Metallurgy of Uranium

Occurrence

Uranium was discovered in 1789 by Martin Klaproth, a German chemist, in the mineral called pitchblende. It was named after the planet Uranus, which had been discovered eight years earlier.

Uranium is a naturally occurring element found in low levels within all rock, soil, and water formed in supernovae about 6.6 billion years ago. This is the highest-numbered element to be found naturally in significant quantities on earth. Uranium occurs in most rocks in concentrations of 2 - 4 ppm and is as common in the Earth's crust as tin, tungsten and molybdenum. Uranium is one of the more common elements in the Earth's crust, being 40 times more common than silver and 500 times more common than gold.

Uranium is not found free in nature. It occurs in the combined state in a few scarce minerals.

Ores of Uranium

It is found in many minerals including uraninite. Most common uranium ores are as;

(i) ***Pitchblende or uraninite*** in which uranium is present as ***U_3O_8 or $2UO_2$. $2UO_3$*** or uranium uranate, **$U(UO_4)_2$**. Uraninite is a major ore of uranium. It contains 75-90% of the oxide and some of the highest grade

uranium ores in the world were found in the *Shinkolobwe mine* in the Democratic Republic of the Congo (the initial source for the Manhattan Project) and in the Athabasca Basin in northern Saskatchewan, Canada.

(ii) ***Carnotite*** $\mathbf{K_2O.2UO_3.V_2O_5.\ 3H_2O}$ or $\mathbf{2K(UO_2)VO_4.3H_2O}$ (potassium uranyl ortho vanadate) which contains both uranium and radium. Carnotite is reported in Congo (Kinshasa), Morocco, Australia (Radium Hill) and Kazakhstan. In Pakistan carnotite occurs in the Upper Miocene middle Siwaliks sandstone (Dhokpathan Formation), in the vicinity of Takhat Nasrati, Karak District.

(iii) ***Antunite,*** $\mathbf{K(UO_2)PO_4.8H_2O}$ (potassium uranyl orthophosphate). It is found in Congo. One of the other locations of autunite includes Autun, France, the type locality and namesake of the mineral. The mineral was formed there as an alteration of uraninite and other uranium bearing minerals. Autunite is also found in Cornwall, Saxony, and North and South Dakota.

(iv) ***Torbernite,*** $\mathbf{Cu(UO_2)_2(PO_4)_2 \cdot 12H_2O}$. A secondary mineral found in the oxidized zones of some uraniferous copper deposits. Often dehydrated to metatorbernite because the transparent crystals can already be metatorbernite. Deposits are found Saxony, Germany.

(v) ***Tyuyamunite*** is a very rare uranium mineral with formula $\mathbf{Ca(UO_2)_2V_2O_8{\cdot}5\text{-}8H_2O}$. It is a member of the carnotite group, bright, canary-yellow color because of its high uranium content named after its type locality, Tyuya-Muyun, Fergana Valley, Kyrgyzstan.

(vi) ***Saleeite*** **.** $Mg(UO_2)_2(PO_4)_2{\cdot}10H_2O$. A secondary mineral occurring in the oxidized zones of uranium-bearing polymetallic hydrothermal, and sedimentary, mineral deposits in Haut-Katanga, DR Congo.

(vii) ***Coffinite*** **.** $U(SiO_4) \cdot nH_2O$. Deposits are found at Colorado, Utah and New Mexico, USA.

(viii) ***Uranophane***. $Ca(UO_2)_2(SiO_3OH)_2.5H_2O$. Typically found at Poland, France, and Ontario, Canada.

(ix) ***Sklodowskite***. $Mg(UO_2)_2(SiO_3OH)_2{\cdot}6H_2O$. Major deposits of are found at Greece, DR Congo and Germany.

Extraction of Uranium from Pitchblende

1. Acid digestion process.

First of all pitchblende is concentrated by gravity process to remove sand, clay etc. and then concentrated ore is roasted in excess of air whereby S, As and Sb are removed as their volatile oxides. Silver, if present in the mineral, is removed, as insoluble AgCI by roasting the mineral at 800°C with NaCl. The roasted ore is digested with dil. H_2SO_4 in presence of MnO_2 (an oxidizing agent) for about 24 hours when Ba, Pb, Ba, etc. are precipitated as sulphates and uranium goes into solution as uranyl sulphate, UO_2SO_4.

$$2U_3O_8 + 6H_2SO_4 + \frac{1}{2}O_2 \longrightarrow 3UO_2SO_4 + 3H_2O$$

Uraninite (mineral) *Uranyl sulphate(Soluble)*

UO_2SO_4 present in solution is converted into *sodium uranyl carbonate,* $N_4UO_2(CO_3)_3$ by the addition of Na_2COa.

