CH0204 Organic Chemical Technology

Lecture 14

Chapter 5 Nuclear Industries

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Overview of topics

Chapter 5 Nuclear Industries

1. Nuclear fuels
2. Nuclear fuel cycle
3. Nuclear reactions
4. Nuclear reactors

Nuclear fuels

Uranium and Thorium are the major source of nuclear fuels.

Uranium is abundant in earth's crust and it is distributed widely.

Thorium, while less widely used than uranium and is suitable as nuclear fuel.

Thorium exists with only one natural isotope, ^{232}Th and is not very rare. Most of it is obtained as by-product of processing of monazite, a complex phosphate .

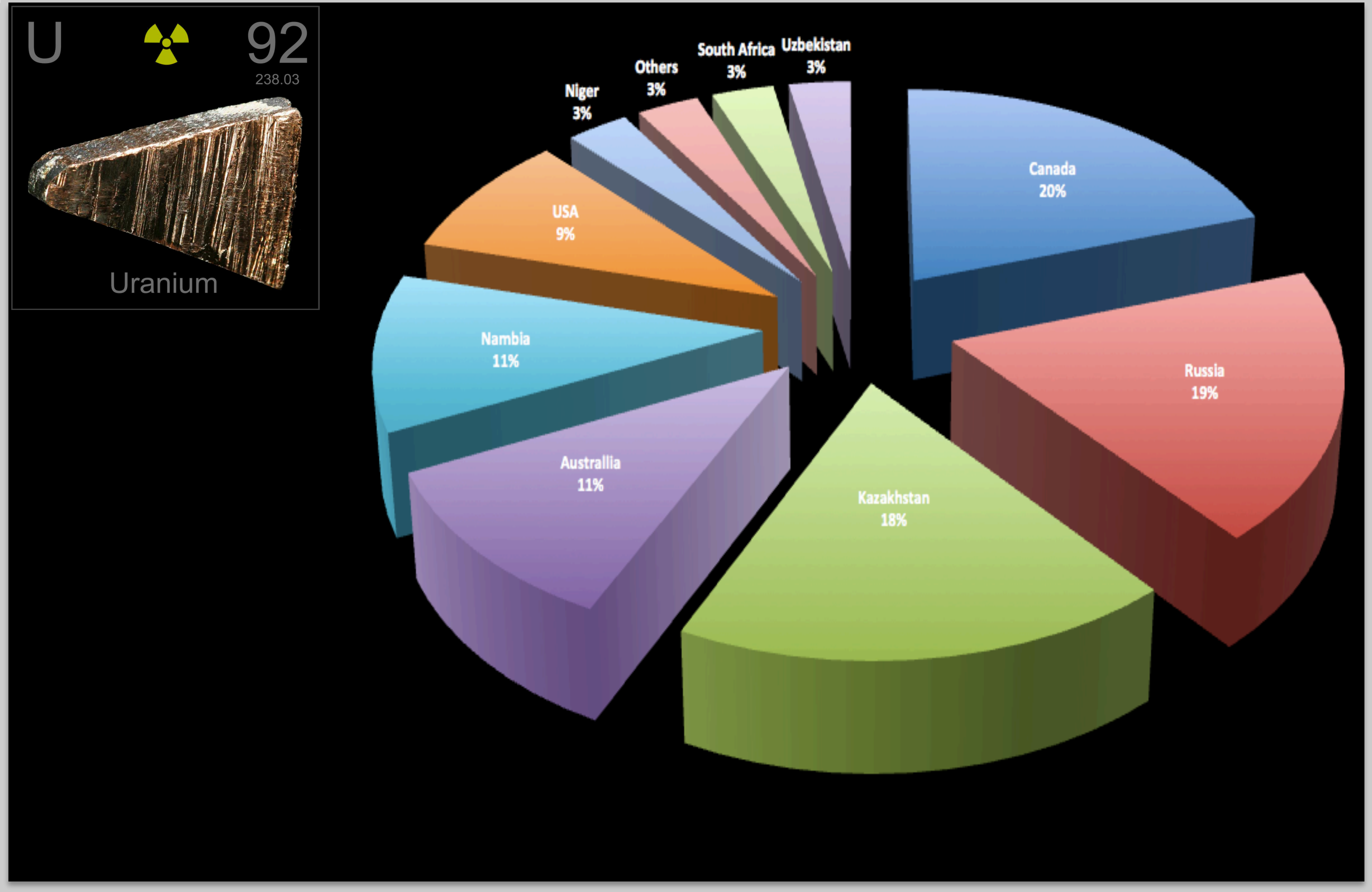
Major deposits are found in India, Brazil, South Africa, Australia, Malaysia and the United States.

