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

by

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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 üretimiyle 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.

## ACKNOWLEDGEMENTS

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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 $165 \times 10^9$ KWh, in the year 2000 the demand,however,willreach to a value of $250 \times 10^9$ KWh. On the other hand,it is estimated that when all known national fossil and hydraulic potential is used to generate electiricity,Turkey will have an energy production potential of $150 \times 10^9$ 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 the se studies have been carried out by different groups and organisations.To our knowledge there has not been a single reference that bring 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 technigues. 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.

# Chapter 2
## 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 temparature, 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 prefered in most commercial power reactors.

Uranium dioxide is the most commen 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-temparature 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 temparature gradient as well as thermal conductivity. Poor thermal conductivity will result in the requirement of large centerline 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.

$UO_2$ powder has good response to some fabrication techniques. Important properties of $UO_2$ are summarized in table 2.1.

Table 2.1. Important Properties of $UO_2$ (2,4).

| Property | $UO_2$ |
|---|---|
| Crystal structure....... | Face-centered cubic |
| Lattice , $°A$ ............. | 5.472 |
| X-ray density g/$cm^3$...... | 10.95 + 10.97 |
| Melting point, $°C$ ....... | 2800 |
| Thermal conductivity.... cal.cm/$°C$.$cm^2$.sec(corrected to 100% density) | 0.02 - $20°C$ <br> 0.008 - 1000 $°C$ |
| Expansivity , $°C^{-1}$ ..... | 10.3 x $10^6$ (25-1000 $°C$) |
| Specific heat, ........ (cal/g/ $°C$ | 0.056 (25 $°C$), 0.078 (1000 $°C$). |
| Heat of formation, .... cal/mole | -259,500 (25-1200 $°C$). |
| Free energy of formation , cal/mole | -246,600 ($25°C$). <br> -218,100 (727 $°C$). <br> -197,700 ($1227°C$). |
| Entropy, cal/mole/ $°C$ .. | 6.67 x $10^{-5}$ (1102 $°C$). |
| Vapor pressure ,mm Hg .. | 9.66 x $10^{-1}$ (2363 $°C$). |
| Tensile strength ....... | c. 5000 p.s.i |
| Modulus of elasticity... | 25x$10^6$ p.s.i |
| Thermal n capture .... cross section | 0.165 $cm^2$ /$cm^3$ (5) |

The crystal sturucture of $UO_2$ is the face-centered cubic fluorite ($CaF_2$) type. Uranium ions occupy corners and faces. The cell dimension was measured to be 5.472 $°A$. The lattice is relatively "open" and the oxygen has a negative partial molal volume. As excess oxygen is added to $UO_2$, 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 liliting power of a fuel element. The melting point of stoichiometric $UO_2$ is shown to be 2865 $°C$ by investigators, although other investigations have found that $UO_2$ melts at 2800 $°C$. Much below this temperature, however, an appreciable vapour pressure is observed. During sintering, $UO_2$ looses weight at temperatures as low as 1400 $°C$. Sinter furnace walls are coloured besides being radioactive indicating its volatility. The volatility of $UO_2$ 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 $1200^0C$ , $U_3O_8$ 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 , $^0C$ | 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 stuructures of oxide compositions are dependent on temperature; the oxide above 500 $^0C$ 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 $^0C$ (7). $U_3O_8$,however,begins to lose oxygen at temperatures above 550 $^0C$-$600^0C$ and turns into $UO_2$ in between the temperatures of $1150^0$ C and $1400^0$ C. At higher temperatures $UO_2$ presents the stable phase.

## 2.2 .CHEMICAL PROPERTIES OF $UO_2$

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 absorbsion and core size, using thick-wall cladding to prevent oxidation hazard will result in a negative effect on reactor economics.

An overriding advantage of $UO_2$ as fuel is its good compatibility with cladding and coolant materials. Both stainless-steel and zircaloy are suitable as cladding materials for $UO_2$ fuel.

Stainless-steel: At temperatures $< 1400\ ^0C$ , $UO_2$ does not react with stainless steel. Even at higher temperatures stainless steel is suitable as cladding material.

Zirconium-$UO_2$ 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 : $UO_2$ reacts with zircaloy-2 less rapidly than un-alloyed Zr.

Aluminium : $UO_2$ reacts with Al. at 600 $^0C$.The reaction is relatively slow at this temperature with $UO_2$ grains larger than 40$\mu$.Reaction products are $UAl_3$, $UAl_4$ and $Al_2O_3$ .

M0,Nb,Ta,Tungsten : $UO_2$ shows good compatibility with these up to their melting points.

Carbon : $UO_2$ in the powder form reacts with C at temperatures as low as 1400 $^0C$. $UC_2$ or $U_2C_3$ are the products.

Hydrogen : $UO_2$ does not react with hydrogen at temperatures up to its melting point.

Silicon : In the temperature range 1900 $^0$- 2100 $^0C$, $UO_2$ reacts with silicon and forms $USi_3$.

Acids : $UO_2$ is soluble in $HNO_3$, not in HCl. The reaction product of $UO_2$ with HF is $UF_4$.

Bases : $UO_2$ does not react with NaOH solutions but is soluble in sodium peroxide forming $Na_2UO_4$.

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 necassary to know the response of $UO_2$ to coolant materials.

Water : $UO_2$ does not react with $H_2O$ at temperatures below 300 $^0C$ and no reaction is expected at higher temperatures. Sintered or

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

$$k = \frac{38.24}{T+129.4} + 4.788 \times 10^{-13} T^3 \ (T.°K)$$

• Out of pile Data
△ Data from grain size analysis



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



$$\% expansion = 1.723 \times 10^{-2} + 6.797 \times 10^{-4} T + 2.896 \times 10^{-7} T^2 \ \text{in range 1000 to 2250 C}$$

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



Melting temperature

Density decrease on melting = 9.6 %

Fig.2.4. Thermal expansion of UO₂(2).



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

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Relatively Unreacted Zirconium

Oxygen Dissolved in Alpha Zirconium

Stained zone

Alpha Uranium + Alpha zirconium

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

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

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

Liquit 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 molat 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) | $\overline{S}_{987}$(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 isotermal elastic moduli of polycrystalline stoichiometric $UO_2$ at $25^0C$ are as follows and given in figure 2.10.

$$E = 2.19 \times 10^8 \text{ kN} / \text{m}^2 \text{ (Young's modulus)}$$
$$G = 8.14 \times 10^7 \text{ kN}/ \text{m}^2 \text{ (Shear modulus)}$$

Polycristalline $UO_2$ 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 $\sim 1200$ $^0C$.The temperature range between 1200-1400 $^0C$ is the region of semibrittle behaviour and at temperatures above 1400 $^0C$ $UO_2$ experiences considerable ductility.
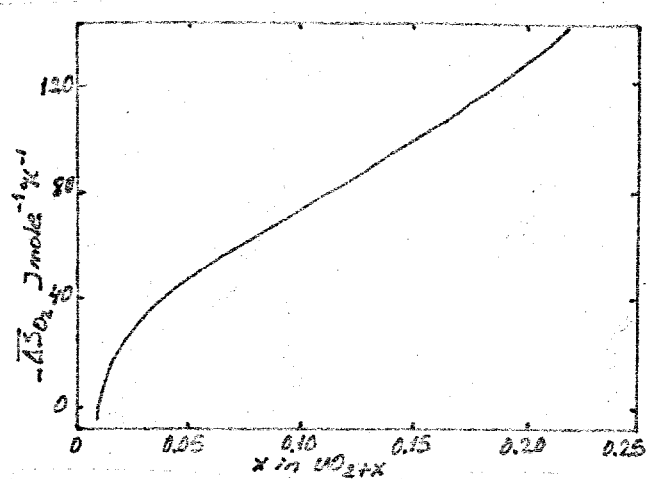
Fig.2.7. Partial molar entropy of oxygen in $UO_{2+x}$ (3).
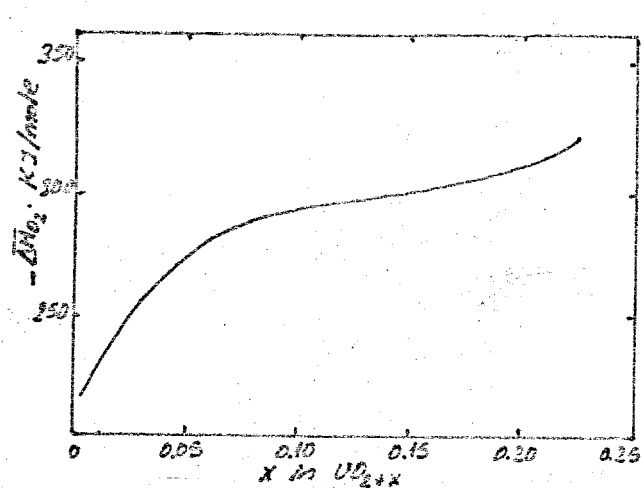


Fig.2.8. Partial molar enthalpy of oxygen in $UO_{2+x}$ (3).
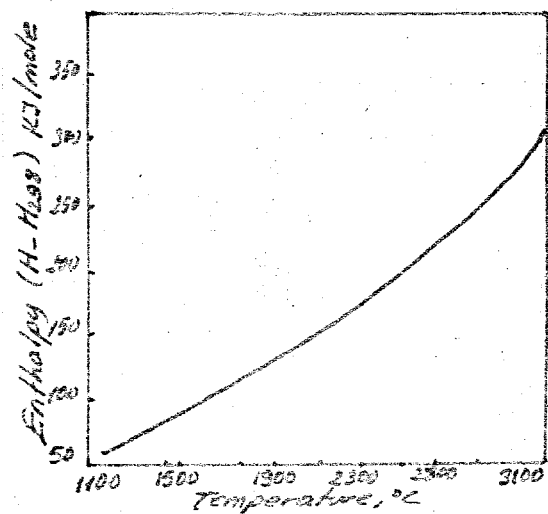


Fig.2.9 Enthalpy- Temperature data for stoichiometric $UO_2$ (4).
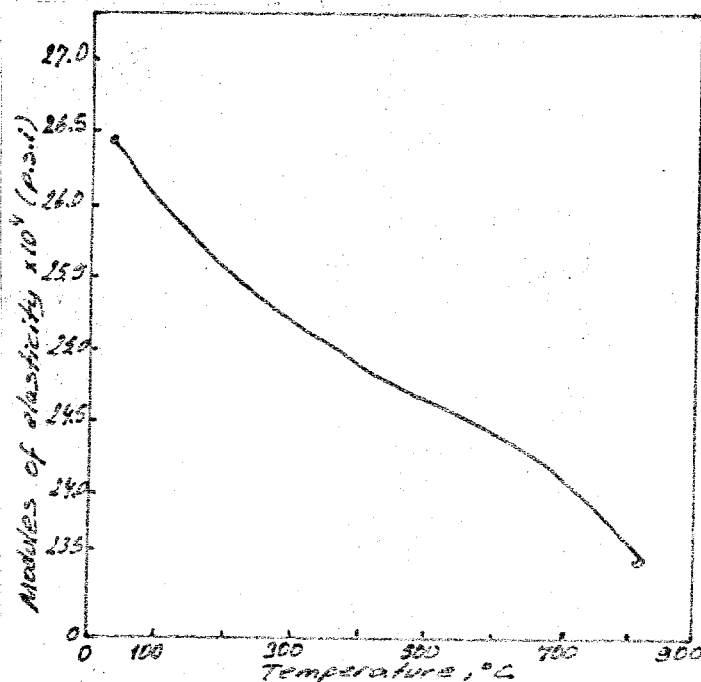


Fig.2.10. Modules of elasticity of sintered $UO_2$ (6).
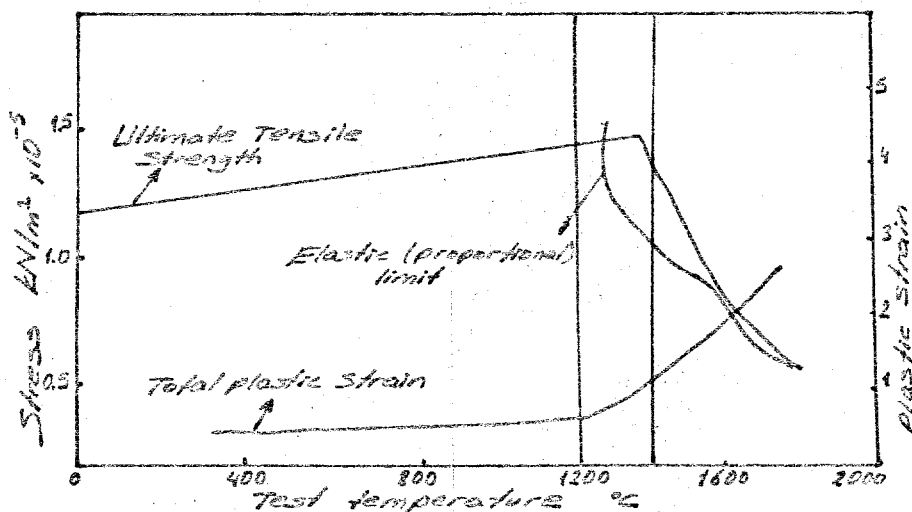


Fig.2.11. Fructure and flow characteristics of $UO_2$ as a function of temperature, ultimate tensile stress, elastic limit, and total plastic strain (3).

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# 3. URANIUM ORES AND DEPOSITS

## 3.1. URANIUM IN THE EARTH'S CRUST

The earth's crust contains about $3 \times 10^{-4}$ % 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 ignerous rocks are summarized in table 3.1.

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

      Ocean waters: $\quad 0.3 \times 10^{-6} - 10^{-5}$ g/l.

      Lake waters: $\quad 3 \times 10^{-8} - 10^{-3}$ g/l.

      River waters: $\quad 3 \times 10^{-8} - 10^{-4}$ g/l.

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

| Uranium Content % | | | | Author and date for determination of uranium content |
|---|---|---|---|---|
| Acid Rocks | Intermediate Rocks | Basic Rocks | Ultrabasic Rocks | |
| $7.01 \times 10^{-4}$ | $5.6 \times 10^{-4}$ | $3 \times 10^{-4}$ | $6 \times 10^{-5}$ | Jeffries (1936) |
| $6 \times 10^{-4}$ | — | — | — | I.O. Komlev (1938) |
| $2.8 \times 10^{-4}$ | — | $9.4 \times 10^{-5}$ | — | Keevil (1938) |
| $4.01 \times 10^{-4}$ | $1.4 \times 10^{-4}$ | $1.1 \times 10^{-4}$ | $6 \times 10^{-5}$ | Goodman and Evans (1941) |
| $2. \times 10^{-4}$ | — | $2 \times 10^{-5}$ | — | Hoffmann (1941 to 42) |
| $3.9 \times 10^{-4}$ | $2.6 \times 10^{-4}$ | — | — | Senftle and Keevil (1947) |
| $4.3 \times 10^{-4}$ | — | — | — | A.O. Vinogradov (1955) |
| $3.4 \times 10^{-4}$ | — | $7 \times 10^{-5}$ | — | Patterson (1955) |
| $2.7 \times 10^{-4}$ | $1.8 \times 10^{-4}$ | $1.8 \times 10^{-4}$ | — | Adams (1955) |
| $5.7 \times 10^{-4}$ | — | $6 \times 10^{-6}$ $2.1 \times 10^{-4}$ | — | I.O. Komlev (1956) |
| $3.5 \times 10^{-4}$ | $1.8 \times 10^{-4}$ | $5 \times 10^{-5}$ | $S \times 10^{-7}$ | A.P. Vinogradov (1962) |
| $4 \times 10^{-4}$ | $1.6 \times 10^{-4}$ | $7 \times 10^{-5}$ | — | 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 sedimantary 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 initimately 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 |
| Tyuyamunite | 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 occuring 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 magnatised rocks with uranite. |
| | II. HYDROTHER- MAL 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 deposites, formed by metasomatosis of lateral rocks. 6. Uranium, uranium-molybdenum and other columnar deposits and veins formed by filling of open cavities and by metasomatosis of lateral rocks. |
| B. EXOGENOUS DEPOSITS | III. SYNGENE- TIC 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. EPIGENE- TIC (INFILTRATION) DEPOSITS IN CONTINETAL 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. METAMORP- HIC DEPOSITS | 13. Lamellar gold-uranium and uranium thorium deposits in pre-paleozoik conglomerates. |
| C. EXOGENOUS DEPOSITS | VI. ANCIENT METAMORPHI- SED ALLUVIAL DEPOSITS | 14. Lamellar gold-uranium and uranium thorium deposits in pre-paleozoik 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.
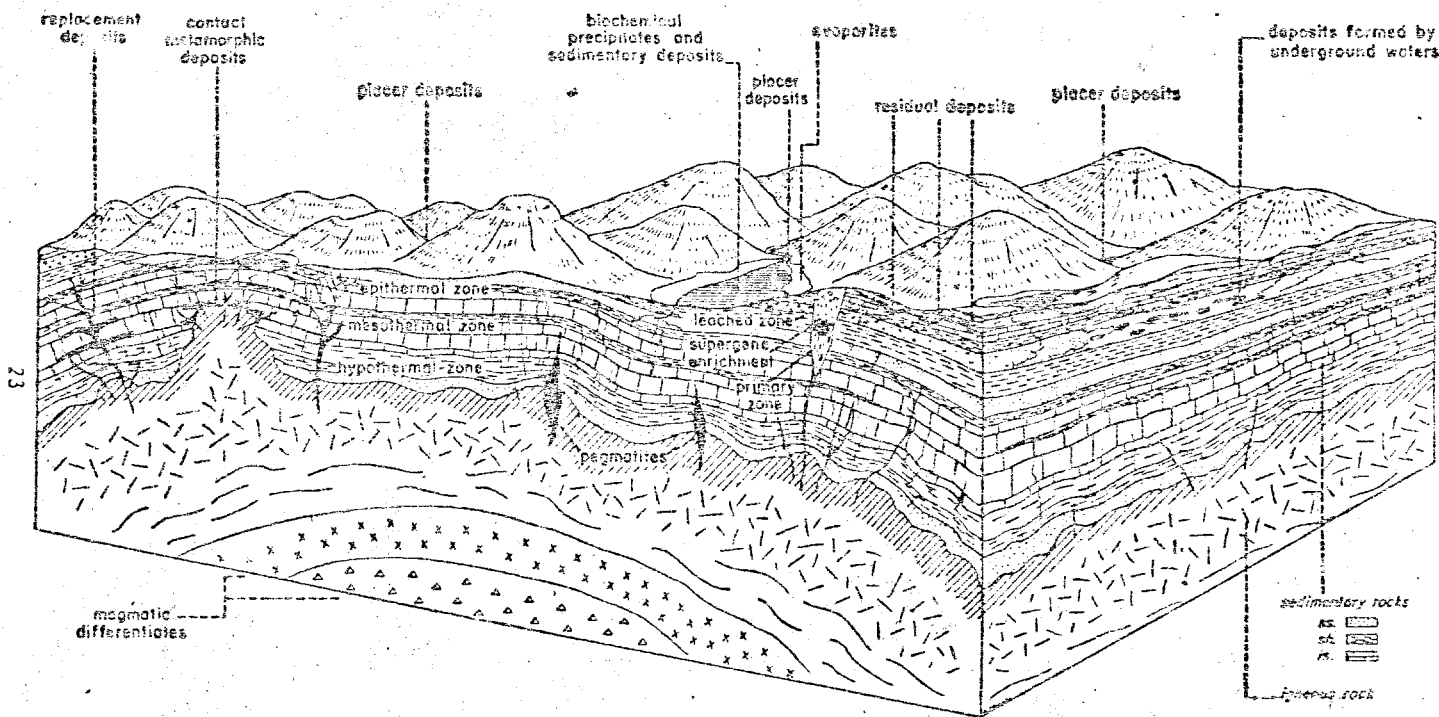
Fig.3.1. Origin and formation of mineral deposits (11).

