractable component depending upon the existence of different distribution coefficients ($D_i/D_j \neq 1$) of the constituents. This kind of operation, however, is called Fractional Extraction. A flow sheet containing a scrubbing section is given in figure 6.6 where each section is made up of many stages such as those shown in figure (6.4.a)

According to the organic solvent used, solvent extraction processes take different names such as AMEX, DAPEX, ELUEX and Mixed Solvent Process. In the AMEX process, an amin is used as organic solvent, which has a uranium extraction capacity of 3-5 gr U_3O_8 /lt. 4% EHPA (di-2 ethyl-hegzil phosphoric acid), 4% TBP (Tri-butylphosphate) and 92% kerosene solution is used in the DAPEX process. However, the organic phase of mixed solvent process is composed

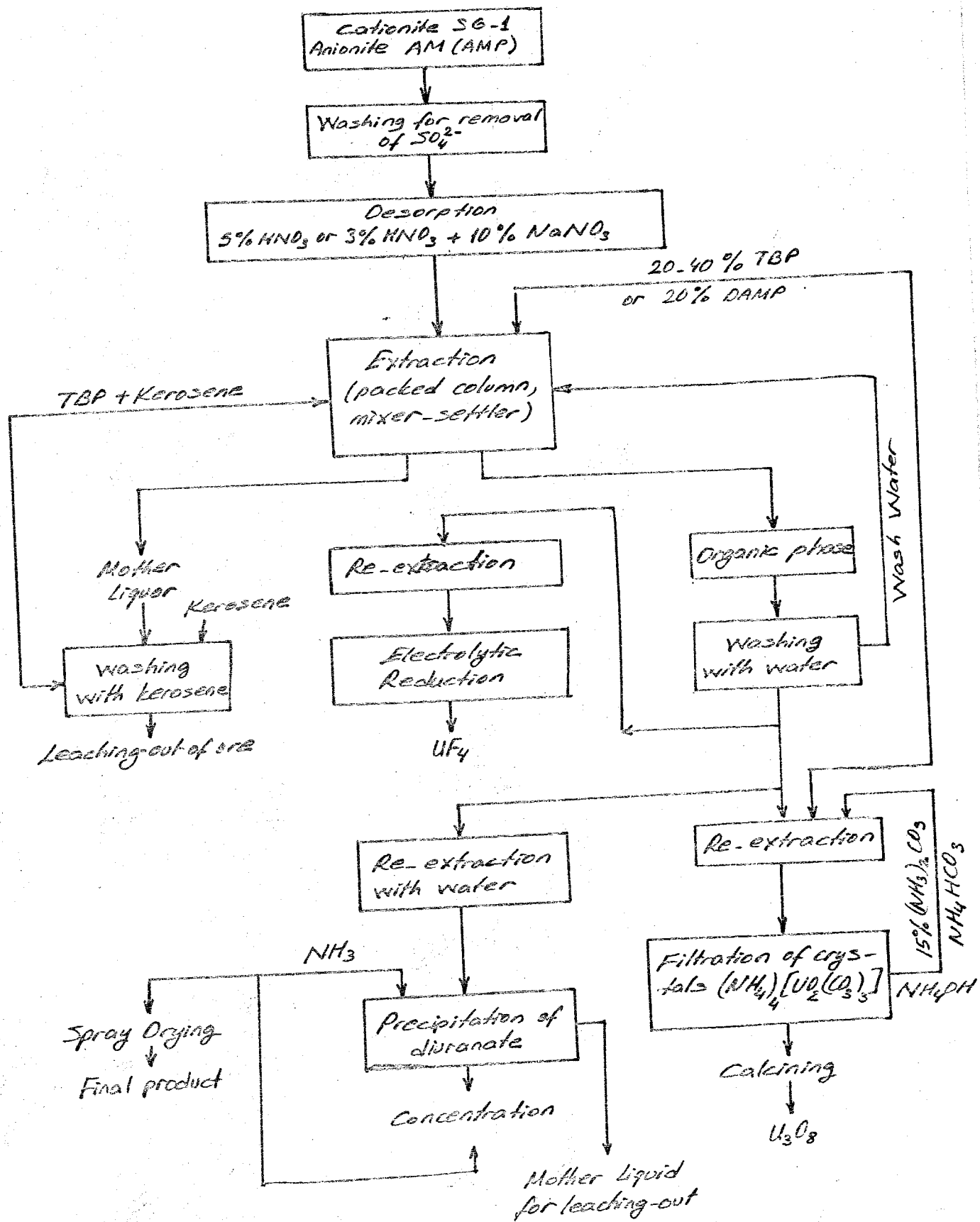


Fig.6.7. Flowsheet of extraction purification of Nitric Acid desorption solutions (8).

of 3.5-4.5% tri-alkylamin, 0.25-1.7% EHPA and 0.75-1.4% HDPA (Heptadecyl phosphoric acid). ELUEX process has a different procedure since AMEX or DAPEX process is applied to uranium solutions obtained from the use of anion exchange resin. PUREX is another extraction process applied for the separation of Pu, U and fission products, where TBP in kerosene is used as an extractant.

The extraction of an inorganic compound is affected by the presence of salting agents, oxidizing or reducing agents and complex-forming anions.

The solvent extraction applied as continuous-multistage operation yields some advantages over the ion exchange. Solvent extraction is applicable to large amounts, has great U extractability and requires less capital (38).

A flowsheet being an example for extraction purification of nitric acid desorption solutions is shown in figure 6.7, where TBP in kerosene is used as extractant and process is carried out in packed columns and in mixer-settlers (see fig. 6.8).

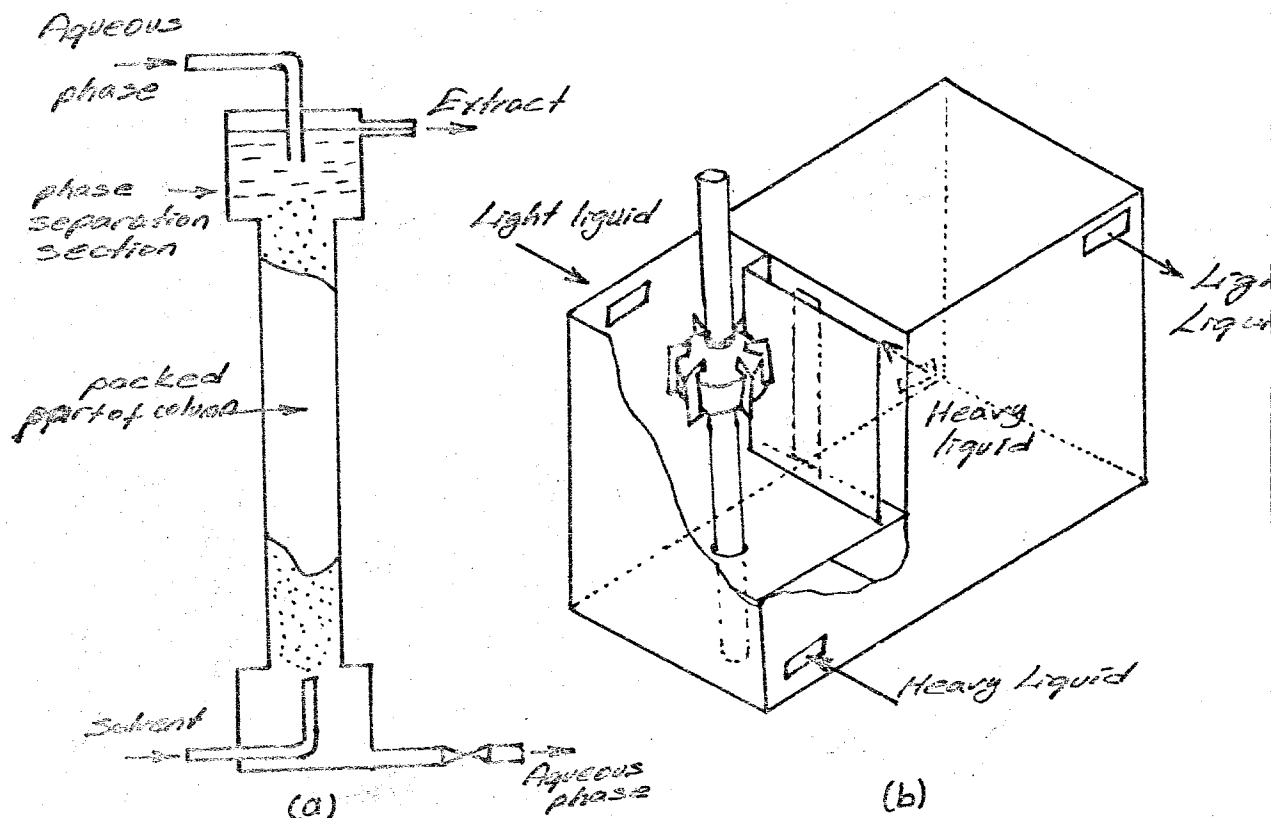


Fig.6.8-a) Packed extraction column,
 b) Pump-Mix Mixer-Settler .(8,26).

Chapter 7

7. PURIFICATION

Neutron economy is of outmost importance for the nuclear reaction maintenance in a reactor. Neutron absorbing admixtures must necessarily be reduced for the successful course of a fission, chain reaction. The content of individual elements with a high neutron capture cross-section in the uranium must not exceed the order of 10^{-5} or 10^{-6} % (8). The permissible content of admixtures can be found in the data provided by the International Atomic Energy Agency (I.A.E.A for short) at Vienna. The data is summarized in table 7.1. The most harmful impurities are ones having high absorption cross sections, and their tolerable amounts are given in table 7.2. The overall hazard coefficient for uranium which is also determined by I.A.E.A, must not exceed 0.25%.

Table 7.1 Permissible Content of Admixtures
in Uranium According to Data of I.A.E.A,
(8).

ADMIXTURE	Content	
	parts per million(max)	Wt%
Aluminum	20	0.002 ₅
Boron	0.2	2×10^{-5}
Cadmium	0.2	2×10^{-5}
Carbon	600	0.06
Chromium	25	0.0025
Cobalt	25	0.0025
Iron	150	0.015
Nickel	80	0.008
Nitrogen	100	0.010
Silicon dioxide	30	0.003
Silicon	40	0.004

Table 7.2 Amount of Impurities in Natural Uranium at Which Neutron Absorption is 0.1% of Neutron Absorption by U^{235} (26)

ELEMENT	Absorption cross section (2200 m/sec) (barns)	Atoms per million Atoms
Rare earths:		
Samarium	6,500	0.8
Europium	4,500	1.1
Gadolinium	44,000	0.1
Dysprosium	1,100	4.5

Considering the atomic energy standards, the uranium concentrate obtained through physical and chemical concentrations mentioned in the previous chapter is not pure enough. Typical composition of chemical concentrates of uranium ores produced at different concentration plants are found in Table 7.3. It is conceivable that further purification has to be adapted to these relatively impure chemical concentrates even though the process causes great difficulties in production technology (37). Consequently, purification process starts with uranium mixed oxide or salts of the uranate type so as to get the high quality uranium metal.

Purification methods are divided into two main groups. The first group includes precipitation methods whereas second group includes extraction methods. The purification process applied in a plant can be composed of one or both of these methods. Absorption methods are not frequently used in the purification stage.

7.1. PRECIPITATION METHODS

Precipitation methods were the most favourable methods used in nuclear industry and still is important since it is simple and does not necessitate expensive reagents. Precipitation methods include crystallisation, carbonate, oxalate and other purification methods (37)

The working principle of crystallization method is based on the fact that uranyl nitrate has different solubilities in water at different temperatures (see fig.7.1). In this method, first of all,

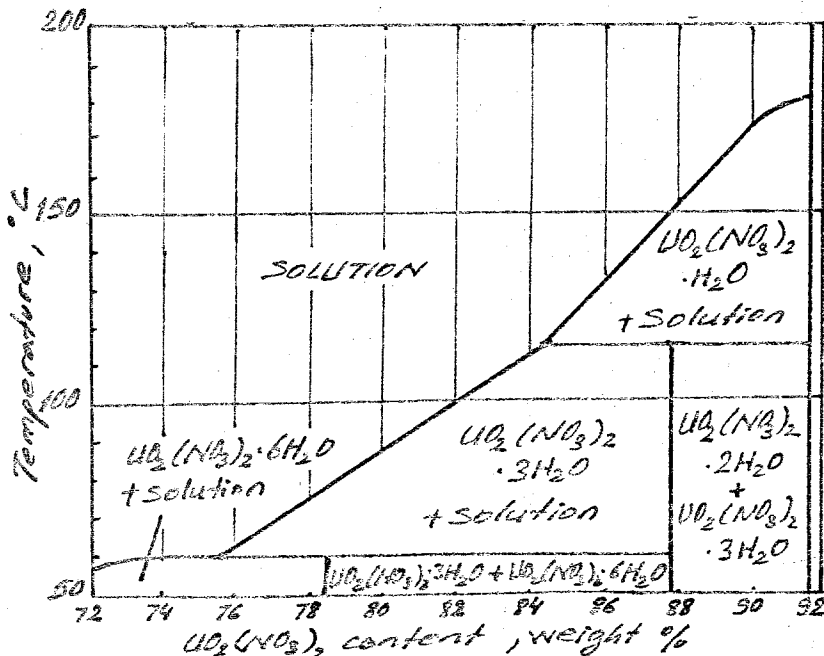


Fig.7.1. $UO_2(NO_3)_2-H_2O$ Phase Diagram (26)

Table 1.3. Typical Compositions of Chemical Concentrates of Uranium Ores (8).

Location of Plant	Component wt %											
	U.S.A			Canada		Africa		Australia				
	New Mexico	Arizona	Colorado	Blind River	Bancroft	Congo	Rep. of S. Afr.	Radium Hill				
Technology	Carbonate Leaching	Acid Leaching	Acid Leaching	Acid Leaching	Acid Leaching	Acid Leaching	Acid Leaching	Acid Leaching				
Compo. Prepn. methods	Alkali precipit.	Extraction	Ion Exchange	Ion Exchange	Ion Exchange	Ion Exchange	Ion Exchange	Ion Exchange				Ion Exchange
U ₃ O ₈	75-78	70-75	65-79	70-80	60-65	48-73	75-85	55-70				
H ₂ O	1-7	0.01-0.1	2-10	<1	<1	0.01-0.5	—	0.2-0.5				
As	traces	0.01-0.1	traces	<0.01	<0.01	<0.02	<0.01	0.02-0.2				
B	<0.005	<0.005	<0.005	0.003-0.004	0.003-0.005	0.008-0.06	0.0002	0.0004-0.004				
Cu	traces-0.25	0.1	<0.03	<0.01	<0.01	0.4-2.0	<0.4	0.01-1.0				
F ⁻	0.03	0.01-0.04	0.03	—	—	—	—	—				
Other halogens	0.03-0.14	0.01-0.4	0.08	0.04-0.22	0.01-0.04	0.02-0.03	0.03	0.05-0.15				
Fe	0.1-0.8	9-13	1-5	0.15-0.45	—	0.4-4.0	7.0	>4				
MoO ₃	0.02-0.06	0.05-1.0	0.02-0.5	0.03-0.04	0.001-0.01	0.2-0.6	0.01	0.01-0.08				
P ₂ O ₅	0.05-0.2	0.2-3.0	1-5.5	0.1-0.13	0.2-0.6	0.25-0.6	0.06	0.1-1.0				
Na	4.5-9.0	0.1-0.5	0.2-4.5	3-4	1-2	0.07-2.0	0.04-0.2	2				
SO ₄ ²⁻	0.2-2.0	1.3-1.0	3.17	0.5-1.5	0.3-0.5	1-37	1-5	0.5-2.5				
U ₂ O ₅	0.05-0.4	0.05-0.3	0.36	<0.002	<0.002	0.002-0.004	0.002	<0.002				
Rare earths	—	—	—	0.0015-0.08	0.005-0.0075	—	—	—				
ThO ₂	—	—	—	0.01-0.85	0.5-0.6	—	—	—				

uranium ore concentrates are dissolved in nitric acid. The insoluble residue is filtered from the uranyl nitrate solution before the solution is evaporated up to saturation. There are soluble residues dissolving like uranium and they too evaporate. After evaporation, cooling is adopted. Using the fact mentioned above, uranium nitrate crystals precipitate and are taken off by filtration. Hence impurities separate out.

Crystallization process made up of dissolving, evaporating and cooling is repeated up to the stage of the pure salt. Fine crystals obtained by rapid cooling are preferred. Since uranyl nitrate can form compounds with alkali metal nitrates and ammonia, the presence of alkali metals in the initial concentrate is not desired. In case of the action of alkali metal and ammonium carbonates on uranyl groups, the method of carbonate purification comes into play.

Carbonate purification method is one of the most important purification methods. In this method, initially the uranium ore concentrate is treated with sulphuric or hydrochloric acid and heated. Then a hot solution of sodium or ammonium carbonate is added. Uranium passes into the solution while the majority of admixtures remain in the mother liquid. Small amounts of iron, aluminum, manganese, yttrium, scandium, boron, phosphorus, vanadium and arsenic admixtures and their compounds also pass into the solution. Therefore, uranium needs to be separated from the solution by precipitation again. Either by salting-out under the action of an alkali metal or ammonia carbonates or by boiling the solution, uranium is precipitated. Figure 7.2 shows the most typical scheme used at Port Hope in Canada.

In order to obtain uranium dioxide and uranium tetrafluoride, uranium concentrates in the form of mixed oxide are subjected to some processes. Oxalate purification permits the mixed oxide. The oxalate purification method has two types. In the first, uranium is obtained as U(IV) oxalate precipitate while in the second type $UO_2C_2O_4 \cdot 3H_2O$ (uranium oxalate) is precipitated. In uranium (IV) oxalate method the concentrate is dissolved in hydrochloric acid in a rubber-lined reactor with continuous mixing. For 100kg concentrate, 300l of acid solution composed of water and 37% hydrochloric acid is used. The solution is filtered. Then the hexavalent uranium is reduced to the tetravalent stage by hydrosulphite and filtered. The oxalic acid with the excess of 10% is added at 80-90°C after a primer of $U(C_2O_4)_2$ is added to obtain a coarsely crystalline precipitate. After the

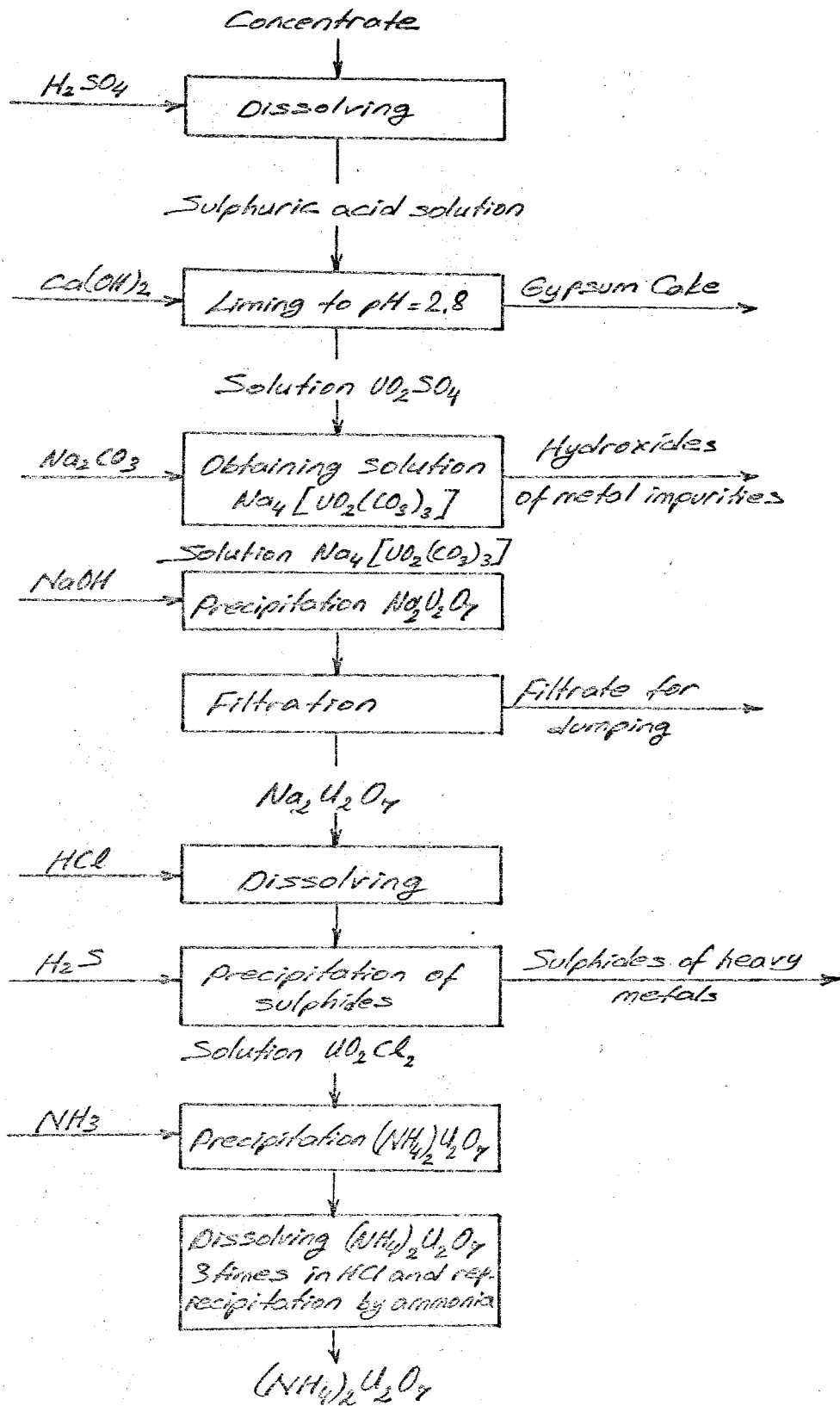


Fig.7.2. Flowsheet of carbonate purification at Port Hope, CANADA (8).

precipitate is filtered and washed, it is treated with a saturated ammonium oxalate solution. Uranium forms a complex compound $(\text{NH}_4)_4 \cdot [\text{U}(\text{C}_2\text{O}_4)_4]$ by passing into the solution. Impurities remaining in the mother liquor are filtered-off. When hydrochloric acid is added to the solution, ammonium urano-oxalate compound forms uranium (IV) oxalate which will be calcined to the oxides. By the use of uranium (IV) oxalate method iron, manganese, vanadium, chromium, phosphorus, silicon, nickel, boron, the alkali-earth metals and alkali metals are separated. High reagent consumption, the difficulty of treating concentrates with a high content of phosphorus, nitrate and arsenic salts and the requirement of rubber-lined apparatus constitute the main disadvantages. In one type of oxalate method, the above disadvantages are eliminated. In this type, the concentrates are calcined at $700-800^\circ\text{C}$ and dissolved in nitric acid. Uranium passes into the solution and forms $\text{UO}_2(\text{NO}_3)_2$. Then, crushed oxalic acid is added to the uranyl nitrate solution with continuous mixing at room temperature. It can be added that oxalic acid consumption is reduced by a factor of two.

Similar to the second version oxalate method, uranium can be precipitated from nitrate solutions by hydrogen peroxide. In the industry, the peroxide method is usually applied in connection with other methods since the starting concentrate must be fairly pure. In France and Belgium, for instance, peroxide method is applied after the extraction method used for uranyl nitrate purification. An important property of the peroxide method of purification is being a rapid process carried out in the cold.

7.2. EXTRACTION METHODS

The working principle of the extraction method used for purifying uranium is the same as it is mentioned in the previous chapter. Extraction methods of purifying uranium expresses some advantages over precipitation and absorption methods (35). Since most of admixtures precipitate together with the uranium, extraction purification results in the purer concentrate than that of precipitation. On the other hand precipitation is long, and complicated process whereas extraction can be carried out automatically. It can also be noted that the extractants are cheaper than resins in absorption methods.