Nuclear fuels

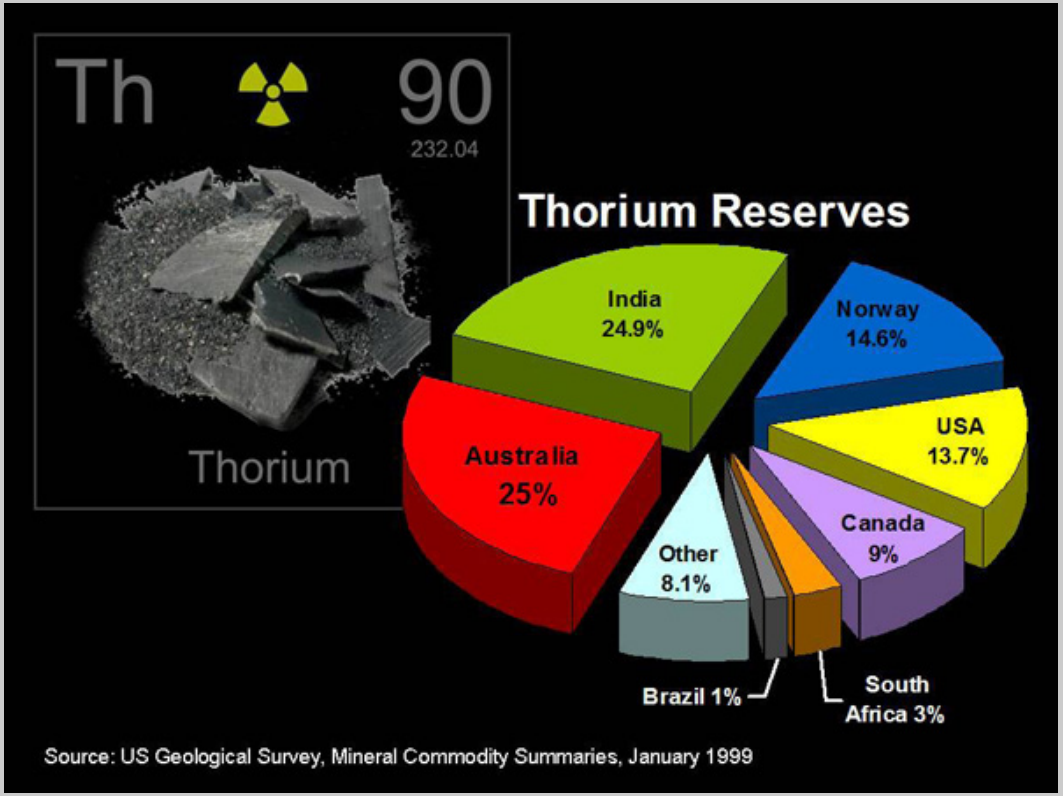
Uranium Ore

Thorium Ore

Nuclear fuels



Nuclear fuels



Thermal breeding advantages for thorium could not be achieved in aqueous solution because of extreme corrosion problem

The complicated decay scheme arises fabrication costs

Lack of technical feasibility

Nuclear fuels

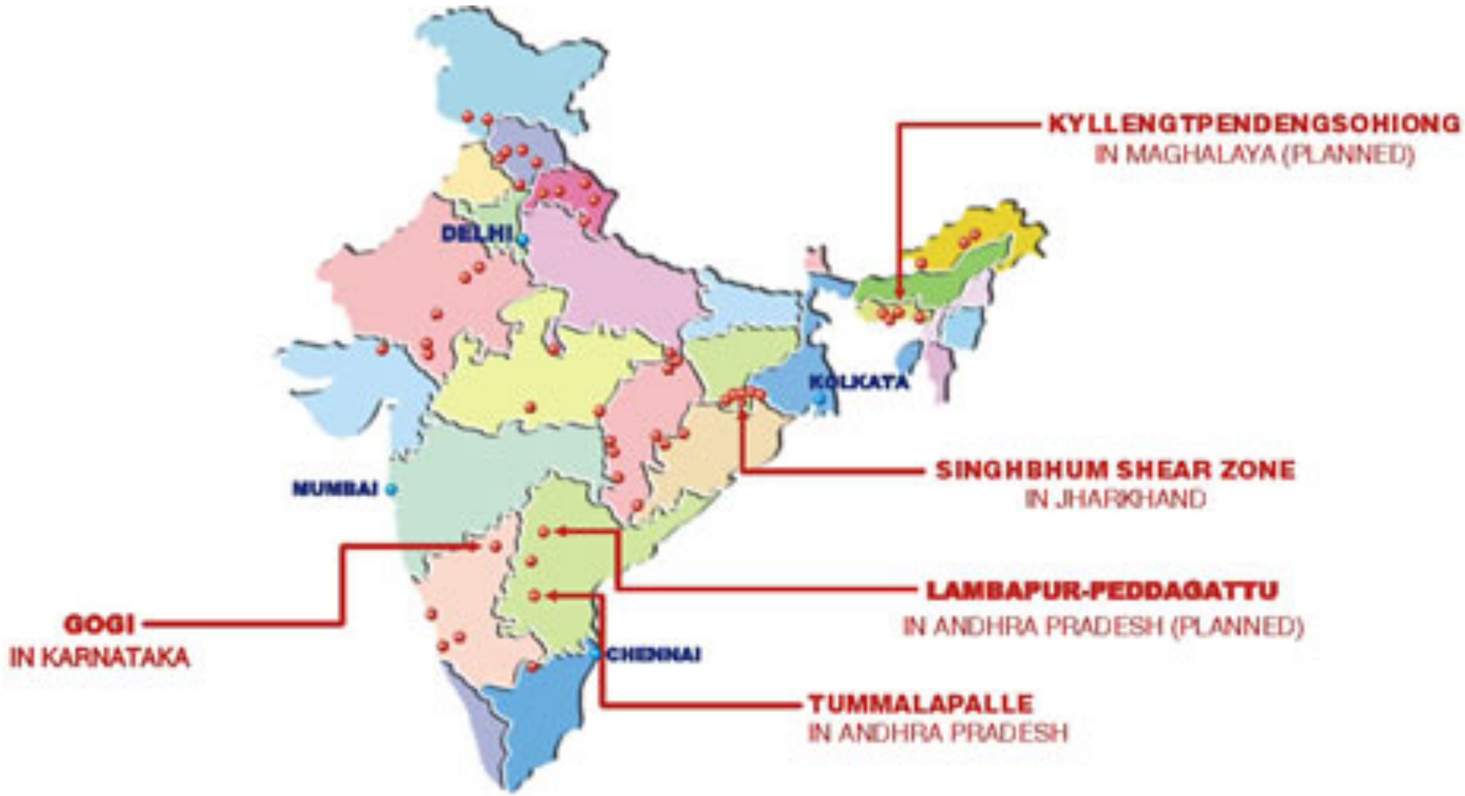
Fissionable isotopes are used as sources of energy in nuclear reactors.

Three isotopes that have a higher probability of fission that capture are ^{233}U, ^{235}U, and ^{239}Pu. Of these isotopes, only ^{235}U occurs in nature. The other two are reactor-synthesized.

These are the common materials that can sustain fission reaction and are therefore called as *nuclear fuels*.