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 catent 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 Reosonable 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 | 1.90 | 6.0 | 16.0 |
| b) Columnar " | 20,000 | 20,000 | 1.90 | 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 | 5,500 | 1,000 | 0.30 | — | — |
| 6. Ancient Conglomerates | 370,000 | 100,000 | 0.08 | 67.0 | 54.0 |
| 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 continiued and reached ∿ 36500t in 1979. On the other hand the maximum production capasities 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 | REGİON |
|---|---|
| U.S.A | Colarado,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/kgU Reasonably Assured 1000 tonnes U | US $130/kgU Reasonably Assured 1000 tonnes U | US $80/kgU Estimated Additional 1000 tonnes U | US $130/kgU 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 | | | 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 | 5 | | | - |
| Finland | 1959 | 1958 | <100 | 0 | 3 | 0 | <1 | | | moderate |
| France | 1945 | 1949 | 29600 | 38 | 54 | 26 | 46 | 4500 | 1986 | moderate/high |
| Gabon | 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(Reb.) | - | - | 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 |
| Sweeden | 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 |
| India | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 |
| Italy | 0 | 0 | 120 | 120 | 120 | 120 | 120 | 120 | 120 | 120 | 120 | 120 |
| 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 |
| Sweeden | 0 | 0 | 0 | 0 | 400 | 400 | 400 | 400 | 400 | 400 | 400 | 400 |
| U.S.A | 19000 | 20900 | 24300 | 27100 | 30900 | 33600 | 34100 | 35000 | 38400 | 40800 | 42600 | 44200 |
| Yugoslavia | 0 | 0 | 120 | 120 | 120 | 130 | 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 aresuggested. 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. Thefield 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 km$^2$)
  Scale of map : 1:250000 to 1:100000
  Photogeological interpratation
  Reconnaissance geology
  Radiometric survey:
    (Gross-count, $\gamma$-ray spectrometry)
    Airborne, carborne
  Geochemical survey:(0.1-1 sample/km$^2$)
    Heavy mineral, lake sediment, stream
    Sediment, water

                    $\downarrow$  $\longrightarrow$  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 interpratation
  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$^2$ )

                 $\downarrow$  $\longrightarrow$  Insignificant anomalies
                                      (Filed)

IV. Detailed Stage (High density)

  Significant anomalies (2-20km$^2$)
  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$^2$)*

                 $\downarrow$  $\longrightarrow$  False anomalies(Filed)

V. Exploration Development Stage

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

                 $\downarrow$  $\longrightarrow$  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 delination 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 $km^2$ 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 $km^2$ 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
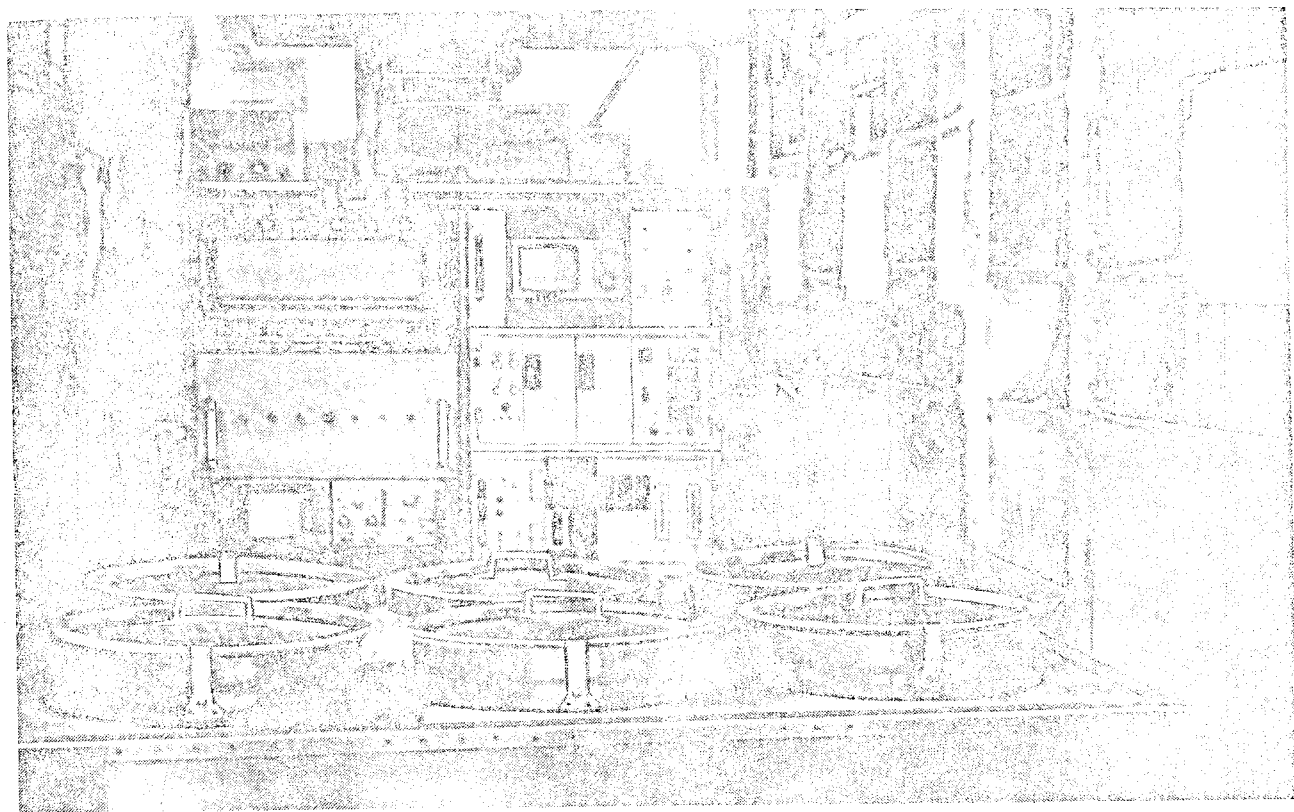
Fig. 4.1. Airborne γ-ray spectrometric system consisting of six large sodium iodide - NaI(TL)-detectors shown here in the foreground of the picture installed inside a survey aircraft, with the associated electronics behind the detectors [14].

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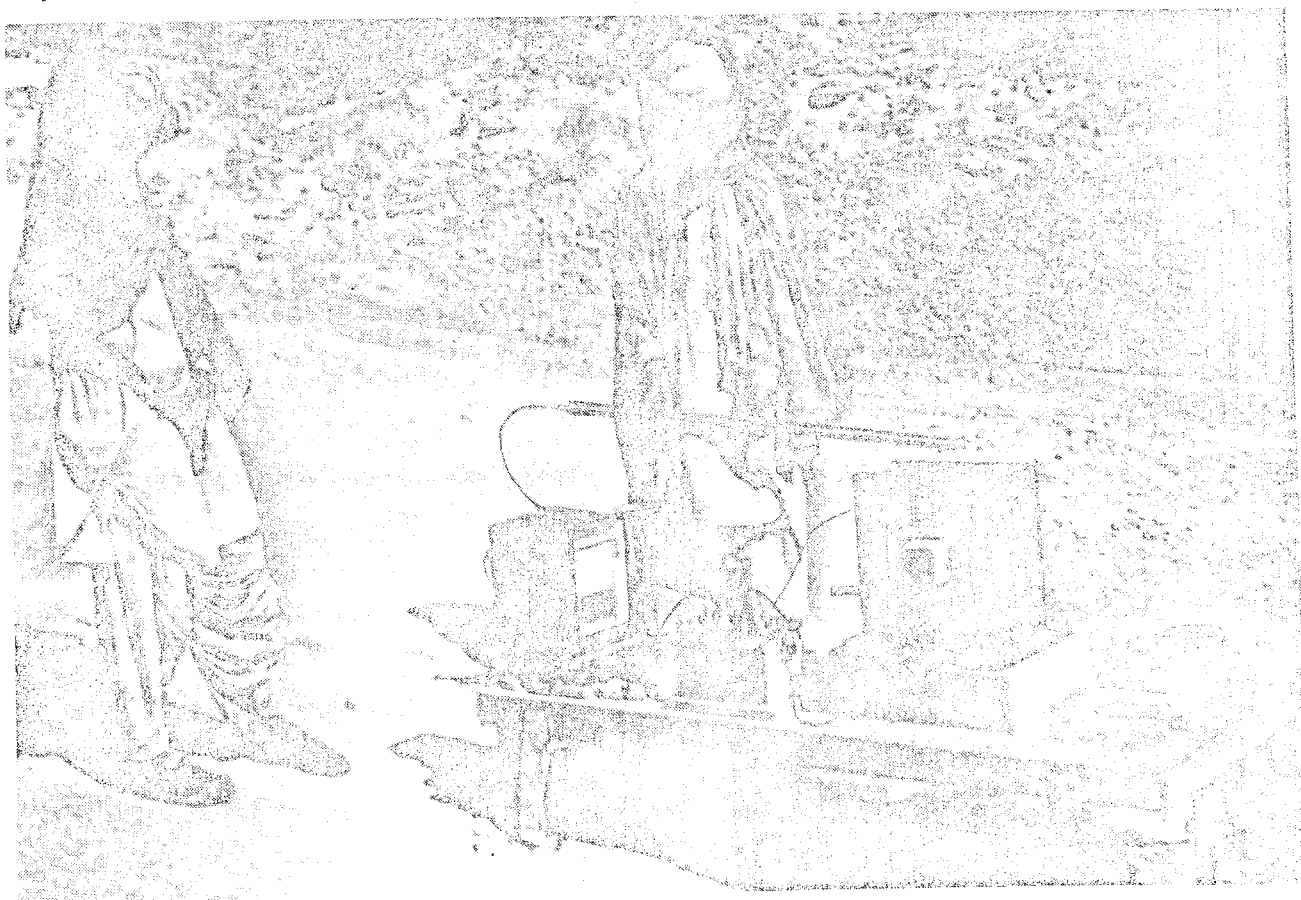
sampled and geological information of anomalous zones is obtained. Then a proper method for further studies is determined in this intermediate phase.

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

This is accomplished by increasing the sampling to 200 samples per $km^2$. The objective of this phase is to distinquish 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 reginal scale. Multispectral reflactance 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 C 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). Int the Blind River region in Canada tracked and trackless undergroundmining methods are applied. Trackless transport is used where the ore beds are inclined at less than 20°; tracked transport for greater inclinations (22).

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[*]At Rossing open-pit mine in Namibia (20)
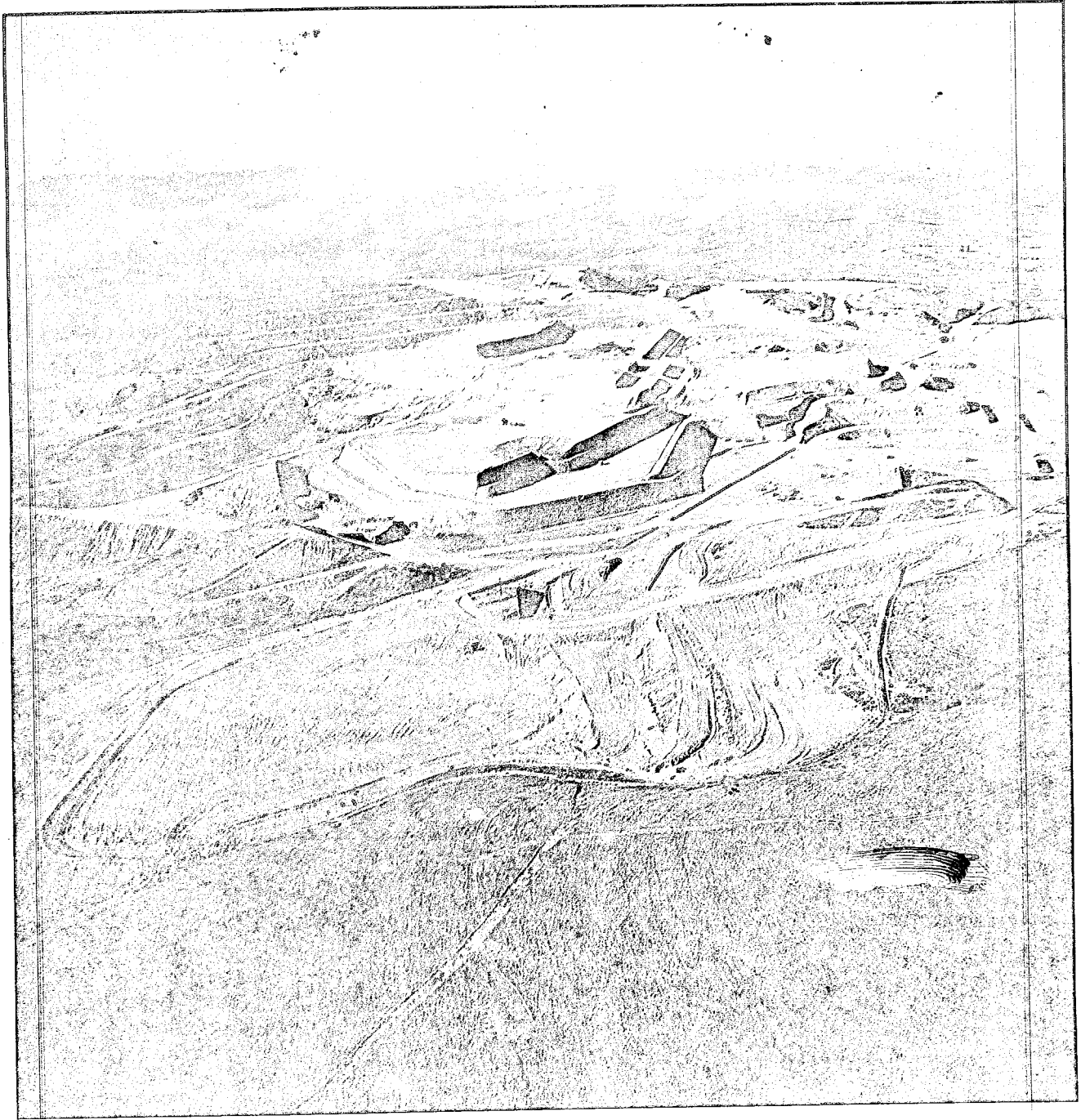
Fig.5.1. The Osamu Utsumi uranium mine in Brasil (21).
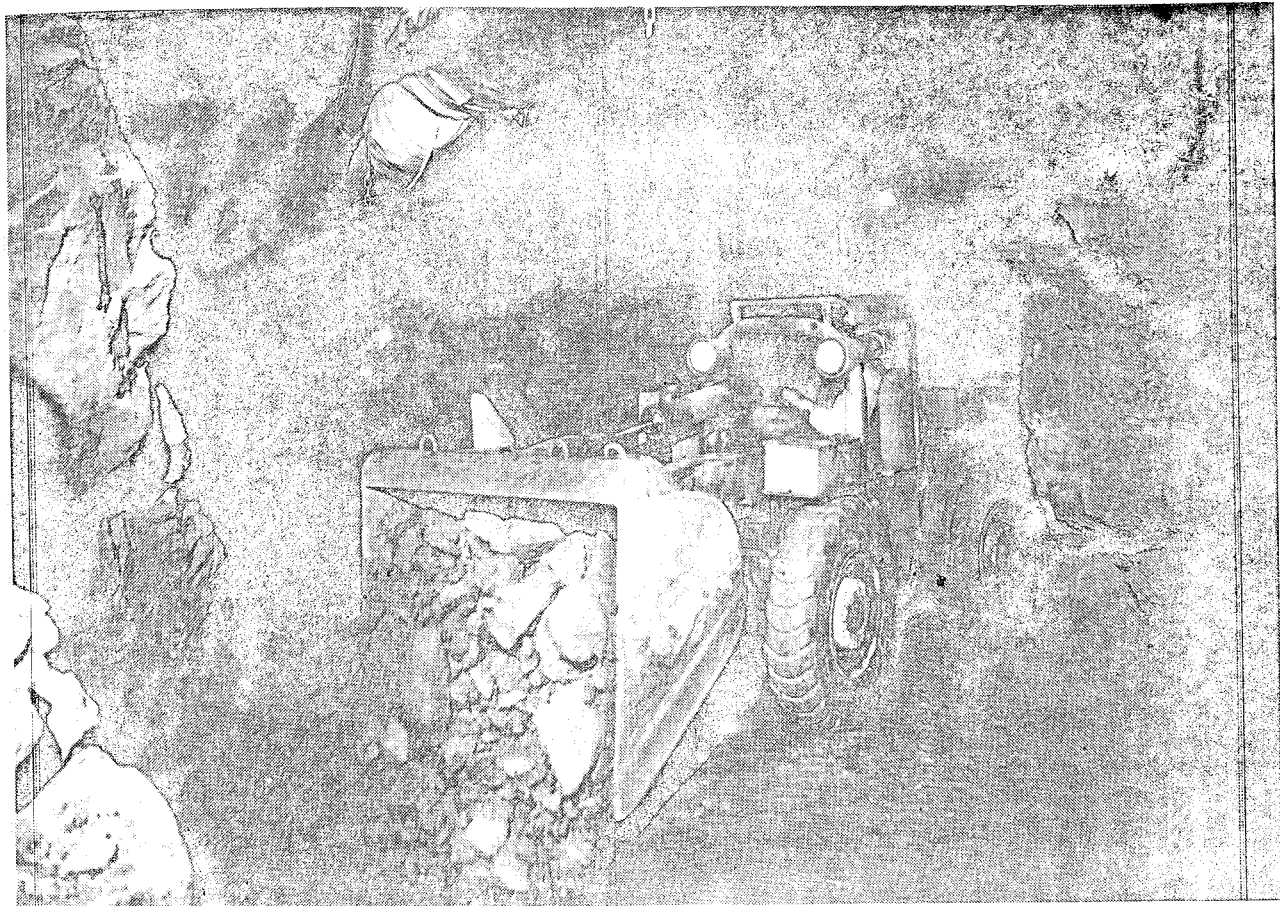
Fig.5.2. Inside an underground uranium mine in the
Vendée region of France (21).
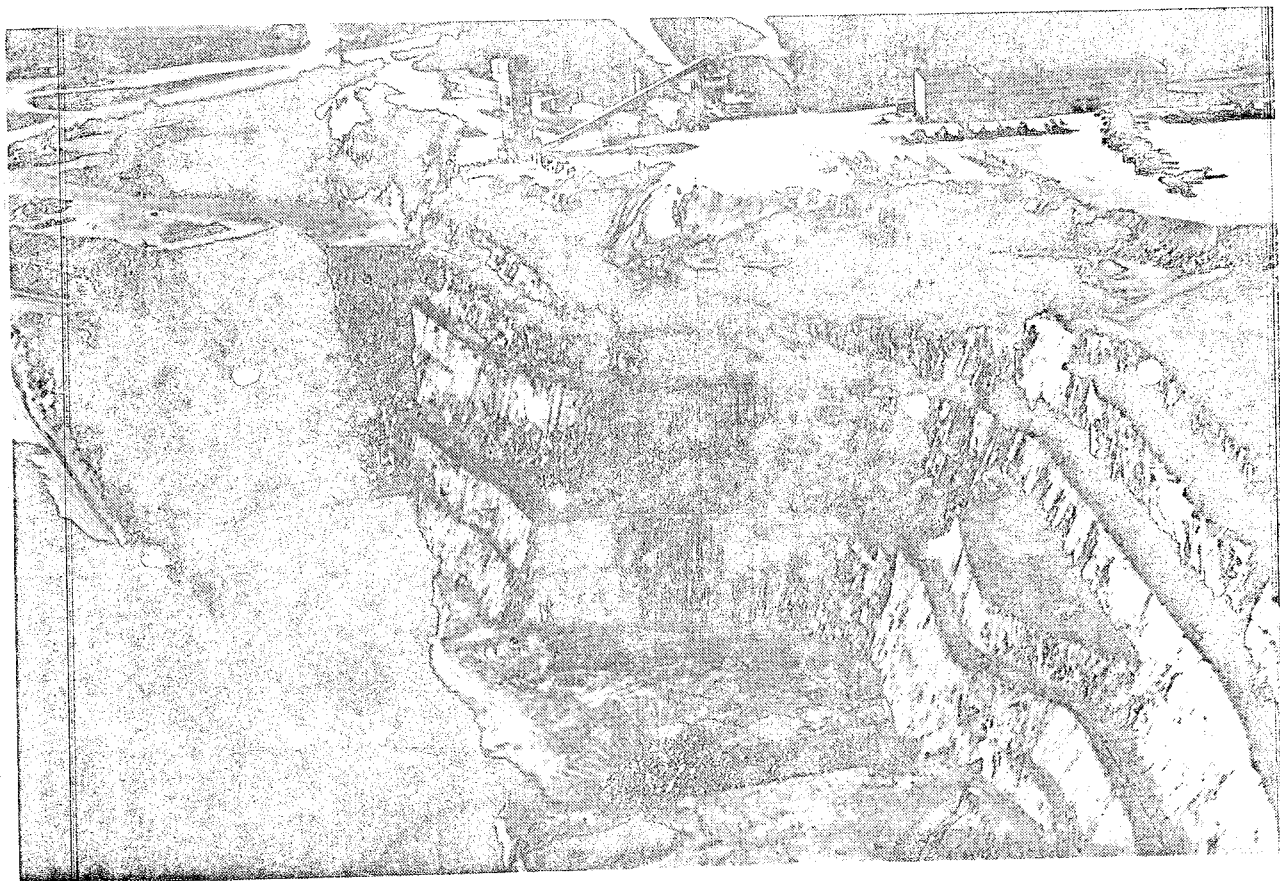


Fig.5.3. An open-pit uranium mine in the Vendée
region of France (21).
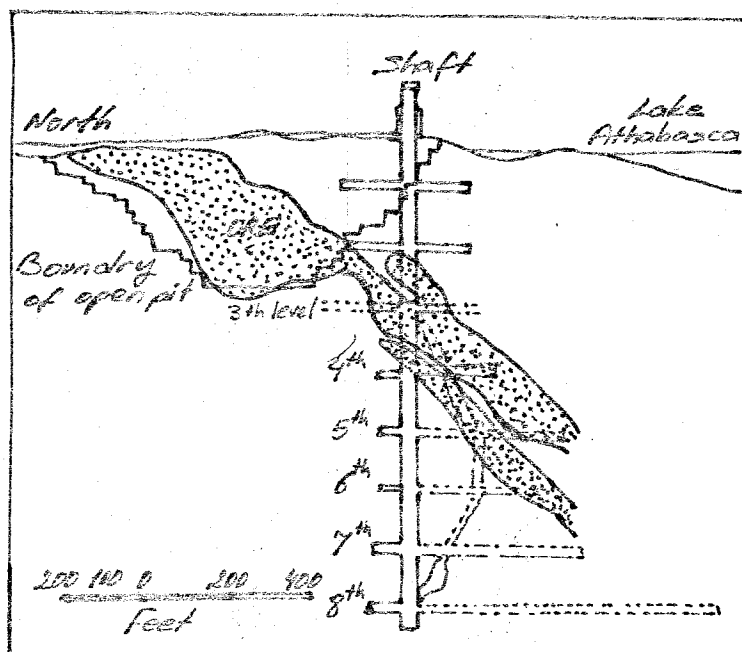
Fig.5.5.Generalized longitudinal sec-
tion along axis of the Gunnar
ore body, looking East(22).
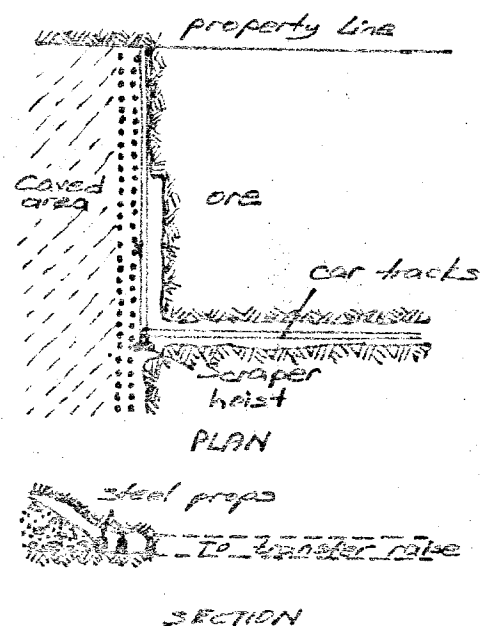
Fig.5.4.Longwall-retreat
mining method, Ra-
don Mine (22).

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)<br>West Water canyon sandstones of the Grants-Ambrossia Lake dist-ricts (New Mexico) |
| 2.Shallow-irregular | Salt Wash Formation (Colorado)<br>White Canyon (Utah) |
| 3.Extensive-Shallow (open-pit mined) | Gas Hills (Wyoming)<br>Grants (New Mexico)<br>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 Härting 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 uranimining (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 $1.6 \times 10^3$ 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).