The extraction methods of purifying uranium depend upon the fact that uranyl nitrate is extracted in a pure state from aqueous solutions by diethylether, methyl isobutyl ketone, and tributyl

phosphate (TBP for short). So, for this reason, uranium concentrates are treated with nitric acid to get uranyl nitrate solution.

In the United States and recently in French process TBP is used as extractor. TBP is a typical complex ether insoluble in water and a colourless, viscous chemically stable fluid. At room temperature, it is non-volatile and non-combustible. Since the density of TBP is very close to the density of water, it is diluted mostly with kerosene which is a complex petroleum distillate.

As it can be followed from the flow sheet given in figure 7.3, when impure uranium concentrate is dissolved in nitric acid, uranyl nitrate is obtained. Uranyl nitrate is sent to the uranium extraction column and mixed with a solution of TBP in kerosene. Then, TBP complex $UO_2(NO_3)_2$ in kerosene is obtained, which is back-extracted with water in the stripping section. In order to remove the traces of admixtures, kerosene solution is washed with dilute nitric acid in scrubbing section before it is sent to the stripping section. Finally the purified uranium is calcined to UO_3 . Stainless-steel pulse columns are used in this process.

In the British process, however, uranyl nitrate is obtained from the dissolution of uranium peroxide in nitric acid after uranium is precipitated as UO_4 by hydrogen peroxide (39). The extracted is diethyl ether. The purified uranium is precipitated as ammonium diuranate by ammonium hydroxide.

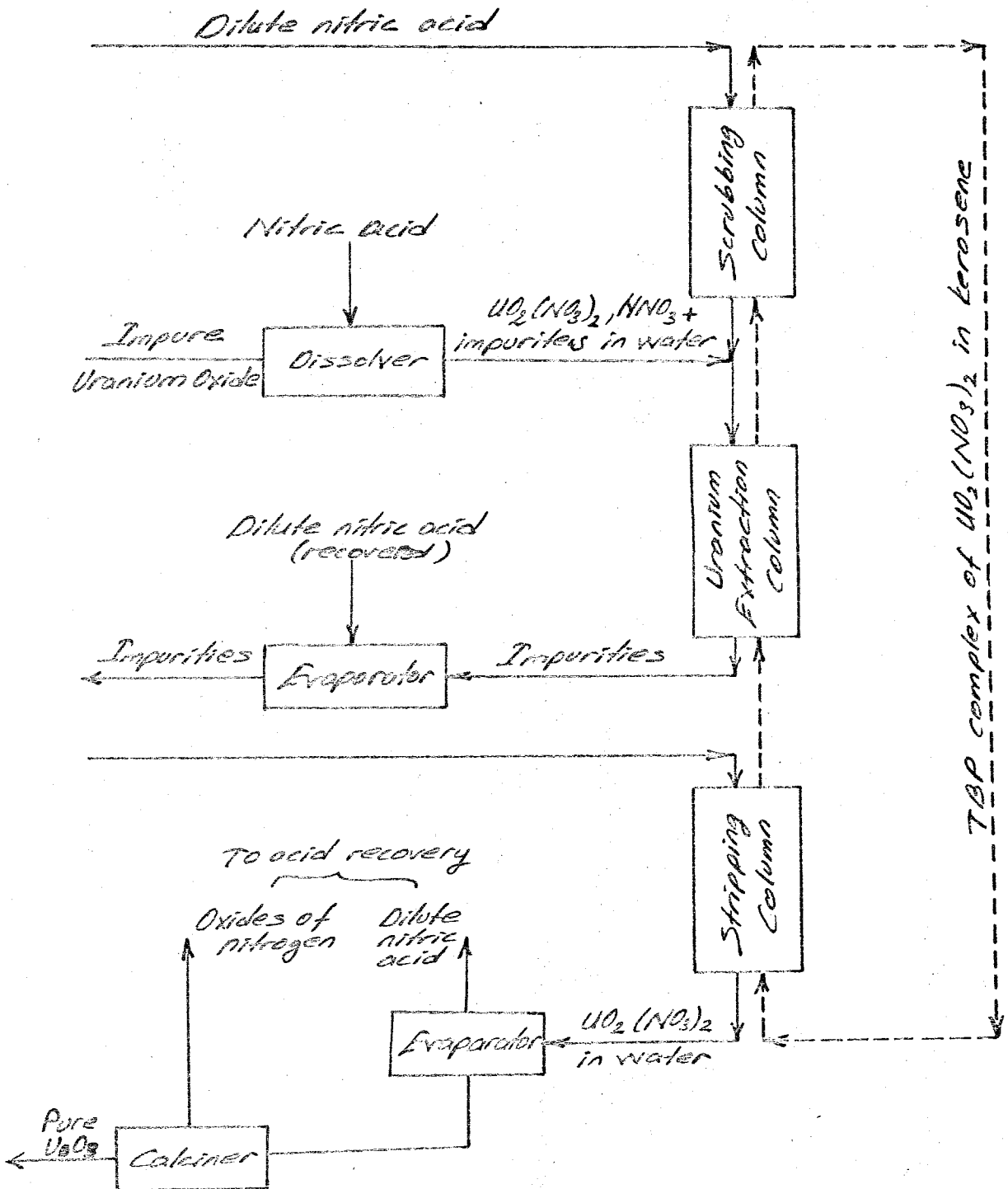


Fig. 7.3. Purification of uranium by solvent extraction with TBP. Solid line, aqueous; broken line, organic (26)

8. CONVERSION AND ENRICHMENT

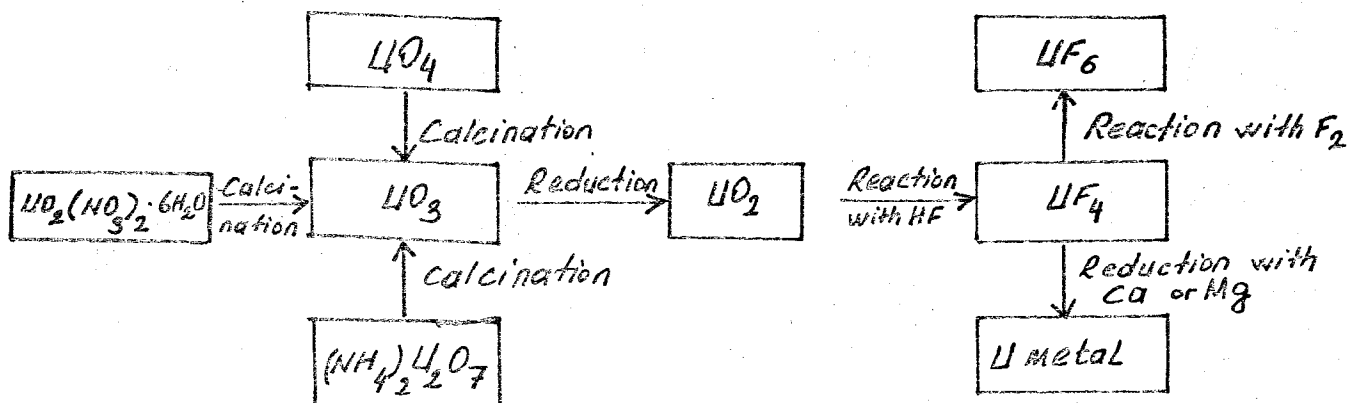


Fig.8.1. Uranium conversion operation (26).

Uranium peroxide UO_4 , uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$, ammonium diuranate $(NH_4)_2U_2O_7$ and uranium trioxide UO_3 are the final products obtained as a result of different purification methods mentioned in the previous chapter. In order to get enriched UO_2 , the principle intermediate products; namely, uranium dioxide UO_2 , tetrafluoride UF_4 and hexafluoride UF_6 are necessarily be obtained. Conversion steps are shown in figure 8.1, where UO_3 is known as "Orange Oxide", UO_2 as "Brown Oxide" and UF_4 "Green Salt".

8.1. CONVERSION METHODS TO UO_2 , UF_4 AND UF_6 8.1.1. CONVERSION TO UO_2

Uranium dioxide is produced by reduction of the UO_3 obtained by calcining either uranium peroxide or ammonium diuranate or uranyl nitrate. The widespread production of UO_2 is from uranyl nitrate solution.

Under industrial conditions uranium content in the uranyl nitrate solution varies from 90 to 280 g/l. Uranium dioxide is produced through the following stages.

The uranyl nitrate solution is evaporated at $120-140^\circ C$. The process is carried out in stainless-steel vertical tubular condensers or in steam-heated boilers. Thermal decomposition of the solution fits the phase diagram of $UO_2(NO_3)_2-H_2O$ given in figure. 7.1.

Denitration is carried out in batch and continuous units which are stainless-steel boilers including mixers and stainless-steel

tube heated by electricity(33). The uranyl nitrate solution is fed into the continuous process apparatus (see fig.8.2).With a jet at the side under pressure,the solution is atomised in the centre of the apparatus.There is a porous diaphragm placed at the base through which hot air is supplied under pressure.Then the atomised drops are converted to UO_3 particles. UO_3 particles fall to the bottom and get discharged.

The following step is the reduction of UO_3 to UO_2 by hydrogen. This process is carried out in batch or continuous units.For the batch reduction,mostly a horizontal stainless-steel tube is used. For the continuous UO_3 reduction,either moving layer reactor or fluidised bed reactor or reactor with material transport by vibration is used.In all zones of the reactor the optimum UO_3 reduction temperature is $650^{\circ}C$.The fluidised bed reactor consists of two vertical stainless-steel tubes having heating and cooling systems. In the first tube,a partial reduction occurs and the product passes into the second tube for the completion of reduction.The uranium content of UO_2 is 87.9% .

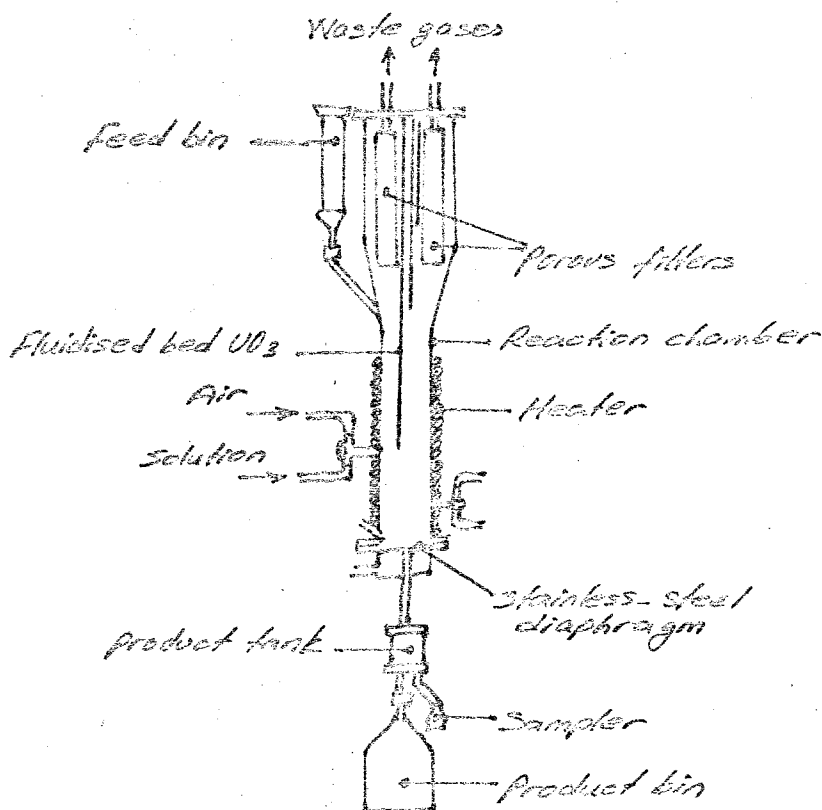


Fig.8.2. Apparatus for denitration according to fluidised bed method (8).

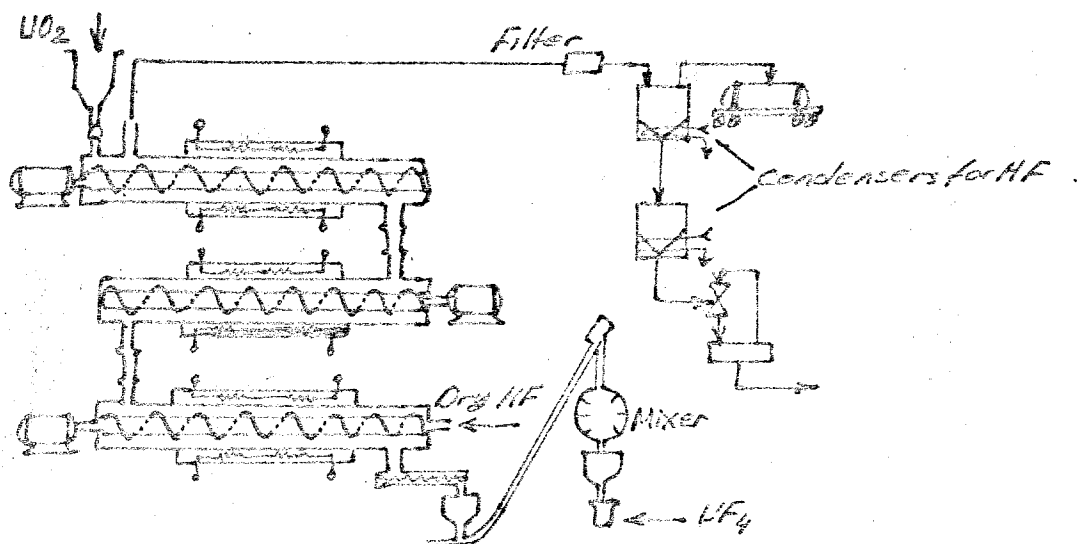


Fig.8.3. Diagram of Hydrofluorination Unit (8).

Uranium tetrafluoride, which is a green crystalline substance, is produced from UO_2 by the use of different methods carried out in the "Dryway" plant. (34). Hydrofluorination, vibration and fluidised bed methods are the basic industrial methods.

Hydrofluorination is the fluorination of uranium dioxide by gaseous hydrogen fluoride. The continuous process apparatus for the hydrofluorination of UO_2 , is shown in fig.8.3. As can be seen from the diagram, the reactor consists of three horizontal tubes placed one under the other and heated by electrical resistance furnaces. The UO_2 enters the reactor in a horizontal worm feeder and passes from tube by means of helical worms. Since the waste gasses, contain UO_2 particles, carbon filters are used.

The vibration method is also a continuous process carried out in the fluorination unit made up of two horizontal tubes. HF from the top of the evaporator is pumped into the unit through a rotameter which automatically controls the delivery.

Three-stage apparatus for fluorination of UO_2 by the fluidised bed method is given in figure 8.4. This apparatus consists of three stages. Each stage is separated by porous diaphragms. UO_2 powder is fed from the top while HF is fed upward from the bottom. As UO_2 powder passes to the lower stages, it reacts gradually with HF .

In different countries, different types of fluorination methods are applied. In the U.S.A, hydrofluorination is used at the Weldon Spring, vibration method and fluidised bed fluorination in the

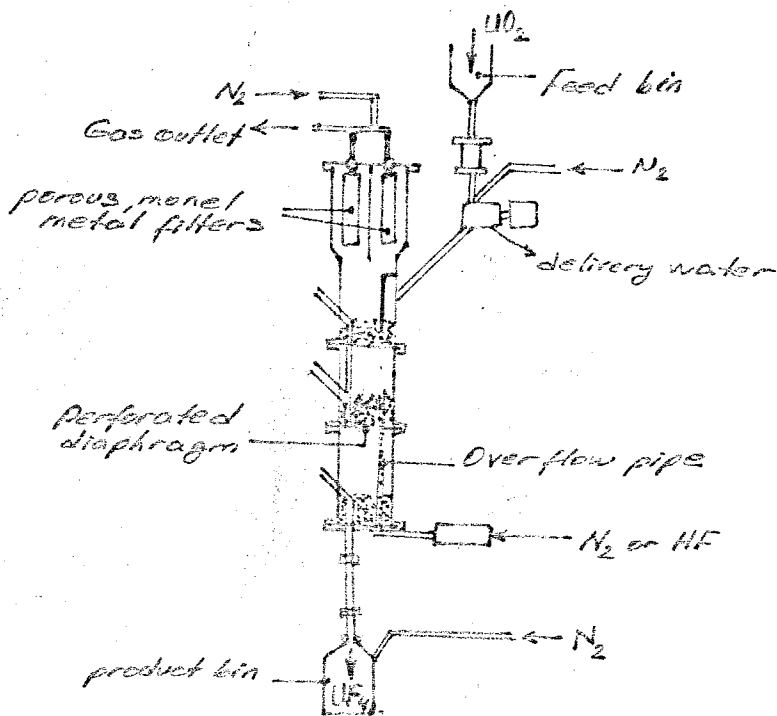


Fig.8.4. Three-stage apparatus according to fluidised bed method (8).

gaseous diffusion plant at Oak Ridge. At the Dryway plant of the United Kingdom Atomic Energy Authority, UF_4 is obtained batch wise from ammonium diuranate. At the new works at Spiring fields this is accomplished by the fluidised bed method.

At the Bouchet Works of the French Atomic Energy Commission, UF_4 is obtained batchwise from UO_4 .

The production of UF_4 by the Belgian process can be followed from the figure 8.5. There, ammonium bifluoride NH_4HF_2 is used instead of HF.

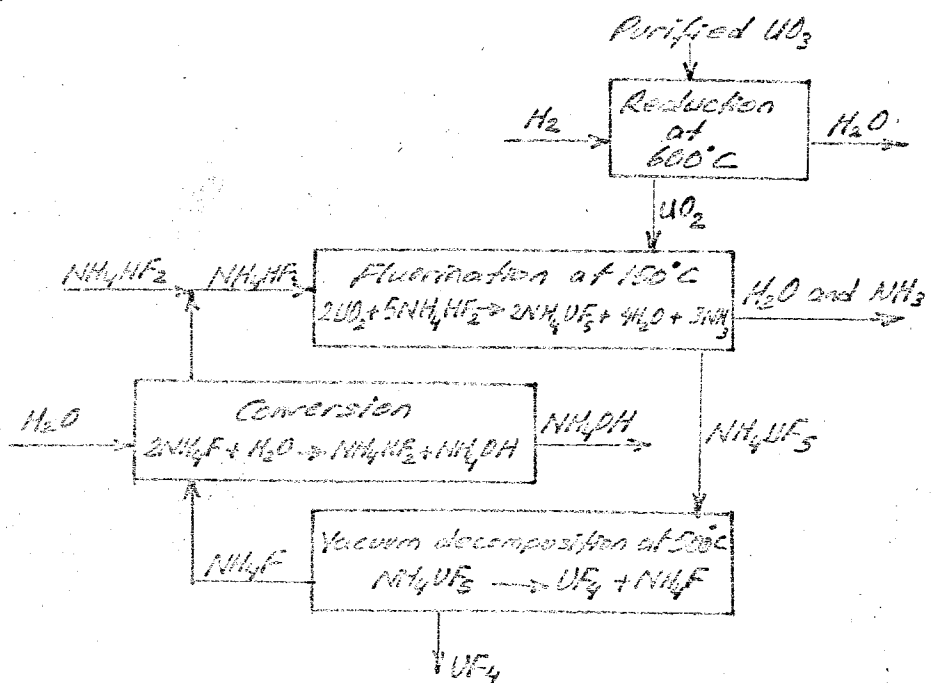


Fig.8.5 Production of UF_4 by the Belgian process (26)

8.1.3. CONVERSION TO UF₆

The importance of uranium hexafluoride UF₆ comes from the fact that it is the only volatile uranium compound at ordinary temperatures. The most important properties of UF₆ are summarized in Table 8.1. Uranium hexafluoride was discovered by Ruff and Heinzelman in 1909(26).

Today UF₆ is produced by the fluorination of UF₄ in a continuous process through the following stages: i. UO₃ in fluidised bed units is reduced to UO₂ by hydrogen; ii. UO₂ is fluorinated to UF₄ by dry HF with warm mixing in reactors and iii. UF₄ is fluorinated to UF₆. Fluorination is carried out in the apparatus which is a monel metal cylinder.(see fig.8.6.).

Table 8.1 Physical and Thermodynamic Properties of UF₆ (8).

Triple point	64.052 °C at 1134 mm Hg
Point of sublimation	56.4 °C at 760 mm Hg
Density:solid	5.06 g/cm ³ at 20.7 °C
Liquid	3.674 g/cm ³ at 65.1 °C
Heat of sublimation	11.495 Kcal/mol at 64.01 °C
Heat of fusion	4.588 Kcal/mol at 64.01 °C
Heat of vaporisation	6.907 Kcal/mol at 64.01 °C
Heat of formation	516 Kcal/mol for UF ₆ (solid)
Heat of solution in water	390,900 cal/g/deg at 25 °C
Critical pressure	45.5 atm.
Critical temperature	230 °C

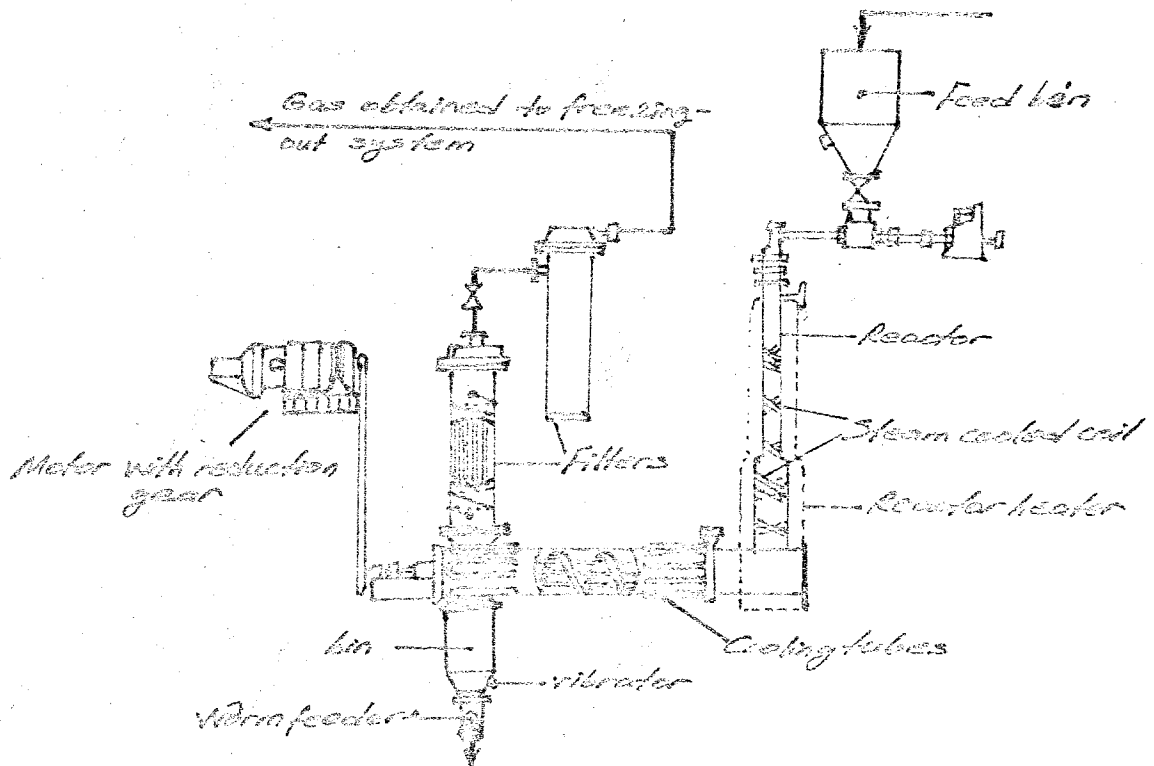


Fig.8.6 Fluorine extraction system(gaseous diff.plant,Oak Ridge, Tennessee,U.S.A) (8).