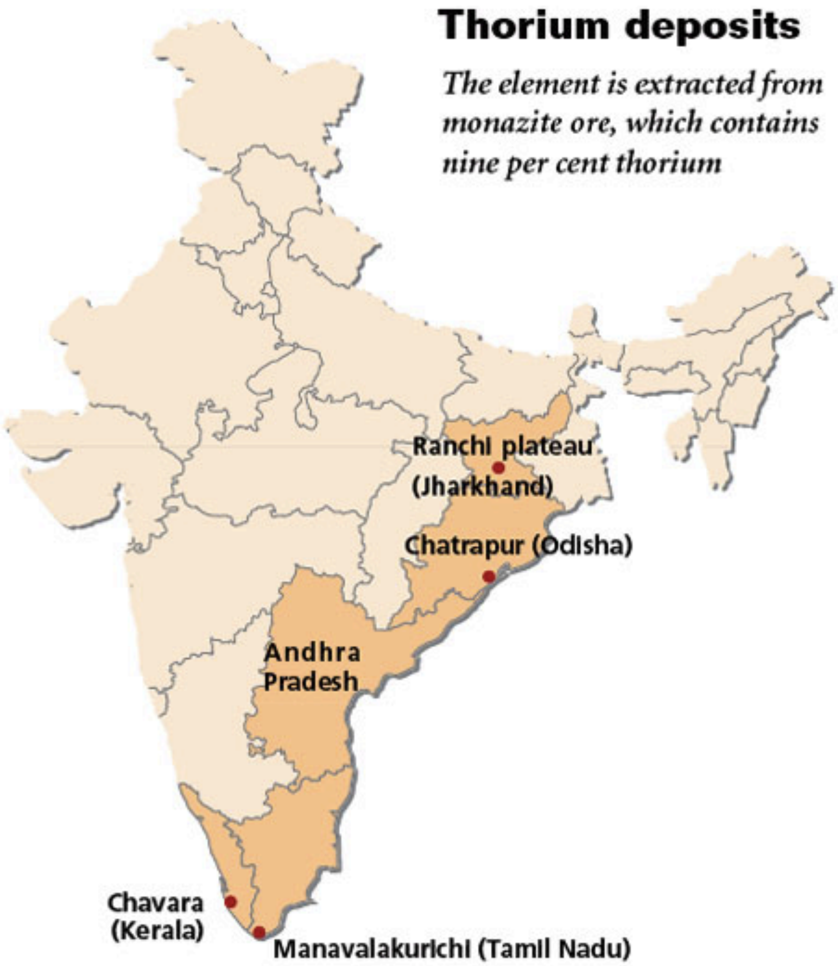
Uranium deposits in India

Uranium deposits in India



Source: UCIL

Uranium deposits in India



Ore to usable nuclear material

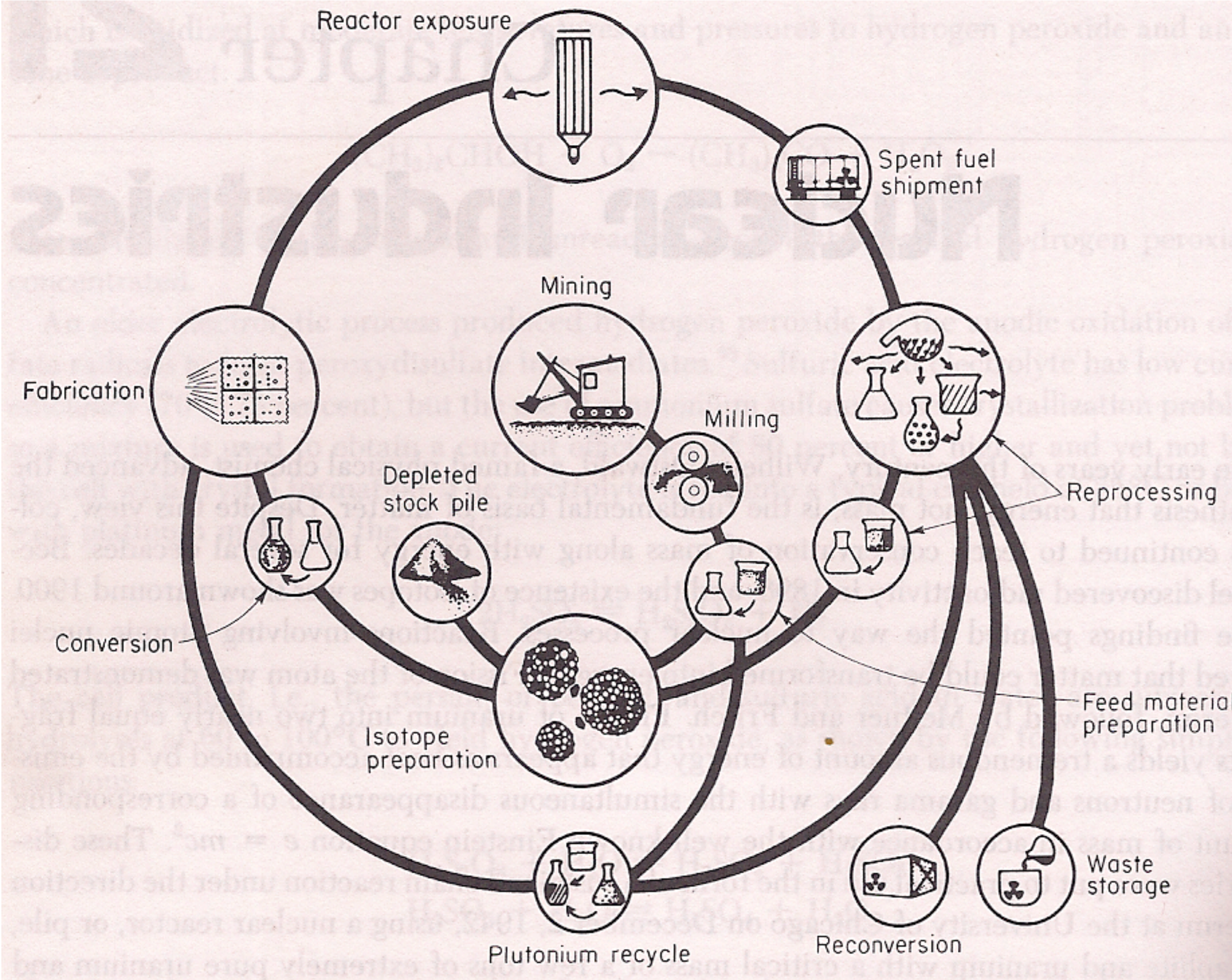
Uranium Ore, a primary Raw material

Yellow Cake impure Triuranyloctoxide (U_3O_8) for refining conversion

Uranium hexafluoride used for isotope enrichment Enrichment

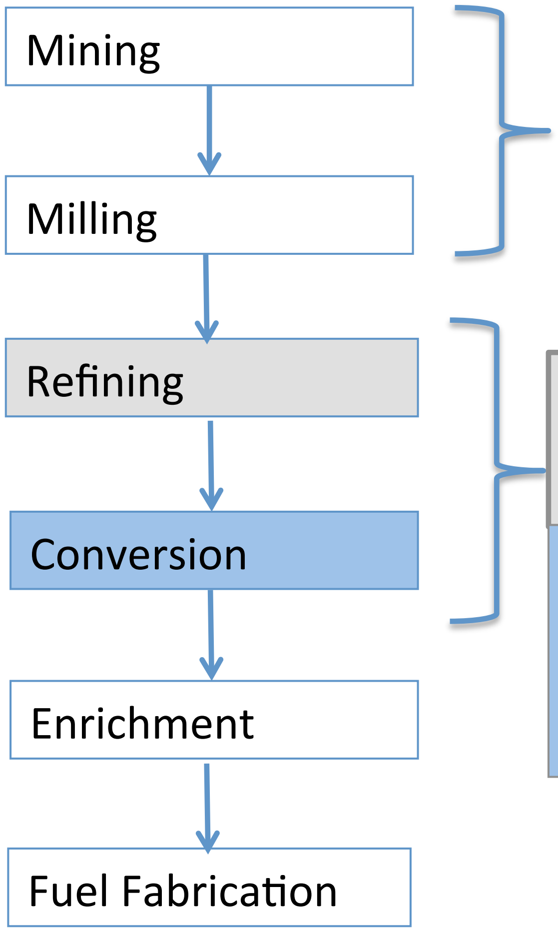
Fabricated, Compact Solid Nuclear Fuel

Flowchart from ore to usable nuclear material



Flowchart from ore to usable nuclear material

Overall Block /Flow Diagram form ore to usable nuclear material



Coversion of ore to yellow cake (triuranium octoxide) U_30_8

Transforming yellow cake (triuranium octoxide-U_30_8) to UO_3

$UO_2(NO_3)_2.6H_2O$	→	**UO_3** + $2NO_2$ + ½ O_2 + $6H_2O$	ΔH = +563 kJ