### Part A. from $U^{238}$

| Nuclide | Historical name | Half-life | Radiation | Atom ratio, ppb in natural U |
|---|---|---|---|---|
| $_{92}U^{238}$ | Uranium I | $4.49 \times 10^9$ years | $\alpha$ | $9.328 \times 10^8$ |
| $_{90}Th^{234}$ | $UX_1$ | 24.10 days | $\beta, \gamma$ | 0.0146 |
| $_{91}Pa^{234}$ | $UX_2$ | 1.175 min | $\beta, \gamma$ | $4.94 \times 10^{-7}$ |
| $_{92}U^{234}$ | Uranium II | $2.48 \times 10^4$ years | $\alpha, (\gamma)$ | $5.48 \times 10^4$ |
| $_{90}Th^{230}$ | Ionium | $8.0 \times 10^4$ years | $\alpha, \gamma$ | $1.77 \times 10^4$ |
| $_{88}Ra^{226}$ | Radium | 1622 years | $\alpha, \gamma$ | 359 |
| $_{86}Em^{222}$ | Radon | 3.825 days | $\alpha$ | $2.32 \times 10^{-3}$ |
| $_{84}Po^{218}$ | Radium A | 3.05 min | $\alpha$ | $1.28 \times 10^{-6}$ |
| $_{82}Pb^{214}$ | Radium B | 26.8 min | $\beta, \gamma$ | $1.13 \times 10^{-5}$ |
| $_{83}Bi^{214}$ | Radium C | 19.7 min | $\beta, \gamma$ | $8.28 \times 10^{-6}$ |
| $_{84}Po^{214}$ | Radium C' | $1.637 \times 10^{-4}$ sec | $\alpha$ | $1.15 \times 10^{-8}$ |
| $_{82}Pb^{210}$ | Radium D | 22 years | $\beta, \gamma$ | 4.86 |
| $_{83}Bi^{210}$ | Radium E | 5.02 days | $\beta$ | $3.04 \times 10^{-3}$ |
| $_{84}Po^{210}$ | Polonium | 138.3 days | $\alpha$ | 0.0838 |
| $_{82}Pb^{206}$ | Radium | Stable | | |

### Part B. From $U^{235}$

| Nuclide | Historical name | Half-life | Radiation | Atom ratio, ppb in natural U |
|---|---|---|---|---|
| $_{92}U^{235}$ | Actinouranium | $7.13 \times 10^8$ years | $\alpha, \gamma$ | $7.15 \times 10^6$ |
| $_{90}Th^{231}$ | Uranium Y | 25.64 hr | $\beta, \gamma$ | $2.94 \times 10^{-5}$ |
| $_{91}Pa^{231}$ | Protoactinium | $3.43 \times 10^4$ years | $\alpha, \gamma$ | 344 |
| $_{89}Ac^{227}$ | Actinium | 22.0 years | $(\alpha), \beta, (\gamma)$ | 0.221 |
| $_{90}Th^{227}$ | Radioactinium | 18.6 days | $\alpha, \gamma$ | $5.11 \times 10^{-4}$ |
| $_{88}Ra^{223}$ | Actinium X | 11.2 days | $\alpha, \gamma$ | $3.08 \times 10^{-4}$ |
| $_{86}Em^{219}$ | Actinon | 3.92 sec | $\alpha, \gamma$ | $1.25 \times 10^{-9}$ |
| $_{84}Po^{215}$ | Actinium A | $1.82 \times 10^{-3}$ sec | $\alpha$ | $5.82 \times 10^{-13}$ |
| $_{82}Pb^{211}$ | Actinium B | 36.1 min | $\beta, \gamma$ | $6.89 \times 10^{-7}$ |
| $_{83}Bi^{211}$ | Actinium C | 2.16 min | $\alpha, \gamma$ | $4.12 \times 10^{-8}$ |
| $_{81}Tl^{207}$ | Actinium C'' | 4.79 min | $\beta, (\gamma)$ | $9.14 \times 10^{-8}$ |
| $_{82}Pb^{207}$ | 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 :

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

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.
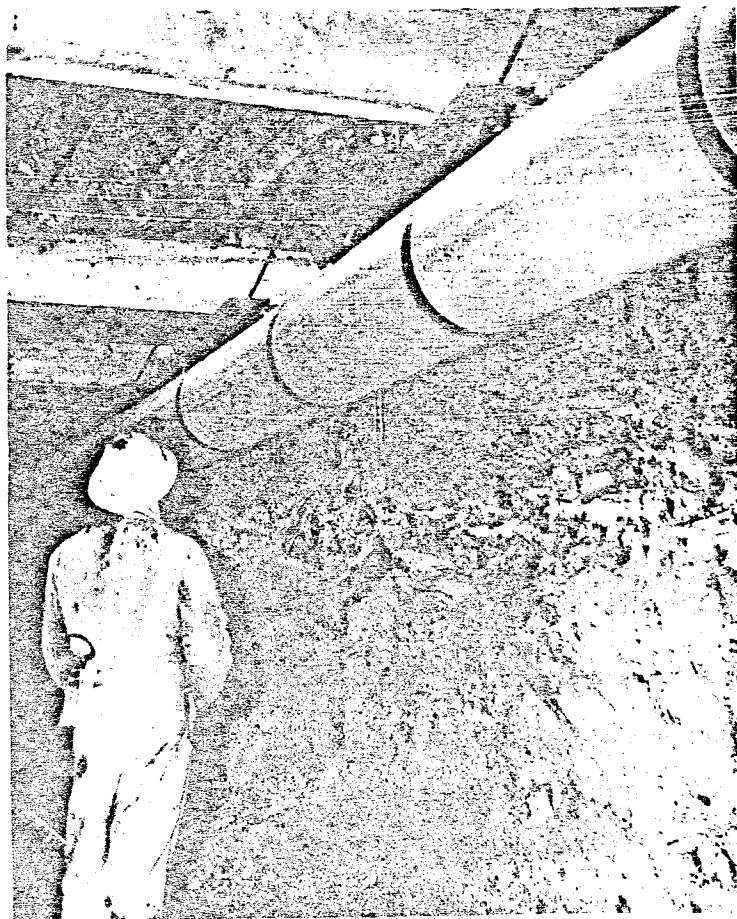


Fig.5.6. 20.in 10m polyethylene duct used
for ventilation of developed headings
(30).

# Chapter 6
## 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 valvable ore. The process defined as separating a metalliferous mineral from gangue is called "CONCENTRATION" or " MILLING".

```
                    Uranium Mineral
                          │
                          ▼
                        Crush
                         and
                        Grind
                          │
                          ▼
                Physical  Concentration
                          │
                          ▼
                       Leaching
                          │
            Acid L.                  Alkali L.
                          │
                          ▼
                      Filter or
                      thickener
                          │
        ┌─────────────────┼─────────────────┐
        ▼                 ▼                 ▼
     Solvent         ion exchan-       ion exchange
    Extraction        ge static         fluidized
        │                 │                 │
        └─────────────────┼─────────────────┘
                          ▼
                    Precipitation
                          │
                          ▼
                       Filter
                          │
                          ▼
                    Uranium ore
                     concentrate
                          │
                          ▼
                        Dryer
                          │
                          ▼
                 Drum  for  shipment
```
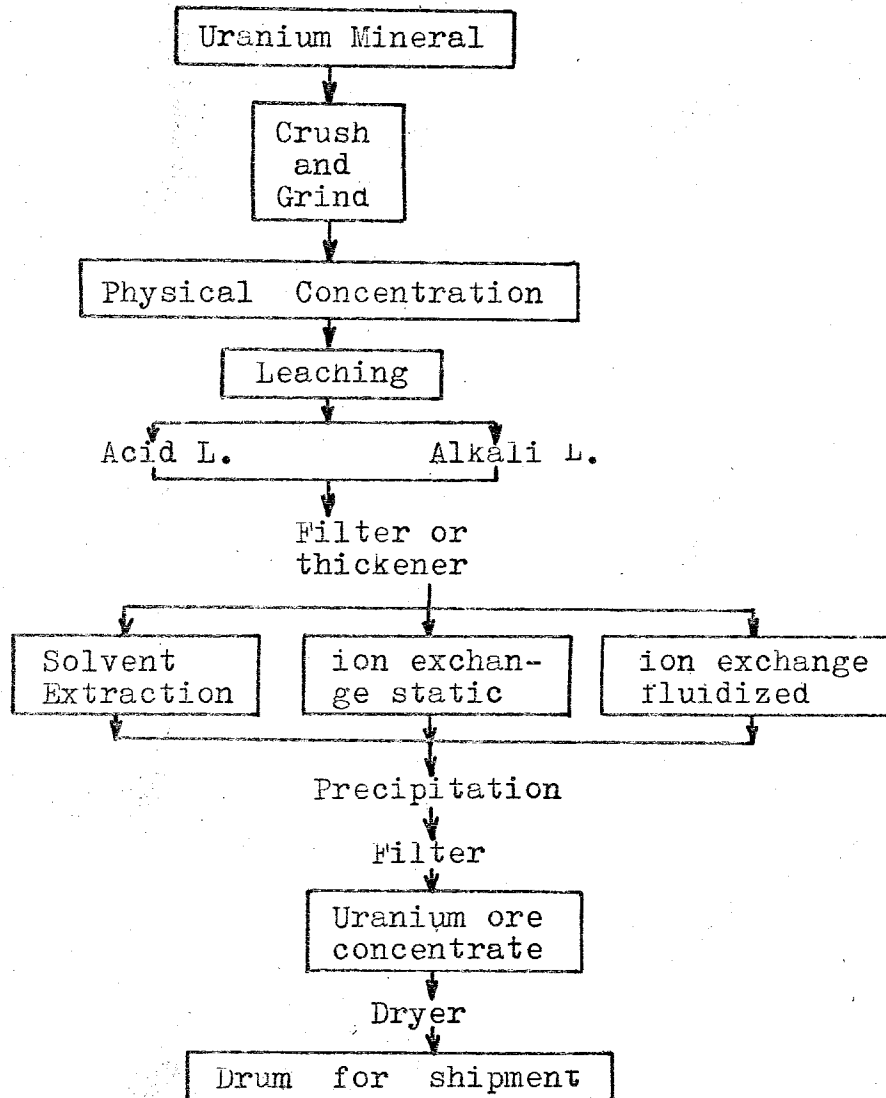
Fig.6.1. Uranium milling steps (31).

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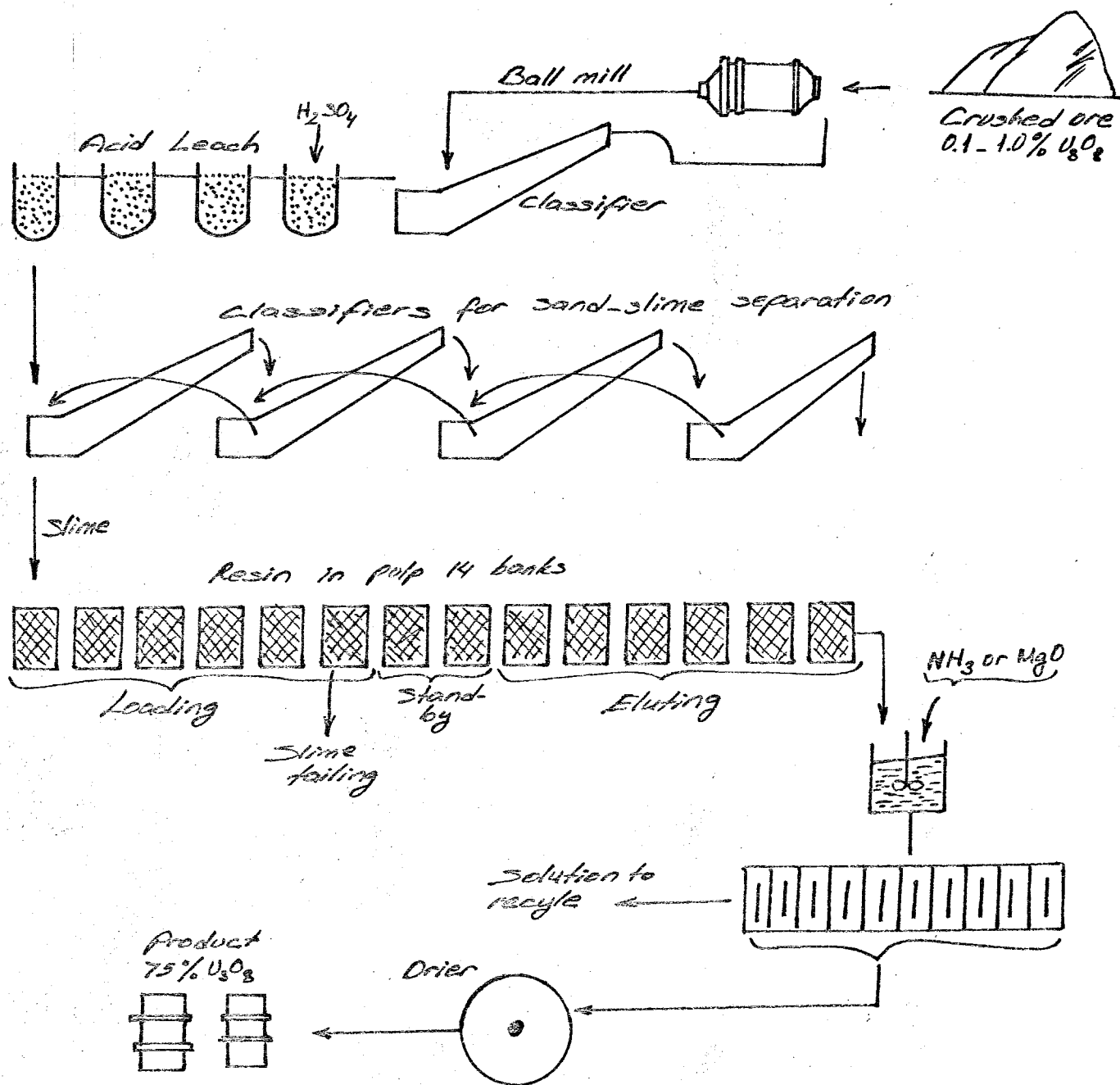
Fig.6.2. Simplified diagram of uranium milling (10).

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

| Characteristic | Country | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | U.S.A† | Canada | S.Africa | Australia | France | Others | Total |
| Number of plants | 25 | 19 | 17 | 5 | 4 | 10(?) | 80 |
| Quantity of ore processed, 1000 t/annum | 7000 | 13,700 | 22,100 | 456 | 1140 | 680 | 45,646 |
| Mean U content, % | 0.22 | 0.037 | 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 | | | | | | | |
| Mechanical concentration‡ | 8 | 3 | 9 | 1 | 2 | 3 | 26 |
| Comprising: | | | | | | | |
| Gravitation | 1 | 1 | | 1 | 1 | 2 | 6 |
| Flotation | 1 | 3 | 9 | 1 | 2 | 1 | 17 |
| Selective Crushing | 6 | 1 | | | | | 6 |
| Acid leaching | 20 | 18 | 17 | 4 | 4 | 5 | 68 |
| Carbonate leaching | 8 | 1 | 1 | | | 1 | 10 |
| Counterflow 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 | 1 | | | 1 | 1 | 8 |
| Extraction | 12 | 2 | | 1 | 1 | 1 | 17 |
| Chemical precipitation | 10 | 1 | | – | 1 | 1 | 13 |

† Many plants have two sections (for silica and carbonate ores) and at 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 seperation 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 minig 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-bottomsstart-stop control under the supervision of the primary crusher tander 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 prefered 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 quard 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 quard 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 then the initial units.here the crushing machines have lower capasity,are more sensitive to size,minerological character,moisture and feed rate variations.Storage in the form of surge bins is offered to ensure constant feed rates. The product is quarded 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 minerological 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 groins,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 op 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,climactic 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.Bal mills are especially used for wet grinding and work  with a combination of a classificator 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 classi-
fiers.The latter is also known as hydraulic classifiers.


### 6.1.5  GRAVITY  CONCENTRATION

A method of separating grains of minerals having different spe-
cific gravities is gravity concentration.Only the richest pichblen-
de ores are susceptible to cocentration 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 par-
ticulate solid.The fluid properties utilized are viscosity and den-
sity while the forces are buoyancy and upward pulse.In other gra-
vity processses the moving fluid impulse is applied to the vertical
action line of gravity and the friction between grains.In all gra-
vity processes, a sizing element works in a closed cycle to separate
different sized particles.Specific gravities of the minerals,vis-
cosity and plasticity of the separating medium,and mechanical met-
hods available are the important criteria for deciding the king
of separation.


### 6.1.6  FLOTATION

Flotation method amoung other physical concentration methods se-
ems to be more applicable and promising for uranium preconcentrati-
on. In the ore preparation,flotation is used to separate some mine-
rals within the ore from others by the use of surface tension pro-
perty.Minerals heavier than water surface due to this property.Sur-
face 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 bubles 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 amoung other acids is cheaper,less corrosive and easily available.It reacts with uranium bearing ore and yields uranil sulfate $(UO_2SO_4)$ or complex uranil sulfate anions $\left[UO_2(SO_4)_3\right]^{-4}$

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.

Ore
↓ (1360 m/24h ; 0.25 % U)
2 crushing stages
↓ −20 mm.

Water
↓
Grinding
$H_2SO_4 + MnO_2$
↓
Leaching out
Fe(metal) ↓ (pH=1; T=164)
↓
Reduction by $Fe^{3+}$
↓
Classification
Sand (yield 80−30 %)      −40μ overflow
Water ↓                          (7%)
Counter current decantation
in 3 stage classifiers      Absorption in containers
sand overflow               (T=100min; capacity 40 kg/m³)
To dump tank                 $NH_4NO_3 + HNO_3$      Resin (KhE−123)
                            Desorption (T=40min)
                            Solution    Resin
$NH_3$    7 g/l. U
↓
Precipitation U
↓ Concentrate
Annealing (t=235°c)
↓
U (Chemical concentrate)
(60% U)

Fig.6.3  Typical flowsheet of acid leaching of uranium with
         Absorbtion 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 $70^0$-$90^0$ under 100 psi pressure. Reaction results in the formation of soluble uranium carbonate anion $UO_3(CO_3)_3^{-4}$. $KMnO_4$ or air in conjunction with copper ammonium ion $Cu(NH_3)_4^{2+}$ 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 lixiviants 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 cosumption | 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 $UO_4 \cdot 2H_2O$.

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 $-NH_2$ ≡ NH or ≡ N groups while cationities contain $-OH, -COOH, -SO_3H$ groups. The ion exchange (adsorpsion) 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 absorbtion 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 phoshates,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 desorpted 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 being start 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, $\rho$ 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

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

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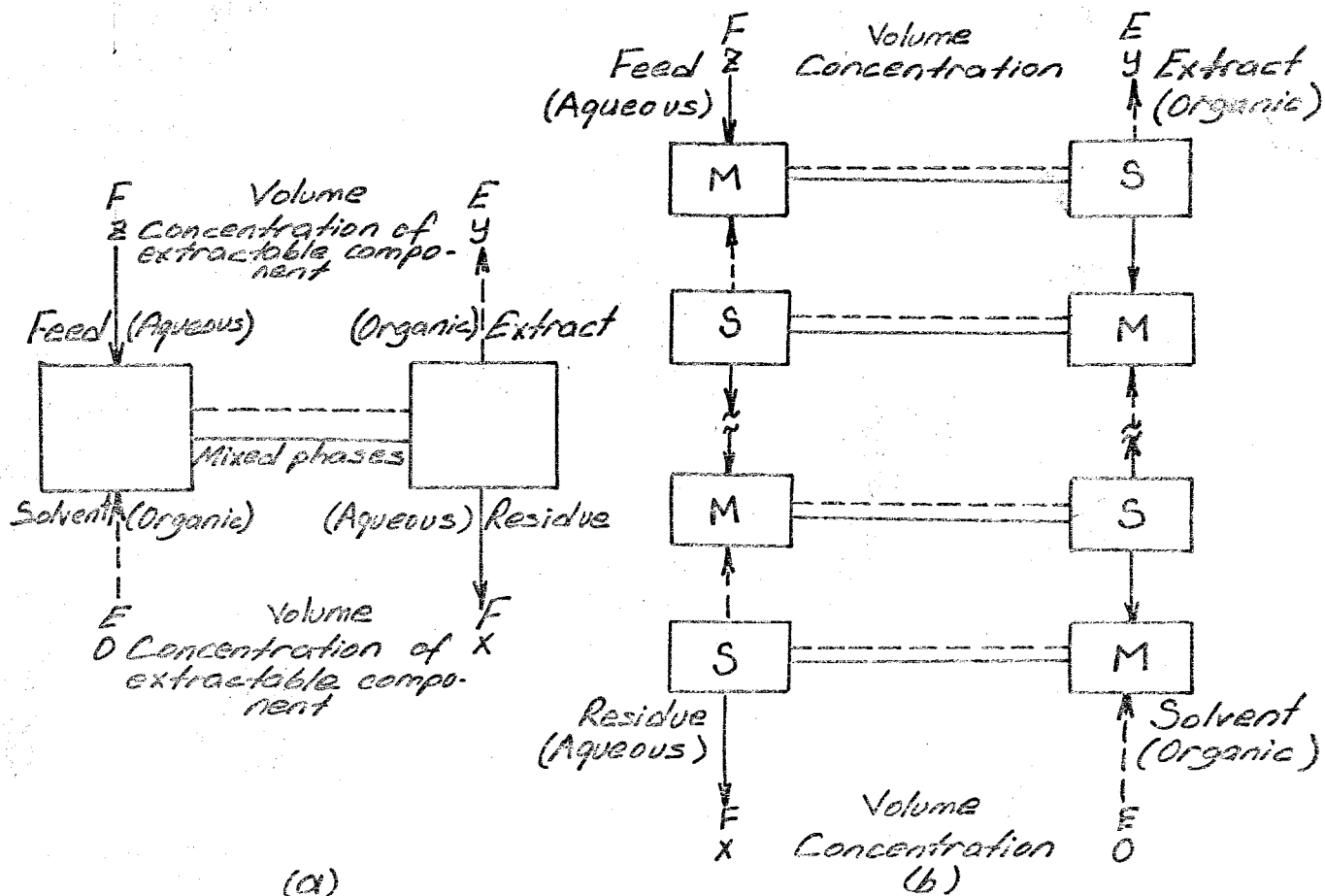
Fig.6.4-a) Single solvent extraction stage , b) Multistage counter current solvent extraction  M,mixer; S, settler.(26).
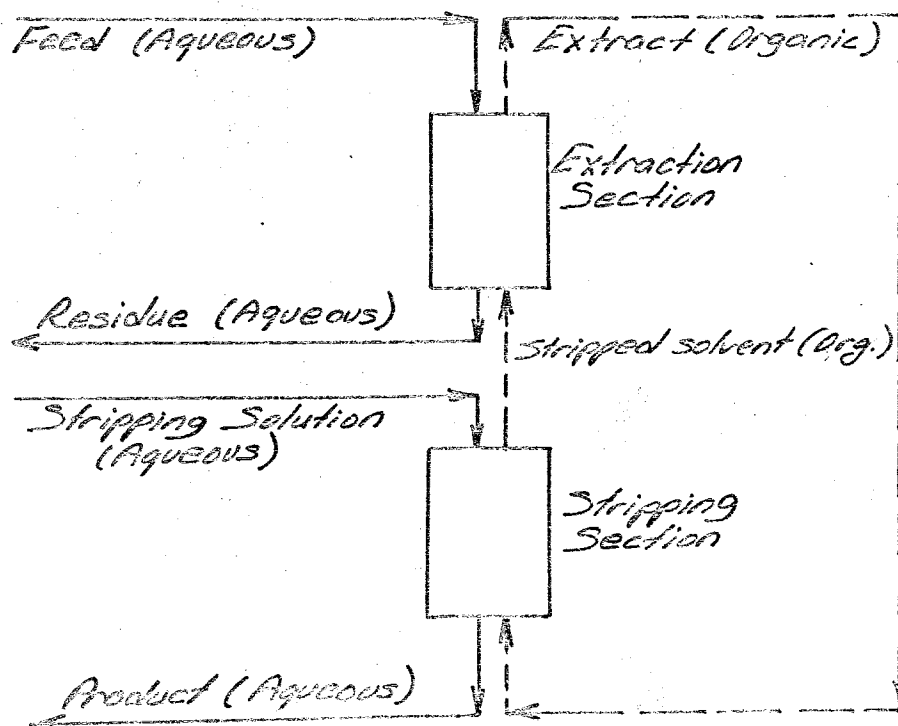