Spiral water cooler is placed around the cylinder. Using four jets, fluorine is fed into the reactor containing solid UF_4 particles. The fluorination product contains about 75 % UF_6 . This is passed through water-cooled tubes. To collect the solid particles, the product is also passed through cyclones and fed into a cooling trap and a condenser. Here the UF_6 changes its state from gaseous into solid. After the accumulation of a sufficient amount of solid product it is remelted and taken into a container.

This method is used in the "Dupont Carbide Corporation", "Paduke", and "Union Carbide Nuclear Co" plants. (8)

Since technically, the compression of UF_6 up to high pressures is very difficult, the extraction of UF_6 from the system needs to be performed by another method. In the absorption method, first of all, gaseous UF_6 is absorbed by an inert diluent (e.g. C_8F_{16}) and secondly UF_6 is separated by fractional distillation. By obtaining UF_6 , pure product is attained since volatile admixtures are eliminated during UF_4 conversion and non-volatiles during UF_6 . (33)

8.2 ENRICHMENT

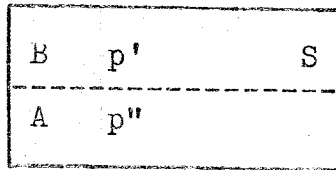
The natural uranium concentration in the earth's crust is about 0.003 percent, and only about 0.7 percent of that is made up of U^{235} , that isotope of uranium which is fissionable by thermal neutrons. The reactors utilizing the heavy water or graphite as moderator can use natural uranium as fuel. However the fuel charged to light water moderator reactors which are the most common type of nuclear reactors operating in the world today have to contain more than 0.7 % U^{235} usually in the range of 2-4 %. The fuel thus containing more U^{235} than natural uranium is called "Enriched Fuel". Since in the milling, purification and conversion processes the isotopic ratio of U^{235} to U^{238} does not change, isotope separation is necessarily done so as to enrich the fuel in U^{235} .

Gaseous diffusion and the gas centrifuge methods are the most widely used methods for U^{235} - U^{238} separation.

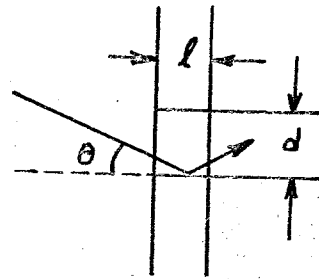
8.2.1 GASEOUS DIFFUSION

The gaseous-diffusion method depends upon the fact that under the same temperature and thermodynamic conditions; different kinds of molecules have different mean velocities. More explicitly, light molecules of a gas mixture travel faster than heavy ones. When the gas mixture meets a wall having minute holes, the lighter mole-

cules flow through the walls more willingly than heavier molecules. This phenomenon is known as "effusion". If the binary gas mixture is confined in a chamber as shown in figure 8.7 and there is a porous barrier placed at the middle, the gas in A flows through the



(a)



(b)

Fig. 8.7 a. Diffusion Chamber shown schematically
b. Diagram of the passage of a molecule through a pore in a very thin barrier (40).

passages due to molecular effusion. The gas pressure is held at a level p'' in A and p' in B. For the diffusion process p'' is required to be markedly higher than p' . The order of magnitude of p'' is chosen such that molecular mean free path λ is long in accordance with the pore mean diameter d (see Table 8.2). As a result of molecular effusion B becomes richer in the light component whereas the gas staying in A is depleted in it. It is conceivable that separation attained in a single stage is not adequate.

Table 8.2 Mean Free Paths (60°F , 1 atm) (26).

GAS	viscosity, centipoise	Mean free path	
		Inches $\times 10^6$	microns
Hydrogen	0.0087	4.7	0.12
Helium	0.0193	7.4	0.19
Methane	0.0108	2.0	0.05
Nitrogen	0.0173	2.5	0.06
Carbon dioxide	0.0144	1.7	0.04
Uranium hexafluoride	0.0200	0.8	0.02

A number of stages, therefore, need to be used. All stages observed in figure 8.7 is arranged in a counter-current cascade as shown in figure 8.8a.b. In each stage, enriched gas is taken to the bottom of the next stage while the depleted one is pumped to the top of the previous stage. At the top end of the cascade, the enriched product is obtained. In separation processes the elementary separation factor q_0 is mentioned. (14). For gaseous diffusion;

$$q_0 \approx \left(\frac{M_2}{M_1} \right)^{1/2} \quad \text{or} \quad q_0 = \frac{M_2 - M_1}{M_2 + M_1} \quad \text{where } M_{1,2} \text{ molecular weights of light and heavy component.}$$

A hundred years ago, the isotope separation using molecular effusion was discovered by Graham (26). The fact that separation factor being proportional to the square roots of the molecular weights of different gas molecules was shown by Maxwell (26).

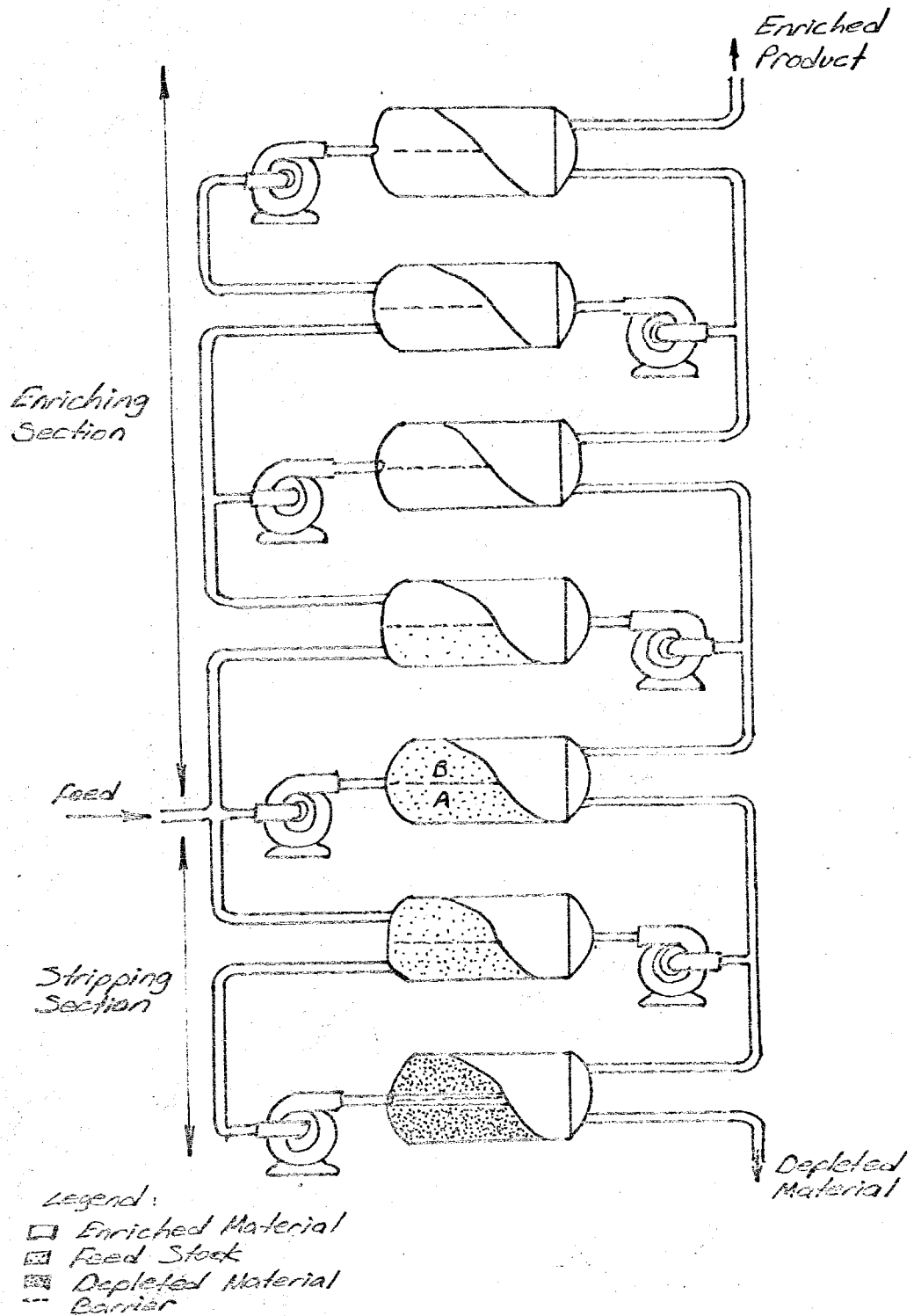


Figure 8.8.a. Schematic Diagram of gaseous Diffusion process (10).

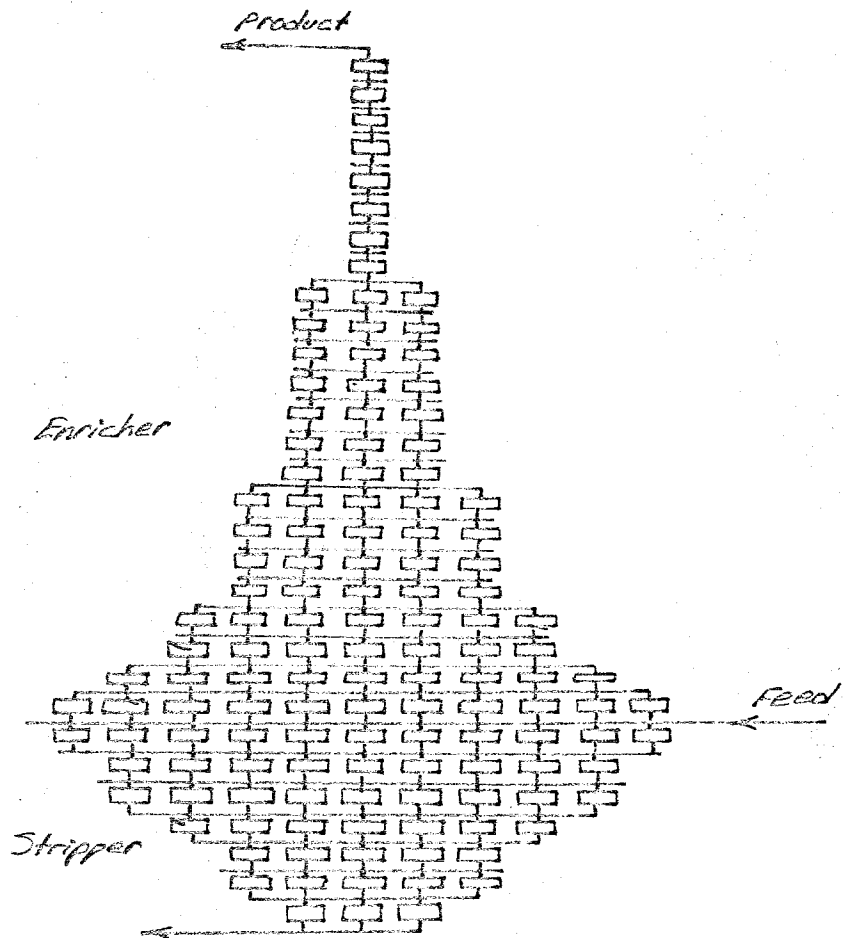


Figure.8.8.b Gaseous Diffusion cascade(10)

A gaseous diffusion plant consists of a cascade of thousands of stages, high-compression-ratio pumps, fine-grained diffusion membranes, coolers and requires to operate at subatmospheric pressure. All these requirements make gaseous diffusion very expensive. But for large-scale U^{235} separation, it is preferable.

Gaseous diffusion plants which were mostly used for military purposes are in the following countries. The United States (Oak Ridge, Tennessee, Paducah, Kentucky, and Portsmouth, Ohio), Great Britain (Copenhurst), France (Pierre Lotte), the Soviet Union, and China.

8.2.2. MASS DIFFUSION

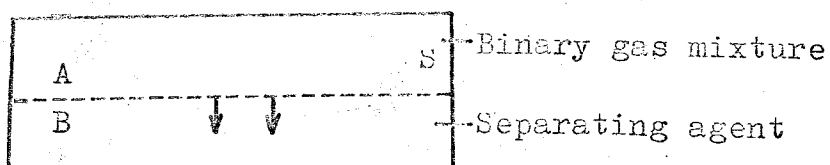


Fig.8.9 Principle of mass-diffusion separation shown schematically (40).

The mass diffusion method makes use of the phenomenon of molecular diffusion to affect separation. Different molecules of a binary gas mixture has different diffusivities in another substance known as separating agent. When the gaseous mixture is confined in a system divided into two by a membrane like in figure 8.9, it comes into contact with the separating agent placed in B. Often, the separating agents are condensable vapors so as to easily separate the agent from the gas component diffusing in A and B parts are under the same pressure. Gas mixture in A, mostly the gas component having greater diffusion coefficient D_1 , flows through the porous barrier. Since D_1 is greater than D_2 , the gas passing into part B is enriched in the component of lower molecular weight in time. Since the gas components are mixed with the separating agent, they are freed by condensation(41). The separation factor in mass diffusion can be expressed by diffusion coefficients of light and heavy components as follows:

$$q_0 - 1 = \frac{2(D_1 - D_2)}{D_1 + D_2}$$

To establish a comparison with the gas-diffusion process, q_0 can also be given as

$$q_0 - 1 = \frac{M_2 - M_1}{M_2 + M_1} \times \frac{M_0}{M_0 + (M_1 + M_2)/2}$$

where M_0 is the molecular weight of separating agent.

The mass diffusion process is carried out either in an individual stage or in a cascade of stages or in a mass-diffusion column. The stage type was developed originally by Hertz (26), which is given schematically in figure 8.10. Since the separation obtained in a single stage is very small, a number of stages are arranged in a counter current cascade of stages (see fig. 8.11). Another type was also introduced by Benedict to provide a greater degree of separation than is obtainable for a single mass-diffusion stage(26). When figure 8.12 is observed, it is seen that separating agent in the innermost chamber is charged over the length of the column instead of only one end. This system has two advantages. The mass diffusion column is more efficient and achieve the degree of separation obtained in many stages in a single column. Consequently, the mass diffusion can be preferred for small scale laboratory separation.

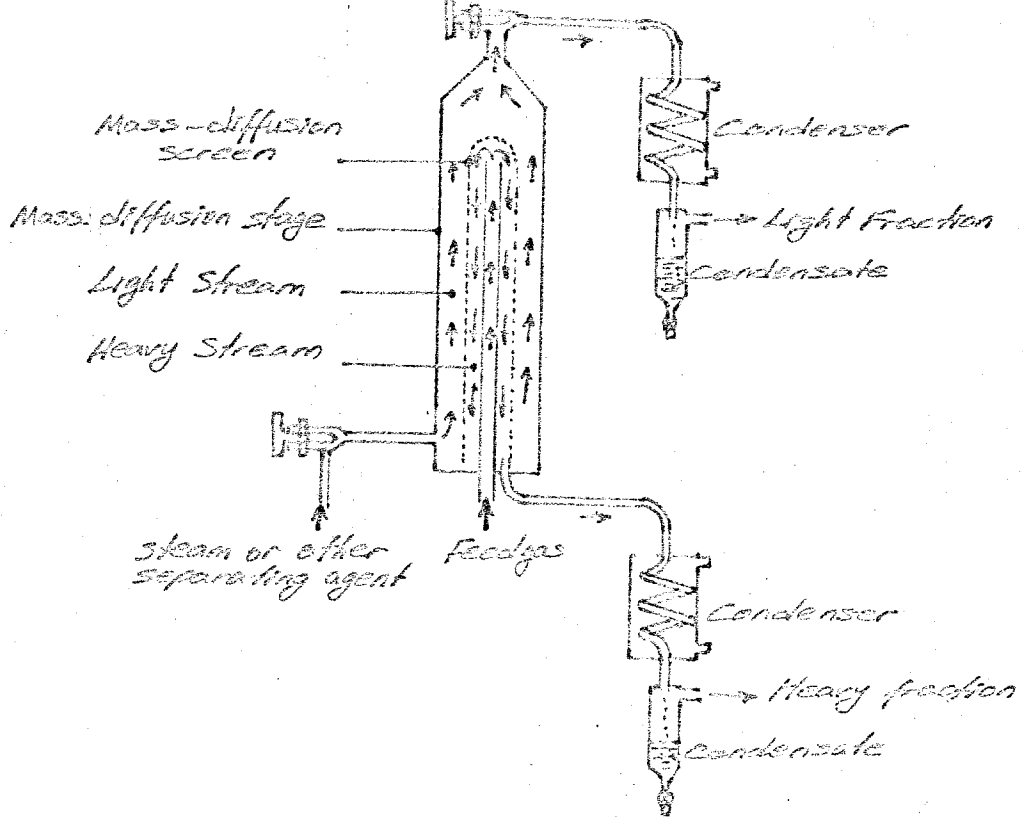


Fig.8.10 Mass-Diffusion stage used by Maier (26).

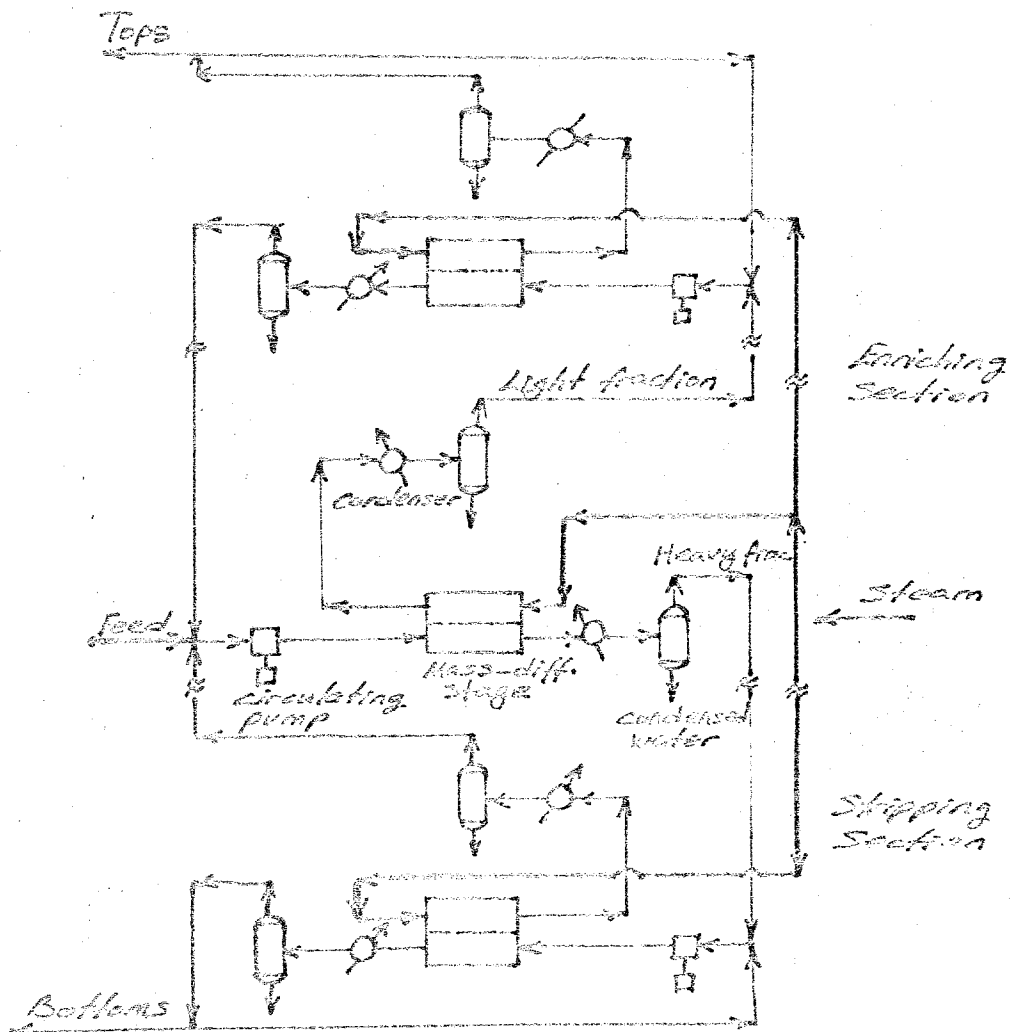


Fig.8.11. Cascade of mass-diffusion stages (26).

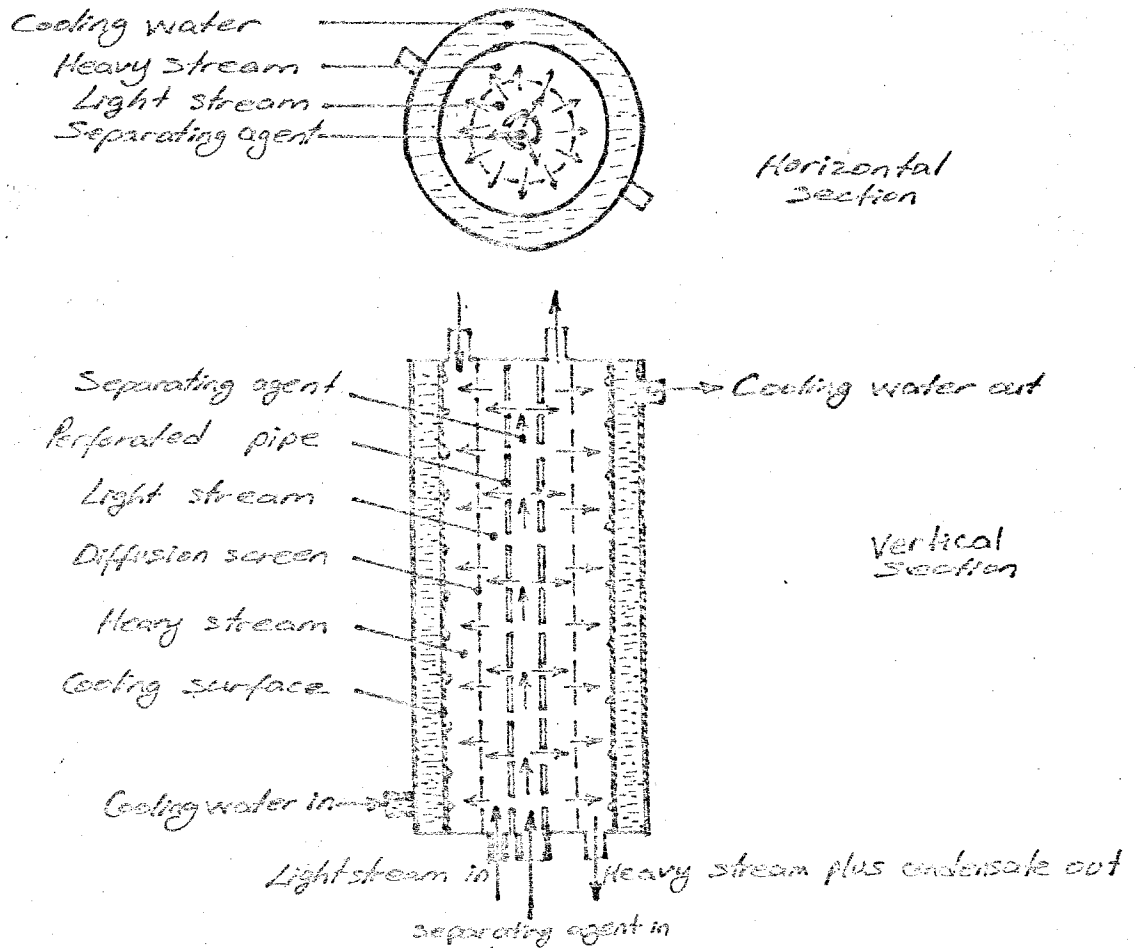


Figure.8.12 Flow in mass-diffusion column (26)

8.2.3 THERMAL DIFFUSION

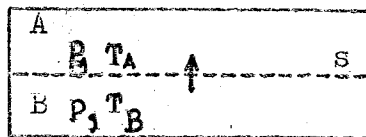
In the process of diffusion of a gaseous mixture, diffusion currents created by a temperature gradient are used for the separation purpose. Assume that a binary mixture is confined in a container as shown in figure. 8.13 divided with a porous barrier. When the temperatures T_A and T_B are different, the gas flows from the cold part to the hot. Since the flow is inversely proportional to the square root of the molecular weight more of the lighter component flows to the hot part. Hence the gas flowing through the membrane to the hot part is enriched in the light component. The elementary separation factor of the thermal diffusion is as follows

$$q_0 - 1 = \left[\frac{x' - x''}{\bar{x} (1 - \bar{x})} \right]_{N_1 = 0} = \bar{\gamma} \ln \frac{T'}{T''}$$

where; x', x'' are light component's mole fraction at hot and cold wall, respectively; \bar{x} is the mean value; N_1 is light component's diffusive molar velocity; $\bar{\gamma}$ is the mean value of thermal

diffusion constant; T' , T'' are the temperatures of hot and cold wall, respectively. Although the thermal diffusion effect was discovered in 1911 by Enskog from the kinetic theory of gases, it was confirmed experimentally by Chapman in 1917 (26).

