Metallurgy of Uranium

DISCOVERY:
Element Uranium was discovered by a German chemist Kaliproth in 1789. Metal Uranium was first prepared by Peligot, who showed that the substance discovered by Kaliproth was the oxide of Uranium.
Location in Periodic Table:
Uranium is a chemical element which symbol is U and atomic number is 92. A Uranium atom has 92 protons and 92 electrons, in which 6 are the valence electrons. It is present in the actinide series of periodic Table having silver grey metal.

NUCLEAR APPLICATION:

Uranium contains only naturally occurring fissionable material, because it is a primary

uclear fuel. In the nuclear applications element uranium is of interest because of its

- Providing energy
- Nuclear properties
- Fission products
- more fissionable material

CANNOT HANDLED LIKE CERTAIN METALS:

Uranium cannot be handled like certain metals such as Fe, Cu etc. because of its;

- Chemical reactivity
- Radioactivity
- Highly Anisotropy
- Radioactivity with consequent health hazards

It may be present in fuel elements such as pure metal, an alloy, or an oxide or other compounds.

NATURAL URANIUM:

Uranium found in nature contains largely two isotopes that is U-235 and other is U-238.

U-235:

The production of energy in nuclear reactors is from fission which comes from splitting of U-235 in this process which releases energy in the form of heat. U-235 is the main fissionable isotope of natural uranium which is fission by thermal neutrons. The uranium isotope U-235 is used for nuclear reactors and nuclear weapons. Natural uranium contains 0.7% 0f U-235 isotope.

U-238:

The isotope U-238 is also important because it absorbs neutron to produce a radioactive isotope that decays to isotope Pu-239 which is fissile.
Natural uranium contains 99.3% of U-238 isotope.

ARTIFICIAL URANIUM:

Artificial isotopes with mass numbers 228 to 239 have been prepared. U-233 is important which is prepared from reaction of neutrons with thorium -232.

$${}_{90}Th^{232} + {}_{0}n^{1} \rightarrow {}_{90}Th^{233} + \text{gamma}$$

$${}_{90}Th^{233} \rightarrow {}_{91}Pa^{233} + {}_{-1}\beta^{0}$$

$${}_{90}Pa^{233} \rightarrow {}_{92}U^{233} + -1\beta^{0}$$

Uranium-235 capture a neutron to form uranium-236 which is undergo a fission into a pairs of atoms. Depending on the pair fission products different number of neutrons are released.

$${}_{92}U^{238} + {}_{0}n^{1} \rightarrow {}_{92}U^{239} + \text{gamma}$$

$${}_{92}U^{239} \rightarrow {}_{93}Np^{239} + {}_{-1}\beta^{0}$$

$${}_{93}Np^{239} \rightarrow {}_{94}Pu^{239} + {}_{-1}\beta^{0}$$

The plutonium and uranium-233 are separated from uranium and thorium respectively.

SOURCES:

- Uranium is widely distributed in the upper crust of the earth which is in the form of thin layer.
- Uranium present in earth crust 2-4ppm. It occurs naturally in low concentrations in rocks, soil and water and is commercially extracted from uranium bearing minerals such as uraninite. It does not occur freely. It is always associated with other minerals.
- Uranium is present in the form of oxides(U_3O_8) associated with the sulphides of silver, lead, cobalt, nickel and iron and radioactive radium. As a secondary mineral uranium is associated with vanadate, phosphates, arsenates etc. the most common is camotite, a potassium uranyl vanadate and autunite, a calcium uranyl phosphate, deposits contain averaging up to 1% uranium oxide.
- Uranium bearing ores have been discovered in India in some places in which ores contains 0.08% U_3O_8, 67%SiO_2, 15% FeO. sea beach sands of Kerala and Tamil Nadu contain some useful radioactive minerals, Moazite which contains thoria,

uranium oxides, phosphate and large percentage of rare earth oxides (9% ThO_2, 0.4% U_3O_8 and 59% RE_2O_3), where RE represent the rare earth metals like scandium, neodymium, holmium etc.

URANIUM METALLURGY:

DEFINITION:

Uranium metallurgy is study of physical and chemical behavior of uranium and its alloys.

OR

Uranium metallurgy is the science of metals; their extraction from ores, purification and alloying, heat treatment and working.