Fig.6.5. Solvent-extraction flow sheet with recycle of solvent (26).
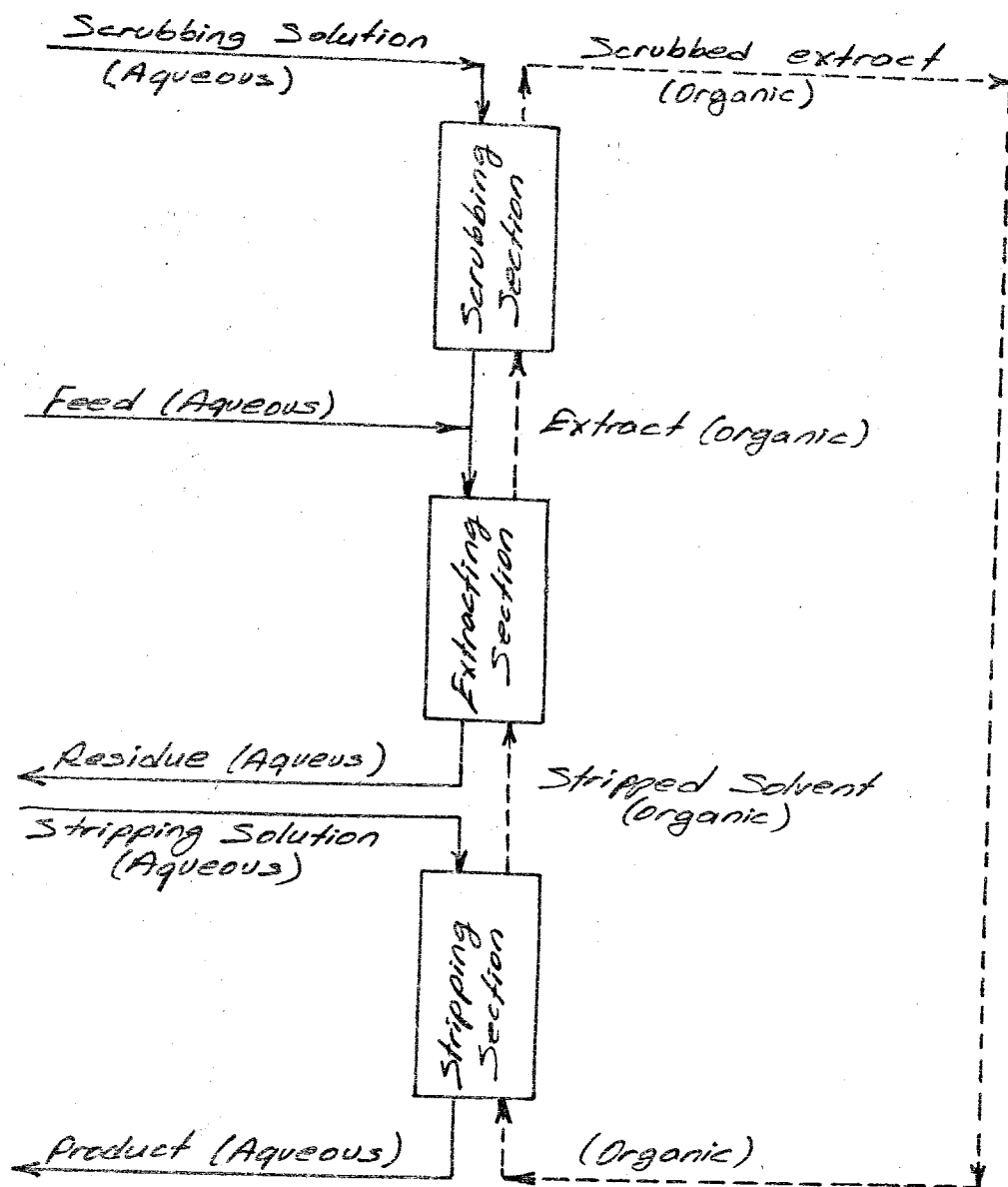
Fig.6.6 Flowsheet for fractional extraction of two
extractable components (26).

enables the separation of more than one extractable component depen-
ding upon the existence of different distribution coefficients
($D_i/D_j$ 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 pro-
cesses take different names such as AMEX, DAPEX, ELUEX and Mixed
Solvent Process. In the AMEX process, an amin is used as organic
solvent, which han a uranium extraction capacity of 3-5 gr $U_3O_8$/lt.
4 % EHPA (di-2 ethyl-hegzil phosphoric acid), 4% TBP (Tri-butylphos-
phate) and 92% kerosene solution is used in the DAPEX process.
However, the organic phase of mixed solvent process is composed
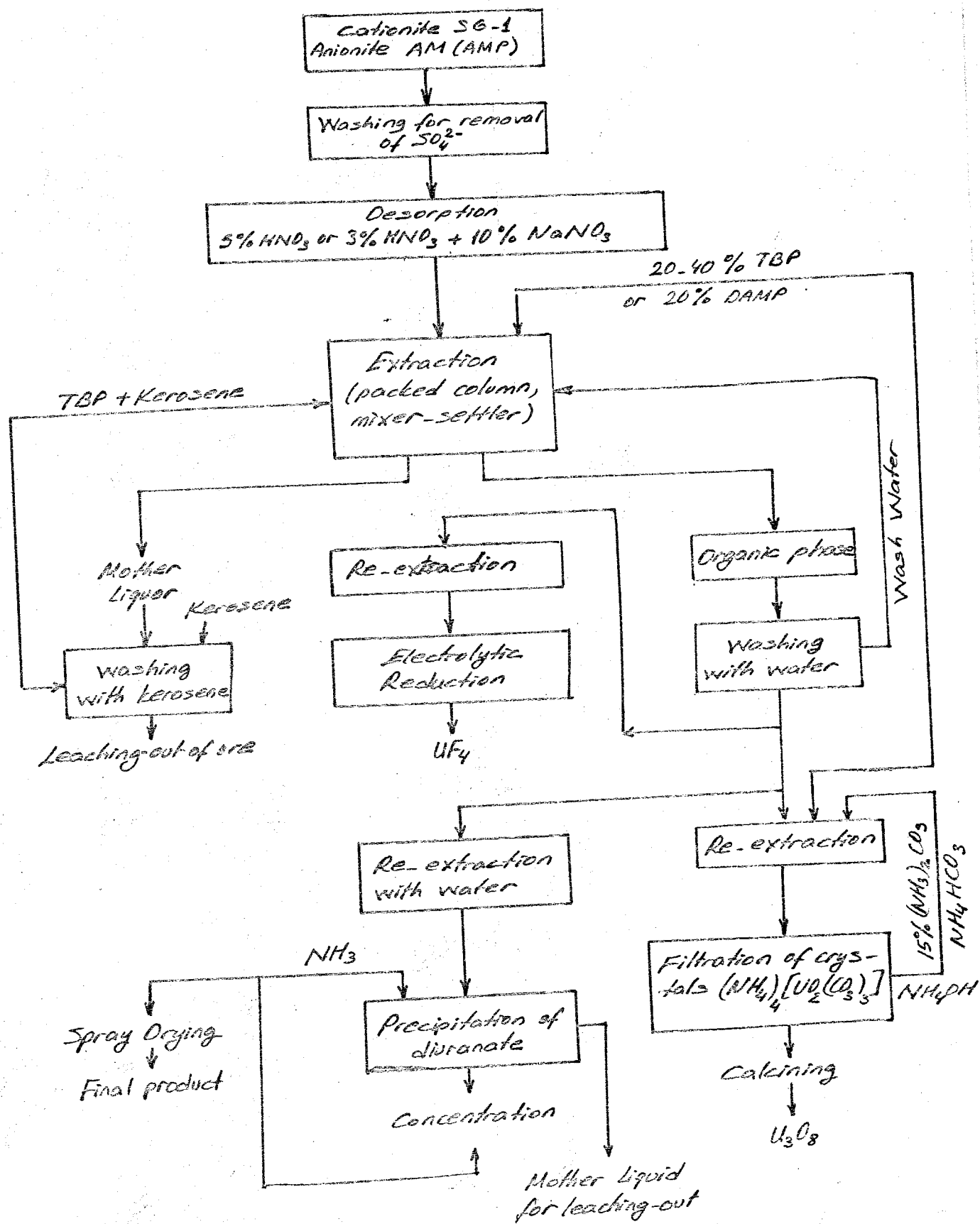
Fig.6.7. Flowsheet of extraction purification of Nitric Acid desorption solutions (8).

of 3.5-4.5% tri-alkilamin,0.25-1.7% EHPA and 0.75-1.4% HDPA (Heptadesel phosphoric acid).ELUEX process has a different procedure since AMEX ar 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).

## 7. PURIFICATION

Neutron economy is of outmost importance for the nuclear reaction maintanance 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 E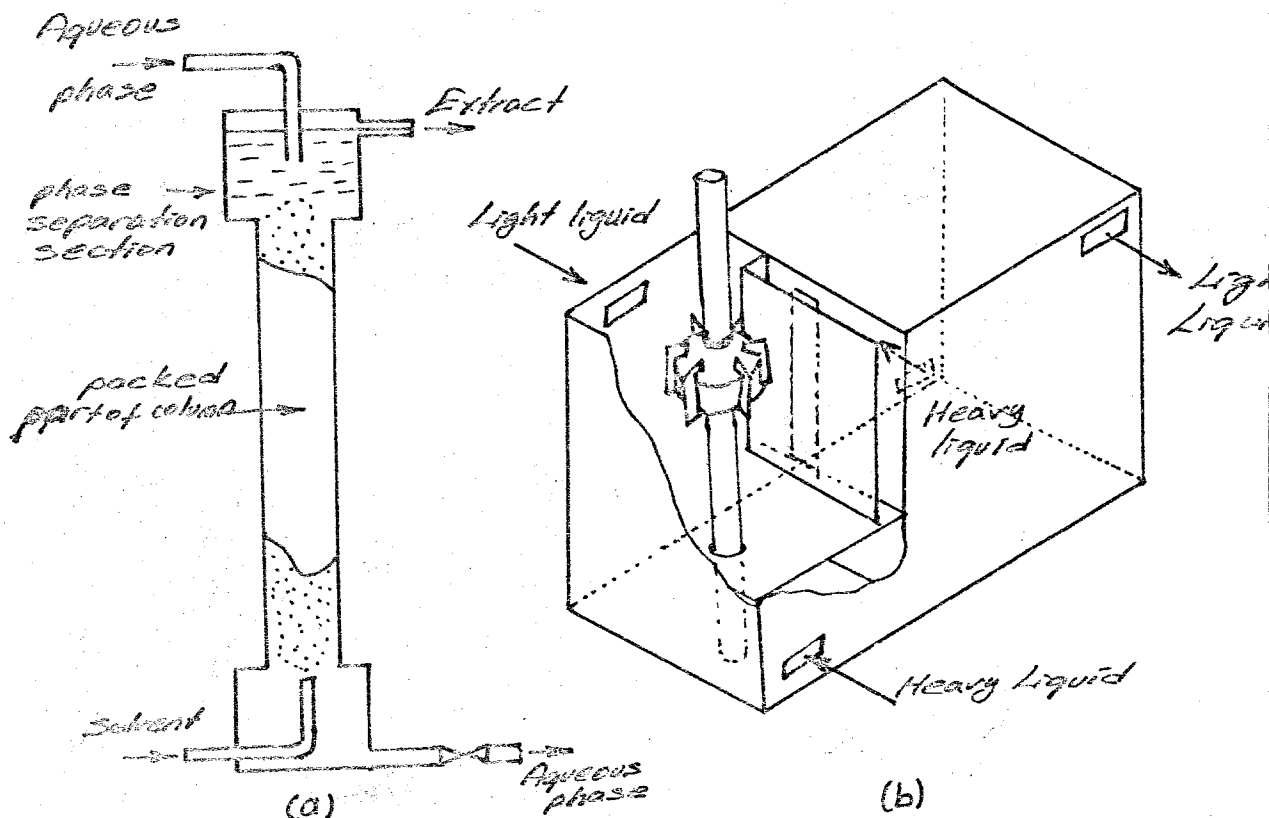nergy Agency (I.A.E.A for short) at Vienna. The data is summarized in table 7.1. The most harmful impurities are ones having high absorption cross sections, and their tolerable amounts are given in table 7.2. The overall hazard coefficient for uranium which is also determined by I.A.E.A, must not exceed 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 | 0.0025 |
| Boron | 0.2 | $2 \times 10^{-5}$ |
| Cadmium | 0.2 | $2 \times 10^{-5}$ |
| 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 Absorp-
sion is 0.1% of Neutron  Absorp-
tion 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 |
| Godolinium | 44,000 | 0.1 |
| Dysprosium | 1,100 | 4.5 |

Considering the atomic energy standarts,the uranium concentrate
obtained through physical and chemical concentrations mentioned in
the previous chapter is not pure enough.Typical composition of che-
mical concentrates of uranium ores produced at different concentra-
tion 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 where as 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 do-
es not necessiate 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
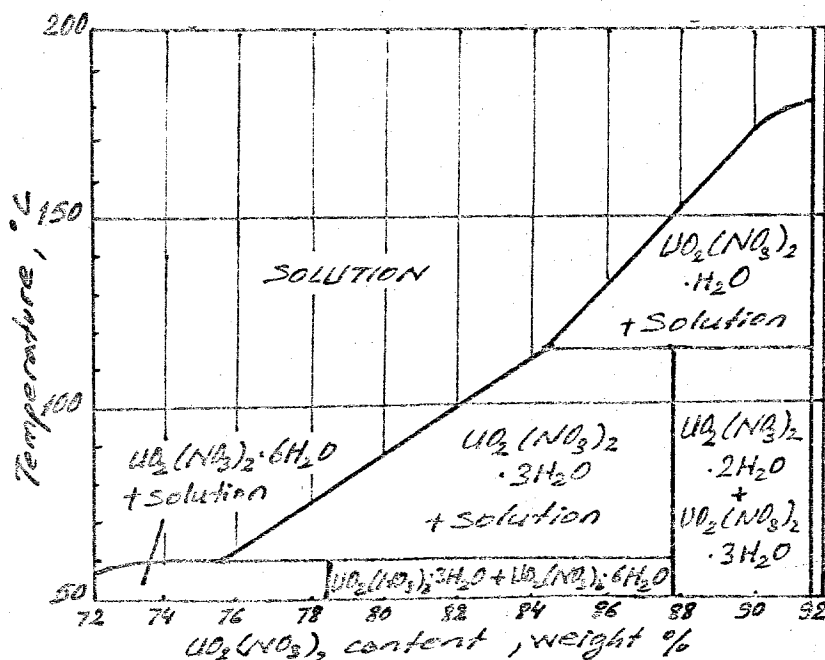different temperatures (see fig.7.1).In this method,first of all,



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

Table 7.3. Typical Compositions of Chemical Concentrates of Uranium Ores (8).

Component wt %

| Location of plant | U.S.A | | | Canada | | Africa | | Australia |
|---|---|---|---|---|---|---|---|---|
| | New Mexico | Arizona | Colorado | Blind River | Bancroft | Congo | Rep.of S.Afr. | Radium Hill |
| Technological process / Components | Carbonate Leaching Alkali precipit. | Acid Leaching Extraction | Acid Leaching Ion Exchange | Acid Leaching Ion Exchange | Acid Leaching Ion Exchange | Acid Leaching Ion Exchange | Acid Leaching Ion Exchange | Acid Leaching Ion Exchange |
| $U_3O_8$ | 75-78 | 70-75 | 65-79 | 70-80 | 60-65 | 48-73 | 75-85 | 55-70 |
| $H_2O$ | 1-7 | 0.01-0.1 | 1.10 | <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 | 0.04-2.0 | <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 | 0.4-0.8 | 9-13 | 1-5 | 0.15-0.45 | ~1 | 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 |
| $P_2O_5$ | 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 | 0.4-0.5 | 0.2-4.5 | 3-4 | 1-2 | 0.07-2.0 | 0.04-0.2 | 2 |
| $SO_4^{2-}$ | 0.2-2.0 | 0.3-4.0 | 3.17 | 0.5-1.5 | 0.3-0.5 | 1.37 | 1-5 | 0.5-2.5 |
| $V_2O_5$ | 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 insolub-
le 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 impuri-
ties 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 presen-
ce of alkali metals in the initial concentrate is not desired.In
case of the action of alkali metal and ammonium carbonates on ura-
nyl 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,mangana-
se,yttrium,scandium,boron,phosphorus,vanadium and arsenic admixtu-
res and their compounds also pass into the solution.Therefore ,ura-
nium 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,ura-
nium 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 $80-90^0C$ after a primer of $U(C_2O_4)_2$
is added to obtain a coarsely crystalline precipitate.After the

Concentrate

$H_2SO_4$ → Dissolving

Sulphuric acid solution

$Ca(OH)_2$ → Liming to pH = 2.8 → Gypsum Cake

Solution $UO_2SO_4$

$Na_2CO_3$ → Obtaining solution $Na_4[UO_2(CO_3)_3]$ → Hydroxides of metal impurities

Solution $Na_4[UO_2(CO_3)_3]$

$NaOH$ → Precipitation $Na_2U_2O_7$

Filtration → Filtrate for dumping

$Na_2U_2O_7$

$HCl$ → Dissolving

$H_2S$ → Precipitation of sulphides → Sulphides of heavy metals

Solution $UO_2Cl_2$

$NH_3$ → Precipitation $(NH_4)_2U_2O_7$

Dissolving $(NH_4)_2U_2O_7$ 3 times in HCl and re-precipitation by ammonia

$(NH_4)_2U_2O_7$

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 $(NH_4)_4 \cdot [U(C_2O_4)_4]$ by passing into the solution.Impurities remaining in the mother liquir 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,manganase,vanadium,chronium,phosphorus,silicon,nickel,boron,the alkali -earth metals and alkali metals are separated.High reagent consumption.the difficulty of treating concentrates with a high concent 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 $700-800^{0}C$ and dissolved in nitric acid.Uranium passes into the solution and forms $UO_2(NO_3)_2$.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 extracter.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 extrac-
tion 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.Fi-
nally 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.
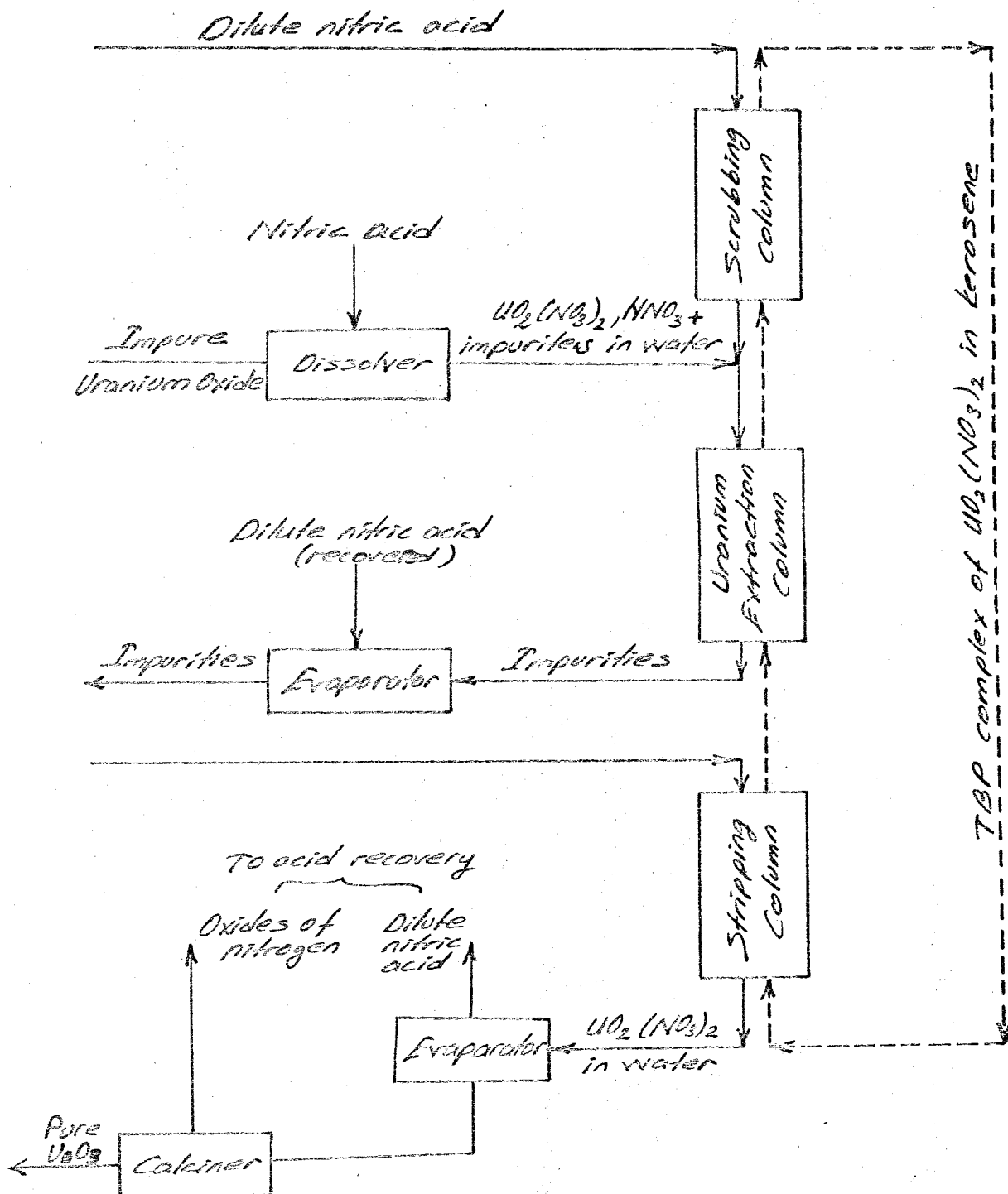
Fig. 7.3. Purification of uranium by solvent extraction with TBP. Solid line, aqueous; brokenline, organic

(26)

# 8. CONVERSION AND ENRICHMENT
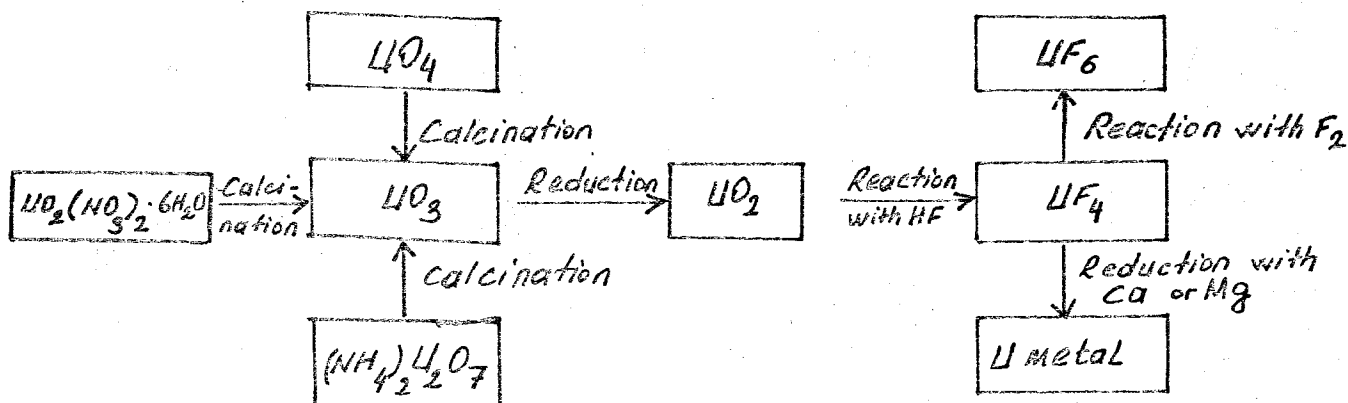


Fig.8.1. Uranium Conversion operation (26).