UO_3 + H_2	→	**UO_2** + H_2O	ΔH = -106 kJ
UO_2 + 4HF	→	**UF_4** +$2H_2O$	ΔH = -181 kJ
UF_4 + 2Mg	→	**U** + $2MgF_2$	ΔH = -350 kJ
UF_4 + F_2	→	**UF_6**	ΔH = -251 kJ

Flowchart from ore to usable nuclear material

Mining:
Physical Mining is done in Large Scale; The ore (containing 2 kg of U_3O_8 per ton) is shipped to the mill to purify further

Milling:
Extraction and Concentration of ore to yellow cake (or triuranium octoxide U_3O_8). The usual process is

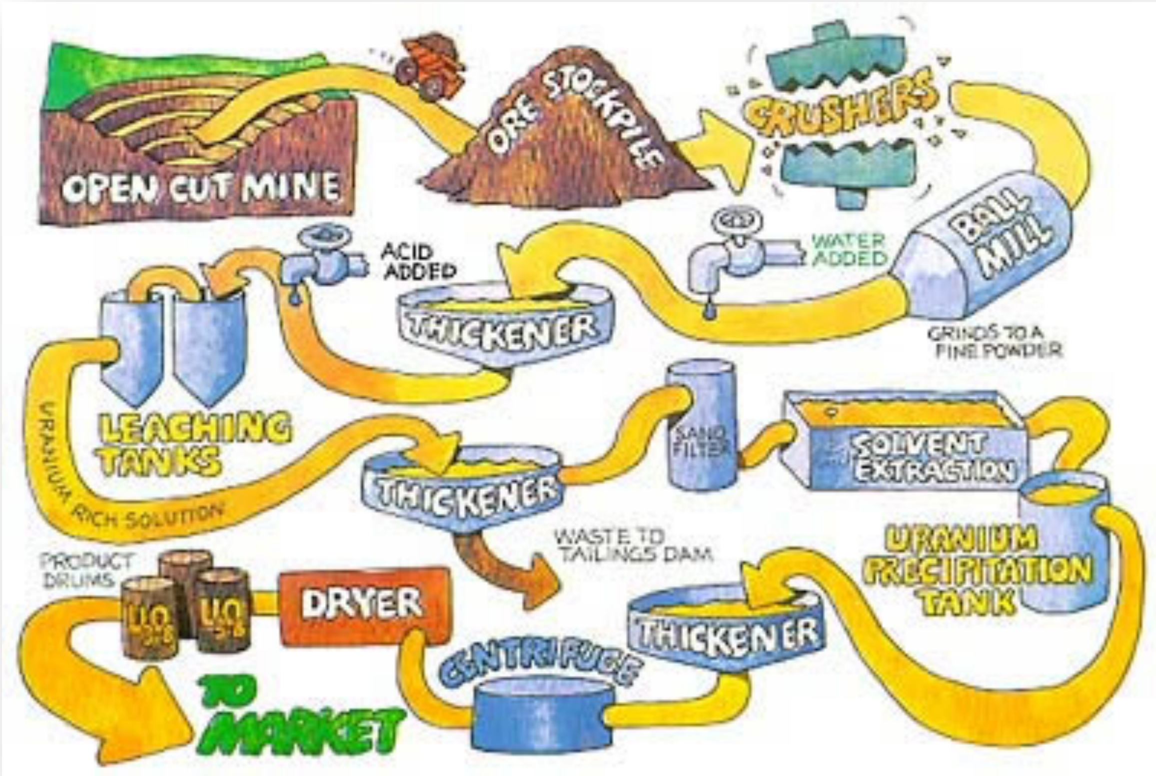
- Sulfuric acid extraction
- Solvent extraction
- Ion exchange and precipitation with caustic soda

Unit Operations involved in producing an impure U_3O_8

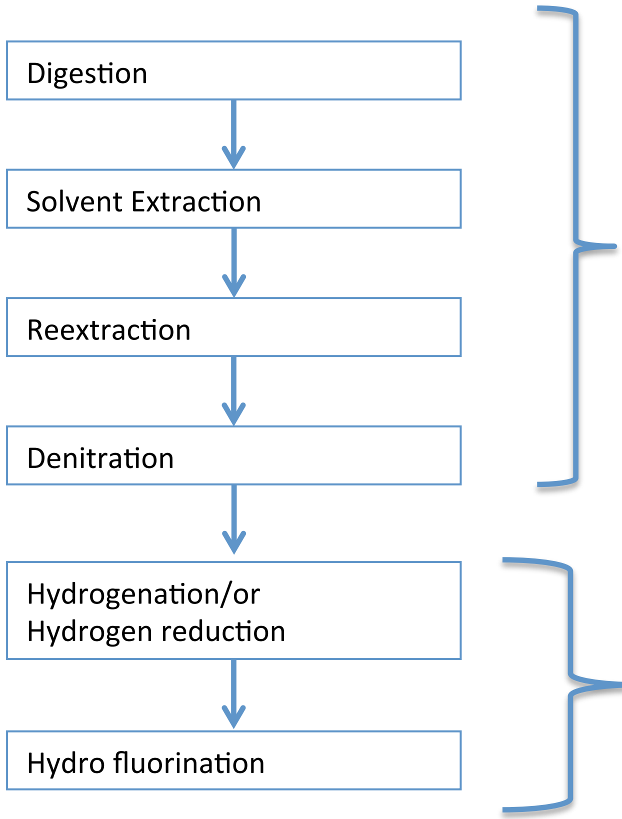
1. Crushing
2. Thickening
3. Leaching
4. Thickening
5. Filtration
6. Solvent extraction
7. Precipitation
8. Thickening
9. Centrifuging
10. Drying
11. Packing