$$UO_2SO_4 + 3Na_2CO_3 \longrightarrow Na_4UO_2(CO_3)_3 + Na_2SO_4$$

Uranyl sulphate *Sad. uranyl carbonate (solution)*

The solution containing $Na_4UO_2(CO_3)_3$ is now neutralized with HCI in order to decompose it into uranyl chloride, UO_2Cl_2 and then saturated with H_2S gas so that Pb, Cu etc. are precipitated as their sulphides. The solution of UO_2Cl_2 is now treated with excess of NH_4OH whereby we get the precipitate of ammonium diuranate, $(NH_4)_2U_2O_7$ which, when strongly ignited in air, gives the oxide, U_3O_8.

$$Na_4UO_2(CO_3)_3 + 6HCI \longrightarrow UO_2Cl_2 + 4NaCI + 3H_2O + 3CO_2$$

Sad. uranyl carbonate *Uranyl chloride (Solution)*

Ignite

$$2UO_2Cl_2 + 6NH_4OH \text{ (excess)} \longrightarrow (NH_4)_2U_2O_7 + 4NH_4CI + 3H_2O$$

$$3(NH_4)_2U_2O_7 \longrightarrow 2U_3O_8 + 6NH_3 + 3H_2O + O_2$$

Ammonium diuranate

When U_3O_8 is reduced by carbon by heating in an electric furnace, uranium is obtained.

$$U_3O_8 + 8C \longrightarrow 3U + 8CO$$

Uraninite (mineral)

98-99% of pure uranium can be obtained by reducing U_3O_8 by Mg, Ca or Al *(Allumino-thermic process).*

$$3U_3O_8 + 16Al \longrightarrow 9U + 8Al_2O_3$$

Burger reduced U_3O_8 by the vapours of calcium in vacuo.

2. Alkali digestion process.

The roasted ore is digested with Na_2CO_3-$NaHCO_3$ mixture solution whereby U3Oa present in the mineral is converted into soluble $Na_4UO_2(CO_3)_3$. The solution containing $Na_4UO_2(CO_3)_3$ is treated with NaOH which precipitates uranium as *sodium diuranate,* $Na_2U_2O_7$.

$$U_3O_8 + 3Na_2CO_3 + 6NaHCO_3 + \tfrac{1}{2}O_2 \longrightarrow 3Na_4UO_2(CO_3)_3 + 3H_2O$$

Tetrasodium tricarbonatodioxouranate

$$Na_4UO_2(CO_3)_3 + 6NaOH \longrightarrow Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O$$

Sod. Diuranate (ppt.)

The precipitate of $Na_2U_2Q_7$ is dissolved in dil. H_2SO_4 and the solution is treated with NH_4OH. The precipitate of $(NH_4)_2U_2O_7$ thus obtained on strong ignition in air gives U_3O_8.

$$Na_2U_2O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2U_2O_7\downarrow$$

Sod. Diuranate (ppt)) *(Soluble)*

$$H_2U_2O_7 + 2NH_4OH \longrightarrow (NH_2)_2U_2O_7 + 2H_2O$$

Ammon. Diuranate

$$3(NH_4)_2U_2O_7 \xrightarrow{Ignition} 2U_3O_8 + 6NH_3 + 3H_2O + O_2$$

Ammon. Diuranate (ppt)

The oxide, U_3O_8, is reduced, as in acid digestion process, to uranium.

Extraction of Uranium from Carnotite

In addition to uranium, Carnotite also contains Ba, V, Fe, Al, Ra etc. From this ore uranium is obtained as a by-product. The ore is treated with cone. HNO_3 at l00ºC. The heating is done by the steam. Most of the ore dissolves in HNO_3 and the solution thus obtained is neutralized by NaOH and then treated with $BaCl_2$ and H_2SO_4 whereby Ba and Ra are precipitated as their sulphate, and U and V are converted into soluble UO_2SO_4 and $VOSO_4$ respectively. This filtrate which also contains Fe and Al is treated with excess of boiling solution of Na_2CO_3 which precipitates Fe and Al (Reject), and UO_2SO_4 and $VOSO_4$ are converted into soluble $Na_4UO_2(CO_3)_3$ and Na_2VO_4 (sod. vanadate) respectively.