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 $120\text{-}140^{O}C$. 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 $650^{0}C$.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% .
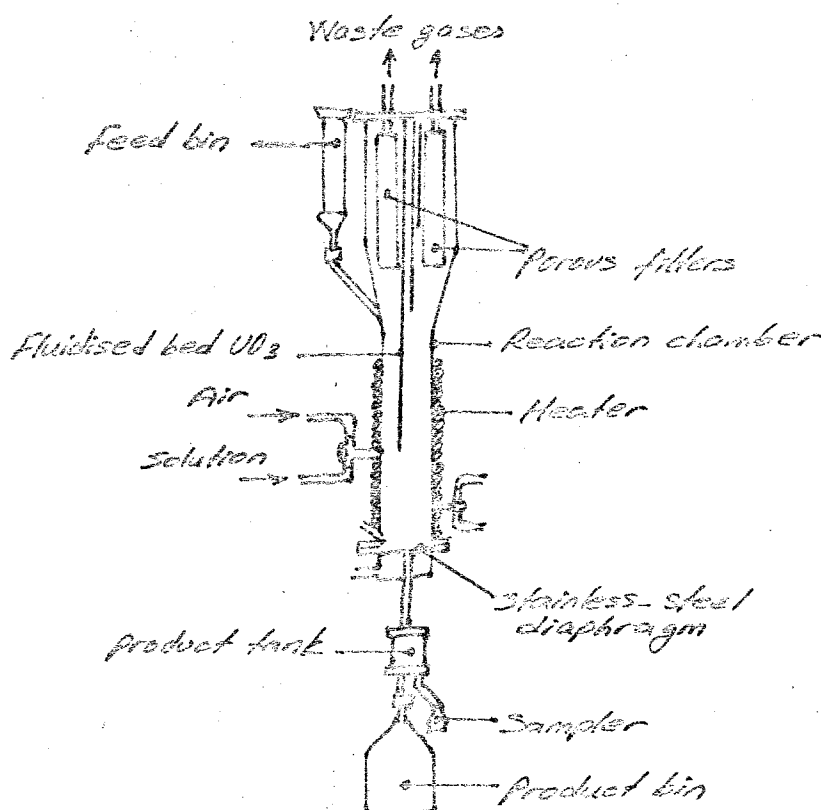


Fig.8.2. Apparatus for denitration according
to fluidised bed method (8).
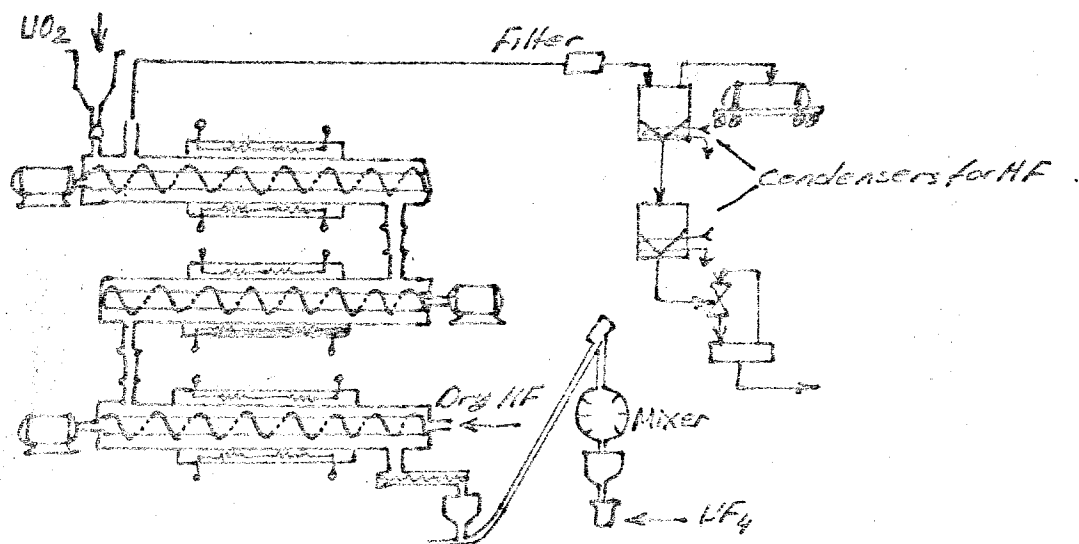
Fig.8.3. Diagram of Hydrofluorination Unit (8).

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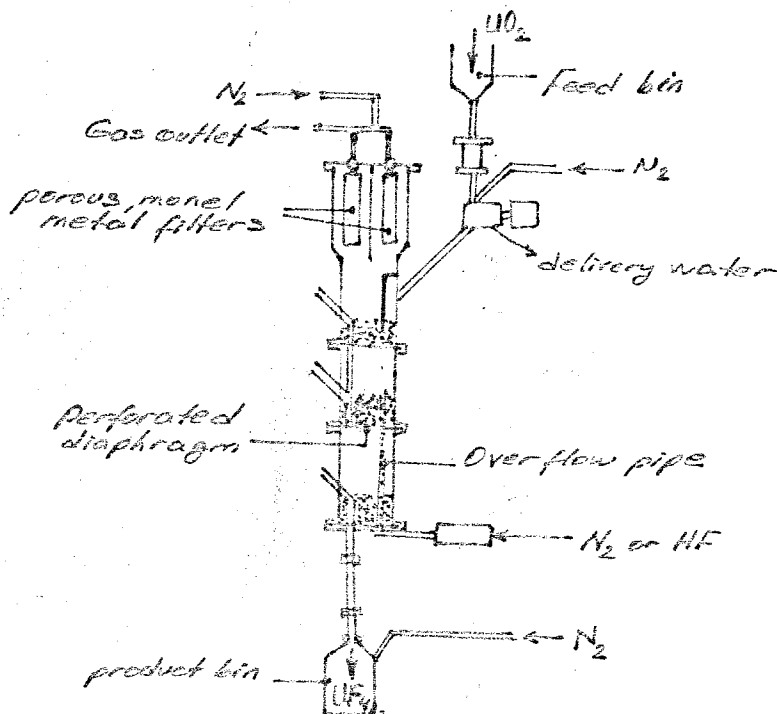
Fig.8.4. Three-stage apparatus according to
fluidised bed method (8).

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 in-
stead of HF.
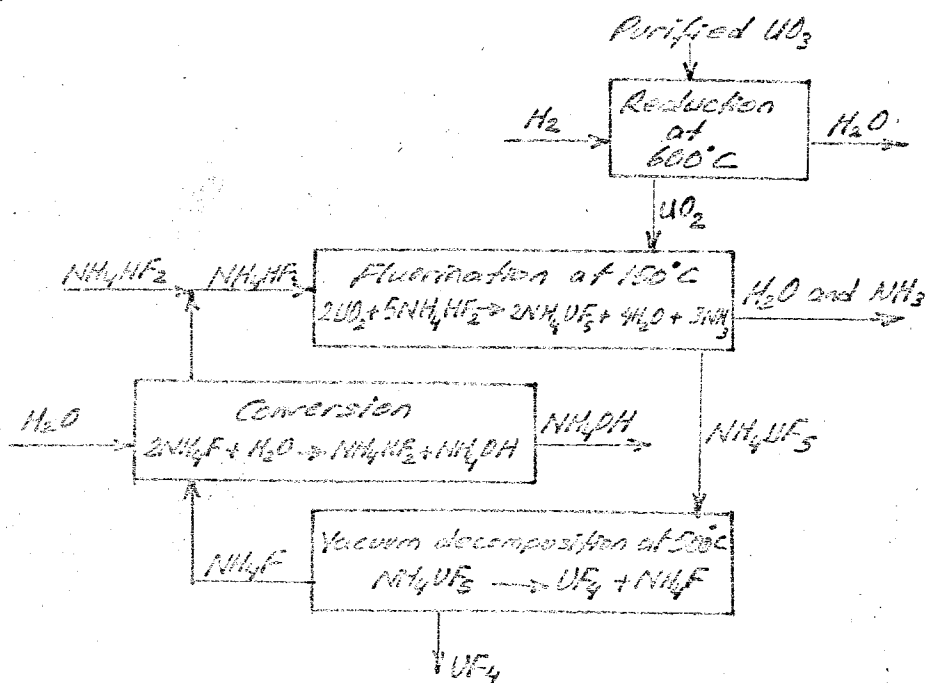


Fig.8.5 Production of $UF_4$ by the Belgian process (26)

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## 8.1.3. CONVERSION TO UF$_6$

The importance of uranium hexafluoride UF$_6$ comes from the fact that it is the only volatile uranium compound at ordinary temperatures. The most important properties of UF$_6$ are summarized in Table 8.1. Uranium hexafluoride was discovered by Ruff and Heinzelman in 1909(26).

Today UF$_6$ is produced by the fluorination of UF$_6$ in a continuous process through the following stages: i. UO$_3$ in fluidised bed units is reduced to UO$_2$ by hydrogen; ii. UO$_2$ is fluorinated to UF$_4$ by dry HF with warm mixing in reactors and iii. UF$_4$ is fluorinated to UF$_6$. 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 UF$_6$ (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 |
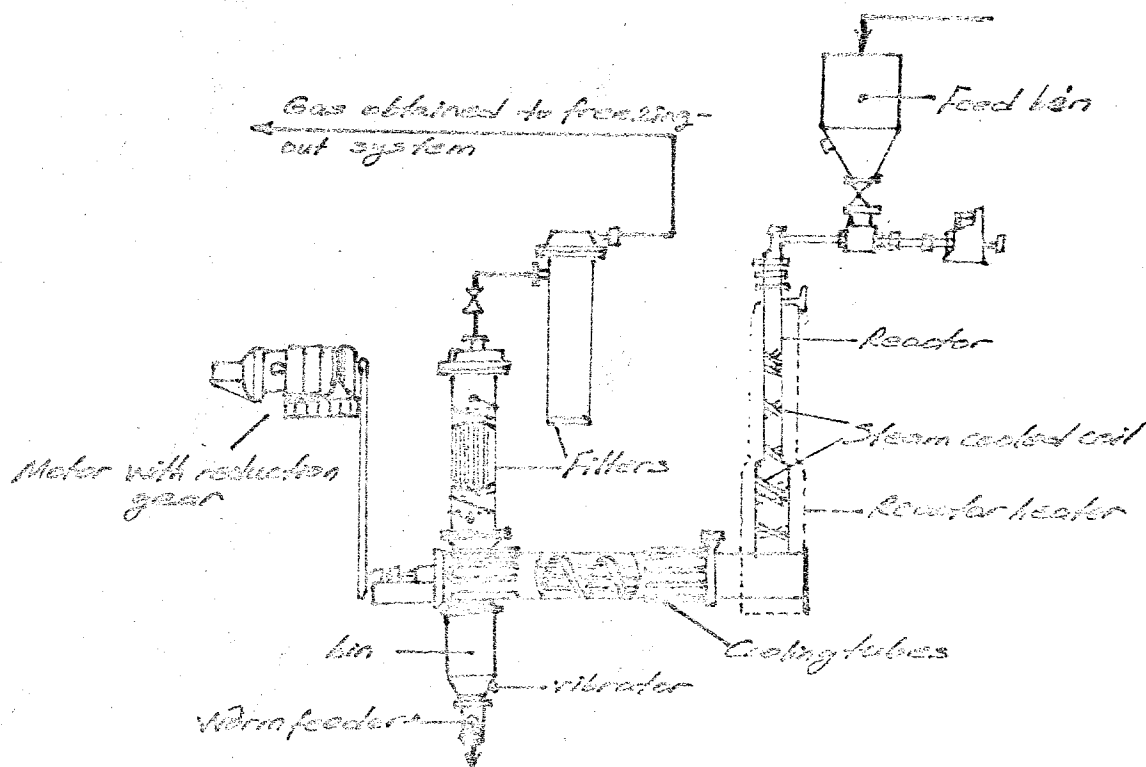


Fig.8.6 Fluorine extraction system(gaseous diff.plant,Oak Ridge, Tennessee,U.S.A) (8).

Spiral water coolor 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 eatrh'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 neecessarily 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 tnah 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
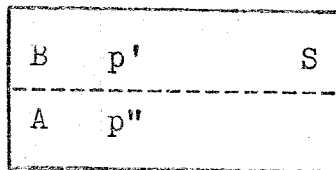


(a)
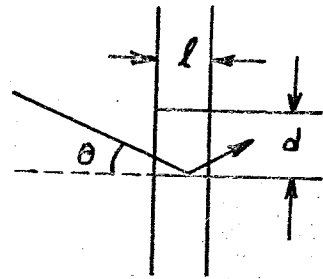


(b)

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 choosen such that molecular mean free path $\lambda$ 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 ($60^O$F,1 atm) (26).

| GAS | viscosity, centipoise | Mean free path | |
|---|---|---|---|
| | | Inches x$10^6$ | 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;

$$q_0 \leq \left(\frac{M_2}{M_1}\right)^{1/2} \quad \text{or} \quad q_0 = 1 + \frac{M_2 - M_1}{M_2 + M_1}$$

where $M_{1,2}$ molecular weights of light and heavy component.

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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).
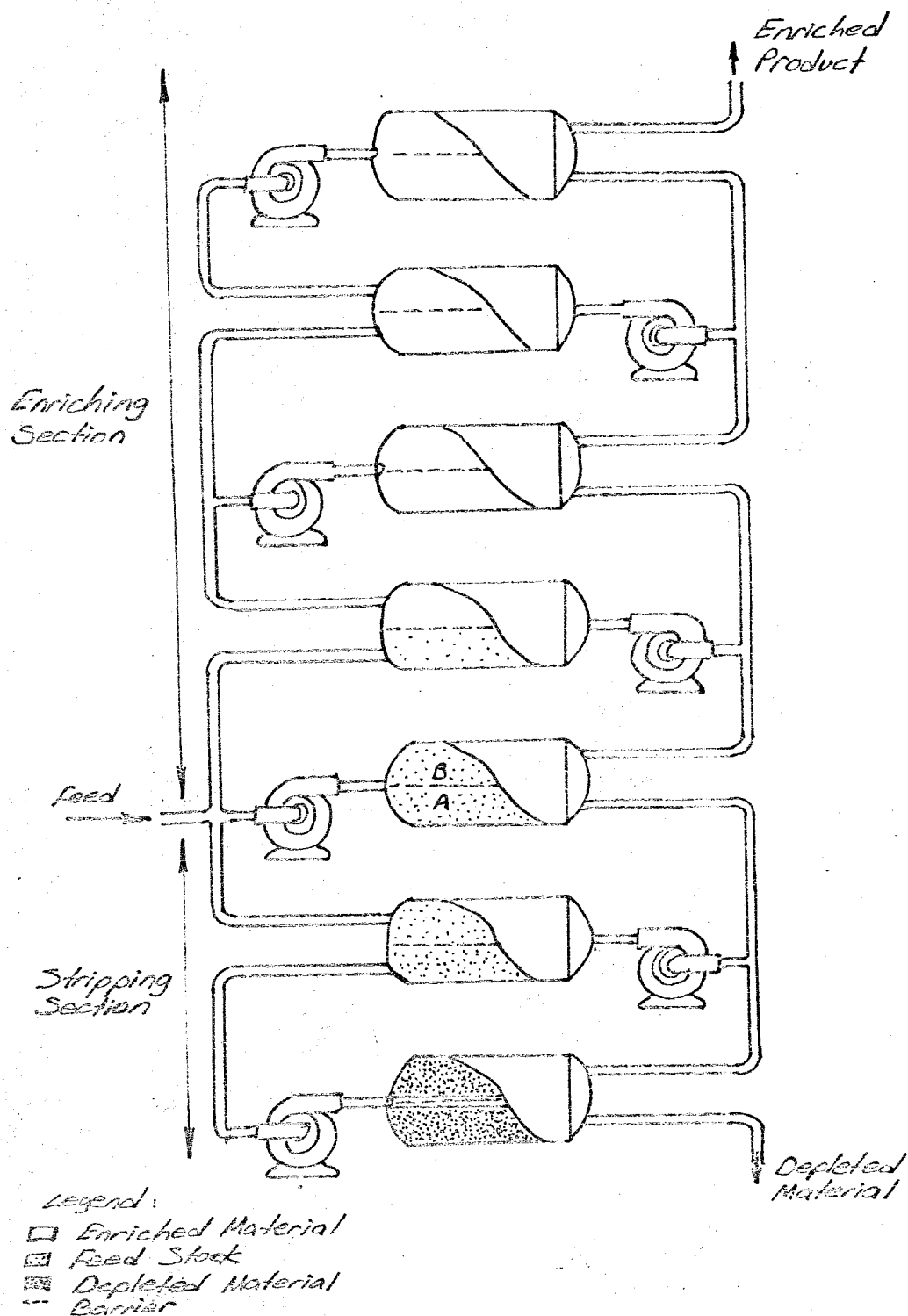


Figure 8.8.a. Schematic Diagram of gaseous diffusion process (10).
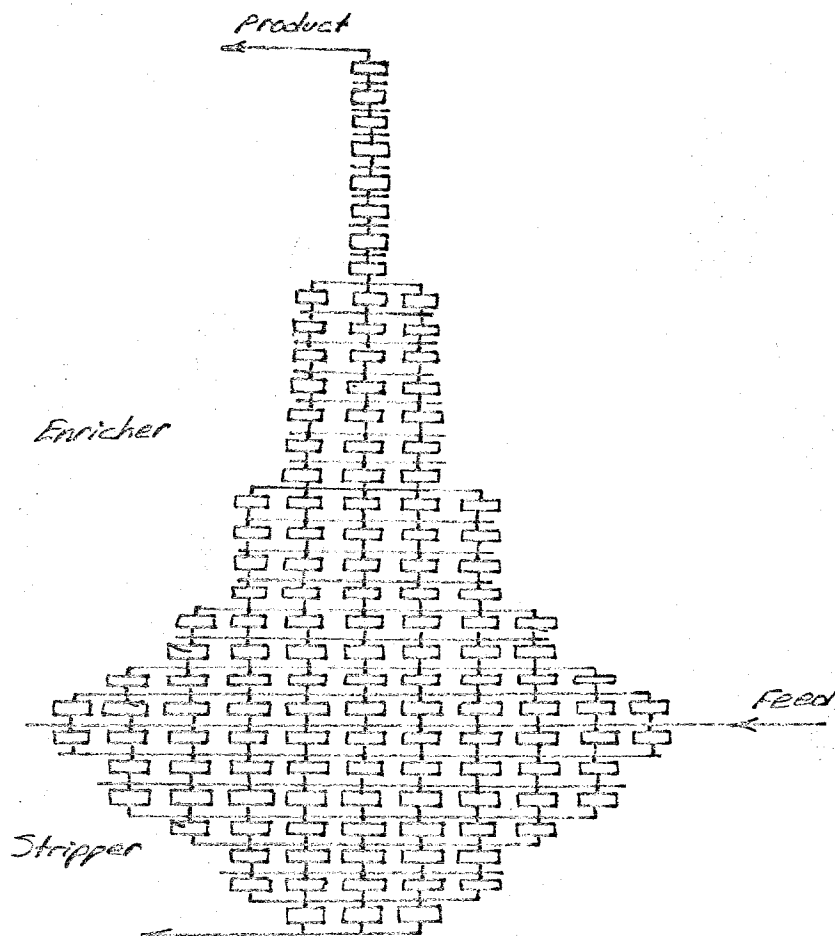
Figure.8.8.b Gaseous diffusion cascade(10)

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, Tennesse,Paducah,Kentucky,and Portsmouth,Ohio),Great Britain(Copenhurst),France(Pierre Lottle),the Soviet Union,and China.

## 8.2.2. MASS DIFFUSION
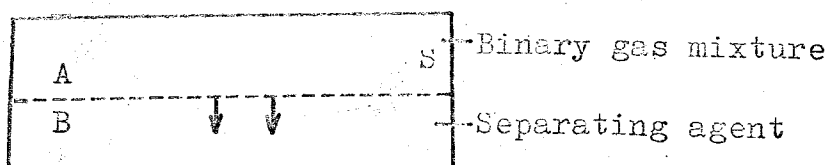


Fig.8.9 Principle of mass-diffusion separation shown schematically (40).