URANIUM METALLURGY METHODS

- The uranium can produce commercially through reduction of uranium halides with alkali or alkaline earth metals.
- Uranium metal can also produce through electrolysis of KuF_5 or UF_4, dissolved in the molten $CaCl_2$ and NaCl.
- Very pure uranium can be produce thermal decomposition of uranium halides on hot filament.
- The main focus of uranium metallurgy is the enrichment of uranium through isotope separation.

EXTRACTION OF URANIUM FROM ORE:

Uranium metal from ore production have following steps. The production of natural and enriched uranium from ore which contains 0.8% U_3O_8, 67% SiO_2, 15% FeO.

1. Acid leaching
2. Ion exchange separation
3. Production of reactor grade nitrate
4. Production of uranium dioxide
5. Metallothermic reduction of uranium compounds

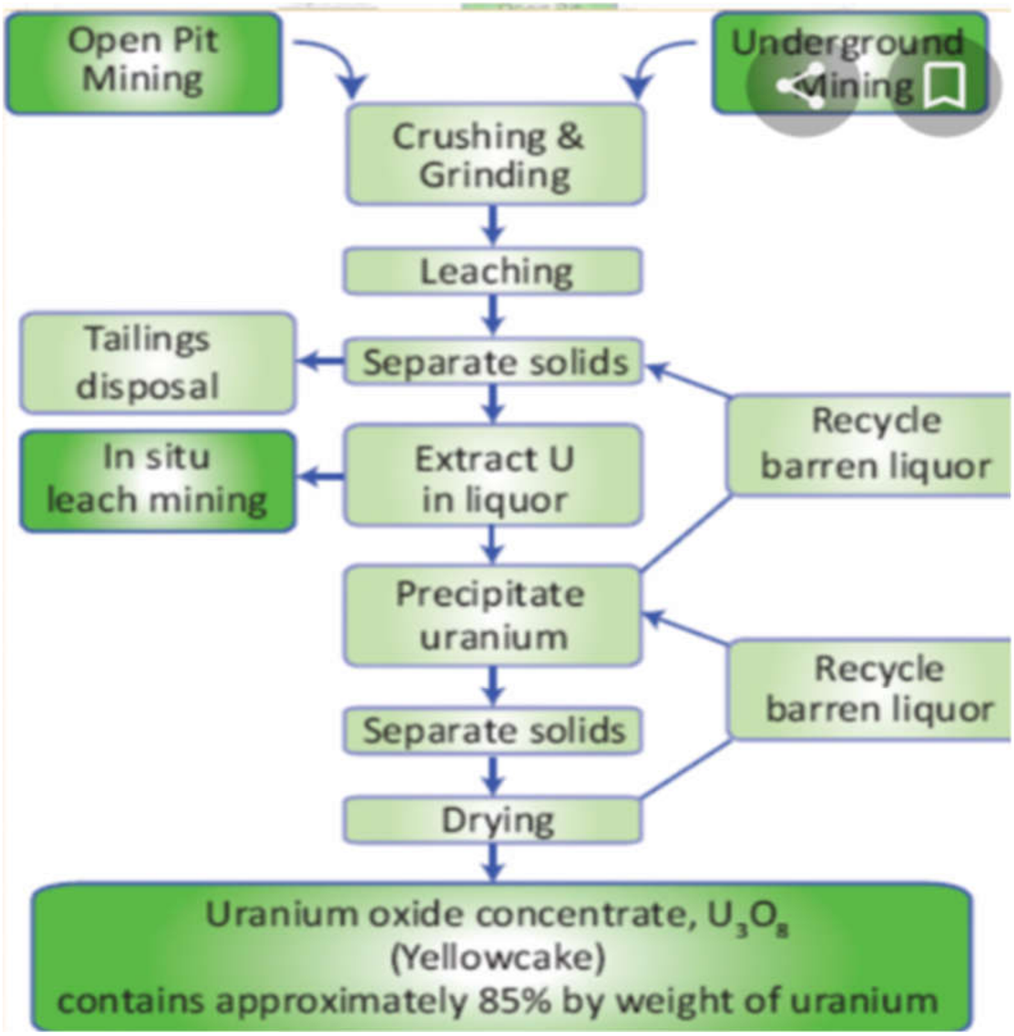
1-Acid Leaching:

The leaching of uranium from ore is done by sulphuric acid(H_2SO_4). The uranium goes into solution as uranyl sulphate.

$$\mathbf{2U_3O_8 + O_2 + H_2SO_4 = 6UO_2(SO_2) + 6H_2O}$$

The oxygen required in the leaching process is indirectly supplied by addition of pyrolusite (60-70%MnO_2). The uranyl sulphate is present in liquor complexes with excess sulphate ions present in the solution and forms negatively charged complexes like $UO_2(SO_4)^{-4}{}_3$ etc.