Flowchart from ore to usable nuclear material

Flow diagram for mining and milling operations



Flowchart from ore to usable nuclear material



Refining and conversion Operations

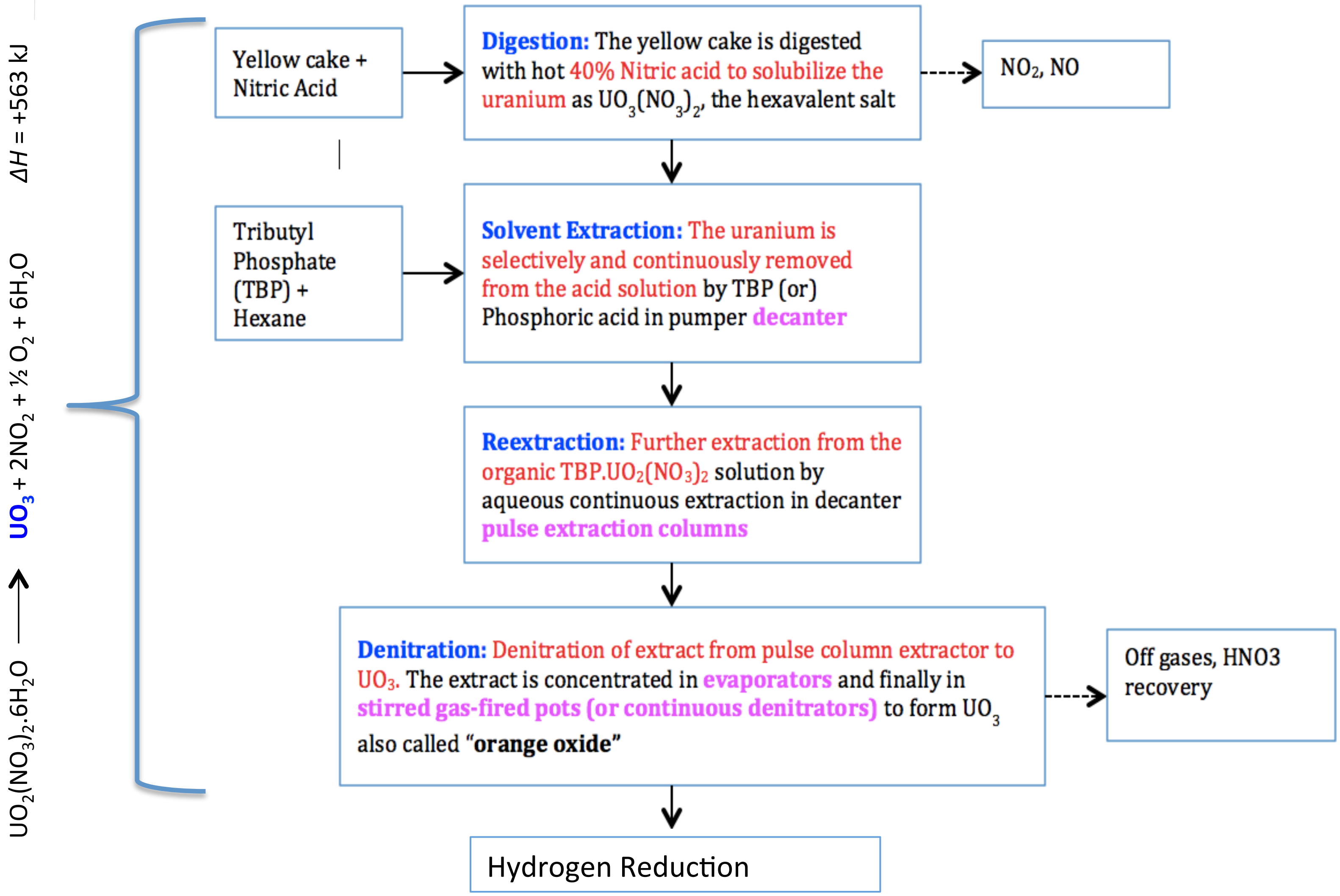
Refining

Further processing of yellowcake from the mill to remove impurities and chemical conversion to UO_3 (uranium trioxide), the feedstock for the next stage of processing.