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:

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

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

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

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 origanally 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 prefferred for small scale laboratory separation.
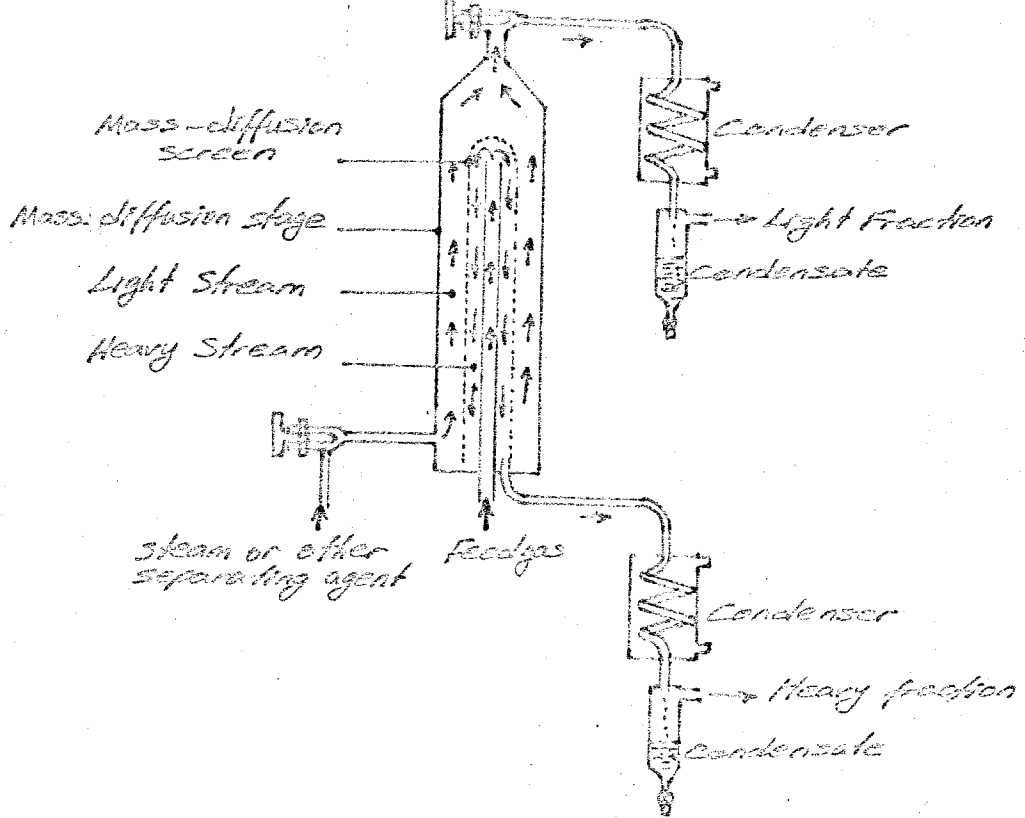
Fig.8.10 Mass-diffusion stage used by Maier (26).
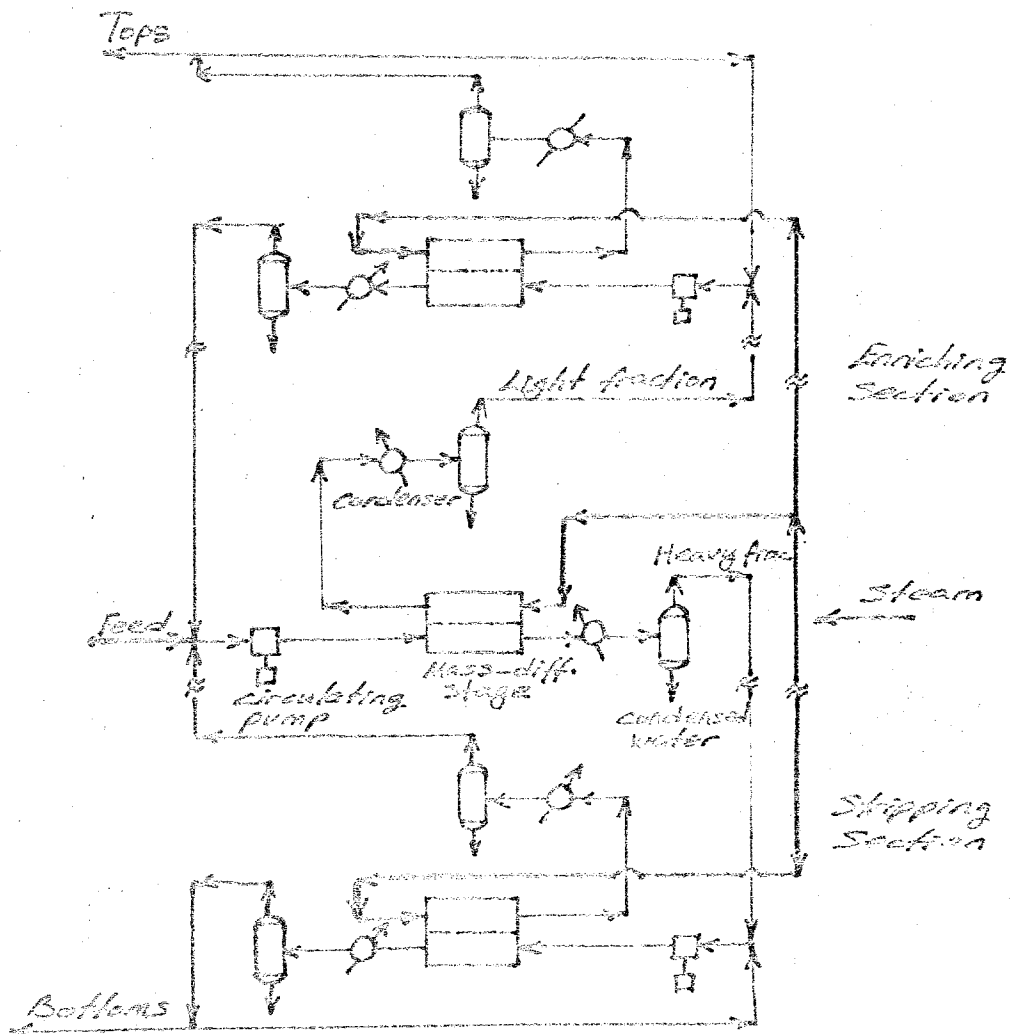


Fig.8.11. Cascade of mass-diffusion stages (26).
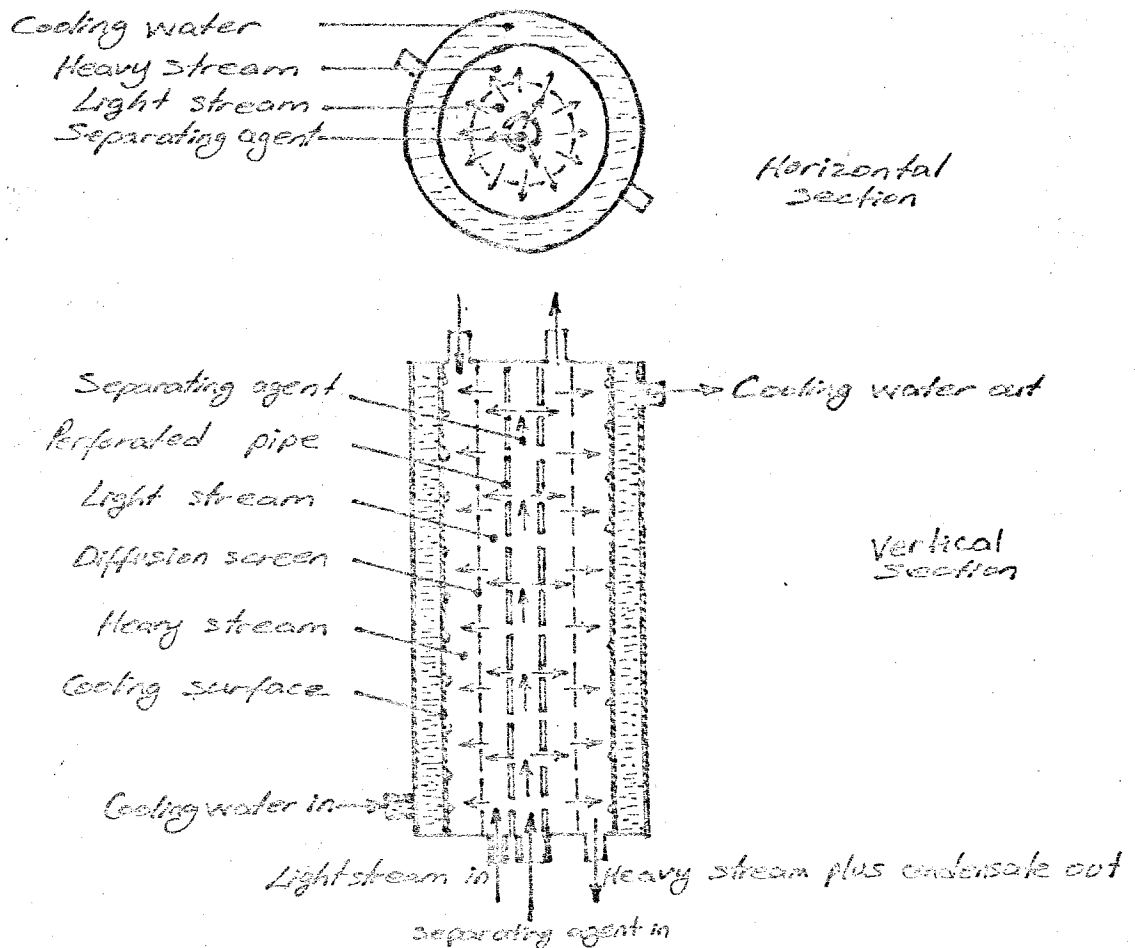
Figure.8.12 Flow in mass-diffusion column (26)

## 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 cofined 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 elemantary 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

-67-

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)
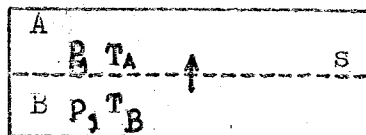


But it still stayed a scientific curiocity until Clasius and Dickel developed their thermal diffusion column in 1938 (2). The thermal diffusion column is illustrated schematically in fig. 8.14. As it can easily be understood, light isotope concentrates near the inner(hot) cylinder which is as close as 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 $M_g \omega^2 r^2$ 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

$$q_o = e^{(M_2 - M_1)\omega^2 r''^2 / 2RT}$$

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, $q_o$ 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 ($300^{\circ}K$).

Means for developing the high peripheral velocity needed for appreciable separation of isotopic mixtures have been developed by Beams and coworkers in the U.S, Khariton in Russia, and Groth and coworkers in Germany (26)
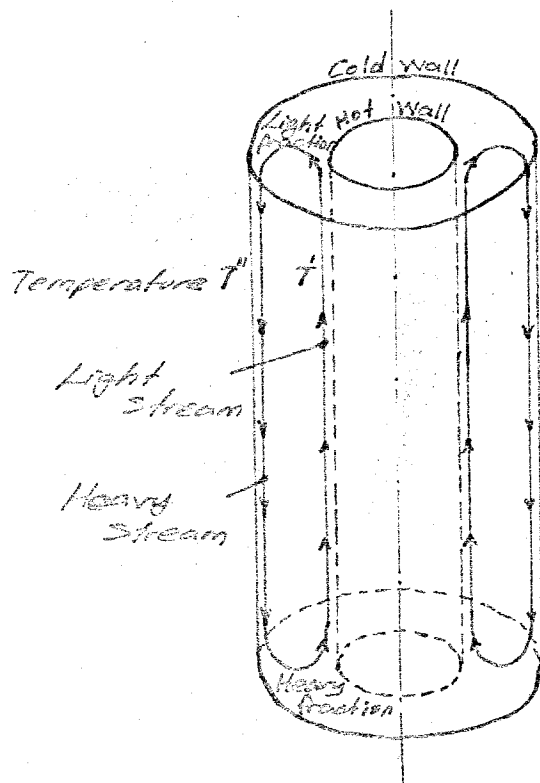
Fig.8.14 Thermal diffusion column (26).
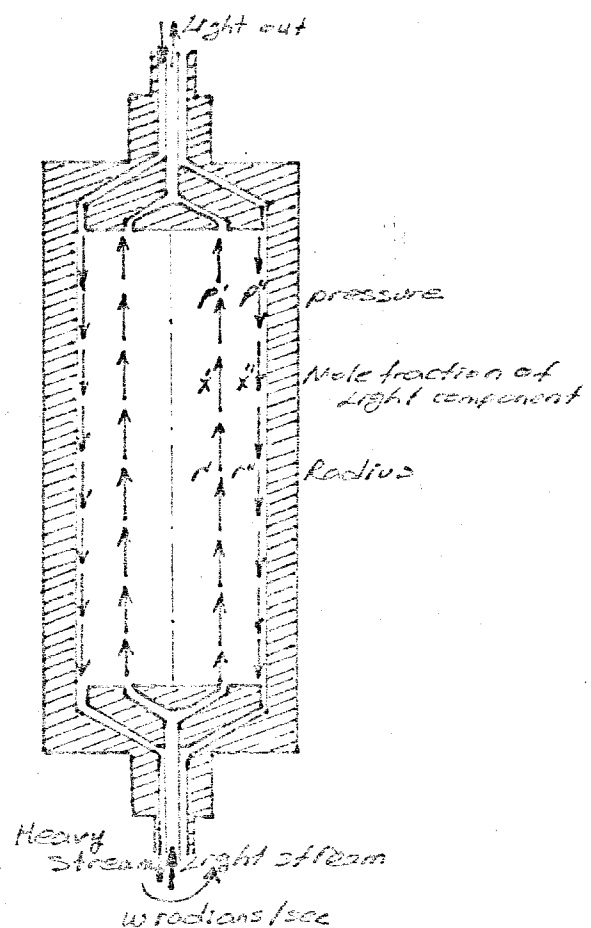


Fig.8.15. Counter current gas centrifuge (26).

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 diffi-
culty of a separation represents the difference in the enriched and
depleted stream compositions.Table 8.4 compares the diffusion proces-
ses applied to $U^{235}-U^{238}$ mixture according to separation factors.The
result of this separation can be concluded as for large-scale separa-
tion 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) | $UF_6 - C_7F_{16}$ | 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 $UF_6$ (37). Teflon is used for the gaskets and accessory parts.

# Chapter 9

## 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, Presurized 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 $^{\circ}$C (42). The size of agglomerates is ultimately 1 to 5 $\mu$ (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.

$$2UF_6 + 2NH_3 + 7H_2O \longrightarrow (NH_4)_2U_2O_7 + 12\ HF$$

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 owen. Dried ADU is taken and sent to a reduction furnace in which the reduction to $UO_2$ happens at 800$^{\circ}$C.(2). After $UO_2$ is cooled in nitrogen atmosphere, easily crushed agglomerates are obtained. The agglomerates having particles rangeing in size from 0.5 to 2 $\mu$ (37), are hammer milled to get fine powder.

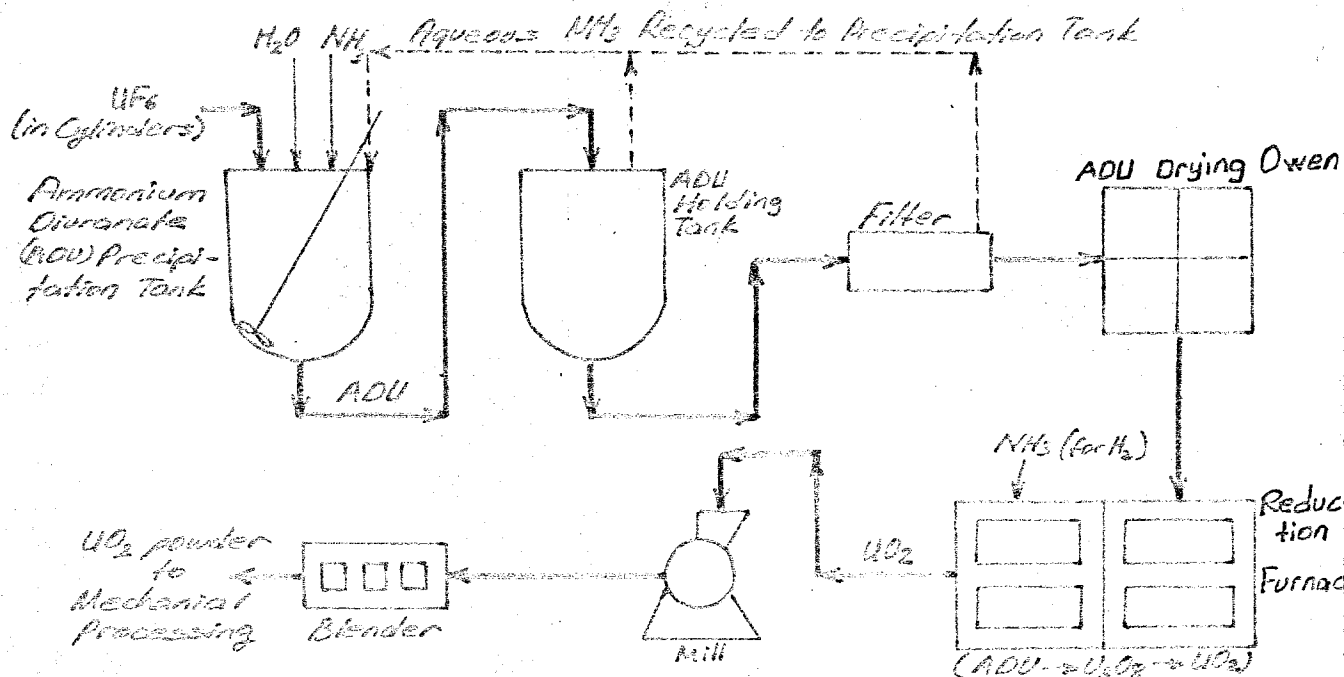To eliminate the aqueous operation, a dry method has been deve-

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:

$$UF_6(g) + 2H_2O(g) \longrightarrow UO_2F_2(s) + 4HF(g).$$

$$UO_2F_2(s) + 2H_2(g) + H_2O(g) \longrightarrow UO_2(s) + 2HF + H_2O(g)$$

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 $1\mu$ is oxidised in air at room temperature to $UO_{2.02}$ in approximately 1 month, whilst powder of particle size $0.06\mu$ 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 coallescense 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
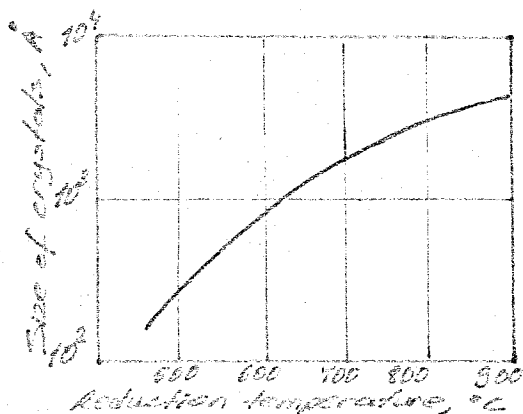the crystalline particles
as a function of the $UO_2$
reduction temperature
(8)


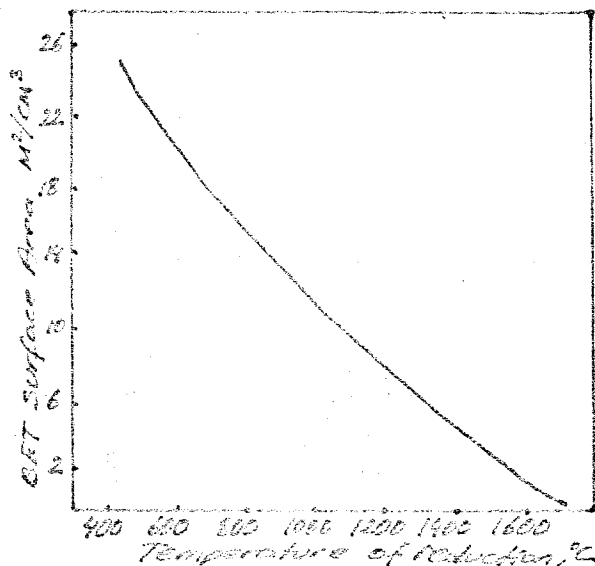
Fig.9.4 BET surface area of $UO_2$
prepared by hydrogen
reduction of $UO_3$ at various temperatures.
(42)



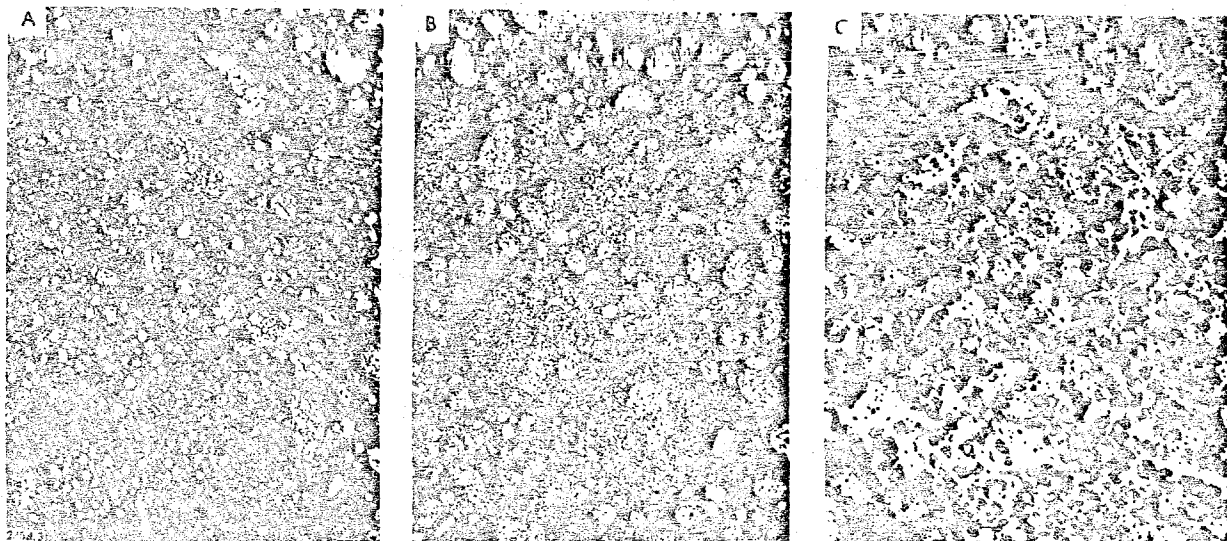Fig.9.3. Effect of reduction temperature on microstructure of
$UO_2$ prepared from $UO_3$ ; A,reduced at $480^{\circ}C$ X160;B,reduced at $800^{\circ}Cx160$; C, reduced at $1650^{\circ}Cx160$ (42).

## 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 fallowed by sintering of ceramic-grade $UO_2$ powders. The process is as follows. The powder is first treated with an organic binder such as polyvinil 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 $70^{o}C$ (2).