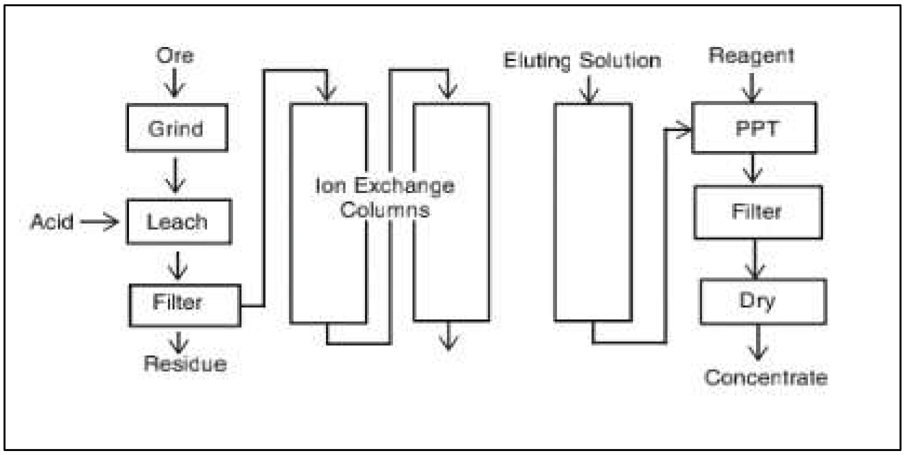
Uranium Processing Flowsheet:



2-Ion Exchange separation:

- In this process of an ion exchange separation the quaternary ammonium anion exchange resin which exhibits a high selectively for the uranyl sulphate anions which is used to concentrate uranium from the sulphuric acid leach liquors.

$$4RCl + UO_2(SO_4)_3^{4-} \quad R_4UO_2(SO)_3 + 4Cl^-$$



- Uranium is absorbed on the anion exchanger in fixed ion exchange columns. The absorbed uranium is passed by strong sodium chloride solution through saturated resin column;

$R_4UO_2(SO_4)_3^{4-}$ + $6OH^-$ $+Mg^{2+}$ = MgU_2O_7 $+6SO_4^{2-}$ $+3H_2O$

- Magnesium diuranate is precipitated from eluate by the addition of $Mg(OH_2)$

$2UO_2(SO_4)_3^{4-}$ + $6OH^-$ + Mg^{2+} = MgU_2O_7 + $6SO_4^{2-}$ + $3H_2O$

3- Production of Reactor Grade Uranyl Nitrate:

- The uranium concentrate is dissolved in nitric acid to obtain solution of uranyl nitrate[$UO_2(NO_3)_2$] firstly.

$MgU_2O_7 + 4HNO_3 \rightarrow UO_2\ (NO_3)_2 + Mg(OH_2) + H_2O$

Uranyl nitrate is soluble in various organic solvents such as diethyl ether, methyl isobutyl ketone and tributyl phosphate(TBP). TBP forms neutral addition complex $UO_2(NO_3)_2.2TBP$ with uranyl nitrate.

$UO_2^{2+}.6H_2O$ + $2NO_3$ + 2TBP $\rightarrow$ $UO_2(NO_3)_2.2TBP$ + $2H_2O$

4-Production of Uranium Dioxide:

This aqueous solution is again dissolved in nitric acid for scrubbing and cleaning by water to form purified uranyl nitrate solution. By passing ammonia gas, ammonium diuranate is precipitated.

$2UO_2(NO_3)_2$ + $2NH_3$ + $3H_2O$ = $(NH_4)_2U_2O_7$ + $4HNO_3$

Ammonium diuranate is at 450C to obtain uranium trioxide.