Fig. 8.13 Schematic diagram of the thermal diff. process (40)



But it still stayed a scientific curiosity until Clarius and Dickel developed their thermal diffusion column in 1938 (2). The thermal diffusion column is illustrated schematically in fig. 8.14. As it can easily be understood, light isotope concentrates near the inner (hot) cylinder which is as close as possible to the cold surface. The operation pressure is near atmospheric pressure. In the thermal diffusion, the degree of separation attained is much smaller than that of other diffusion processes.

8.2.4. GAS CENTRIFUGE

The $M_2 \omega^2 r^2$ is the well known centrifugal force per unit volume which is directly proportional to the mass the components. It is inevitable that a component having greater mass than the other is pushed aside by a stronger centrifugal force than that effecting the light one. This phenomenon is the working principle of the gas centrifuge isotope separation method. When a binary mixture is confined in a cylinder rotating about its axis with a high angular velocity (see fig. 8.15) the light and heavy components tend to separate. Light stream will move near the center whereas the heavier one near the outside.

The elementary separation factor is $q_0 = e^{(M_2 - M_1) \omega^2 r^2 / 2RT}$

where; $\frac{1}{2} \omega^2 r^2$ is known as the centrifugal potential and r'' is the outer radius. Since the separation factor includes the mass difference,

q_0 is the same for light and heavy element isotopes under the same conditions. Table 8.3 lists the separation factors for differences of mass from 1 to 3 for various peripheral velocities at ambient temperature (300°K).

Means for developing the high peripheral velocity needed for appreciable separation of isotopic mixtures have been developed by Blams and coworkers in the U.S., Khariton in Russia, and Groth and coworkers in Germany (26)

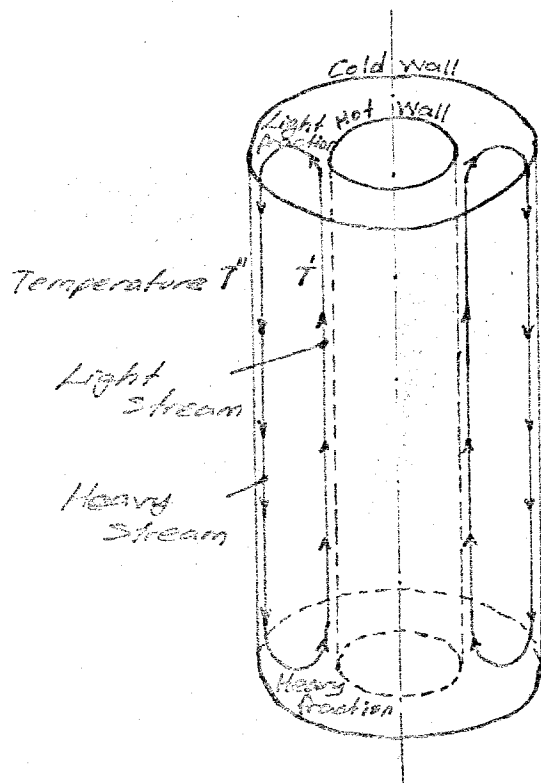


Fig.8.14 Thermal diffusion column (26).

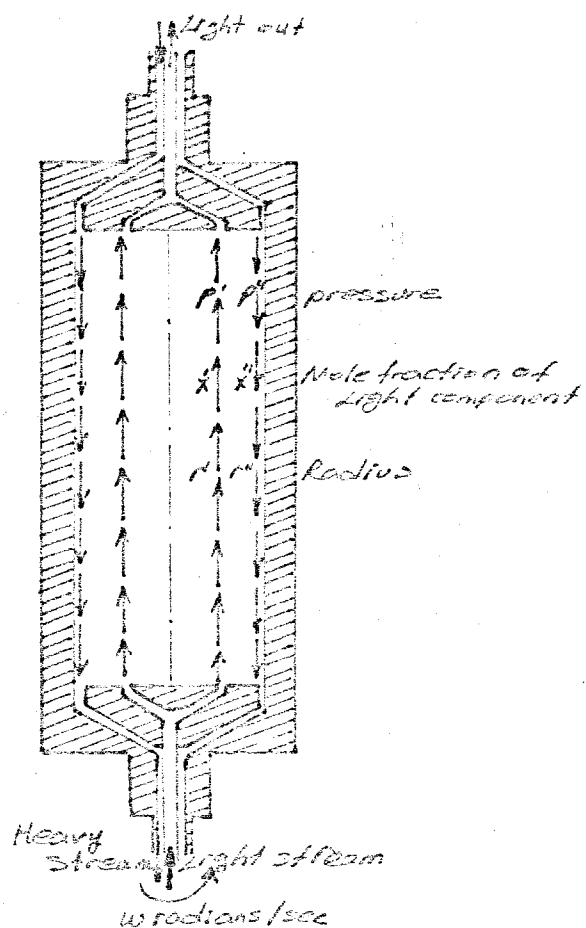


Fig.8.15. Counter current gas centrifuge (26).

Table.8.3 Elementary Separation Factors (40).

$M_2 - M_1$	300 m/sec	350 m/sec	400 m/sec	450 m/sec
1	1.018	1.049	1.069	1.085
2	1.037	1.104	1.144	1.177
3	1.057	1.159	1.198	1.278

8.2.5 COMPARISON OF PROCESSES AND PLANT FEATURES

The separation factor being the best single measure of the difficulty of a separation represents the difference in the enriched and depleted stream compositions. Table 8.4 compares the diffusion processes applied to U^{235} - U^{238} mixture according to separation factors. The result of this separation can be concluded as for large-scale separation of the heaviest elements, gaseous diffusion and the gas centrifuge are the most economical. For intermediate -scale work, mass diffusion is advantageous.

In recent years, different separation methods have been investigated.

Laser separation, Chemical Exchange and Electromagnetic Separation methods are the most familiar ones.(41).

Table 8.4 Comparison of Separation Factors (26).

SEPARATION METHOD	Isotopes U ²³⁵ - U ²³⁸	
	Working Substances	Separating factor
Gaseous diffusion (min.power)	UF ₆	1.0042
Mass diffusion (min.power)	UF ₆ - C ₇ F ₁₆	1.0022
Thermal diffusion (min.power)	UF ₆	?
Gas centrifuge* (min length)	UF ₆	1.026

* peripheral velocity 25,100 cm/sec.

The most striking feature of isotope-separation plants is the large number of identical pieces of equipment due to low separative duty of the individual units. Another feature of these plants is the requirement of a long time to reach a steady production. To give an idea, it can be said that start up times are of the order of 50 to 100 days. Enormous electricity consumption is of course another important feature of isotope separation plants. Therefore the thermodynamic efficiency of these processes is very low.

Alloys of Al, Cu, and SS are chief materials used in construction of the components coming into contact with UF₆ (37). Teflon is used for the gaskets and accessory parts.

9. THE FABRICATION TECHNIQUES OF UO_2 SHAPES

Nuclear reactors for commercial power production are mostly fed by either natural or enriched uranium dioxide. Enriched uranium reactors are mainly of three types; namely, Pressurized Water Reactors (PWR), Boiling Water Reactors (BWR) and Advanced Gas Reactors (AGR) whereas Canadian Heavy Water Reactors (CANDU) and some Gas Cooled Reactors in U.K (G.C.R) use natural uranium.

Uranium dioxide powders being either natural or enriched is needed to have sufficient ceramic activity to start the machining. Therefore production of ceramic-grade UO_2 powders prior to the fabrication of UO_2 into shapes is required.

9.1. PREPARATION OF CERAMIC - GRADE UO_2 POWDERS

Although there is a variety of other methods, two main large-scale industrial preparation methods have been used. According to these methods, ceramic-grade natural UO_2 and enriched UO_2 are produced from uranyl nitrate and uranium hexafluoride, respectively.

As it is mentioned in chapter 8, uranyl nitrate is the most suitable pure compound to produce natural uranium dioxide powder. After uranyl nitrate is denitrated to UO_3 , UO_3 is reduced to UO_2 by hydrogen reduction at 650-800 °C (42). The size of agglomerates is ultimately 1 to 5 μ (37) and are more difficult to breakdown for getting the required particle sizes.

The starting material for enriched UO_2 powder is obviously UF_6 enriched in U^{235} . The schematics of production route for enriched UO_2 powder is shown in figure 9.1. The process starts with the contact of UF_6 with NH_3 and steam according to the following reaction.



where $(NH_4)_2U_2O_7$ is the ammonium diuranate (ADU) which precipitates as a yellow precipitate. Then the ADU is transferred from the precipitation tank in which UF_6 is held at a temperature of well above its boiling point. After the ADU is taken to a holding tank, it is sent to a filter and a drying oven. Dried ADU is taken and sent to a reduction furnace in which the reduction to UO_2 happens at 800 °C (2). After UO_2 is cooled in nitrogen atmosphere, easily crushed agglomerates are obtained. The agglomerates having particles ranging in size from 0.5 to 2 μ (37), are hammer milled to get fine powder.

To eliminate the aqueous operation, a dry method has been deve-

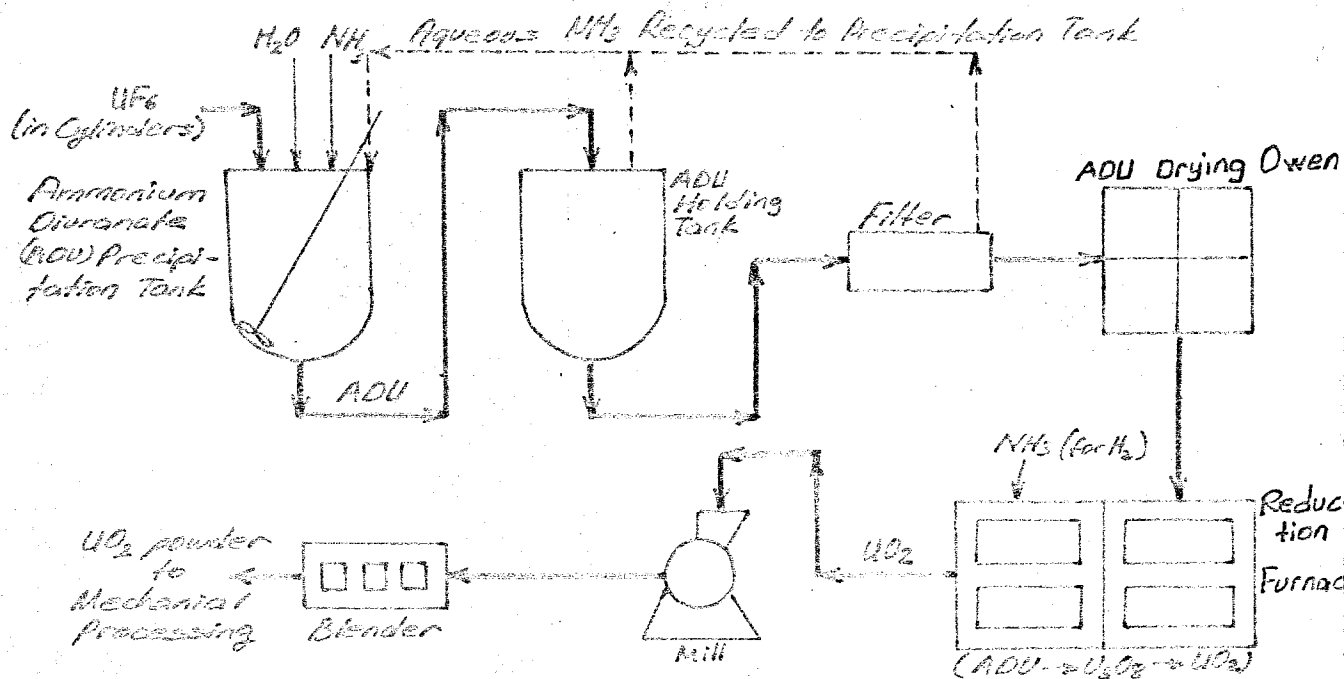


Fig.9.1. Flow sheet for the manufacture of ceramic-grade uranium dioxide (2)

veloped for obtaining UO_2 from UF_6 . In this method, UF_6 in gaseous phase is brought into contact with steam at $130^\circ C$ and then with hydrogen and steam in the ratio 2:1 at $550^\circ C$ (8) as follows:



This and a variety of other methods including hydrogen reduction of UO_3 and U_3O_8 , oxidation of uranium metal have been studied on an experimental scale, but none of them has been put into large-scale production.

UO_2 powders for ceramic use should have a very fine particle size. The size of the individual particles of UO_2 varies depending on the particle size of the higher oxide and the reduction temperature. Size-temperature relation can easily be observed from figure 9.2 where the reduction temperature increase results in the larger sized crystal production. The particle size is important when the stoichiometric composition of UO_2 is concerned (31). The smaller the powder size, the more rapidly oxidation occurs. Powder with a dioxide particle size of around 1μ is oxidised in air at room temperature to $UO_{2.02}$ in approximately 1 month, whilst powder of particle size 0.06μ is oxidised to $UO_{2.135}$ only after 1 day (8).

Figure 9.3 illustrates the effect of reduction temperature on microstructure of UO_2 prepared from UO_3 , where pore coalescence is observed. Surface areas of UO_2 powders from UO_3 reduction and reduction temperature yield apparent relationship (see fig.9.4) whilst UO_2 powders obtained from ammonium diuranate do not show a similar correlation.

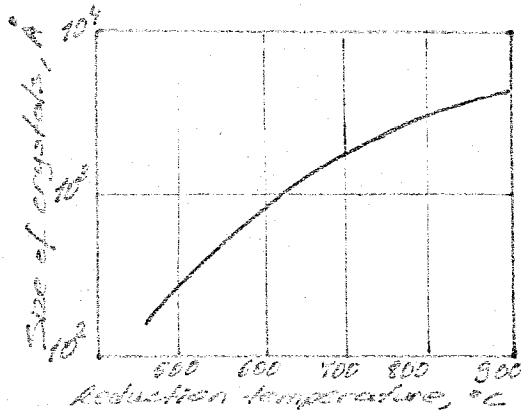


Fig.9.2 Graph of the sizes of the crystalline particles as a function of the UO_2 reduction temperature (8)

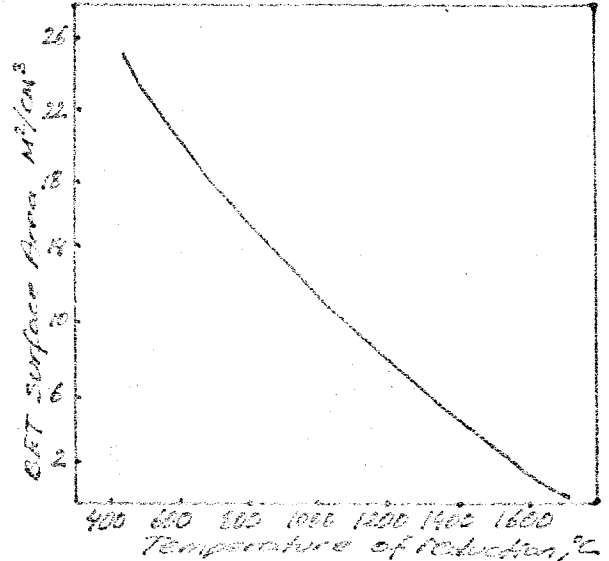


Fig.9.4 BET surface area of UO_2 prepared by hydrogen reduction of UO_3 at various temperatures. (42)

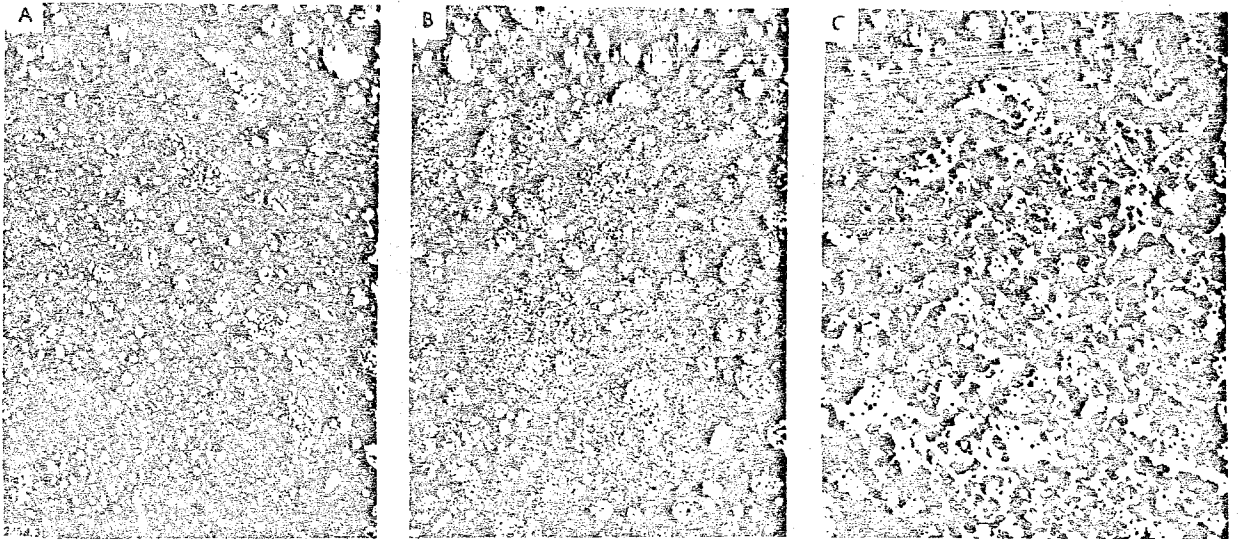


Fig.9.3. Effect of reduction temperature on microstructure of UO_2 prepared from UO_3 ; A, reduced at 480°C X160; B, reduced at 800°C X160; C, reduced at 1650°C X160 (42).

9.2. THE FABRICATION OF UO_2 INTO SHAPES

Ceramic UO_2 fuel elements are fabricated by a number of techniques such as; cold pressing and sintering, hot pressing, cold binder extrusion, vibratory compaction, swaging and hot extrusion.

9.2.1 COLD PRESSING AND SINTERING

The most widely used technique for the fabrication of UO_2 is the cold pressing followed by sintering of ceramic-grade UO_2 powders. The process is as follows. The powder is first treated with an organic binder such as polyvinyl alcohol (PVA) in order to get the free-flowing granules. A lubricant, such as hydrogenated vegetable-oil lubricant (sterotex), zinc stearate or stearic acid, is also blended in the powder. After blending, the batch is transferred to a coarse mesh screen and given a preliminary drying at $70^{\circ}C$ (2).

Granulated UO_2 obtained by forcing the dried batch through a finer mesh sieve is fed into the pressing apparatus. The press is double-acting, that is, both upper and lower punch move to exert equal pressure on the powder from top to bottom. Its punch faces are slightly convex and made out of tungsten carbide. The compacts are pressed to 50 to 65 per cent of their theoretical density (37). Before being sintered, the compacts are heated in a flowing CO_2 atmosphere at $800^{\circ}C$ for 2 hours (43) to remove the binder and lubricant. Pellets which are sintered partly during dewaxing are fed into a molybdenum-wound hydrogen atmosphere furnace and sintered. The sintering operation is performed in dry hydrogen atmosphere in a typical temperature range of $1600-1750^{\circ}C$ (3). The density of the sintered ceramic depends to a great extent on temperature, particle size of the original oxide powder, compacting pressure and time. Figure 9.5 indicates the effects of these variables on product.

Some data summarizing the sintering capacity of UO_2 powders obtained by different methods are shown in table 9.1. On sintering non-stoichiometric uranium dioxide in a nitrogen atmosphere, high ceramic densities were obtained at a sintering temperature of $1200-1300^{\circ}C$ (8). Effects of different atmospheres on sintering of uranium dioxide is obvious when the data on table 9.2 is observed. When the non-stoichiometric uranium dioxide is briefly held in a hydrogen atmosphere at the same temperature, the stoichiometric UO_2 can be recovered. Sintered uranium dioxide can be machined by wet polishing to remove the surface cracks with a tungsten carbide instrument.