$$UO_2SO_4 + 3Na_2CO_3 \longrightarrow Na_4UO_2(CO_3)_3 + Na_2SO_4$$

(Soluble)

$$2VOSO_4 + 5Na_2CO_3 + ½O_2 \longrightarrow 2Na_3VO_4 + 3Na_2SO_4 + 5CO_2$$

Vanadium oxysulfate (Soluble) *Sod. vanadate*

The solution containing $Na_4UO_2(CO_3)_3$ and Na_3VO_4 is neutralized by HNO_3 and treated with NaOH. This treatment precipitates uranium as $Na_2U_2O_7$

$$Na_4UO_2(CO_3)_3 + 6HNO_3 \longrightarrow UO_2(NO_3)_2 + 4NaNO_3 + 3H_2O + 3CO_2$$

Tetrasodium tricarbonatodioxouranate

$$2UO_2(NO_3)_2 + 6NaOH \longrightarrow \underset{(ppt)}{Na_2U_2O_7} + 4NaNO_3 + 3H_2O$$

The precipitate of $Na_2U_2O_7$ is converted into $(NH_4)_2U_2O_7$ as in alkali digestion process.

$$Na_2U_2O_7 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2U_2O_7$$

$$H_2U_2O_7 + 2NH_4OH \longrightarrow \underset{(ppt)}{(NH_4)_2U_2O_7\downarrow} + 2H_2O$$

$(NH_2)_2U_2O_7$ on strong ignition in air gives U_3O_8 which can be reduced to uranium as already discussed.

Properties

The metal uranium resembles nickel in appearance. The pure sample is white, but on contamination with some nitride, it assumes yellow tint. It is malleable, takes polish, is softer than steel, but becomes hard and brittle when alloyed with carbon and chilled. It melts at 1850^{O}C. The powdered metal burns in air when heated to 160^{O}C, in chlorine at 150^{O}C and in fluorine at the room temperature. It also burns in iodine, sulphur vapour and nitrogen at higher temperature. It also decomposes water though slowly at the room temperature, yet rapidly on boiling.

It reacts with ammonia at higher temperatures to give out nitrogen, dissolves in dilute mineral acids, giving out hydrogen, and evolves sulphur dioxide from concentrated sulphuric acid. The caustic alkalies have no action upon the metal. Uranium will displace mercury, silver, copper and tin from the solution of their salts. When a solution of uranium salt is exposed to light, it shows fluorescence. Uranium is a radioactive element and gives a series of disintegration products. Nitrogen combines directly with uranium at 1000^{O}C forming uranium nitride, U_3N_4. Carbon also directly combines with uranium giving uranium carbide, UC_2.

Uses

In ceramics, uranium compounds are sometimes used to give coloured glasses, orange or yellow. Its salts have also been used as mordant for silk and wool. The metal and its carbide are one of the best catalysts in the Haber's synthesis of ammonia. Uranyl nitrate is used as a reagent in volumetric determination of phosphate and arsenates. Uranium steels are also of technical importance. The metal is used in nuclear reactors.

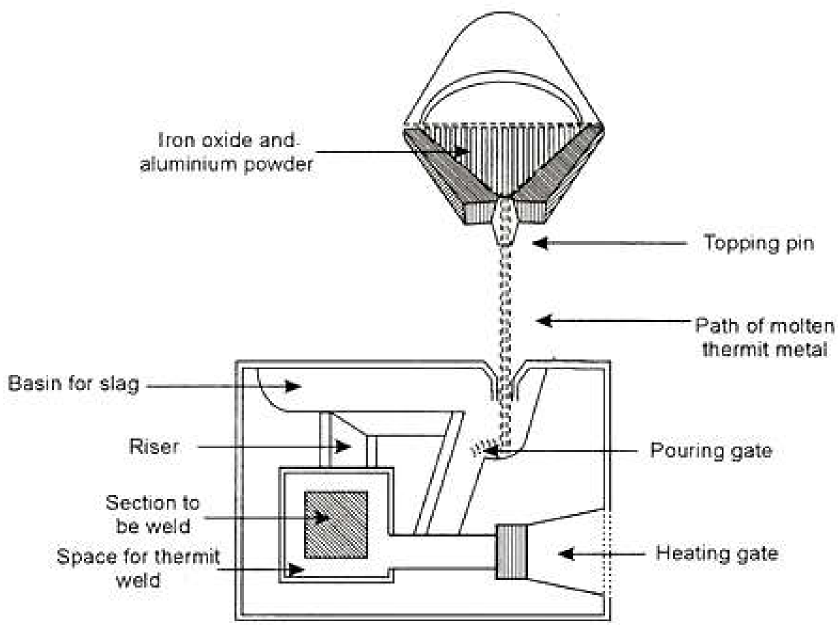

Fig. 22.1 Thermit Weld