$(NH_4)_2U_2O_7$ = $2UO_3$ + $2NH_3$ + H_2O

5-METALLOTHERMIC REDUCTION OF URANIUM CPMPOUNDS:

- Pure uranium metal is difficult to prepare because of its affinity to attach with other metals such as oxygen, halogen, nitrogen and carbon.so, reduction of uranium is performed in closed systems to avoid atmospheric contamination.

If uranium dioxide has used as the starting material for preparation of metal, then it shows that it is a very high reducing agent because it has large negative energy for the formation of uranium dioxide.

UO_2= -514.6 KJ/g-atom of O_2 AT 25 C

Hydrogen require a very high H_2/H_2O ratio in gas mixture and cannot consider a practical reducing agent.

Reduction with **carbon** requires vacuum and leads to contamination by carbide formation.

*Thermodynamically, uranium dioxide can be reduced to uranium metal **by reducing agent calcium and magnesium but the product formed is***

- inconvenient to handle
- impure product formed

this method is not used to produce uranium. And refractory oxides product does not melt in this process and uranium is dispersed as a fine powder through slag matrix.

Halides are more suitable than **oxides** as starting materials for metal preparation.

- Additional heat is evolved
- Halide by-product has a lower melting point
- Halide melts and permits the dense uranium metal to settle at the bottom.

Fluoride reaction is universally applicable to obtain uranium metal.

5.1-PREPARATION OF URANIUM TETRAFLUORIDE:

Uranium tetrafluoride is less hydroscopic and less volatile than chloride and preferred halide intermediate. It is prepared by hydro fluorination of uranium dioxide.

$$UO_2 + 4HF = UF_4 + 2H_2O \qquad \Delta H_{298}=-266.1KJ$$

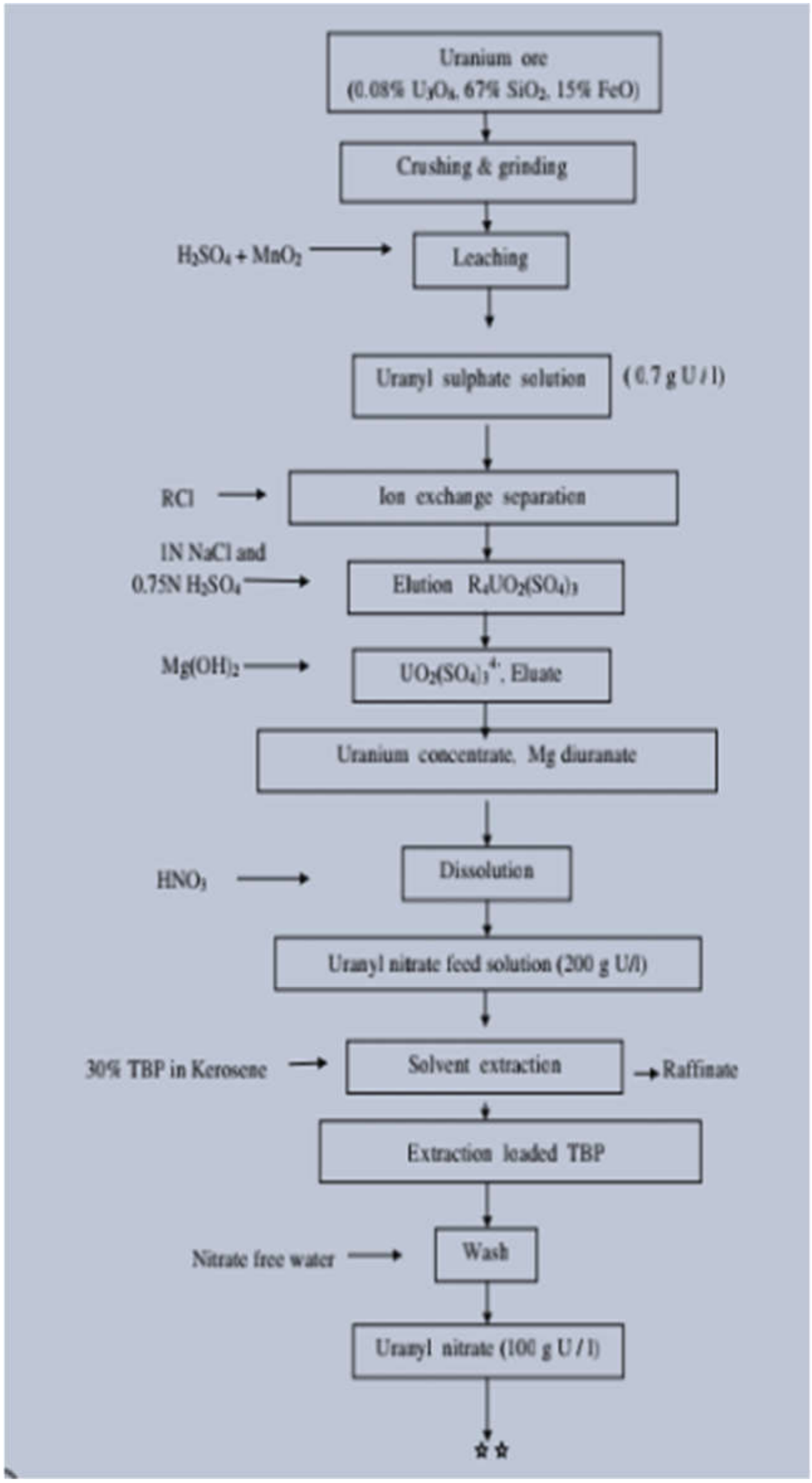
- Carried out in magnesium –lined inclined rotary reactors.
- Temperature at 600·c
- Complete conversion of UO_2 to UF_4
- Highly exothermic