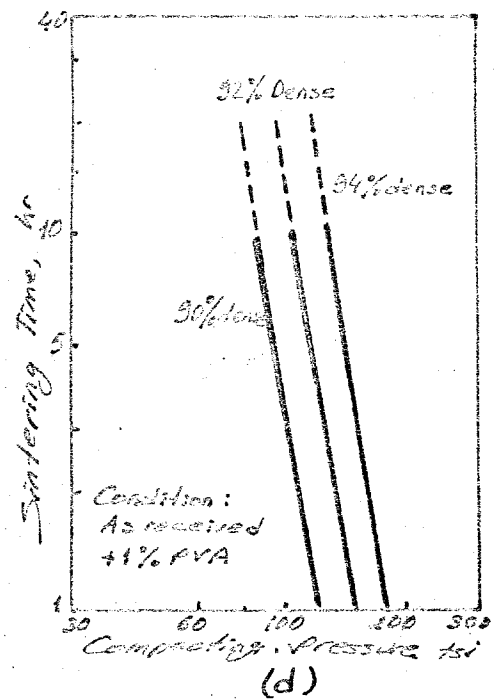
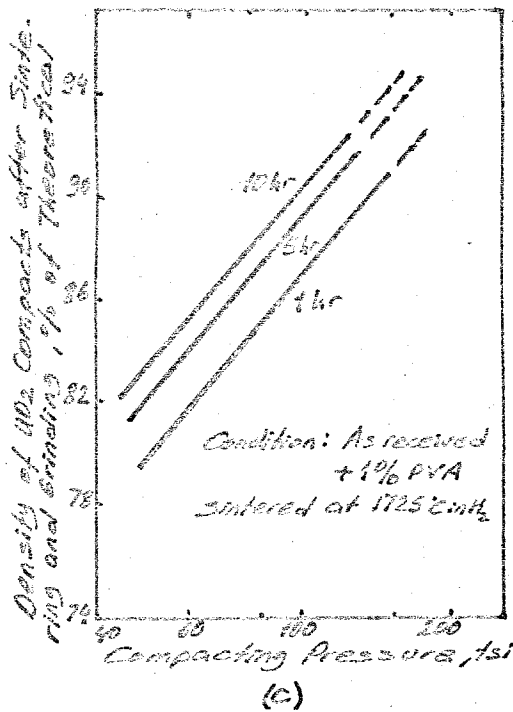
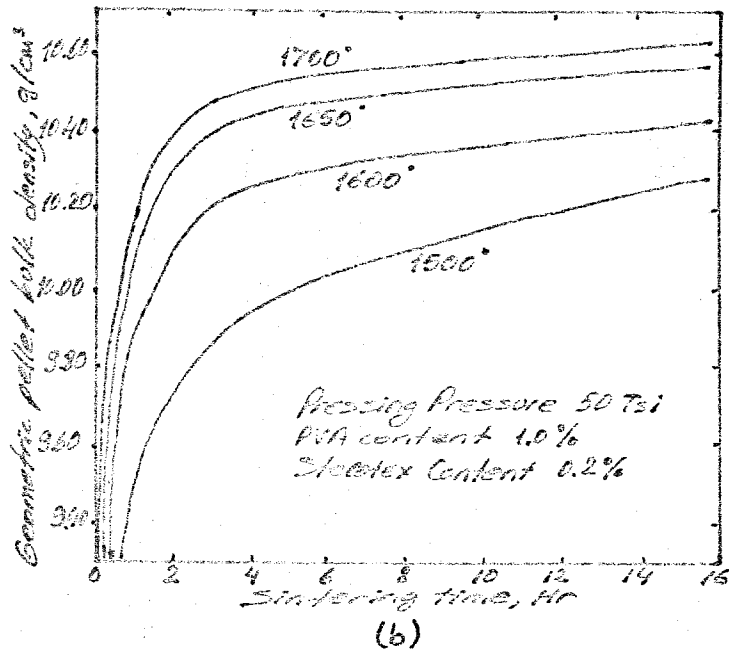
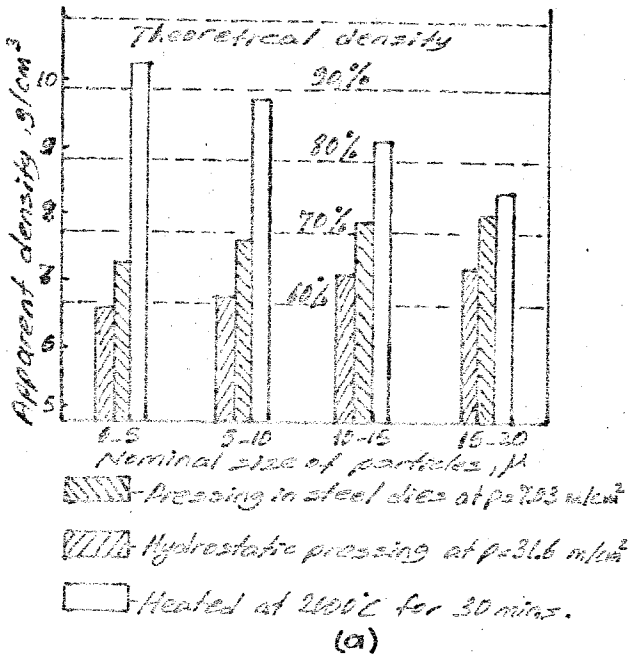


Fig. 9.5 Effects of processing variables on the sintered density of UO₂ compacts. *a*) Change in density of UO₂ objects as a function of particle size in different stages of treatment (2), *b*) Effect of sintering time and temperature (2), *c*). Sintered density as a function of compacting pressure and sintering time (43), *d*). Sintering time as a function of pressure and density (43).

Table 9.1. Sintering Capacity of UO_2 Powders Obtained by Different Methods (8).

Method of Production	Specific Surface M^2/g	U/O atomic ratio	Pressing Pressure kg/cm^2	Sintering Temperature (in H_2) $^{\circ}C$	Max. value of density of sintered material, g/cm^3
Denitration of $UO_2(NH_4)_2$, H_2 -reduction at $800^{\circ}C$	0.62-2.75	2.02-2.06	28.3	1700 (30 min)	7.8-9.2
Hydration of UO_2 , obtained by denitration of $UO_2(NH_4)_2$, with wet crushing in a ball mill, H_2 -reduction at $800^{\circ}C$	1.9-7.9	2.04-2.16	28.3	1700 (30 min)	10.4-10.8
Precipitation of $(NH_4)_2U_2O_7$ at 60°C and pH=9-9.3 from concentrated solutions, calcining and H_2 -reduction at $800^{\circ}C$	3.8	2.18	28.3	1600-1650 (60-90 min)	9.5-10.8 (greater part above 10.2)
Precipitation of UO_4 peroxide, H_2 -reduction	—	—	8.15	1750 (50 min)	11.7
Hydrolysis of UCl_6 by steam at $130^{\circ}C$ and reduction by a steam hydrogen mixture at $150^{\circ}C$	—	—	31.5	1600 (4 hr)	10.8
Continuous precipitation of $(NH_4)_2U_2O_7$ at pH=7-7.5 and low rates of reaction, quenching and H_2 -reduction at $800^{\circ}C$	4.8	—	28.3	1600-1650 (10-30 min)	8.1-10.7

Table 9.2 Effect of Atmosphere on Sintering of Uranium Dioxide (43).

Atmosphere	% of theo. density	O/U ratio	Atmosphere	% of theo. theo. dens.	O/U ratio
H_2 only	81.2	2.00	62 H_2 + 38 H_2O only	83.4	2.01
Air (1400-1500)°C	86.9	2.00	98 H_2 + 2 H_2O (1400-1500°)C	97.3	2.00
Steam (1400-1500)°C	97.7	2.01	43 H_2 + 57 H_2O (")	97.7	2.00
Steam only	82.2	2.10	98 H_2 + 2 H_2O only	86.3	2.09
98 H_2 + 2 H_2O only	85.8	2.00	98 H_2 + 2 H_2O (1400-1500°)C	85.6	2.01
84 H_2 + 16 H_2O only	85.8	2.00	98 H_2 + 2 H_2O only	82.9	2.11

9.2.2 HOT PRESSING

The pressing results in compaction of powder since the applied force compresses the material surrounding the pores by slip deformation. Pressing at 1650°C in induction-heated graphite dies at 8500 psi has produced compacts 95 % of theoretical density (2) Figure 9.6 compares the 10 minute hot pressing characteristics of both American UO_2 and British $\text{UO}_{2.13}$ with cold pressed and sintered $\text{UO}_{2.13}$. It is easy to see that the maximum density of 10.25 g/cc of the British oxide is approached at 1400°C and above 1800°C the density again increases slightly to 10.55 g/cc (4).

Since the hot pressing eliminates the shrinkage of the objects on sintering, it is used to produce long rods, plates and other objects with accurate sizes. But this method is rarely considered owing to the fact that the reaction between the graphite die and the surface of compact causes differential densification.

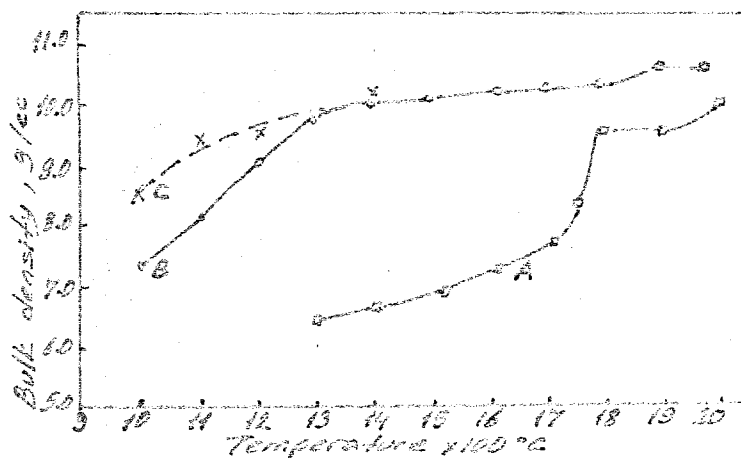


Figure.9.6 Hot-pressing characteristics of uranium oxide

A- UO_2 , B- $\text{UO}_{2.13}$, C- Cold-pressed and sintered $\text{UO}_{2.13}$ (4)

9.2.3 COLD BINDER EXTRUSION

In the U.S and Europe, successful cold binder extrusion of uranium dioxide to produce cylindrical rods having large length-to-diameter ratios has been reported. Cold binder extrusion process starts blending of the virgin ceramic-grade powder with a plasticizer, such as Carbopol, polyvinyl alcohol, cornstarch, methyl cellulose and polyethylene glycol. This blended feed is introduced into a muller-mixer where it is mixed with water or water-glycerine mixture. A plastic mass is obtained as a result of this mixing. Then the plastic mass is obtained as a result of this mixing. Then the plastic mass is placed in a ceramic extrusion press and be freed of air. The pressure extruding the mass varies in the range of 3000 to 20,000 psi. Extruded

rods are dried within 48 hr. Similar to the previous processes, dried rods are sintered in hydrogen or cracked ammonia atmosphere. Final step is centerless grinding. The densities attained by extrusion and steps of various extrusion procedures are summarized in table 9.3 and 9.4 respectively.

Table 9.3 Densities of Extruded Uranium Dioxide Powders (43).

UO ₂ powder type	Surface area m ² /g	Average diameter μ	Percent of theoretical density		
			Green	Sintered	Density increase (Green to sintered)
Ceramic grade	2.0	1.25	56	96	40
Ceramic grade	1.4	1.65	56	95	39
Ceramic grade	0.4	4.10	57	80	23
PWR (milled 8 hr)	0.8	1.50	56	93	27
PWR (milled 64 hr)	2.3	0.90	59	93	34
PWR (milled 8 hr) ^b	2.1	1.28	59	93	34
Hanford depleted ^a	5.2	4.80	52	90	38

a-Sintered in H₂ atmosphere for 8 hr at 1750°C.

b-Treated by a controlled oxidation-reduction process

Table 9.4 Steps in Fabrication of Uranium Dioxide Extruded Rods (43).

Material	Plasticizer (Carbonol 934) wt. %	Ball-milling time hr.	Liquid added wt. %	Blended in Rubber mill	Extrusion Pressure psi	Drying time hr.	Sintering time at 1750°C hr.	Percent of theoretical density	
								Green	Sintered
PWR-grade UO ₂	1.2-1.7	24-48	6-8	No	12-25	48	8-16	56-59	85-93
PWR-grade UO ₂ (oxidation-reduction process)	1.4	3	8	Yes	20	48	8	57-58	93
Hanford-depleted UO ₂	2.6	3	12	Yes	15	48	8	51-52	89-91
Ceramic-grade UO ₂ of high surface area per unit volume	2.0-2.5	3	10-13	Yes	15-25	48	1-8	51-56	91-96
Ceramic-grade UO ₂ of low surface area per unit volume	1.2	3	7	Yes	15	48	8	51-58	79-80

9.2.4 VIBRATORY COMPACTION

In the vibratory compaction technique, ceramic-grade UO_2 powders are placed in a tubular jacket unit and subjected to a vibrational load.

Vibrations can be produced by either an electrodynamic shaker or a pneumatic vibrator (see fig.9.7). The tube in which blended fuel is placed serves as covering for the fuel. The fuel material is added slowly and initially vibrated at low levels (less than 10 g's acceleration), while the vibration frequency range from 500 to 4000 cycles per sec is traversed rapidly (2). Accelerations up to 80 g's and a pressure of 25 to 50 psi on the fuel column are applied (10). Total time required to load and densify an 8-ft rod is about 3 min (2). UO_2 powder in stainless-steel jacket can be impacted at $1100^{\circ}C$ to $1200^{\circ}C$ in a high-velocity impact machine (Dyngpak). In this case 99 % of theoretical density is obtained.

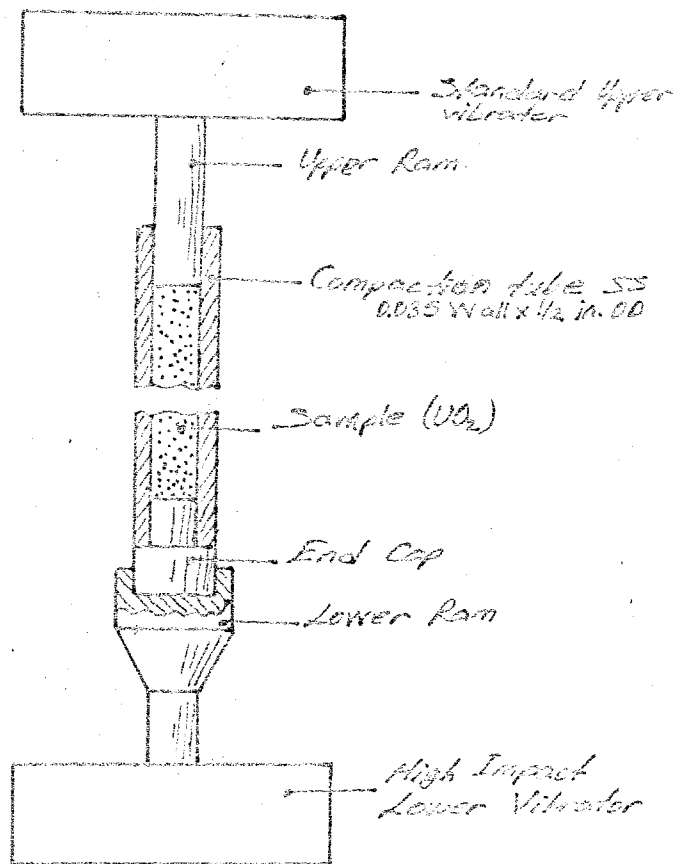


Fig.9.7 Pneumatic compaction apparatus for producing fuel units (2).

Lower manufacturing cost, remote control possibility, dimensional tolerance relaxation for clad tubes and fabrication ability for producing fuel having complex cross sections are the major advantages of vibratory compaction.

9.2.5 SWAGING

Swaging can be cold or hot swaging. This method consists of compacting UO_2 powder in tubes by hammering. First of all ceramic-grade UO_2 powders are clad with stainless-steel, zircaloy and aluminium alloys successfully. In fact, canning the uranium dioxide in one operation is an important advantage of this technique.

By cold and hot swaging methods, powder densities achieved are listed in table 9.5 and 9.6 according to various cladding materials and swaging temperatures. It must be added that during compaction of powder, the metal sheet deforms only slightly and the wall thickness increases. The wall thickness, elongation and density of hot and cold swaged fuel rods as a function of reduction of rod is illustrated in figure 9.8

Table 9.5 Densities of UO_2 Swaged with Various Cladding Materials (43).

Table 9.6 Densities of Uranium Dioxide with Various Swaging Temperatures (43).

Cladding Material	Wall thickness of cladding before swaging in.	Maximum UO_2 density after swaging, % of theoretical	Cladding Material	Swaging Temperature °C	UO_2 density % of theoretical
304L Stainless steel	0.065	87	0.035-in. SS (304L)	Room temp.	86
304L stainless steel	0.035	86	0.035-in. SS (304L)	600	91
Zircaloy 3	0.030	84	0.030-in. Zircaloy-3	Room temp.	84
Aluminium	0.060	82	0.030-in. Zircaloy-3	400	86
			0.030-in. Zircaloy-3	600	88

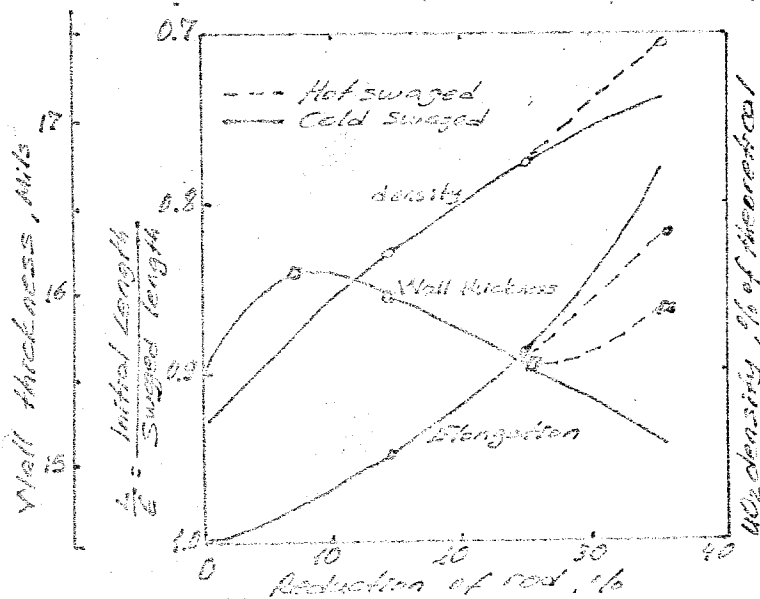


Fig. 9.8. Wall thickness, elongation and density of hot and cold swaged fuel rods as a function of reduction (2).

9.2.6. HOT EXTRUSION

Hot extrusion represents an interesting technical accomplishment besides a promise for low-cost high-quality ceramic fuel elements. Hot extrusion method is composed of following steps.

Uranium dioxide and cladding material which could be tantalum, molybdenum, zircaloy and stainless-steel are heated separately. Their heating temperatures are obviously different since high temperatures give sufficient plasticity to fuel whereas canning material can not bear the same temperatures. When the plastic equivalency is obtained between UO_2 and clad, co-extrusion is applied. In order to supply the adequate strength to cladding material, a heavy can such as mild steel is necessarily provided outside of it. This can is removed after extrusion by nitric acid application. The fuel core of the resulting rod has a density of 99-100 % of theoretical, (43). The rod obtained has a uniform outer surface, but the clad inner surface is rough and has non-uniform wall thickness.

9.2.7 OTHER TECHNIQUES

There is a variety of techniques employed to ceramic UO_2 fabrication. They are dealt with briefly.

During pressing step if ceramic-grade UO_2 powders are enclosed in a pliable sheath, immersed in a fluid and then pressurized, this process takes the name "Isostatic Pressing". Clearly the exerted force is passed uniformly to enclosed powder, and hence a uniform density is obtained.

"Slip Casting" method has not been applied extensively to fabricate fuel elements, but it has been used to make special shapes. In this process, first of all a low-viscosity water suspension is prepared. The suspension is filled into a plaster of Paris mold (Porous mold). Water is extracted by capillary motion through these pores. Hence a solid casting is obtained in the plaster and taken out for drying and sintering.

"Vibratory Compaction" can be connected with swaging or isostatic pressing to get a dense product and clad having less damage.

A series of fuel rods starting with fused UO_2 have been made by "tandem rolling" at room temperature and excellent surface properties have been obtained.

No matter what the fabrication technique is, finished elements are examined before assembling and using in a reactor. Mainly dimensional checks, high temperature water or steam out-of-clave tests, helium leak tests, X-ray examination, ultrasonic and visual tests

are applied

There is an important aspect of UO_2 manufacturing due to the fact that uranium dioxide is one of the heavy metal compounds being chemically poisonous. Since uranium oxide is α radioactive compound, it is harmful if inhaled. During UO_2 fabrication adequate dust collection and recovery procedures are of vital importance for protecting the health of the workers.

Chapter 10

10. NUCLEAR FUEL PRODUCTION POSSIBILITIES OF TURKEY

On May 3, 1955, the White House announced the approval of a proposed agreement between the governments of the Republic of Turkey and the United States for cooperation in the field of research in the peaceful uses of atomic energy (44). In Turkey on June 10, 1955, Peaceful Uses of Atomic Energy Agreement was approved by the law No. 6864, and later modified by the law No. 317 on July 17, 1961 (44).

The Turkish Atomic Energy Commission (TAEK) was established by the law No. 6821 on September 4, 1956, and was attached to the Prime Minister's Office. TAEK on March 6, 1958 decided to establish a LMW swimming pool type of research reactor at Küçük Çekmece, Istanbul. On May 27, 1962, this reactor became critical and Çekmece Nuclear Research and Training Center, (ÇNAEM) was opened. The center included a number of research groups (44).

Up to now, close cooperation has been maintained between the TAEK and the IAEA, and a number of governments in establishing a number of laboratories in Ankara and Istanbul and independently in the universities, (44).

10.1. URANIUM DEPOSITS IN TURKEY

Studies of uranium exploration and research in Turkey is under the responsibility of Mineral Research and Exploration Institute which is called MTA for short. In 1935, MTA was founded by M. Kemal Atatürk with the law No. 2804. As a result of reorganization in 1957, Radioactive and Rare Metals Technology Services were also brought under the auspices of MTA.

Uraniferous deposits in Turkey according to the first results obtained and reported fall mainly into three groups (44).

- i. Ore appearing as a result of crystallization of secondary uranium minerals,
- ii. Ore formation as a result of uranium entering into opal, limonite and phosphorite sediments in the form a gel by engrossing ties.
- iii. Sedimentary ores.

The exploration studies were started after 1956. The uranium deposits were met in Western and South-western Anatolia. Turkey's uranium reserves are mainly located in the following regions:

1. Manisa, Salihli-Köprübaşı region:

The most important basin is placed in this region. Two types of ore are observed.

- i. Kasar ores: These are composed of secondary uranium minerals as Meta-autunite and autunite which are mainly composed of silicates. Since Kasar uranium ores are disseminated in neogene sediments, its grade varies from 0.052 to 0.01 % U_3O_8 (45). The reserve in the Ecinlitaş location is assumed to be an extension of the Kasar ores. The thickness of the ore being under ground and having a lense shape is about 1.5-3 metres.
- ii. Taşharman ores: In Taşharman conglomerate and tuffite ores, uranium is in dahlite which is a phosphate mineral. Taşharman ores are disseminated in fine sediments. The grade of the ore is about 0.045 % U_3O_8 (44).

2. Uşak-Güre-Fakılı region:

Secondary uranium mineralizations are observed. Uranium beds are in local Fakılı formation containing tuff, gypsum, pyrite and sandstone layers. It is poor in uranium content 0.025 % U_3O_8 (45).

3. Aydın-Koçarlı-Kuşukçavdar region:

The crystallization of secondary uranium minerals are found in Menderes massif. The grade of the ore is about 0.05 % U_3O_8 (46).

4. Çanakkale-Ayvacık-Küçükkuşu region:

Similar to Taşharman ore, uranium ores found in this region is in dahlite form. Uranium beds are placed inside old tuffs. Uranium content is about 0.05 % U_3O_8 (46).

5. Giresun-Şebinkarahisar region:

In the old eosen sedimentary formations, autunite mineralization is realized. Its grade is about 0.04 % U_3O_8 (44).

The uranium reserves of Turkey amounts to approximately 5100 (47) (4600, 46-47) metric tons of U_3O_8 equivalent in the reasonably assured category. Locations of these reserves according to the latest MTA report are as follows (48).

Manisa-Salihli-Köprübaşı	: 3040 t U_3O_8
Uşak-Fakılı	: 510 t U_3O_8
Aydın-Koçarlı	: 1000 t U_3O_8
Çanakkale-Ayvacık-Küçükkuşu	: 250 t U_3O_8
Giresun-Şebinkarahisar	: 300 t U_3O_8
TOTAL	: <u>5100 t U_3O_8.</u>

10.2. POSSIBLE URANIUM RESOURCES OF TURKEY

Turkey's possible resources can be summarized in six groups. These are as follows:

1. Black Sea:

Sea waters contain about 3.3 ppb uranium (49). Uranium in the sea waters is in the form of soluble ion complexes. The most important ion complex is tricarbonatouranilate by which 98 per cent of total uranium in sea waters is included. Black sea does not show different characteristics in this sense (50).

Black sea sediments also contain uranium. The base of Black sea has a depth of 2000 m, and an area of 150000 km² (51). Black sea sediments were made in 5000 years and a layer of 1 m, deep contains about 2 million tonnes of uranium (51) (According to German scientist E.T Degens: 6.7 million tons of uranium exist (46). Uranium in Black Sea sediments was formed by microorganisms in H₂S medium. Carrying out the sediments and extracting uranium efficiently constitute the initial problems to be surmounted. It can be said that uranium production from Black Sea sediments will not be economical in the near future.

2. Istanbul Strait:

In March-April 1971, scientists on Atlantis II, an American ship, proved that Black sea waters reaches Marmara sea at a rate of 6100-12600 m³/sec due to natural streams in Istanbul strait. (52). This flow rate means approximately 800 million tons of sea water per day.

