Chemistry of Uranium

Uranium is found in sea water at about 0.003 parts per million (ppm) and in rocks of the Earth's crust at up to 4 ppm. It is incorporated into many minerals as uraninite (UO2) or pitchblende (U3O8) or as secondary minerals (complex oxides, silicates, phosphates, vanadates).

Fast Facts

- U3O8 is a stable complex oxide: U2O5.UO3.
- Uranium is fairly soluble and uranium oxide precipitates from uranium-bearing groundwaters as they enter a reducing environment.
- Uranium can be mobilized (redissolved) in situ by oxygenated leach solution.
- Australian ores are up to 0.5% U3O8.

Extraction of Uranium in Australia

The ore is crushed and ground to liberate the mineral particles. It is then leached with sulphuric acid:

UO3 + 2 H+ ---------- UO2 2+ + H2O

UO2 2+ + 3SO4 2- ----------UO2(SO4)3 4-

The UO2 is oxidized to UO3.

Two methods have been used for concentration and purification of uranium: ion exchange and solvent extraction. Early operations in Australia used ammonium type resins in polystyrene beads for ion exchange, but solvent extraction is now in general use.

In solvent extraction, tertiary amines are placed in a kerosene dilutent and the phases move counter-currently. The loaded solvents can then be treated to remove impurities.

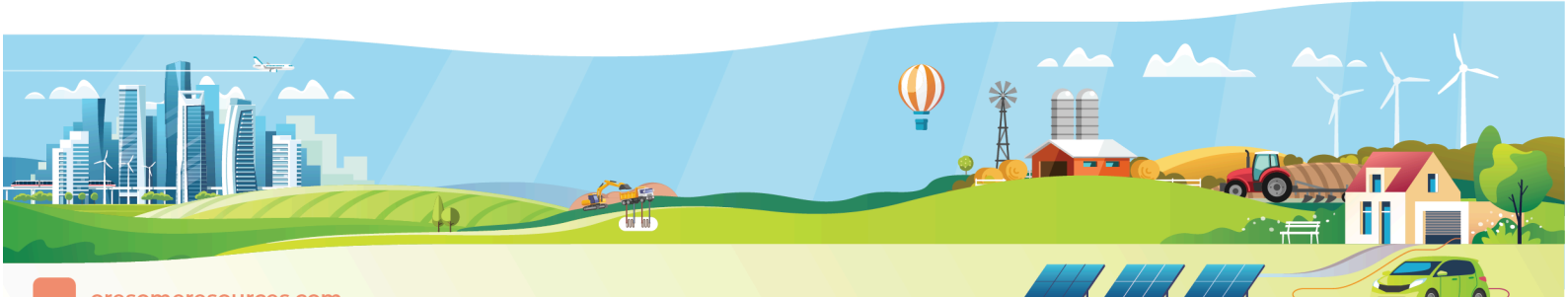
First cations are removed at pH 1.5 using sulphuric acid and then anions are dealt with using gaseous ammonia. The solvents are then stripped in a counter-concurrent process using ammonium sulphate solution.

(R3NH)4UO2(SO4)3 4- + 2(NH4)2SO4 ----------4R3N + (NH4)4UO2(SO4)3 + 2H2SO4

Precipitation of ammonium diuranate is achieved by adding gaseous ammonia to neutralize the solution:

2NH3 + 2UO2(SO4)3 4----------(NH4)2U2O7 + 4SO4 2-

The diuranate is then dewatered and roasted to yield U3O8 product, which is the form in which uranium is marketed and exported.



In Situ Leaching

In situ leaching, also known as solution mining or in situ recovery, involves leaving the ore in the ground and recovering the minerals from it by dissolving them and pumping the pregnant solution to the surface where the minerals can be recovered.

The uranium is recovered by circulating weakly acidified groundwater with oxygen added through injection and recovery wells. In the plant, the pregnant liquor then deposits uranium on a plastic ion exchange resin. The loaded resin is washed with sulphuric acid, hydrogen peroxide is added and uranyl peroxide precipitated. With low temperature drying, this then becomes U3O8.