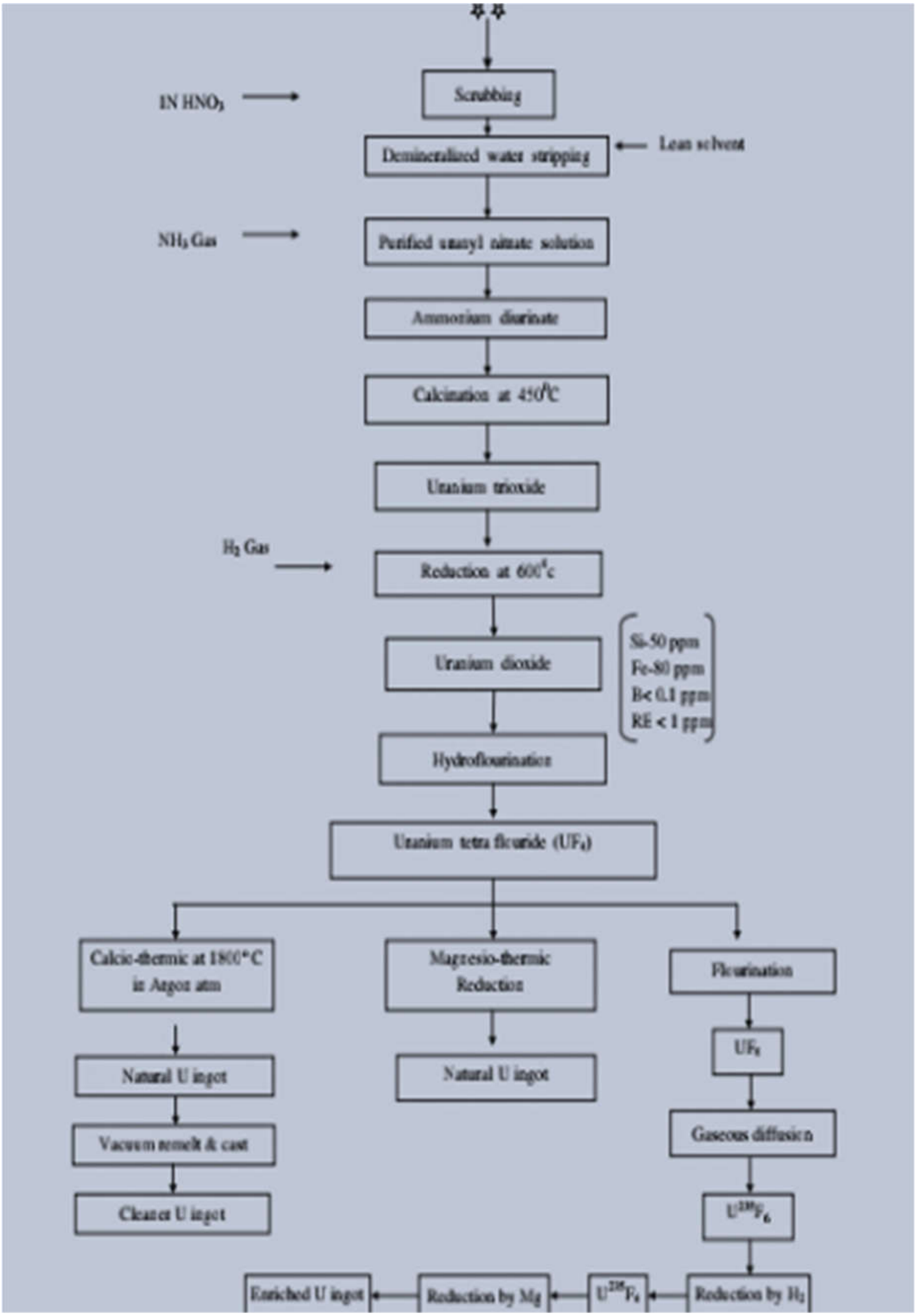
5.2-REDUCTION OF UF_4

I. **CALCIOTHERMIC REDUCTION OF UF_4:** Reduction with calcium is simpler because of high temperature i.e. 1800 C and high heat reaction.

$$UF_4 + 2Ca = U + 2CaF_2 \quad \Delta H_{298} = -575.7 Kj$$

General flow sheet for production of natural and enriched uranium from ore:




1N HNO3
Scrubbing
Demineralized water stripping
Lean solvent
NH3 Gas
Purified uranyl nitrate solution
Ammonium diurinate
Calcination at 450°C
Uranium trioxide
H2 Gas
Reduction at 600°c
Uranium dioxide
Si-50 ppm
Fe-80 ppm
B< 0.1 ppm
RE < 1 ppm
Hydroflourination
Uranium tetra flouride (UF4)
Calcio-thermic at 1800°C in Argon atm
Magnesio-thermic Reduction
Flourination
Natural U ingot
Natural U ingot
UF6
Vacuum remelt & cast
Gaseous diffusion
Cleaner U ingot
Reduction by H2
Reduction by Mg
Enriched U ingot

In this slag-metal separation will be good. Uranium ingots are obtained in the product which are usually remelted in vacuum electric furnace and cast into cleaner agents.

II. **MAGNESIOTHERMIC REDUCTION OF UF_4:** Magnesium is easier to get high purity. heat of reaction is low and external heat supply is required for good metal slag separation. Mg is preferred for uranium production.

$$UF_4 + 2Mg = U + 2MgF_2 \quad \Delta H_{298} = -372.4kJ$$

III. **PRODUCTION OF UF_6**:UF_4 is reacted with fluorine gas to form UF_6