Granulated $UO_2$ obtained by forcing the dried batch trough 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 $800^{o}C$ for 2 hours (43) to remove the binder and lubricant. Pellets which are sintered partly during dewaxing are fed into to a molybdenum-wound hydrogen atmosphere furnace and sintered. The sintering operation is performed in dry hydrogen atmosphere in a typical temperature range of $1600-1750^{o}C$ (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 $1200-1300^{o}C$ (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.
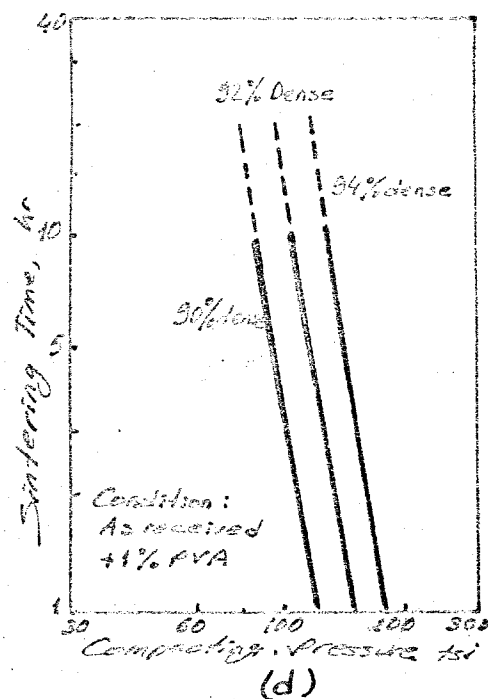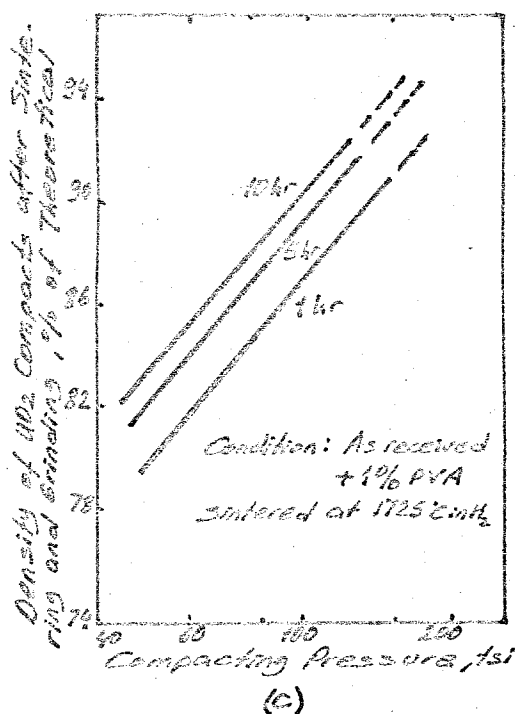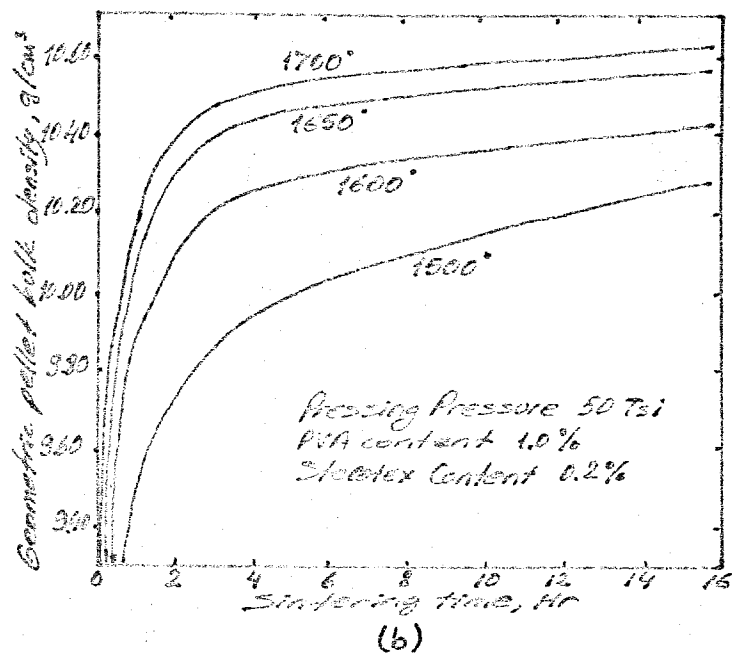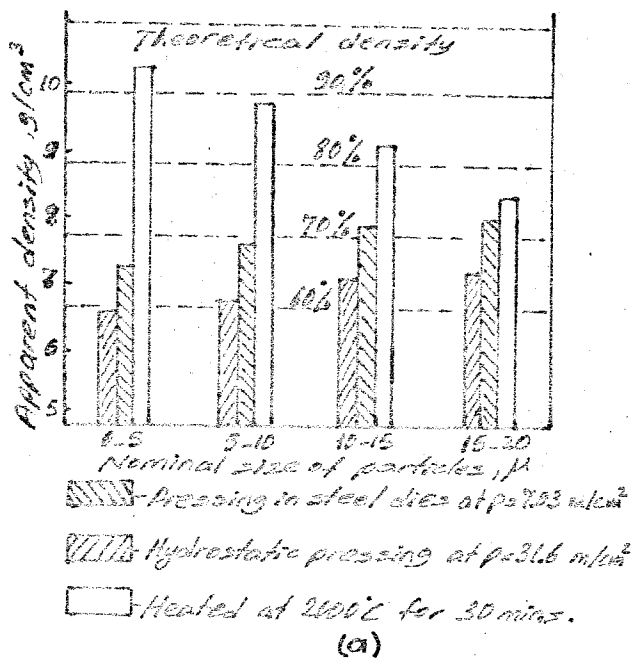
Fig.9.5 Effects of processing variables on the sintered density
of UO₂ compacts. a) Change in density of UO₂ objects as a
function of particle size in different stages of treat-
ment (2). b) Effect of sintering time and temperature(2),
c). Sintered density as a function of compacting pres-
sure and sintering time (43), d). Sintering time as a func-
tion of pressure and density (43).

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

| Method of Production | Specific Surface M²/g | U/O atomic ratio | Pressing Pressure kg/mm² | Sintering Temperature (in H₂), °C | Max. value of density of sintered material, g/cm³ |
|---|---|---|---|---|---|
| Denitration of UO₂(NO₃)₂, H₂-reduction at 800°C | 0.62-2.75 | 2.02-2.16 | 28.3 | 1700 (30 min) | 7.8-9.2 |
| Hydration of UO₃, obtained by dehydration of UO₂(NO₃)₂, with wet crushing in a ball mill, H₂-reduction at 800°C | 1.9-7.9 | 2.04-2.16 | 28.3 | 1800 (30 min) | 10.4-10.8 |
| Precipitation of (NH₄)₂U₂O₇ at 60°C and pH=9-9.3 from concentrated solutions, calcining and H₂-reduction at 900°C | 3.8 | 2.18 | 28.3 | 1600-1600 (60-30 min) | 9.5-10.8 (greater part above 10.2) |
| Precipitation of UO₄ peroxide, H₂-reduction | — | — | 8.15 | 1750 (90 min) | 10.7 |
| Hydrolysis of UF₆ by steam at 130°C and reduction by a steam hydrogen mixture at 150°C | — | — | 31.5 | 1600 (4 hr) | 10.8 |
| Continuous precipitation of (NH₄)₂U₂O₇ at pH=7-7.5 and low rates of reaction, quenching and H₂-reduction at 900°C | 1.8 | — | 28.3 | 1600-1650 (40-90 min) | 8.1-10.7 |

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

| Atmosphere | % of theor. density | O/U ratio | Atmosphere | % of theor. tral dens. | O/U ratio |
|---|---|---|---|---|---|
| H₂ only | 81.2 | 2.00 | 62H₂+38H₂O only | 88.4 | 2.21 |
| Air (1400-1500)c | 86.9 | 2.80 | 98He+2H₂O (1400-1500°c) | 97.3 | 2.10 |
| Steam (1400-1500)c | 97.7 | 2.01 | 43He+57H₂O ( " ) | 97.7 | 2.00 |
| Steam only | 82.2 | 2.10 | 38H₂+2H₂O only | 86.3 | 2.09 |
| 98H₂+2H₂O only | 85.8 | 2.00 | 98N₂+2H₂O (1400-1500°c) | 85.6 | 2.01 |
| 84H₂+16H₂O only | 85.8 | 2.00 | 38N₂+2H₂O 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 $1650^{o}C$ 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 $UO_{2.13}$ with cold pressed and sintered $UO_{2.13}$. It is easy to see that the maximum density of 10.25 g/cc of the British oxide is approached at $1400^{o}C$ and above 1800 $^{o}C$ the density again increases slighty 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.
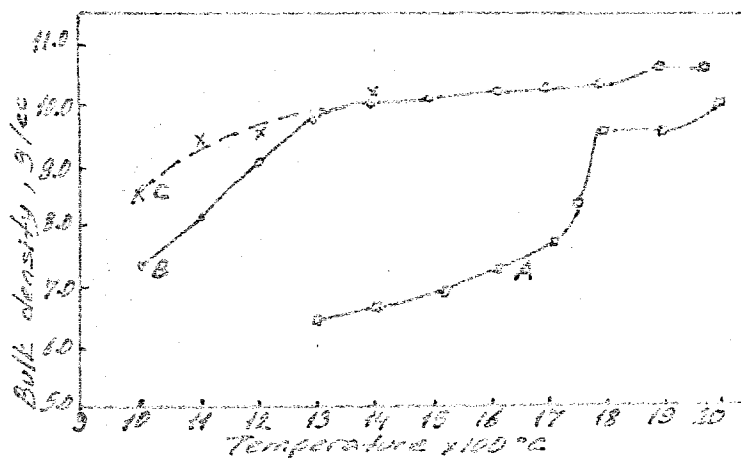


Figure.9.6 Hot-pressing characteristics of uranium oxide
A-$UO_2$, B-$UO_{2.13}$, C- Cold-pressed and sintered $UO_{2.13}$(4)

## 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 $\mu$ | 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 | 83 | 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 Hz 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 (Carbopol 934) wt.% | Ball-milling time hr. | Liquid added wt.% | Blended in Rubber mill | Extrusion Pressure t.s.i | Drying time hr | Sintering time at 1750C 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 | 54-56 | 91-96 |
| Ceramic-grade $UO_2$ of low surface area per unit volume | 1.2 | 3 | 7 | Yes | 15 | 48 | 8 | 56-58 | 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(Dynpak). In this case 99 % of theoretical density is obtained.
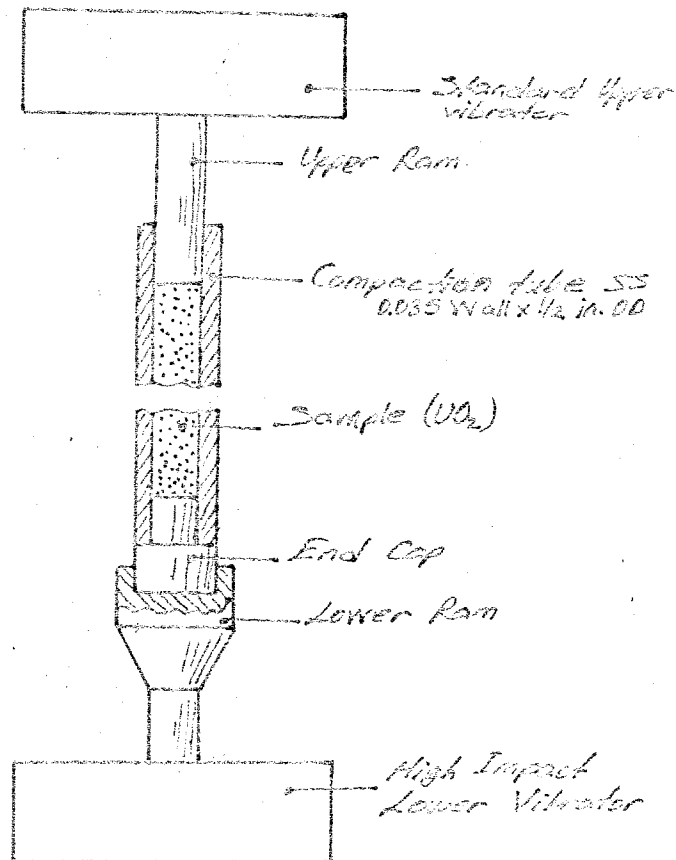


Fig.9.7 Pneumatic compaction apparatus for producing fuel units (2).

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,zircoloy 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 UO₂ Swaged with Various Cladding Materials (43).

| Cladding Material | Wall thickness of cladding before swaging in. | Maximum UO₂ density after swaging, % of theoretical |
|---|---|---|
| 304L Stainless steel | 0.065 | 87 |
| 304L Stainless steel | 0.035 | 86 |
| Zircaloy 3 | 0.030 | 84 |
| Aluminum | 0.060 | 82 |

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

| Cladding Material | Swaging Temperature °C | UO₂ density % of theoretical |
|---|---|---|
| 0.035-in. SS (304L) | Room temp. | 86 |
| 0.035-in. SS (304L) | 600 | 91 |
| 0.030-in. Zircaloy-3 | Room temp. | 84 |
| 0.030-in. Zircaloy-3 | 440 | 86 |
| 0.030-in. Zircaloy-3 | 600 | 88 |
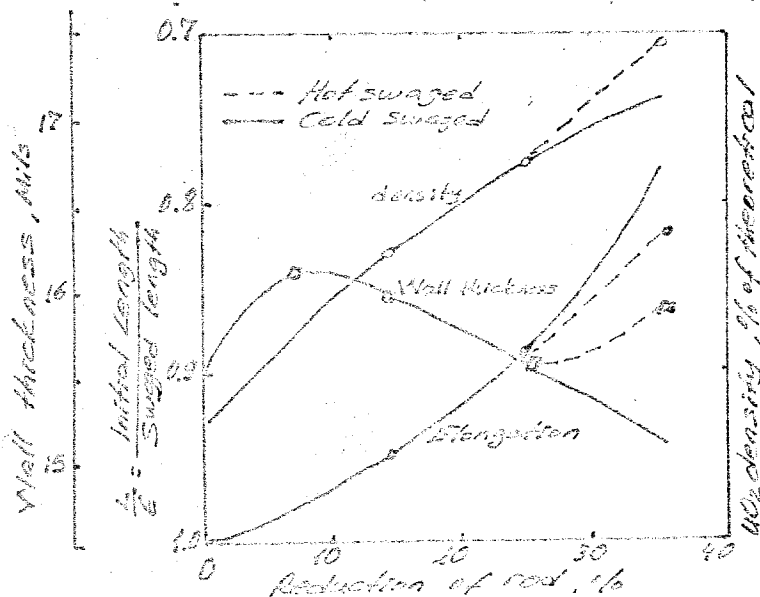


Fig.9.8. Wall thickness, elongation and density of hot and cold swaged fuel rods as a function of reduction (2).

## 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 outher 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 etxracted 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 outaclave 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 $\alpha$ 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.

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 1MW swimming pool type of research reactor at Küçük Çekmece,Istanbul. On May 27,1962 ,this reactor became critical and Çekmece Nuklear 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.Sedimantary ores.

The exploration studies were started after 1956.The uraniferous 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 assummed 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. Urainum 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-Kuçukçavdar 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-Kuçükkuyu 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 sedimantary formations ,autunite mineralization is realized.It's 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-Küçükkuyu | : 250 t $U_3O_8$ |
| Giresun-Şebinkarahisar | : 300 t $U_3O_8$ |
| TOTAL | : 5100 t $U_3O_8$. |

## 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 $km^2$(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 $H_2S$ 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 $m^3$/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 |
| Adsorpsion surface required | $10^6$ $m^2$ |
| Adsorpsion pool number | 60 |
| Total pool volume | $4.2 \times 10^5$ $m^3$ |
| Sea water flow rate in pool | 27 m/hr |
| Initial amount of Titannium oxihydrate (which is the most suitable substance to adsorb uranium ion complexes from sea water.) | $7.2 \times 10^4$ 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, 15 ppb uranium (49) has been found. Since Demirköprü Dam passes aproximately 700 million $m^3$ 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 hydralic 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 $P_2O_5$/year. Turkey's phosphate reserves inclusive of the prospective reserves amounts to 416.000.000 m.tons of 7-21.5% $P_2O_5$, 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 87 %,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-Kasrık 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.Asphalties and Other Minerals:

Asphalties are formed by techtonic 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 ,Ottowa, Canada and MTA on January 11,1960 for magnetic and radiometric airborne exploration  covering an area of 140000 $km^2$ namely the Aegean,the Central Anatolia,and East Touros 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 wiht 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 elavation 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 sedimantation.
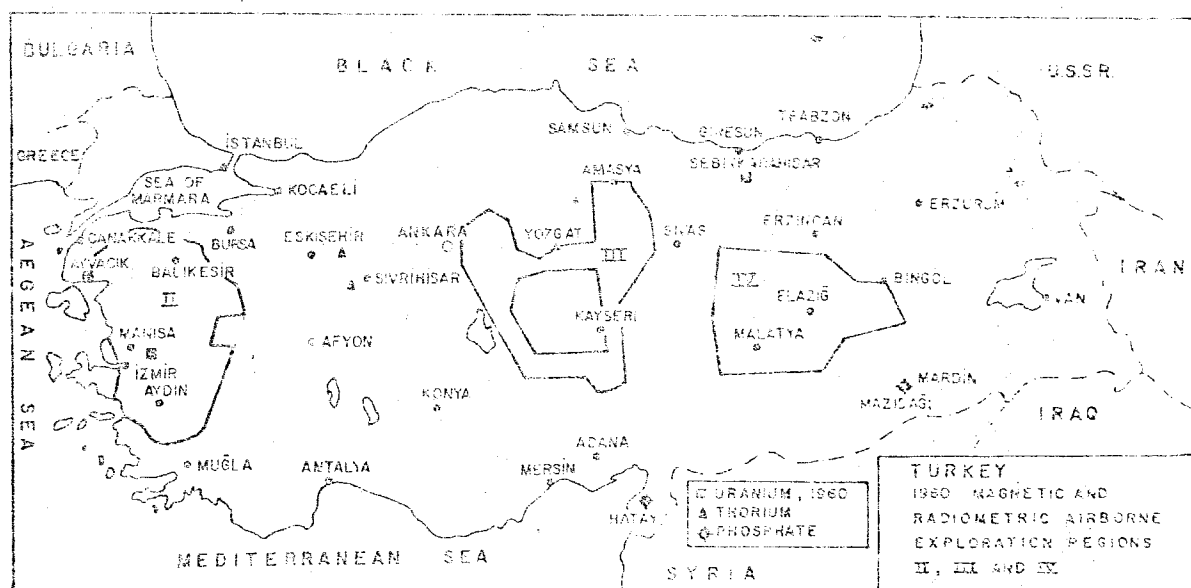


Fig.10.1. Uranium(1960),Thorium and Phosphate(1960) Deposits; also shown are the magnetic a radiometric airborne explorations mainly intended for iron investigations of 1960 in three regions II,III,and IV amounting to a total 140 000 Km² in Turkey (44)

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,horizantal and under ground such that
no direct samples can be obtained.Uranium ores prospecting in Tur-
key are sandstone types.

IAEA-MTA project carried out in South-West Anatolia is a good
example for a project applying modern exploration methods.The pro-
ject area is given in figure 10.2. In this project,drilling areas
were chosen according to geological mapping,aerial and surface ra-
diometric 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
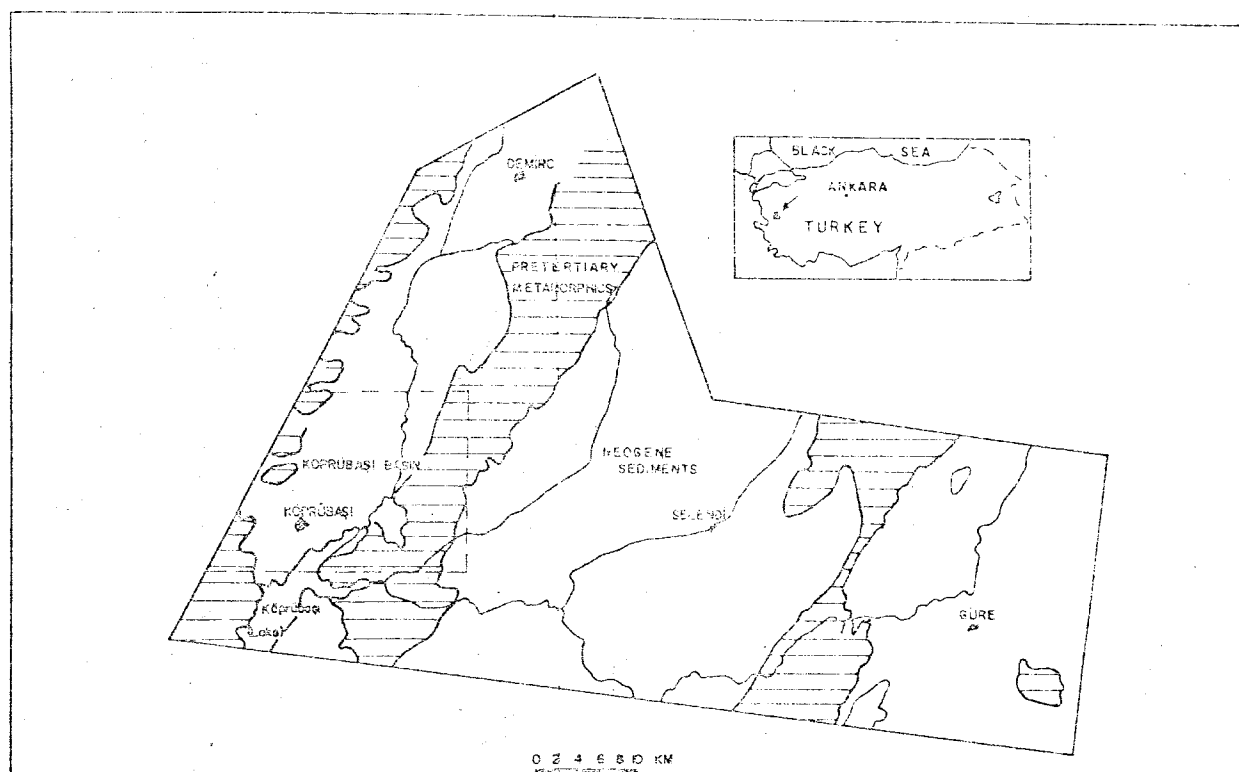


Figure 10.2. UNDP Project area for uranium exploration (44).

stream sediments for determining the uranium and radon concents
(see fig.10.3).Results of laboratory tests were prepared by com-
puter and labelled on maps.Figures 10.4 and 10.5 illustrate such
maps.In the project region ,the area having high radioactive ano-
malies occupied an area of 30 $km^2$.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,continuous-
ly.Basic subsurface data were taken into consideration to obtain
lithologic interpretation and stratigrafic correlations.A geologist
noted the properties and tested the minerology of fragment samples