On the other hand in 1975, Llewelyn determined the possible locations where uranium could be extracted by natural conditions from world seas and prepared a list. Istanbul strait was not only one of the locations in the list but also it was the first one (52).

Since the stream waters contain two times more uranium than that of sea waters, the stream waters coming from Black sea contain about 5.9-7.0 ppb uranium (49). When the amount of water flowing and this uranium content are taken into consideration, it is easily said that 5.6 tons of uranium in a day passes the strait.

Under the light of above concepts, table 10.1 summarizing the features of a possible plant has been prepared. Expected cost of 1kg of uranium produced in this plant is about 93 \$ (according to 1979 price) (49).

3. Lake Van and Demirköprü Dam:

The waters of Lake Van being a closed lake contain about 90 ppm (46) uranium which is 30 times more than that of sea waters. The sediments of Lake Van also contain 8 ppm uranium. The results obtained by today's technology are not economic. Thus the uranium production from Lake Van waters and sediments does not seem feasible

at this time. This is the same for Demirköprü dam sediment also.

Table 10.1 Expected Technological Characteristics of an Uranium Production Plant to be Constructed on Istanbul strait. (49).

Production capacity	1.4 tU/day
Amount of sea water used	280 million m ³ /day
Adsorption surface required	10 ⁶ m ²
Adsorption pool number	60
Total pool volume	4.2 x 10 ⁵ m ³
Sea water flow rate in pool	27 m/hr
Initial amount of Titanium oxihydrate (which is the most suitable substance to adsorb uranium ion complexes from sea water.)	7.2 x 10 ⁴ t
Adsorption time	4 days
Washing and elusion	1 day
Estimated titanium loss	3.5 kg Ti/kgU
Efficiency	80 %
Uranium content in the sea water	6 ppb

Demirköprü dam is located at the region between Gördes, Demirci, Selendi and Kula. It has been determined that the most important uranium resources and anomalies are placed at the same region. It has also been known that uranium is one of the mobile elements. Considering these facts, MTA tested the water samples taken from the outlet of Demirköprü Dam. As a result, 15ppb uranium (49) has been found. Since Demirköprü Dam passes approximately 700 million m³ water per year, 8.7 tons of uranium per year with an efficiency of 80 % can be obtained. The energy equivalent of this amount of uranium will taken be greater than the hydraulic energy obtained from the dam.

4. Phosphate Reserves and Phosphoric Acid Production:

Uranium can be obtained as a by-product of phosphoric acid production. Although Turkey meets its phosphate requirements through imports, the capacity of phosphoric acid production is 400,000 tons P₂O₅/year. Turkey's phosphate reserves inclusive of the prospective reserves amounts to 416.000.000 m.tons of 7-21.5% P₂O₅, and the amount of uranium contained in them is 0.02-0.002 % (44).

The production from Turkey's own phosphates at Mazıdağı will also be started in 1985. Then the production capacity will reach a value of 947,780 tons P_2O_5 /year (46). The amount uranium ending up in phosphoric acid is 81 %, while the efficiency of uranium gain from acid is about 93%. It can be concluded that uranium gain as a by-product of phosphoric acid production in Turkey constitutes an important reserve (see table 10.2)

Table 10.2 Possible Uranium Production from P_2O_5 in Turkey (46).

YEAR	ton U_3O_8 average
1979	91
1980	109
1981	125
1982	133
1983	135
1984	135
1985	182
1986	201
1987 and future	213

Foundations work with 80 % capacity

By considering the time required to implement these studies, it is expected that the earliest uranium production will be in 1989 at 213 tons U_3O_8 (46). According to experiments applied to Batı-Kasrik phosphate concentrates, the cost of 1kg yellow cake containing 75 % U_3O_8 production is estimated as 30 T.L. (53). In view of the rising costs of uranium, this offers a possibility of production of uranium from phosphates.

5. Fuel Ashes:

Especially lignite ashes are reasonably important in uranium content. Muğla-Yatağan lignite deposit is located in South-west Anatolia where important anomalies were observed. The average uranium content of the lignite is in the order of 0,01 % U_3O_8 (13). Since the lignite reserve in the Muğla-Yatağan region is about 30 million tons, total uranium is estimated as 2700 tons (9). Results obtained from lignite ashes taken from different are summarized in table 10.3.

6. Asphaltics and Other Minerals:

Asphaltics are formed by tectonic movements of earth's crust such that petroleum changes its place and flows into the cracks

of rocks. In Turkey, asphaltite resources are around Mardin-Siirt regions, which contain 100 ppm uranium.

Some important metallic minerals contain uranium as impurity. Two minerals express this property in Turkey. The first mineral is thorium and rare earth metals found in Eskişehir-Beylikahır region, which includes 0.02 % U_3O_8 (40). Second mineral, although found in small quantities, consists of 0.73 % Cu and 0.195 % U_3O_8 (50) in Uşak-Fakılı region.

Table 10.3 Analysis of Lignite Ashes (50).

REGION	U_3O_8 (%)
Afşin-Elbistan	rare
Beypazarı	0.0010-0.0025-0.0040
Bursa : Orhaneli-Burnu	0.0060
Orhaneli	0.0040-0.0090
Keleş-Davutlar	0.0010
Çanakkale-Çan	0.0005
Çankırı-Orta Linyit	0.0035
Edirne-Demirhanlı	0.0025
Gölbaşı	0.0010-0.0020
Erzurum-Hınıs	0.0120
Kütahya-Seyitömer	0.0013
Tekirdag-Saray	0.0050
Soma : E1	0.0110
E2	0.0120
Siirt-Şırnak	0.0200

10.3. URANIUM EXPLORATION IN TURKEY

Effective uranium exploration efforts in Turkey started after 1957. At the beginning, MTA carried the exploration projects in cooperation with some countries. The purpose of these studies was to train Turkish personnel about modern exploration techniques as well as to explore uranium in Anatolia.

A contact was signed between the Canadian Aero Services Ltd, Ottawa, Canada and MTA on January 11, 1960 for magnetic and radiometric airborne exploration covering an area of 140000 km² namely the Aegean, the Central Anatolia, and East Taurus regions (44). Reports and contour maps were completed in December 1960.

In South-West Anatolia, uranium exploration project has been carried out by the corporation of UNDP /IAEA with MTA institute since 1974.

10.3.1. EXPLORATION METHODS USED IN TURKEY

In uranium exploration, the first step is to determine the geological properties of regions. Areas of interest are evaluated by aerial radiometric prospecting. Fig.10.1 illustrates the radiometric airborne exploration regions in 1960. Aerial survey enables the initial evaluation of regions and hence suitable locations for exploration are determined. Detailed aerial surveys, mapping, surface radiometric surveys, geological-geochemical surveys and probably radon surveys and botanical prospecting are used to find out the level of importance of these chosen regions. Gathering of all the information, the geologist responsible for the project settles the most applicable procedure according to ore type. Uranium exploration procedures for vein and sandstone type deposits have revealed basic differences(54). During sandstone type ore exploration, studies must be directed to find out the locations of uranium sedimentation.

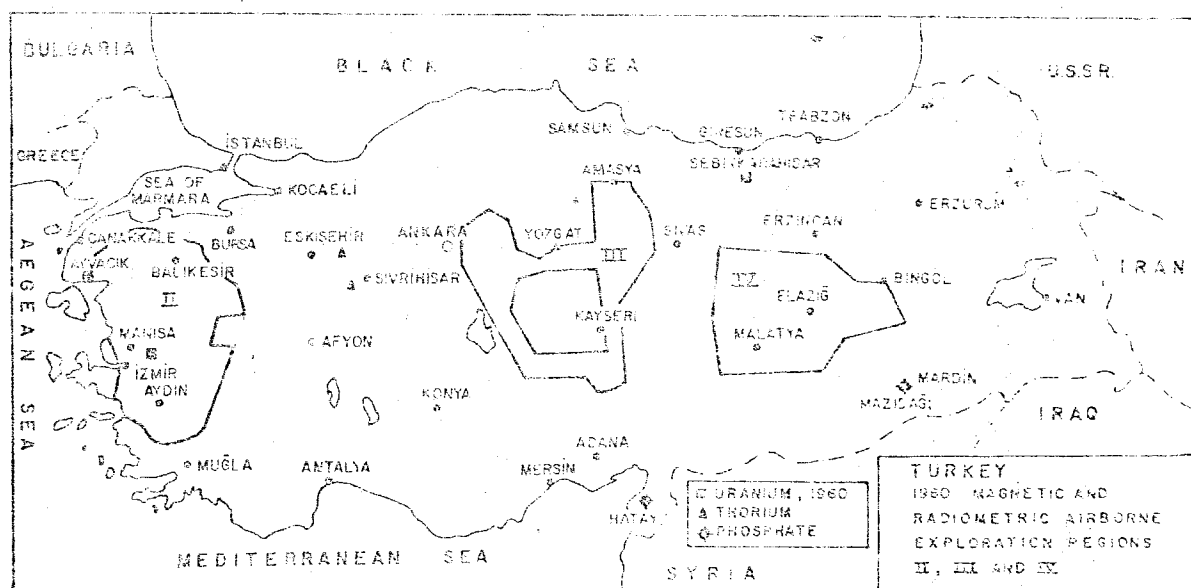


Fig.10.1. Uranium(1960), Thorium and Phosphate(1960) Deposits; also shown are the magnetic and radiometric airborne explorations mainly intended for iron investigations of 1960 in three regions II, III, and IV amounting to a total 140 000 Km² in Turkey (44)

Conversely, mineralisation of vein type ores can easily be observed on the surface. Vein deposits, on the other hand, show point instances

since they are tubular in shape having great inclination. Sandstone deposits, however, are shallow, horizontal and under ground such that no direct samples can be obtained. Uranium ores prospecting in Turkey are sandstone types.

IAEA-MTA project carried out in South-west Anatolia is a good example for a project applying modern exploration methods. The project area is given in figure 10.2. In this project, drilling areas were chosen according to geological mapping, aerial and surface radiometric surveys. During aerial surveys, in order to determine the exact place of radioactivity, the route of aircraft was controlled by an automatic camera. Samples were taken from waters, soil and

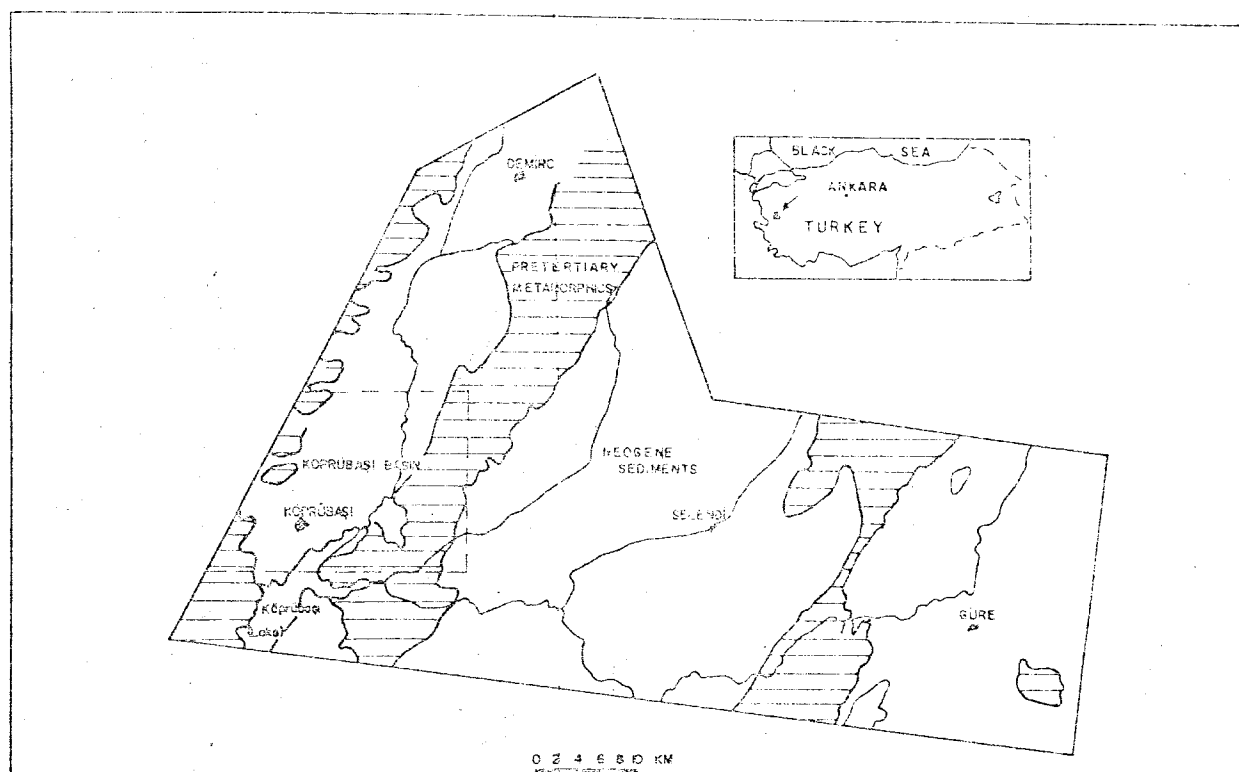


Figure 10.2. UNDP Project area for uranium exploration (44).

stream sediments for determining the uranium and radon contents (see fig.10.3). Results of laboratory tests were prepared by computer and labelled on maps. Figures 10.4 and 10.5 illustrate such maps. In the project region, the area having high radioactive anomalies occupied an area of 30 km². Drilling studies, in this part, started and applied with intervals of 1 km. A different feature of this drilling studies was to use the subsurface geology, continuously. Basic subsurface data were taken into consideration to obtain lithologic interpretation and stratigraphic correlations. A geologist noted the properties and tested the mineralogy of fragment samples



Figure 10.3 Sampling water from a domestic well in Turkey to analyse its uranium and radon content (14).

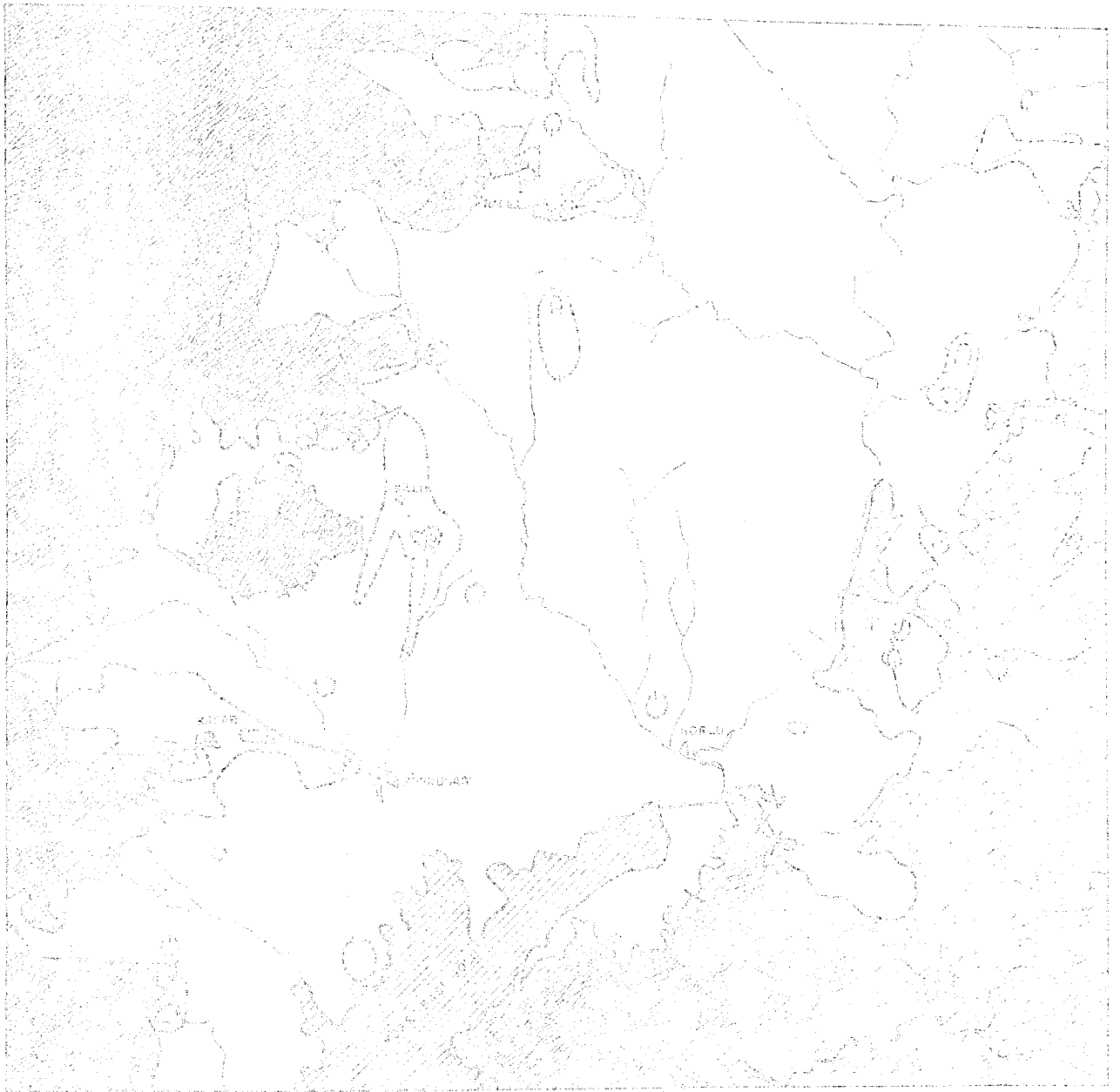
taken from each meter. Their copies were attached to other maps, reports of the same location as a reference. All results have been compiled and kept by MTA. Table 10.4 gives an idea about radioactive element geological prospecting studies conducted by MTA between 1964 and 1968. More recently, Turkey has taken advantage of the remote sensing geological mapping of U.S Satellite Programme(44).

10.3.2. TURKEY'S URANIUM RESERVE SITES AND EXPLORATION RESULTS

in Uranium reserves have either been found or are expected to be found in the following regions in Turkey (57). The order in which they are listed below is not necessarily the order of importance for these regions. One can observe that the studies conducted by MTA in the years 1964-68 and listed in table 10.4 are mostly carried out in the regions given below.

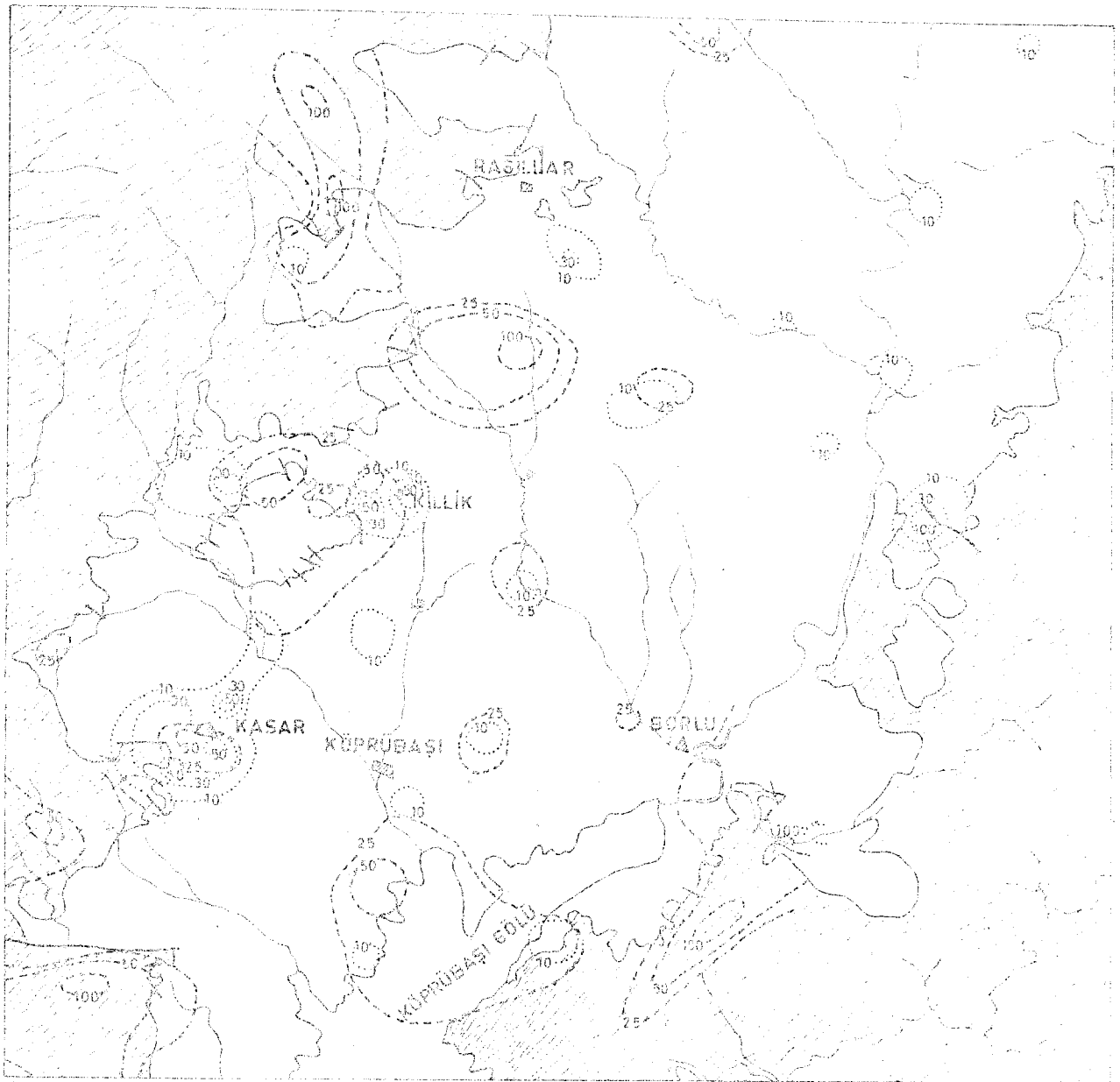
1. Trakya Region :

Trakya region is the North-Western part of Anatolia extending in Europe. It is expected that studies carried out in the Western part of the regions will give a good result. Geochemical and radon measurements are still being continued through Lalapaşa-Çatalca line.



Neogene Sediments
 Pretertiary
 Metamorphics
 (---) U Concentration Contours (ppm)

Fig.10.4. Uranium content in stream sediments at Kôprubaga basin (55).



- Heogene Sediments
- ▨ Proterozoic Metamorphics
- U Concentration Contours (ppm)
- Rn Concentration Contours (ppb)

0 1 2 3 KM.

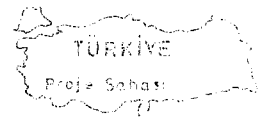


Fig.10.5. uranium and radon contents in waters taken from Köprülübaşı basin (bb).

Table 10.4. MTA Studies Between 1964-1968 (56).