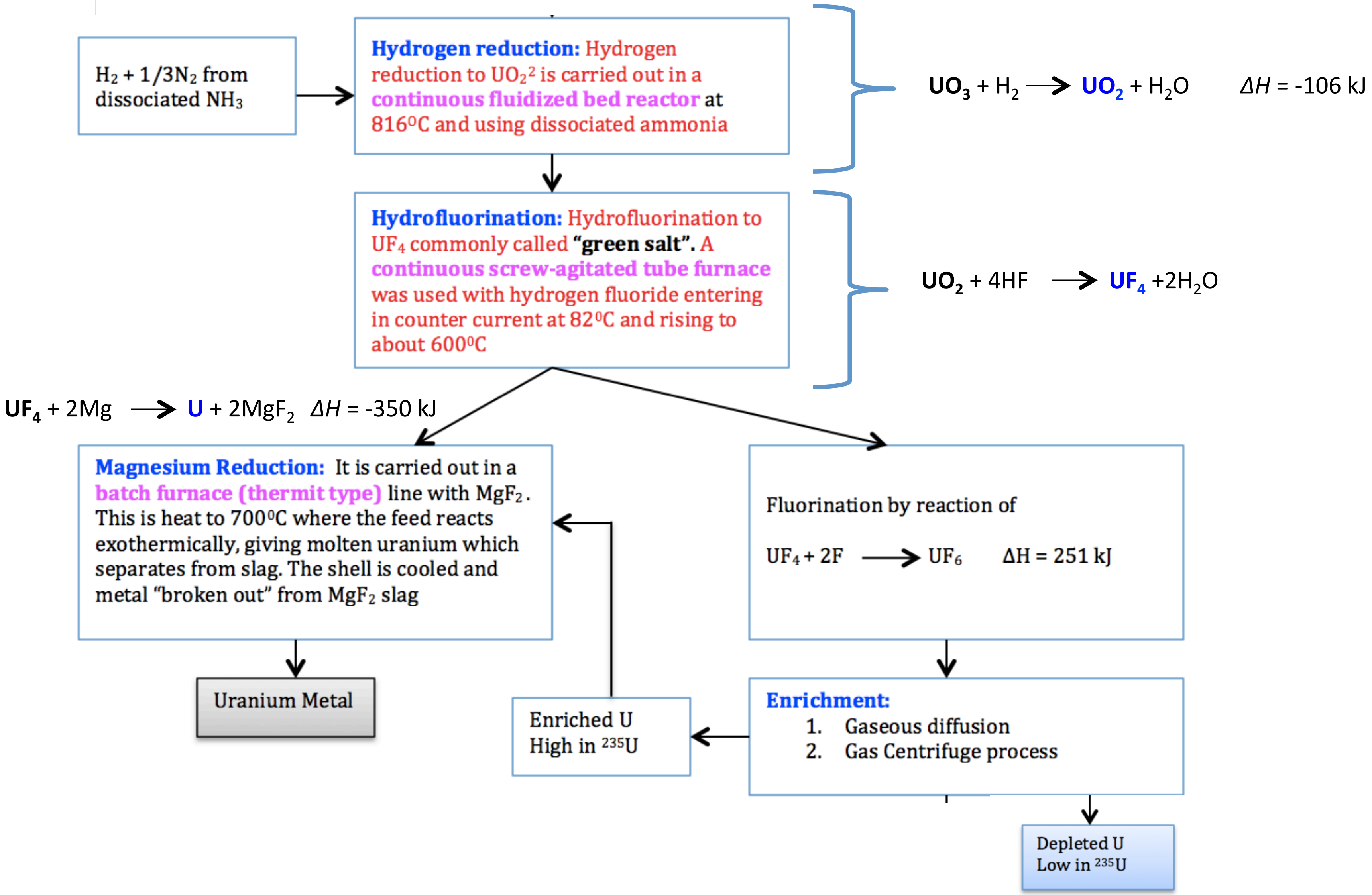
Conversion

A chemical process to convert UO_3 from a refinery into UF_6 (uranium hexafluoride) as feedstock for enriched light water reactor fuel or UO_2 (uranium dioxide) for heavy water reactor fuel.

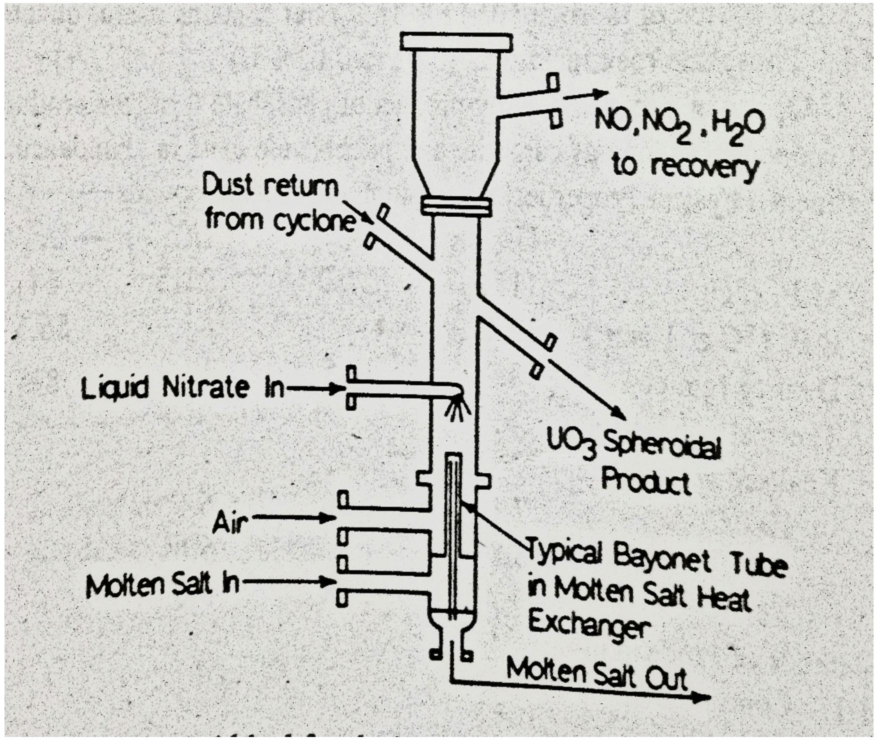
Refining, Conversion, Enrichment and Fabrication of Uranium Ore



Refining


$H_2 + 1/3N_2$ from dissociated NH_3
Hydrogen reduction: Hydrogen reduction to $UO_2{}^2$ is carried out in a **continuous fluidized bed reactor** at 816^{0}C and using dissociated ammonia
$UO_3 + H_2 \rightarrow UO_2 + H_2O$ ΔH = -106 kJ
Hydrofluorination: Hydrofluorination to UF_4 commonly called **"green salt"**. A **continuous screw-agitated tube furnace** was used with hydrogen fluoride entering in counter current at 82^{0}C and rising to about 600^{0}C
$UO_2 + 4HF \rightarrow UF_4 + 2H_2O$
$UF_4 + 2Mg \rightarrow U + 2MgF_2$ ΔH = -350 kJ
Magnesium Reduction: It is carried out in a **batch furnace (thermit type)** line with MgF_2. This is heat to 700^{0}C where the feed reacts exothermically, giving molten uranium which separates from slag. The shell is cooled and metal "broken out" from MgF_2 slag
Uranium Metal
Fluorination by reaction of
$UF_4 + 2F \rightarrow UF_6$ ΔH = 251 kJ
Enrichment:
1. Gaseous diffusion
2. Gas Centrifuge process
Enriched U
High in ^{235}U
Depleted U
Low in ^{235}U

UO_3 Production Using Fluidized Beds



High turbulent mixing is ensures uniform temperature distribution

Good heat transfer because of internal heat exchanger

A free flow of product with high bulk density achieved is suitable for subsequent process steps