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

taken from each meter.Their copies were attached to other maps,re-
ports of the same location as a reference.All results have been
compiled and kept by MTA. Table 10.4 gives an idea about radioac-
tive element geological prospecting studies conducted by MTA bet-
ween 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 re-
gions. 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 regi-
ons 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 measu-
rements are still being continued through Lalapaşa-Çatalca line.
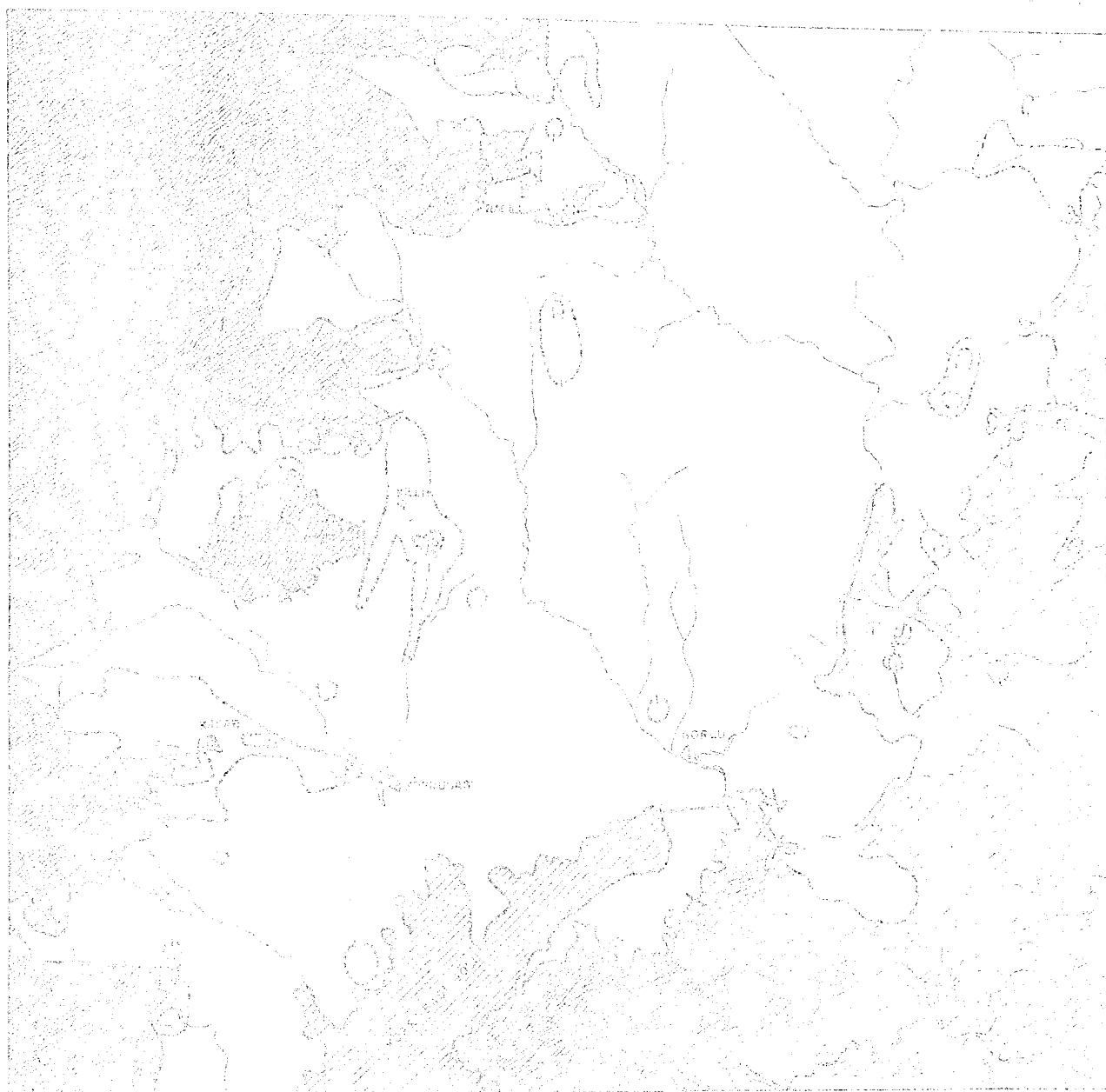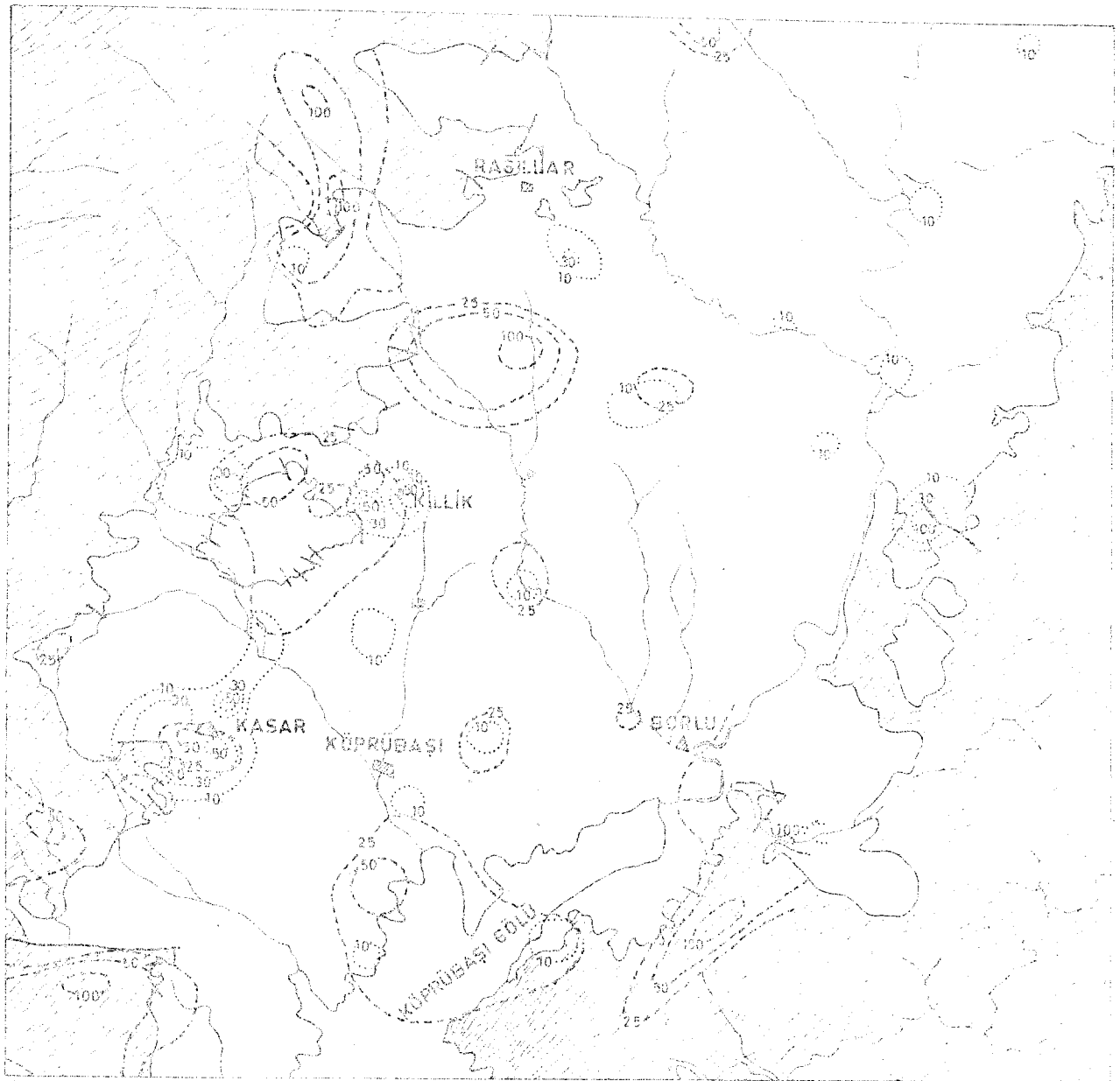
Fig. 10.4. Uranium content in stream sediments of Köprübaşı basin (65).

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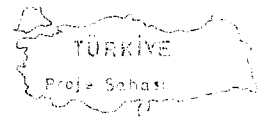- Pretertiary Metamorphics
- U Concentration Contours (ppm)

Fig.10.5. Uranium and radon contents in waters
taken from Küprübaşı basin (55).

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

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

Table 10.4. (continued)

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

11. Giresun-Şebinkarahisar-Koyulhisar Region :

Regional prospections and drilling studies were completed initially. Regions yielding radioactive anomalies are Eskine 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-İkizdere Region :

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

13. Bitlis Massive Region :

This region is surrounded by Bingol, Mus, 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 minerologic 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 $^{\circ}$ 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% eventhough 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).

| Region | ORE | Reserve U₃O₈ (ton) | Mineral | LABORATORY Agitation Leaching Sample:250gr(-65mesh) B/L=2/3, Time:4hr, Temp:25 U₃O₈ % | H₂SO₄ kg/ton-Ore | Efficiency U₃O₈ % | Column Leaching Sample:10kg(-2cm) S/L=2/1 Time:5-10 days, Temp:25°C U₃O₈ % | H₂SO₄ kg/ton-Ore | Efficiency U₃O₈ % | PILOT Heap Leaching (Orig. Grain Size) U₃O₈ % | Amount of Ore (ton) | H₂SO₄ kg/ton-Ore | Leaching Time (day) | Solution (ton) | Washing Time (day) | Solution (ton) | Efficiency According to Solution U₃O₈ % | Disposal U₃O₈ % | Efficiency According to Disposal U₃O₈ % | Commercial Production (-,+) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K. Byrükköl | KAŞAR | | Metaautunite - Autunite | 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 | |
| | ÇETINBAŞ | | | 0.150 | 40 | 89.1 | 0.150 | 40 | 88.7 | 0.030 | 50 | 30 | 4 | 6 | 35 | 22 | 96.6 | 0.0003 | 97.0 | + |
| | KAYRAN | | | 0.038 | 40 | 87.5 | 0.038 | 40 | 94.7 | 0.093 | 84 | 40 | 15 | 30 | 48 | 42 | 83.7 | 0.0014 | 84.9 | + |
| | TOPALLI - Conglomerate | 3040 | | 0.105 | 20 | 96.6 | 0.105 | 40 | 98.0 | 0.076 | 72 | 30 | 4 | 5 | 53 | 75 | 93.8 | 0.0062 | 91.3 | + |
| | TOPALLI - Tuffit | | | 0.020 | 20 | 73.0 | 0.020 | 20 | 85.6 | 0.052 | 134 | 20 | 7 | 26 | 38 | 51 | 98.0 | 0.0053 | 89.8 | + |
| | TOMAŞA | | | 0.020 | 20 | 96.0 | 0.020 | 20 | 90.5 | 0.020 | 57 | 20 | 5 | 6 | 28 | 30 | 91.2 | 0.0024 | 88.0 | + |
| | ECINLITAŞ (80-150 m) | | | 0.010 | 28 | 90.0 | 0.010 | 30 | 99.0 | Sampling is impossible | | | | | | | | | | |
| | TAŞHARMAN Conglomerate | | Uranium in Dolbite | 0.040 | 75 | 89.0 | 0.030 | 100 | 49.1 | 0.030 | 110 (-5cm) | 100 | 14 | 70 | 10 | 35 | — | 0.0130 | 56.6 | |
| | TAŞHARMAN Tuffit | | | 0.041 | 75 | 92.7 | 0.120 | 100 | 32.0 | 0.055 | 67 (-5cm) | 100 | 13 | 50 | 9 | 35 | — | 0.0200 | 63.6 | |
| | KAŞA/TAŞHARMAN-Cong/Tuff | | | — | — | — | 0.038 62kg | 80 | 93.3 | 0.060 | 100 2/1/1 | 85 | 8 | 18 | 16 | 110 | 70.3 | 0.023 | 61.6 | |
| MANISA | YARDERE | | Uranium in Carbonate | 0.038 | 25 | 94.1 | 0.038 | 80 | 88.7 | 0.036 | 50 | 80 | 30 | 40 | 18 | 30 | 40.0 | 0.018 | 50.0 | — |
| | TÜLLÜCE | | | 0.027 | 80 | 92.6 | 0.027 | 80 | 64.2 | x | x | x | x | x | x | x | x | x | x | — |
| | KOCADÜZ | | | 0.022 | 392 | 93.5 | x | x | x | x | x | x | x | x | x | x | x | x | x | |
| | GÖRDES | | | 0.030 | 320 | 26.7 | x | x | x | x | x | x | x | x | x | x | x | x | x | |
| | MANISA Alaşehir-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 | — |
| | UŞAK Fatih | 510 | gamma 12 gap. | 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 Koçarlı-Küçükçavdar | 1000 | Metaautunite | 0.380 | 20 | 96.4 | 0.450 | 20 | 95.7 | Sampling after detailed analysis | | | | | | | | | | + |
| | AYDIN Koçarlı-Arapsu | | | 0.850 | 20 | 95.0 | 0.850 | 20 | 98.0 | | | | | | | | | | | + |
| | GIRESUN Şebinkarahisar-Esbine | 300 | | 0.230 | 20 | 95.1 | 0.230 | 20 | 93.0 | | | | | | | | | | | + |
| | ÇANAKKALE Küçükkuyu-Örencik | 250 | U in phospho. | 0.160 | 1000 | 93.1 | Since P₂O₅:30%, Phosphoric acid production is taken as the base | | | | | | | | | | | | | |
| | ÇANAKKALE Küçükkuyu-Karaothi | | | 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 preliminery 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°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-Küçükkuyu :

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-KÖPRÜBAŞI-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 amounth 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-

H₂SO₄ : 20 kg / ton of ore

"KASAR"
URANIUM ORE INPUT
[Approx. 10 cm.]
[Coarse Ore]

URANIUM ORE
ORIG. SOLUTION

POOL

LEACHING
BY SULPHURIC
ACID SOLUTION

COLLECTING
POOL
1

COLLECTING
POOL
2

COLLECTING
POOL
3

SETTLING
TANK

SETTLING
TANK

ALAMINE 336
KEROSENE
ISO OCCANOL
} ORGANIC SOLVENT
CIRCULATION
20 lt/Hr

ORGANIC
SOLVENT

PREGNANT
SOLUTION
1.5 gr U₃O₈ /lt
PH : 1
90 lt/Hr

MIXER — SETTLER

X       X       X

X       X       X

SOLVENT
EXTRACTION

NaCl
SOLUTION
PH : 1

4 lt/hr

REJECT
SOLUTION
U₃O₈ : 1-5 ppm.

CaO/
Ca(OH)₂

NEUTRALIZA
TION
TANK

CONCENTRATED
PREGNANT
SOLUTION
15-18 gr U₃O₈/lt

YELLOW
CAKE
PH : 5-6

MgO/
Mg(OH)₂

TAILING
DISPOSAL

FILTERING

YELLOW CAKE
OUTPUT
50 kg SACKS
MgU₂O₇
~75 % U₃O₈ (e)

105°C

DRYING

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.
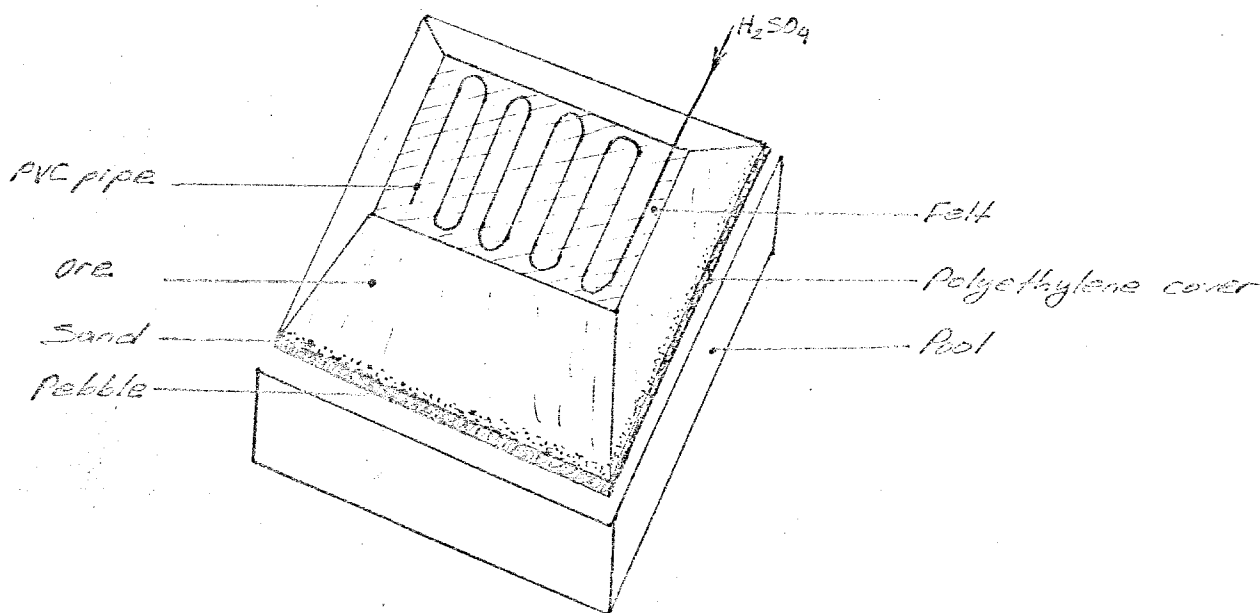


Fig.10.7. Preparation of a heap at MTA-Köprübaşı
pilot plant (61).

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/lt $U_3O_8$ concentration becomes a concentrated solution containing 15-18 gr/lt $U_3O_8$(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/lt $U_3O_8$ 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 $^{\circ}C$ in an owen. 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 analized. 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.

Inspite 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.
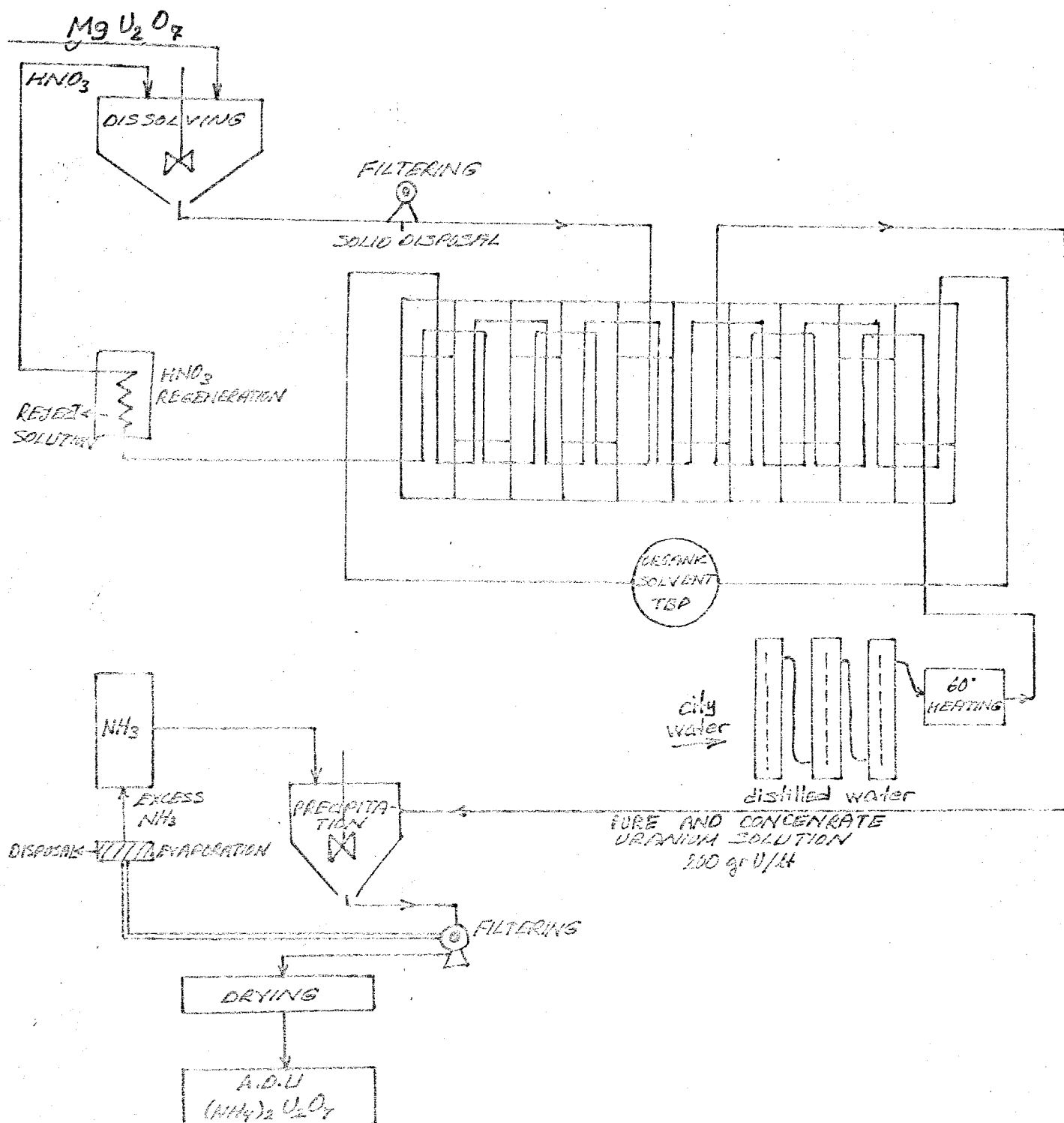
Fig. 10.8. Flow diagram of ammonium di uranate (ADU) production at laboratory scale at MTA-Köprübaşı pilot plant (47,64).

# 11. CONCLUSIONS AND RECOMMANDATIONS 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 LMFBR'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 develope 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 |
| LWFBR | 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 reliabilty 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 Feasibility Studies (Etibank+MTA) | Contracting of Engineering Services (Etibank) | Contracting of Main plant (Etibank) | Construction of the Main Plant and Preparation for Commercial Production (Etibank) | | | Commercial Production (Etibank) | Commercial Production (Etibank) |
| MANISA Plapehir | Evaluation of Pilot Plant Studies (MTA) | | Field Studies and Drilling (MTA) | | | | Commercial Production (Etibank) | " |
| UŞAK Fakılı | " | " | " | " | " | " | " | " |
| AYDIN Koşarlı | Laboratory Studies (MTA) | Pilot Plant Studies (MTA) | | Field Studies and Drilling (MTA) | | | " | " |
| GİRESUN Şebinkarahisar | " | " | " | " | " | " | " | " |
| ÇANAKKALE Küçükkuyu | Laboratory (MTA + A.E.K) | | Pilot Studies (MTA) | Field Studies, Drilling and Preliminary Feasibility (MTA) | | | " | " |

(1) Laboratory and pilot plant studies of Taşharman and Yardere locations which are considered to be problem areas, will continued.

(2) If samples could be obtained, pilot plant studies will be conducted at Köprübaşı Ecinlikaşı 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.

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