YEAR	LOCATION	REMARKS
1964	Gördes-Demirci	Systematic Prospecting Trenching : 9
1965	Gördes-Taşharman-Manisa Gürün-Başviran Antalya, Trabzon, Erzincan, İspir Aydın Afyon-Şuhut, Adana-Mağara, Kütahya, Salihli-Köprübaşı, Giresun-Suşehri, Ordu, Ele- zığ-Keban, Bingöl, Menemen, Aliaga.	Trenching : 661 m ³ Systematic Prospecting Trenching : 8 Aerial Pros. : 24000 km ² Aerial Pros. : 13000 km ² Surface Pros. : 11340 km ² General Pros. : 105 km ² Detailed Pros. : 555 km ² Surface Pros. : 600 km ²
1966	Alaşehir, Manisa, Akhisar, Denizli, Bandırma Söke-Besparmak-Aydın, Bäre- mit, Bergama, Sındırgı, Ba- lıkesir, Küçükkuyu, Ayvacık, Trabzon, Gümüşhane, Malatya Hekimhan, Uşak-Eşme, Beyli- kahır-Eskişehir Gördes-Topallı-Temaşa-Kayran Çetinbaş-Yardere-Killik-Kı- nık-Dövişviran-Mestanlı-Bey- namaz	Aerial Pros. : 72000 km ² General pros. : 770 km ² Surface Pros. : 650 km ² Location : 231 Drilling : 7619.80 m Trenching : 535.5 m ³
1967	Ağrı, Bitlis, Tunceli, Bin- göl, Hınıs, Palu, Van Simav-Gediz-Demirci-Alaşehir (Kütahya, Manisa). Uşak-Banaz Kula-Simav-Selendi Edirne-Lalapasa Gördes-Yardere, Mezargedigi, Akcaalan, Tüllüce-tepe, Taş- harman-Kocadüz, Gökburun, Karaoglan Ayvalık-Küçükkuyu	Aerial pros. : 20000 km ² Surface Pros. : 6000 km ² Detailed Pros. : 158 km ² Trenching : 73-(263m ³) Detailed Pros. : 201 km ² Trenching : 45-(165m ³) Anomalies : 200-8000 C/s General Pros. : 250 km ² Detailed Pros. : 145 km ² Trenching : 11-(40m ³) Drilling : 13396 m Hole : 3 (46)m Total Reserve : 1900 tU Location : 125 Hole : 2 Trenching : 20-(370m ³)

Table 10.4. (continued)

YEAR	LOCATION	REMARKS
1967	Hekimhan-Malatya	Detailed Pros.: 126 km ² Trenching : 25-(153m ³)
	Beylikahır-Eskişehir	Trenching : 18-(100m ³)
1968	Kütahya-Afyon-Uşak-Trakya Uşak-Banaz	Aerial Pros. : 40000 km ² Detailed Pros.: 70 km ² Trenching : 113 m ³ Anomalies : 500-2500 C/s
	Kula-Selendi	Detailed Pros.: 160 km ² Anomalies : 450-900 C/s
	Giresun-Şebinkarahisar	General Pros. : 75 km ² Detailed Pros.: 130 km ² Trenching : 160 m ³
	Ağrı-Bitlis	Location : 60 km ² (pros.)
	Trakya Region	Detailed Pros.: 150 km ² Trenching : 43-(60m ³) Anomalies : 100-1000 mr/hr
	Kazdağ masif (Ezine-Geyikli)	Surface Pros. : 80 km ²
	Afyon	Detail Pros. : 100 km ² Trenching : 150 m ³ Anomalies : 600-5000 C/s
	Manisa-Gördes-Köprübaşı	Locations : 160 Drilling : 8764 m Hole : 1-(15 m) Total reserve reached to 2400tU
	Manisa-Kula-Selendi	Detailed prospecting is started Drilling : 1461 m
	Uşak-Eşme-Güre	Drilling : 46-(2515 m) Reserve of 200tU
	Edremit-Küçükkuyu	Detailed Pros.: 10 km ² Locations : 44 Drilling : 1593 m Trenching : 32 m ³ Reserve of 300tU Studies will be continued

2. Kocaeli Region :

The region extending from Istanbul in the West to Gebze in the East is worth to be considered. Radioactive anomalies were obtained in the granites of the North-Western part of Gebze.

3. Biga Peninsula and Surrounding Region :

There are uranium beds in old tuffs in Ayvacık-Küçükkuyu region. Uranium is inside dahlite mineral.

4. Şanlı-Susurluk-Orhaneli-Domaniç Region :

This region consists of six separate areas lying from the West to the East. Susurluk and Orhaneli granites show important anomalies.

5. Balıkesir-Ayvalık Region :

Kozak granite massive, the West of Çandarlı gulf and volcanic areas show radioactive anomalies.

6. Eskişehir-Sivrihisar-Beypazarı Region :

Sivrihisar and Beypazarı regions are interesting from uranium and Thorium point of view. Studies will be continued.

7. Menderes Massive Region :

This region is bounded with Salihli-Alaşehir in the North, Denizli-Muğla in the East, Muğla-Lake Bafa in the South and Aegean sea in the West. Aerial and surface radiometric surveys have been completed. In some regions drilling tests have already been made. Especially, around Beşparmak mountains high radioactive anomalies have been observed. Uranium ore beds have been determined in neogene cavities.

8. Uşak-Kula-Demirci-Köprübaşı Region :

This is the most important region in Turkey. As a result of explorations mentioned in section 10.3.1, the formations containing uranium were determined. Then, possible underground uranium beds were searched by the use of drilling techniques.

9. Afyon-Sandıklı Region :

Studies have been continuing for many years. Geologic structure and the existence of a number of local uranium concentrations present a promising region.

10. Kırıkkale-Sorgun-Şereflikoçhisar-Kırşehir Region :

It has been tried to determine the vein type uranium ores in granite and cyonites and points having high activities. Reliable results however, have not been obtained. Only in Bahşilli village in South-West Kırıkkale, some anomalies were observed in granites.

11. Giresun-Şebinkarahisar-Koyulhisar Region :

Regional prospecting and drilling studies were completed initially. Regions yielding radioactive anomalies are Eskişehir plateau, Giresun-Kümbet region and the region around Karagöl mountain. At Çukurova location, a reserve of 200 tonnes U_3O_8 with a grade of 0.04 % was estimated. Anomalies were also detected around Arpa, Tatarköy and Tutakdağ area.

12. Gümüşhane-Trabzon-Ikizdere Region :

Aerial prospecting of the region is necessary since the region is steep and woodland.

13. Bitlis Massive Region :

This region is surrounded by Bingöl, Muş, South Lake Van, Bayhan, Lice and Palu. The results of aerial surveys are not encouraging. But in the North-West Bitlis, high anomalies were observed at many places.

14. Kars-Pasof-Şavşat-Sarıkamış Region :

Detailed prospecting is required to make a decision.

10.4. MILLING IN TURKEY

10.4.1. TECHNOLOGICAL CLASSIFICATION OF TURKEY'S URANIUM ORES

Technological methods used for reserve classification are determined by the ore grades, size and distribution of reserve and mineralogic composition. Technologic evaluation inevitably results in an economic investigation.

In order to produce yellow cake from ores found, initially grain size, kind and amount of chemical reagents used, temperature, time, rate of solid/liquid and the effect of oxidant are determined. Then, static column tests are carried out to get preliminary results for heap leaching. All these works are in laboratory scale.

Technological classification of uranium ores in Turkey is given in table 10.5. Important features of each from the point of view of yellow cake production are as follows :

1. Manisa-Köprübaşı :

Technological experiments yield three type uranium ores.

i. Carbonaceous Ores : The preliminary laboratory tests show that Kocadüz, Gördes ores are carbonaceous ores. Although expensive conditions such as fine grinding, excess amount of acid or alkaline and 65 ° C temperature were applied, uranium extraction was hard and at a very low level. These ores need to be studied more.

ii. Taşharman Ores : Since uranium is in Dahlite, uranium dissolution rate is about 60% even though more acid and fine grinding conditions are applied (58). Mother solutions contain about 0.4gr U_3O_8 /lt. Therefore the yellow cake obtained has a low grade. Generally the production cost of Taşharman ores is higher than that of Kasar ores. According to some laboratory tests, blended samples of Taşharman ore with Kasar ore give some economical leaching values. HCl for leaching and capillary dissolution methods are applicable (59). The production cost of 1 kg uranium as UF_4 is 905 TL or 434 TL in case of uranium extracted from Taşharman ore alone or from a blended ore, respectively.

iii. Kasar Ores: Uranium is produced from these ores at a reaso-

Table 10.5 Technologic Classification of Uranium Ores in Turkey (48,50).

ORE	Reserve U ₃ O ₈ (ton)	Mineral	LABORATORY						PILOT											
			Agitation Leaching			Column Leaching			Heap Leaching (Orig. Grain size)											
			Sample: 250 gr (-65 mesh) S/L = 2/3, Time: 4 hr, Temp: 25°			Sample: 10 kg (-2cm) S/L = 2/1 Time: 5-10 days, Temp: 25° C			U ₃ O ₈ %	Amount of ore (ton)	H ₂ SO ₄ kg/ton-ore	Leaching		Washing		Efficiency According to Solution U ₃ O ₈ %	Disposal U ₃ O ₈ %	Efficiency According to Disposal U ₃ O ₈ %	Commercial Production (-, +)	
			U ₃ O ₈ %	H ₂ SO ₄ kg/ton-ore	Efficiency U ₃ O ₈ %	U ₃ O ₈ %	H ₂ SO ₄ kg/ton-ore	Efficiency U ₃ O ₈ %				Time (day)	Solution (ton)	Time (day)	Solution (ton)					
MANISA - K. Ördübaşı	3040	Metavanadinite - Turunite	0.050	20	96.3	0.100	20	98.1	0.056	100	20	10	32	38	32	97.3	0.0052	90.7	+	
									0.024	1000	20	20	83	32	290	85.4	0.0040	83.4		
			0.150	40	89.1	0.150	40	89.7	0.030	50	30	4	6	35	22	96.6	0.0003	97.0	+	
			0.038	40	87.5	0.038	40	94.7	0.093	84	40	15	30	48	42	83.7	0.0014	84.9	+	
			0.105	20	96.6	0.105	40	98.0	0.076	72	30	4	5	53	75	93.8	0.0062	91.3	+	
			0.020	20	73.0	0.020	20	85.6	0.052	134	20	7	26	38	51	98.0	0.0053	89.8	+	
			0.020	20	96.0	0.020	20	90.5	0.020	57	20	5	6	28	30	91.2	0.0024	88.0	+	
			0.010	28	90.0	0.010	30	99.0	Sampling is impossible											
			0.040	75	89.0	0.030	100	49.1	0.030	110 (-5cm)	100	14	70	10	35	—	0.0130	56.6		
			0.041	75	92.7	0.120	100	32.0	0.055	67 (-5cm)	100	13	50	9	35	—	0.0200	63.6		
			—	—	—	0.038 62kg	80	93.3	0.060	100 21111	85	8	18	16	110	70.3	0.023	61.6		
			0.038	25	94.1	0.038	80	88.7	0.036	50	80	30	40	18	30	40.0	0.018	50.0	-	
			0.027	80	92.6	0.027	80	64.2	x	x	x	x	x	x	x	x	x	x	x	-
0.022	392	93.5	x	x	x	x	x	x	x	x	x	x	x	x	x	x	-			
0.030	320	26.7	x	x	x	x	x	x	x	x	x	x	x	x	x	x	-			
MANISA Arazehin-Yeşilyurt	—	—	0.025	80	92.4	0.012	100	85.0	0.012	77	100	16	67	7	30	30.3	0.008	34.0	-	
USAK Fakih	510	8 in the sample	0.025	25	91.0	0.029	40	89.6	0.029	82	40	7	42	9	93	90.3	0.0026	91.0	+	
AYDIN Kozanlı-Kışıkbaşlar	1000	Metavanadinite	0.380	20	96.4	0.450	20	95.7	} Sampling after detailed analysis											+
AYDIN Kozanlı-Arapsu			0.850	20	95.0	0.850	20	98.0												+
BİRESLİN Sebincarahisar-Estine			0.230	20	95.1	0.230	20	93.0												+
GANAKKALE Kışıkbaşlı-Kocacık	250	U in phosphate	0.160	1000	93.1	Since P ₂ O ₅ : 30% , Phosphoric acid production is taken as the base														
GANAKKALE Kışıkbaşlı-Kocacık			0.180	1000	84.0															
TOTAL : Σ	5100																			

nable price. There is no major problem during the production stage. Detailed yellow cake production process will be mentioned in the following section.

2. Uşak-Fakılı :

Laboratory and pilot scale tests yield that the same procedure applied to Kasar ores is applicable. The heap leaching performed with 82 tons of ore and 40 kg H_2SO_4 /ton-ore resulted in 90% U_3O_8 uranium solution after sixteen days. But, since the ore absorbed the solution, uranium content in the mother solution was 0.5 gr U_3O_8 /lt. This problem was solved by the use of ion exchange plus solvent extraction or TBP purification.

3. Aydın-Koçarlı :

In preliminary tests of samples taken from Küçükçavdar and Arapsu formations, efficiency of 90% U_3O_8 can be obtained by the use of 20kg H_2SO_4 /ton-ore. No problem is observed during solvent extraction and purification steps. Since the grade is very high, uranium in mother solutions containing 30gr U_3O_8 /lt is directly precipitated by ammonia. Then, yellow cake obtained is purified by TBP.

4. Giresun-Şebinkarahisar-Eskine :

For 90% efficiency following conditions are required : 20kg H_2SO_4 per ton-ore, grain size = -2 cm, solid/liquid = -1/8, temperature = $25^\circ C$, dropping rate 80-100 cc solution/hour, permeability 500lt/day/ m^2 , (kg) H_2SO_4 /(kg) U_3O_8 11.1. Mother solution contains 1-2 gr U_3O_8 /lt-solution. As a result of solvent extraction whose organic reagent is composed of 10% Alamine 336, 3% Decanol and Kerosene, yellow cake of 75% U_3O_8 was obtained. It can be concluded that the technological process used for Kasar ores is suitable for these also.

5. Çanakkale-Küçükuyu :

Since the samples include 30% P_2O_5 , phosphoric acid production constitute the base. When 1000kg H_2SO_4 /ton-ore is used in 6-stage-operation, 1% P_2O_5 is left in the residue. Special procedures are obviously required. That's why detailed P_2O_5/U_3O_8 separation tests must be performed.

6. Manisa-Alaşehir-Yeşilyurt :

Although the laboratory tests did yield reasonable results, Heap leaching at pilot scale had an efficiency of 31% U_3O_8 .

The difference in results indicates the requirement of tests at pilot scale and at large volumes. On the other hand high rate liquid absorption of ore and its low grade cause weak intermediate solutions which is a problem in solvent extraction and precipitation processes. Both chemical and drilling studies were cancelled.

10.4.2. MTA-KÖPRUBAŞI-PILOT PLANT

Laboratory experiments started in 1970 brought about the requirement of pilot scale studies. MTA has established a pilot beneficiation plant for the production of yellow cake U_3O_8 in 1974 (44). Since Köprübaşı, Manisa is at the center of regions including Kasar, Ecinlitaş, Tomaşa, Yardere, Topallı, Taşharman and Kocadüz ores, the pilot plant was constructed at Köprübaşı. Studies are carried out by 13 chemical engineers and 5 technicians (48). Three of the chemical engineers are responsible for uranium analysis.

Main purposes of the pilot plant can be summarized as follows :

- i. To collect data used for a main plant by the use of experiments carried out at larger scale than laboratory ones.
- ii. To examine the equipment and materials produced in Turkey.
- iii. To make the quality control of yellow cake obtained from different ores and to search the possibilities for production of uranium compounds at nuclear purity.
- iv. To educate qualified personnel.

At Köprübaşı-Pilot Plant (see Fig.10.6), the yellow cake production process is mainly composed of three steps ; leaching, solvent extraction, and precipitation.

1. Leaching Step :

Studies at pilot scale started with Kasar ore. In order to dissolve uranium, initially coarse ore is placed inside dissolving cells. Optimum dissolving conditions are found for leaching processes at large scale.

i. Cell Leaching : At Köprübaşı Pilot Plant there are six dissolving cells of 24 tons capacity each. Ore placed in a cell is washed first by a solution coming from the previous cell, then by a solution consisting of the previous cell solution washed with water plus acid at a rate of 20 kg H_2SO_4 /ton-ore. Finally, the ore is washed with water. Since solution obtained after the first washing contains the highest amount of U_3O_8 , this solution is passed to solvent extraction process. Due to the swelling of minerals with clay, expansion in cell is limited and permeability decreases much. It was noted that such cell leaching processes took 4 months (60).

ii. Heap Leaching :

Utilizing the results of cell leaching, open heap leaching is applied on ore heaps of 50-100-1000 tons. Heap leaching has some advantages. These can be summarized as follows : a. Crushing, grinding, screening and disposal of waste are not required, b. Since it is not con-

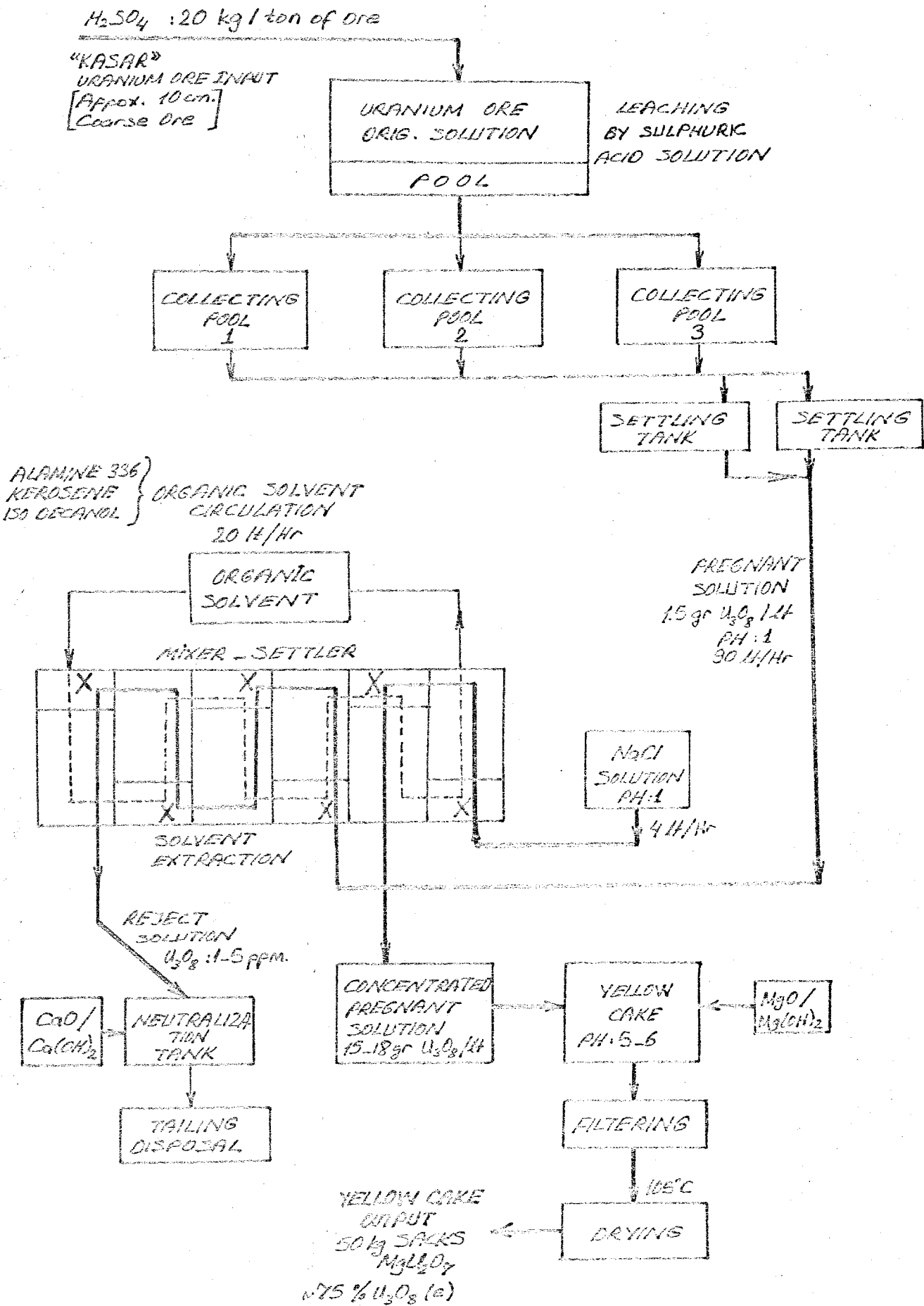


Fig.10.6. Flow diagram of uranium yellow cake production at MTA-Köprübaşı Pilot Plant (44,48).

fined in equipment, heap can have different dimensions, c. Except frost, at any weather condition, leaching continues, and d. Acid solution is given temporarily. Disadvantages of heap leaching are leakage from bottom due to excess loading, low extraction efficiency in case of poor permeable ore leaching and long leaching time.

In this process, first of all a polyethylene cover is placed on a 5% inclined area (see Fig.10.7). In order to prevent the cover tearing, pebble and then sand is situated under the ore heap. PVC pipes are installed on the felt covering at the top in such a way that there is 50 cm interval between the two pipes. Through these pipes acid solution is sent at a rate of 20 kg H_2SO_4 per ton of ore. Leach liquor is taken to collecting pools to get rest. Impurities precipitate in the pools to some extent.

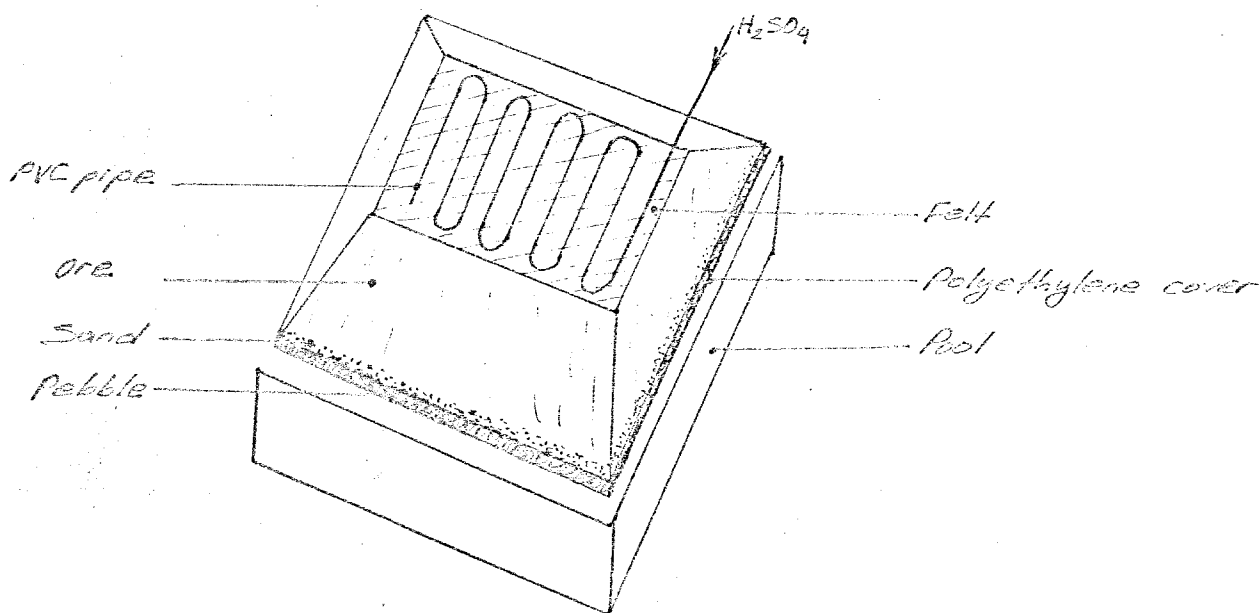


Fig.10.7. Preparation of a heap at MTA-Aöprübaşı pilot plant (61).

It was noted that leaching time was 40 days for a Kasar ore heap of 100 tons and uranium solubility was 83% (60).

2. Solvent Extraction Step :

Impurities such as Fe, Al, SiO_2 , PO_4 , Ca and Mg also pass into the leach liquor. Therefore, the leach liquor needs to be purified. It is taken into mixer-settler units for solvent extraction process. Organic solvent used is composed of Alamine 336, Kerosene and Decanol. After uranium passes into organic phase, it is re-extracted into liquid phase by stripping with a solution of sulphuric acid and NaCl. And hence the pregnant solution entering the system at 1-2 gr/lit U_3O_8 concentration becomes a concentrated solution containing 15-18 gr/lit U_3O_8 (61).