A closed system with no moving parts
Minimizes the possibility of personal exposure to dust and fumes

Separation of isotopes or Uranium enrichment

Two major process are used today to separate the uranium isotope i.e. ^{235}U from ^{238}U

1. Gaseous diffusion process and
2. Gas centrifuge process

Separation of isotopes or Uranium enrichment

Gas diffusion process

The gaseous diffusion process is based on differences in the diffusion rate between $^{235}UF_6$ and $^{238}UF_6$ through porous barriers

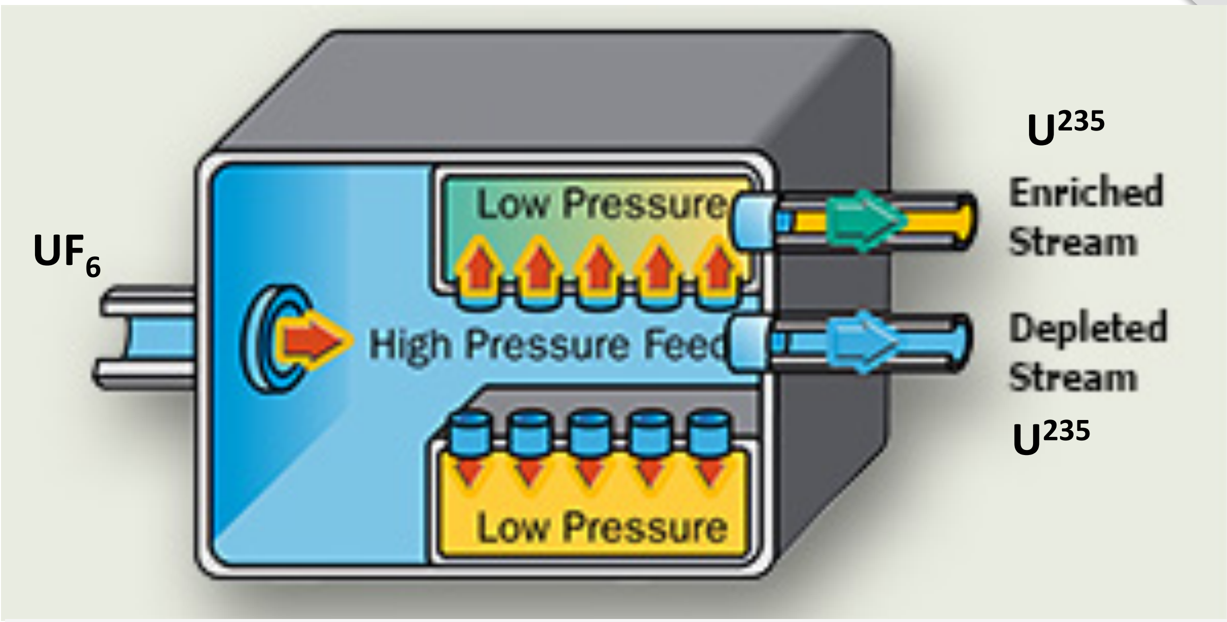
Gas centrifuge process

The gas centrifuge process depends on centrifugal force for the separation

Separation of isotopes or Uranium enrichment

Energy Intensive Process

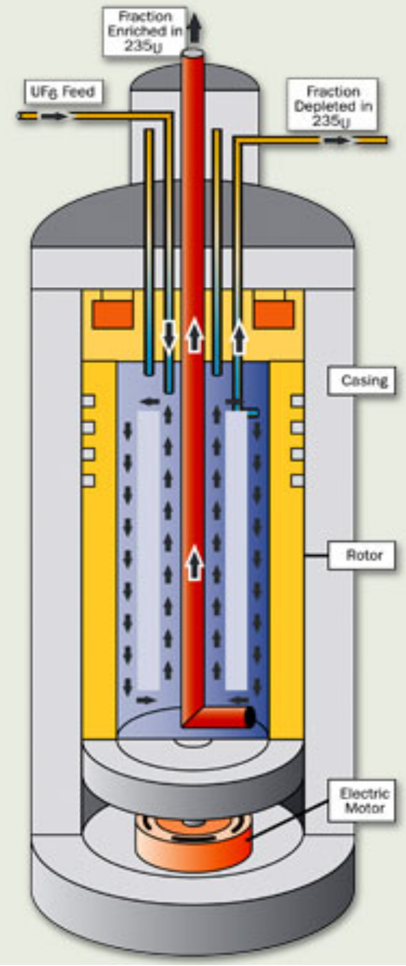
Gaseous Diffusion



As the gas moves, the two isotopes are separated, increasing the concentration of U^{235} to the desired level and decreasing the concentration of U^{238}

Separation of isotopes or Uranium enrichment

- Gaseous UF_6 is pumped into a centrifuge (a cylindrical container that spins the UF_6 at high speeds).
- Centrifugal force pushes the heavier U^{238} particles to the outside of the centrifuge.
- The lighter U^{235} particles concentrate at the center.
- A number of centrifuges are connected together in an arrangement known as a “cascade”.
- As the UF_6 passes through successive cascades, the concentration of U^{235} gradually increases.



Gaseous Centrifuge

Source: http://www.cameco.com/uranium_101/fuel-processing/enrichment/

Summary

Gaseous diffusion is a technology used to produce enriched uranium by forcing gaseous uranium hexafluoride (UF_6) through semipermeable membranes.

This produces a separation between the molecules containing uranium-235 (^{235}U) and uranium-238 (^{238}U).