$$UF_4 + F_2 = UF_6$$

BY THE GASEOUS DIFFUSION to form $U^{235}F_6$ reduced by hydrogen

$$U^{235}F_6 + H_2 = U^{235}F_4 + 2HF$$

The further reduction is done by magnesium to get enriched uranium.

$$U^{235}F_4 + 2Mg = U^{235} + 2MgF_2$$

HIGH PURITY OF URANIUM:

- Small ingots of uranium pure are made by vacuum melting of high purity crystals of uranium in uranium oxides crucible.
- These crystals are prepared by electrolysis in an argon atmosphere.
- The electrolyte is fused salt comprising a mixture of LiCl, KCl and 30% UF_4 AT 400-450 C.
- The cathode is molybdenum and anode is ordinary vacuum cast uranium.

Enrichment of Uranium:

Uranium enrichment is a process that is necessary to create an effective nuclear fuel out of uranium by increasing percentage of uranium-235 which undergoes fission with thermal neutrons. This is a complex and difficult procedure. Uranium 235 and 238 have same chemical properties but different in the physical properties. In the enrichment procedures u-235 proportion has been increased around 4%

Enrichment commercially methods:

There are two main methods;

- Gaseous diffusion
- Ultra centrifugation

In both of these two procedures uranium must first convert into uranium hexafluoride which becomes gaseous when heated to over 80 degrees Celsius. This chemical is highly corrosive.