Rest of the pregnant solution includes 1-5 ppm U_3O_8 (60). The capacity of the system, rate of pregnant solution, rate of organic phase and rate of re-extraction solution are 100lt/hr, 90lt/hr, 20lt/hr and 4 lt/hr, respectively (44,61).

Sulphuric acid is supplied from Etibank, but Alamine 336 and Decanol are imported.

3. Precipitation Step :

Concentrated solution having 15-18 g/lit U_3O_8 is taken into precipitation tanks. Uranium is precipitated by MgO solution at pH :5-6 as " MgU_2O_7 " (62). This yellow cake is in the form of mud. Therefore it is dried at 105 °C in an oven. Dried yellow cake is packed in sacks of 50 kg each. A sample of 1 kg is taken from every 50 kg yellow cake and analyzed. According to these analyses the U_3O_8 content of the product is about 60-70 % (60).

The first yellow cake was produced on January 17, 1975 and by the end of January 1976 an output of 350 kg yellow cake was obtained(44, 60). Working in three shifts and in the open heap leaching yearly uranium cake production is estimated to be 1.7-2 tons U_3O_8 equivalent(44).

10.5. FUEL ELEMENT PRODUCTION STUDIES

BEYOND MILLING

Yellow cake produced at MTA-Köprübaşı Pilot Plant is the end of the chain of fuel cycle reached in Turkey. Further progress is under the responsibility of Turkish Atomic Energy Organization. At this time, however, there has not been any solid decision about completing the front end of the nuclear fuel cycle and production of nuclear fuel in Turkey.

In spite of this uncertainty, individual applications concerning some segments of the remaining part of the fuel cycle have been determined. Research for ore concentration conditions of different types of ores and their mixture, experiments for purification of yellow cake obtained at the pilot plant, sintering studies of UO_2 powders using ceramic powders other than UO_2 in the laboratory and ADU production at laboratory scale can be mentioned within these individual applications (48,63,64,65). ADU production at laboratory scale is supplied through the flowsheet given in Fig.10.8.

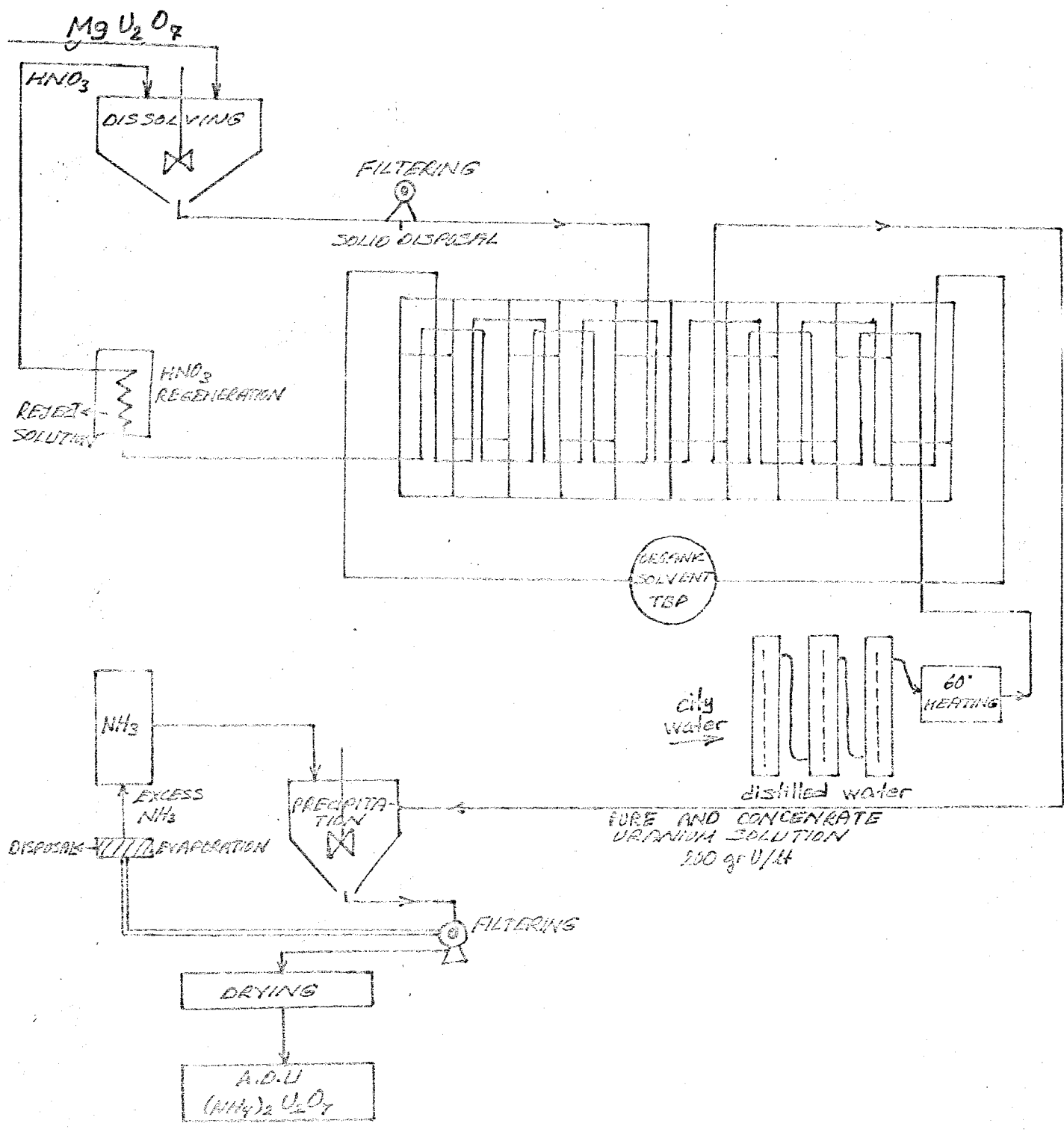


Fig.10.8. Flow diagram of ammonium di uranate (ADU) production at laboratory scale at MIA-Köp-rübaşı pilot plant (47,64).

Chapter 11

11. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDY

1. Literature survey has been performed to examine the basic uranium dioxide nuclear fuel element production steps and to combine these steps to obtain a complete procedure.

2. Uranium reserves and existing fuel production studies in Turkey have been researched and the data has been collected in a suitable manner.

3. The known uranium reserves found in Turkey must be evaluated with respect to the nuclear fuel requirements of one or more reactors. Table 11.1 lists the U_3O_8 demands of various type 1000 MWe nuclear reactors. We see that a 1000 MWe PWR or BWR uses 5000 tons of U_3O_8 and CANDU type PHWR uses about 3500 tons of U_3O_8 over its lifetime. HTGR's, LWBR's and LWFER's need smaller amounts, but their technology is far more advanced. It is more likely for the first generation reactors in Turkey to be PWR, BWR or PHWR.

Turkey's available uranium reserves as outlined in chapter 10, seem to be sufficient to fuel one or at most two nuclear reactors. Therefore, the exploration studies have to be emphasized and continued to develop the national reserves. Presently known uranium reserves must be handled seriously.

Table.11.1 U_3O_8 Demand for Inventory and 1000 MWe Reactor Operation(44).

REACTOR TYPE	INVENTORY PER REACTOR (tons)	40-YEAR OPERATION (tons)
PWR	548	5000
BWR	580	5000
PHWR	225	3500
HTGR	456	2400
LWBR	1140	1140
LWFER	1500	1500

4. Since after 1980's the shortage of yellow cake production is predicted (2), Turkey must enlarge her yellow cake production capacity. Certain amount of production, even though at low level, can of course be desirable as far as the commercial relations and reliability of supply is concerned. According to the timing of technological studies and yellow cake production prepared by MTA and Etibank (see table 11.2), Turkey will start the commercial yellow cake production as early as 1986. These plans should be put into

Table 11.2 The Timing of Technologic Studies and Yellow Cake Production (48).

URANIUM ORES	1980	1981	1982	1983	1984	1985	1986	1987
MANISA Köprübaşı	Preliminary Contracting Feasibility of Engineering Studies (EtiBank-MTA)	Contracting of Main Plant (EtiBank)	Contracting of Main Plant (EtiBank)	Construction of the Main Plant and Preparation for Commercial Production (EtiBank)	Construction of the Main Plant and Preparation for Commercial Production (EtiBank)	Commercial Production (EtiBank)	Commercial Production (EtiBank)	Commercial Production (EtiBank)
MANISA Alerpehir	Evaluation of Pilot Plant Studies (MTA)	Field Studies and Drilling (MTA)	Field Studies and Drilling (MTA)	Field Studies and Drilling (MTA)	Field Studies and Drilling (MTA)	Commercial Production (EtiBank)	Commercial Production (EtiBank)	Commercial Production (EtiBank)
UŞAK Fakılı	"	"	"	"	"	"	"	"
AYDIN Kocanlı	Laboratory Studies (MTA)	Pilot Plant Studies (MTA)	Pilot Plant Studies (MTA)	Field Studies and Drilling (MTA)	Field Studies and Drilling (MTA)	"	"	"
GİRESUN Şebinkarahisar	"	"	"	"	"	"	"	"
ÇANAKKALE Küçükkuyu	Laboratory (MTA + A.E.K.)	Pilot Studies (M.T.A)	Pilot Studies (M.T.A)	Field Studies, Drilling and Preliminary Feasibility (M.T.A)	Field Studies, Drilling and Preliminary Feasibility (M.T.A)	Field Studies, Drilling and Preliminary Feasibility (M.T.A)	Field Studies, Drilling and Preliminary Feasibility (M.T.A)	Field Studies, Drilling and Preliminary Feasibility (M.T.A)

- (1) Laboratory and pilot plant studies of Taşharman and Yarabere locations which are considered to be problem areas, will continue.
- (2) If samples could be obtained, pilot plant studies will be conducted at Köprübaşı Ecinliyaş area.

operation soon or at least any delays beyond the times shown on table 11.2, shouldn't be allowed.

5. It has already been mentioned that the last step reached in Turkey is the yellow cake production step. Further steps to be taken after the yellow cake production is an unknown since Turkey does not have a certain nuclear energy policy. Nuclear fuel production has many uncertainties in the near future due to governmental changes and regulatory obstacles. For the realization of nuclear technology in Turkey, the first step might be the organisation of a nuclear fuel services group. A number of complex problems faced in nuclear fuel technology can effectively be handled by such a nuclear fuel services group concerned with the future nuclear energy supply of Turkey.

6. To bridge the future energy gap, accelerated efforts should to be directed to construct a national nuclear fuel production policy. A country can furnish its own fuel cycle technology within 10-20 years depending upon the level of industrial development. Today most of the European countries having nuclear technology have developed their fuel technology through licencing agreements with the countries leading in this area. This might be a route to follow for Turkey, also. The most important aspect of this choice is to try to develop the transferred technology with national means and to adapt to national goals and priorities.

REFERENCES

1. TUNABOYLU,KAHRAMAN ; "Nükleer Yakıt Çevrimi,Sorunları ve Bu Alanda Türkiye'de Yapılabilecek Çalışmalar",Proceedings of Türkiye 3. Genel Enerji Kongresi, p.548-585, ANKARA,1978.
2. HOLDEN,ROBERT B. ; "Ceramic Fuel Elements",Gordon & Breach Science Publishers, NEWYORK,1966.
3. OLANDER,DONALD R. ; "Fundamental Aspects of Nuclear Reactor Fuel Elements",Published by ERDA Technical Information Center, Oak Ridge,Tennessee, U.S.A,1976.
4. FINNISTON,H.M. & HOWE,J.P. ; "Metallurgy and Fuels",Pergamon Press Ltd.,LONDON,1956.
5. SHAPPER,PETER T.B. & HAWSNER,HENRY H. ;"Plenum Press Handbooks of High-Temperature Materials,No:1 Material Index",Plenum Press, p.370,NEWYORK,1963.
6. INTOSH,A.B MC & HEAL,T.J. Ed's ; "Materials for Nuclear Engineers", Interscience Publishers,NEWYORK ,1960.
7. KATZ,JOSEPH J. & RABINOWITZ,EUGENE ;"The Chemistry of Uranium The Element,Its Binary and Related Compounds",Dover Publications Inc.,Chap.13,NEWYORK,1951.
8. YEMEL YANOV, V.S & YEVSYUKHIN, A.I. ;"The Metallurgy of Nuclear Fuel",Pergamon Press, GERMANY,1969.
9. HEPSİN,TUNCER ;"Muğla Yatagan Bölgesindeki Uranyumlu Linyitlerden Uranyumun Değerlendirilmesi",Çekmece N.A.E.M Matbaası,İSTANBUL, 1976.
10. WILLS,J.GEORGE ;"Nuclear Power Plant Technology",John Wiles & Sons Inc, U.S.A,1967.
11. NININGER,ROBERT D. ;"Mineral for Atomic Energy",D.Van Nostrand Company Inc.,CANADA,1956.
12. BOXER,L.W.,HAUSSERMANN,W.,COMERON,J.,ROBERTS,J.T. ;"Uranium Resources,Production and Demand",Proceedings of the Fourth International Energy Conference ,Geneva,Published by IAEA,Vol.8,p.3-11,AUSTRIA 1972.

13. HANSEN, M.V. ; "World Uranium Resources", Proceedings of International Atomic Energy Agency Bulletin, Vol.23, No.2, p.10, VIENNA, 1981.
14. BARRETTO, P.M. ; "Recent Developments in Uranium Exploration", Proceedings of The International Atomic Energy Bulletin, Vol.23, No.2, p.15-20, VIENNA, 1981.
15. MININGER, ROBERT D. ; " Exploration For Nuclear Raw Materials", Mac Millan and Co.Limited, part.2, U.S.A, 1956.
16. CLAYTON C.G. ; "Applications of Radioisotope X-ray Fluorescence Analysers in Metalliferous Mineral Exploration and In Mining", Proceedings of a Panel on Nuclear Techniques and Mineral Resources in Developing Countries, p.27, CRACOW, 1969.
17. HAMBLETON, B.B. & JONES, D. ; "Theory and Practice of Geochemical Prospecting For Uranium", Proceedings of Minerals Sci. Engng, Vol.10, No.3. July, 1978.
18. IPEKOGLU, B., ERDINE, H., UZEMEN, R. ; "Radyoaktif Minerallerin Arama Metodleri ve Son Gelistmeler", C.N.A.E.M Rapor No:186, ISTANBUL, 1978.
19. ROBERTSON, JOHN F. ; "The Atomic Energy Deskbook", Reinhold Publ. Corporation, U.S.A., 1963.
20. SEIDEL, D.C. ; "Extracting Uranium From Its Ores", Proceedings of International Atomic Energy Agency Bulletin, Vol.23, No.2, VIENNA, 1981.
21. I.A.E.A Bulletin, Vol.23, No.2, Front Cover, p.7, p.30, VIENNA, 1981.
22. GITTUS, J.H. ; "Metallurgy of Rarer Elements: Uranium", William Clowes & Sons Limited, Chap.2, Sec.2.4, LONDON, 1963.
23. STEWART, C.G. & SIMPSON, S.D. ; "The Hazards of Inhaling Radon 222 and Its Short-Lived Daughters", Proceedings of the Symposium on Radiological Health and Safety in Mining and Milling of Nuclear Materials, Printed by I.A.E.A, Vol.1, VIENNA, 1964.
24. SCHRAUB, A. ; "Introductory Remarks Concerning Health and Safety in Uranium Mines", Proceedings of the Same Symposium as in Reference 23.

25. HOLADAY, D.A. ; "Some Unsolved Problems in Uranium Mining", Proceedings of the Same Symposium as in Reference 23.
26. BENEDICT, MANSON & PIGFORD, H. THOMAS. ; "Nuclear Chemical Engineering", Mc Graw-Hill Book Company, U.S.A, 1957.
27. BELLAMY, R.G. & HILL, N.A. ; "Extraction and Metallurgy of Uranium, Thorium and Beryllium", Pergamon Press, Chap.6, NEWYORK, 1963.
28. AHMED, J.U. ; "Occupational Radiological Safety in Uranium Mines and Mills", Proceedings of I.A.E.A Bulletin, Vol.23, No.2, VIENNA, 1981.
29. EICHHOLZ, G.G. ; "Airmonitoring During Uranium-Steel Fabrication Processes", Proceedings of the Same Symposium as in Reference 23.
30. SMITH, C.F. ; "The Control of Radiation Hazards in Canadian Uranium Mines and Mills with Specific References to the Beaverlodge Operation of Eldorado Mining and Refining LTD.", Proceedings of the Same Symposium as in Reference 23.
31. COOPER, A.R. ; "Chemical Processing In the Atomic Energy Industry", Iliffe Books Ltd., LONDON, 1964.
32. TAGGART, ARTHUR F. ; "Handbook of Mineral Dressing", John Wiley & Sons Inc., U.S.A, 1945.
33. FLAGG, JOHN F. ; "Chemical Processing of Reactor Fuels", Academic Press Inc., Chap.II, NEWYORK, 1961.
34. GURINSKY, H.DAVID & DIENES, G.J. ; "Nuclear Fuels", D.Van Nostrand Company Inc. NEWYORK, 1956.
35. BURKIN, A.R. ; "The Chemistry of Hydrometallurgical Processes", E F.N. Spon Ltd., Chap.1, LONDON, 1966.
36. GLASSTONE, SAMUEL & SESONSKE, ALEXANDER. ; "Nuclear Reactor Engineering", Van Nostrand Reinhold Company, NEWYORK, 1967.
37. KOPELMAN, B. ; "Materials For Nuclear Reactors", Mc-Graw-Hill Book Comp., U.S.A, 1959.
38. BOLTAX, ALVIN. ; "Nuclear Materials", Mc-Graw-Hill Book Comp., Chap.4, U.S.A, 1964.

39. "BRITAIN'S ATOMIC FACTORIES" Prepared by the Ministry of Supply and the Central Office of Information, LONDON, 1954.
40. VILLANI, STELIO. ; "Isotope Separation", Publ. by The American Nuclear Society, Chap. 3, 5, U.S.A, 1976.
41. VILLANI, STELIO. ; "Uranium Enrichment", Springer-Verlag Berlin Heidelberg, GERMANY, 1979.
42. BELLE, J. ; "Basic Metallurgy and Fabrication of Fuels", Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. 6, p. 12404, U.Nations, GENEVA, 1958.
43. KAUFMANN, ALBERT R. ; "Nuclear Reactor Fuel Elements, Metallurgy and Fabrication", John Wiley Sons, Inc. Chap. 6, U.S.A, 1962.
44. EVCİMEN, TURHAN HİPZİ & ÇETİNÇELİK, MUAMMER ; "The Importance of Radioactive Minerals In Turkey for Future Nuclear Energy Production", Proceedings of the Tenth World Energy Conference, Division: 3, p. p-3.2, ISTANBUL, 1977.
45. SAGDIK, UTKU ; "Türkiye'nin Nükleer Yakıt Yapımı Olanaklarının Araştırılması", Proceedings of Türkiye 3. Genel Enerji Kongresi, Sec: 1, p. 596-601, ANKARA, 1978.
46. BİRSEN, NEVZAT ; "Dünya Uranyum Kaynakları, Yeterliliği ve Türkiye'nin Uranyum Potansiyeli 1980", AEK Teknik rapor No: 1 ANKARA, 1980.
47. YARMAN, TOLGA ; "Enerji: Nükleer Enerji ve Alışılmamış Enerji Kaynakları , Dünya ve Türkiye", Bulletin of Bogaziçi University, Vol. 7, ISTANBUL, 1979.
48. SAGDIK, UTKU ; MTA , ANKARA (Private Communication).
49. UZKUT, İSMET ; "Deniz Suyundan Uranium Elde Edilimi ve Türkiye İçin Önemi", Proceedings of 6. Türkiye Madencilik Bilimsel ve Teknik Kongresi, T.M.M.O.B Maden Mühendisleri Odası Yayınları, ANKARA, 1979.
50. SAGDIK, UTKU ; "Türkiye'de Sarı Pasta Üretimi için Mevcut Potansiyelin Değerlendirilmesi", MTA Enstitüsü Teknoloji Dairesi, p. 6-12, ANKARA, 1981.

51. ALTIN, VURAL & ENGİNOL, TURAN.B. & BORAK, FAHİR & GREEN, MICHAEL, D. SANCAKTAR, SELİM ; "Karadeniz Dip Çamurundaki Uranyumun Değerlendirilmesi", Proceedings of Türkiye 3. Genel Enerji Kongresi, Sec. 1, p. 384-389, ANKARA, 1978.
52. UZKUT, İSMET ; "Yeni Bir Nükleer Enerji Hammadde Kaynağı, Boğazlar", Proceedings of 5. Türkiye Madencilik Bilimsel ve Teknik Kongresi, T.M.M.O.B Maden Müh. Odası Yayınları, ANKARA, 1977.
53. ONAL, GUVEN ; "Mazıdağı Fosfat Cevherlerindeki Uranyumdan Yararlanma Olanakları".
54. KING, JOHN .W. ; "Türkiye'de Uygulanmakta Olan Modern Uranyum Arama Yöntemleri", Proceedings of 5. Türkiye Madencilik Bilimsel ve Teknik Kongresi, T.M.M.O.B Maden Müh. Odası Yayınları, ANKARA, 1977.
55. KING, JOHN & TOUCHID, MOHAMMED & FREY, DORREL & BASSET, MARCEL ÇETİNTURK, İBRAHİM AYDINOZ, FEVZİ KEÇELİ, BİLSEL ; "Güney Batı Anadolu'da Uranyum Aramaları" Tercüme No:35.
56. "Dünya Maden Haberleri" Bulletins of MTA, 1964-1968, ANKARA.
57. KALAFATÇIOĞLU, ADNAN ; "Uranyum Kaynakları ve Türkiye'nin Muhtemel Uranyum Bölgeleri", Ayyıldız Matbaası A.Ş., Energy World Bulletin Special Publication, ANKARA, 1976.
58. UTKU, SADIK ; "Taşharman Uranyum Cevherlerinin Teknolojik Değerlendirilmesi", Proceedings of 5. Türkiye Madencilik Bilimsel ve Teknik Kongresi, T.M.M.O.B Maden Müh. Odası Yayınları, ANKARA, 1977.
59. UZMEN, REŞAT ; "Türkiye Uranyum Cevherlerini Değerlendirme Çalışmalarına Katkı", Ç.N.A.E.M Rapor No:185, p.103-summary, İSTANBUL, 1979
60. SAGDIK, UTKU & ÇIRALI, BAYRAM & BILGEN, NAZIM & ONGEL, MEHMET & MENTEŞE, FAHİR & GURBÜZALIK, ERCAN & ALKAN, HALİL & AKKAŞ, MUZAFFER ; "Kasar Uranyum Cevherlerinin Pilot Çapta Değerlendirilmesi", Proceedings of 5. Türkiye Madencilik Bilimsel ve Teknik Kongresi, T.M.M.O.B Maden Müh. Odası Yayınları, ANKARA, 1977.
61. KASA, BAYRAM & İPEKOĞLU, BEDRİ & İKİZOĞLU, FEVZİ ; "Salihli-Köprübaşı MTA Uranyum Pilot Tesisinde 28-30.9.1977 Tarihinde Yapılan Gezi Raporu", Ç.N.E.A.M Yayınları, 1977.

62. EVCİMEN, TURHAN HIFZİ ; "Türkiye'de Planlanan Nükleer Elektrik Üretiminin Dayandığı Birincil Kaynakları ve Bazı Nükleer Yakıt Sorunları", Proceedings of Türkiye 3. Genel Enerji Kongresi, Sec.1, p. 492-517, ANKARA, 1978
63. BIRSEN, NEVZAT ; T.A.E.K., ANKARA (Private Communication).
64. KOPUZ, BAYRAM ; Ç.N.E.A.M., İSTANBUL (Private Communication).
65. İPEKÖĞLU, BEDRİ ; Ç.N.E.A.M., İSTANBUL (Private Communication).