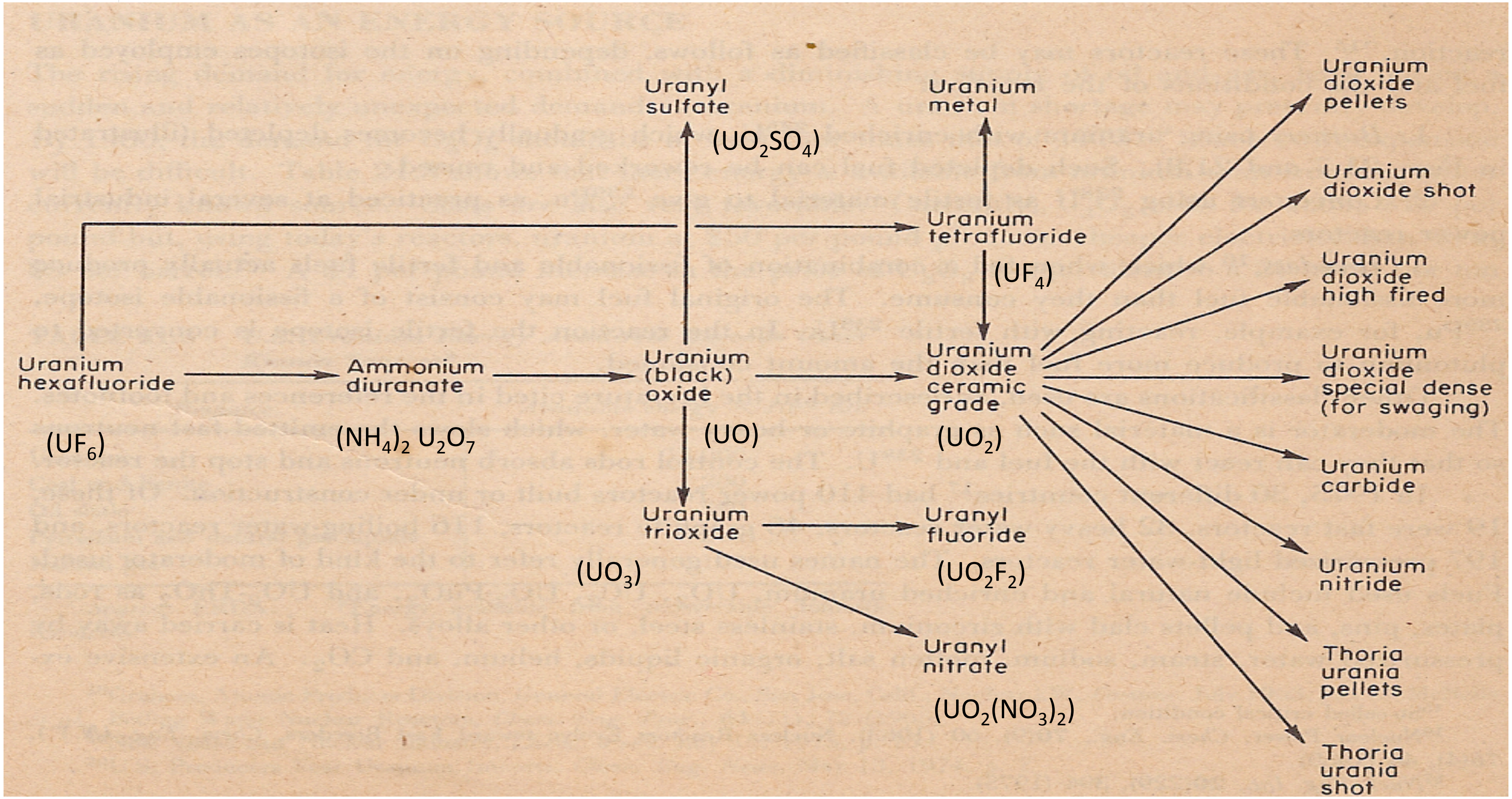
Energy intensive

A centrifuge relies on the principles of centripetal force accelerating molecules so that particles of different masses are physically separated in a gradient along the radius of a rotating container.

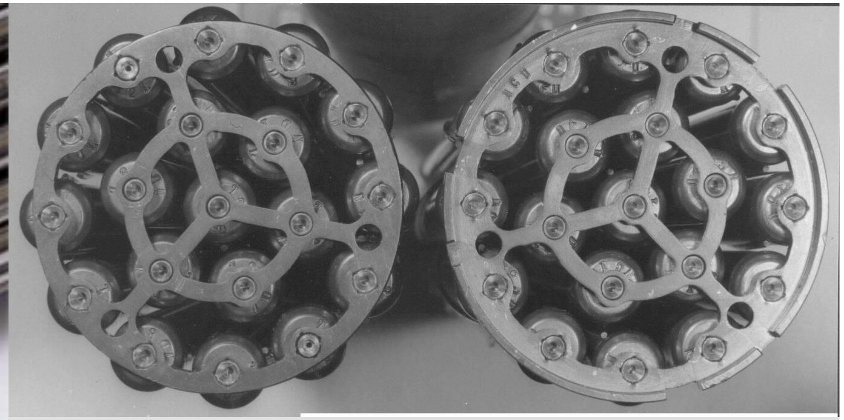
A prominent use of gas centrifuges is for the separation of uranium-235 from uranium-238

Less Energy

Uranium Metal Production – Final Fabrication



Uranium Metal Production – Final Fabrication



End-plates of the first 3 inch diameter fuel bundles. These were the first 19 element fuel bundles built in Canada for Nuclear Reactor

Nuclear Reactions

Overall reaction

$$U_3O_8 + HNO_3 \longrightarrow NO_3-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{U}}-NO_3\cdot 6H_2O \longrightarrow UO_3 \longrightarrow UF_4 \longrightarrow U$$

Reactions in refining

$$U_3O_8 + 8HNO_3(aq) \longrightarrow 3UO_2(NO_3)_2(aq) + 2NO_2 + 4H_2O \qquad \Delta H = -41.4 \text{ kcal}$$

$$UO_2(NO_3)_2 6H_2O \longrightarrow UO_3 + 2NO_2 + \tfrac{1}{2}O_2 + 6H_2O(g) \qquad \Delta H = +134.6 \text{ kcal}$$

$$UO_3(s) + H_2(g) \longrightarrow UO_2(s) + H_2O(g) \qquad \Delta H = -25.3 \text{ kcal}$$

$$UO_2(s) + 4HF(g) \longrightarrow UF_4(s) + 2H_2O(g) \qquad \Delta H = -43.2 \text{ kcal}$$

$$UF_4 + 2Mg \longrightarrow U + 2MgF_2 \qquad \Delta H = -83.5 \text{ kcal}$$

$$UF_4(s) + F_2(g) \longrightarrow UF_6(g) \qquad \Delta H = -60 \text{ kcal}$$

References

1. Dryden C. E, *Outlines of Chemical technology – for the 21st Century*, 3rd edition, East-West Press (2004)

2. Austin G. T, *Shreve's Chemical Process Industries*, 5th edition, Mc Graw Hill International editions (1984)

3. www.cameco.com

4. Benedict. M, Thomas H. Pigford, Hans W. L, *Nuclear Chemical Engineering*, 2nd edition, Mc Graw Hill, 1981.