1-GASEOUS DIFFUSION:

It is a technology used to produce enriched uranium by forcing gaseous uranium hexafluoride through semipermeable membranes. This separate mixture of uranium 235 nd 238 by their mass difference. U-235 which is lighter travel more distance and pass through semipermeable membrane and separate. It is more energy consuming.

2-Gaseous Ultracentrifugation:

It is a technique introduced after second world war. It involves spinning a hollow cylinder containing uranium at a very high speed. The centrifugal force drives heavier hexafluoride U-238 move to upper side and U-235 in inner side. We get separate U-235 at inner wall. Less energy consuming than gaseous diffusion.

PROPERTIES:

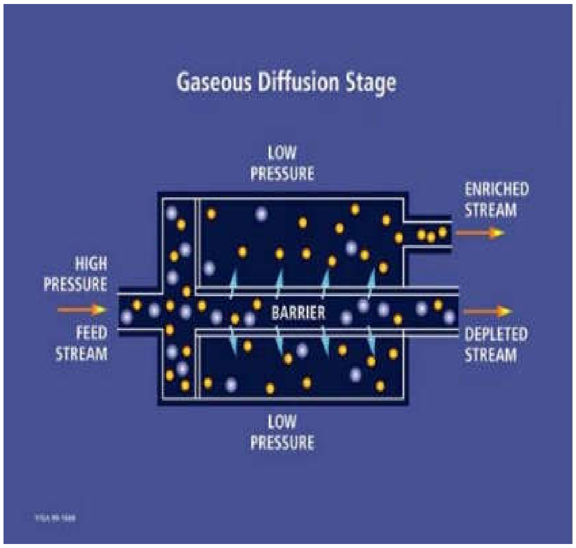
- It is a silver-grey luster when freshly prepared.
- It readily reacts with other elements or metals and when it readily exposure to atmosphere it formed oxide formation.
- Uranium is a dense, moderately hard metal.
- It has attractive properties such as high specific gravity and thermal conductivity.
- It is malleable and ductile.
- The specific gravity of uranium depends on amount of carbon and other low impurities present in uranium.
- The specific gravity of uranium is 19.05 and for wrought uranium is 18.7-19.1.
- The melting and boiling point of uranium metal are 1132 C and 3813 C respectively.
- Uranium can be cast and fabricated into desired shapes such as rolling, drawing, extrusion.
- Uranium has three allotropic form; orthorhombic, tetragonal,

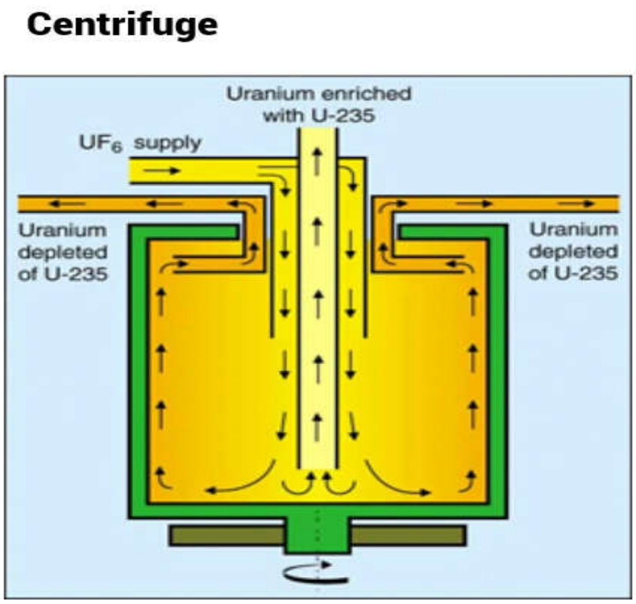
APPLICATIONS:

- In the atomic energy reactors uranium metal is cast into rods approximately 2.5cm in diameter using vacuum melting technique in a high electric frequency furnace.
- Uranium and plutonium discovered almost during world war that, why attention going to military angle.
- Used in nuclear power station.
- Used in the nuclear weapons
- Used as fuel in nuclear power reactors for electricity generation.
- There are many other uses in production of radio isotopes including;

- Used for diagnosis diseases
- Used in cancer therapy
- Used in food processing industry
- Used in metallurgy, automobiles, aeronautics for inspection of safety and quality.

Used in space to operate places far away from sun.





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