Refining and Conversion to UF6 prior to Enrichment (Europe and America)

The mixed uranium oxide concentrate U3O8 received by the refinery is dissolved in nitric acid. The resulting solution of uranium nitrate UO2(NO3)2.6H2O is fed into a countercurrent solvent extraction process, using tributyl phosphate dissolved in kerosene or dodecane. The uranium is collected by the organic extractant, from which it can be washed out by dilute nitric acid solution and then concentrated by evaporation. The solution is then calcined (heated strongly) to produce pure UO3.

Most nuclear reactors require uranium to be enriched from its natural isotopic composition of 0.7% U-235 (most of the rest being U-238) to 3.5-4% U-235. The uranium therefore needs to be in a gaseous form and the most convenient way of achieving this is to convert the uranium oxides to uranium hexafluoride.

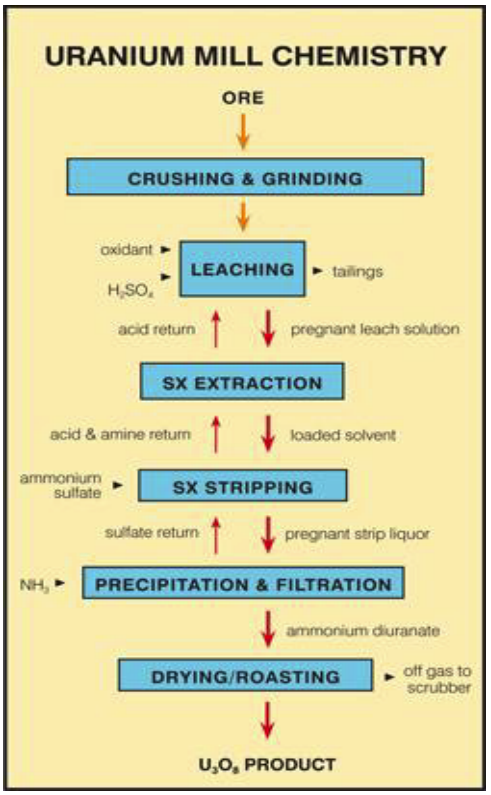
After purification, the uranium oxide UO3 is reduced in a kiln by hydrogen to UO2.

UO3 + H2 ====> UO2 + H2O ..... delta H = -109 kJ/mole

This reduced oxide is then reacted with gaseous hydrogen fluoride in another kiln to form uranium tetrafluoride, UF4, though in some places this is made with aqueous HF by a wet process.

UO2 + 4HF ====> UF4 + 2H2O ..... delta H = -176 kJ/mole

The tetrafluoride is then fed into a fluidised bed reactor with gaseous fluorine to produce uranium hexafluoride, UF6. Hexafluoride is condensed and stored.



UF4 + F2 ====> UF6

Enrichment is a physical process using either centrifuges or fractionation by diffusion of the gaseous uranium hexafluoride.

The Reactor Fuel

After enrichment, the hexafluoride is turned into UO2, and then made into pellets, which are assembled into fuel rods for the reactor. In the reactor, the nuclear fission chain reaction produces neutrons which cause further fission in U-235 atoms, which typically release about 200 MeV, or 3.2 x 10- 11 Joule. This fission reaction produces products such as Ba, Kr, Sr, Cs, I and Xe with atomic masses distributed around 95 and 135.

Some of the U-238 in the reactor core becomes plutonium-239 and Pu-240. The Pu-239 is fissile in the same way as U-235. Fuel is usually left in the reactor for three years, after which time two thirds of the Pu-239 is fissioned with the U-235, leaving a high proportion of Pu-240.

Reprocessing of Spent Fuel

Used fuel is reprocessed to recover the uranium and plutonium in it. The highly radioactive fuel is chopped up and dissolved in hot concentrated nitric acid. The first stage separates the uranium and plutonium in the aqueous nitric acid stream from the fission products by a counterconcurrent solvent extraction process, using tributyl phosphate dissolved in kerosene or dodecane.

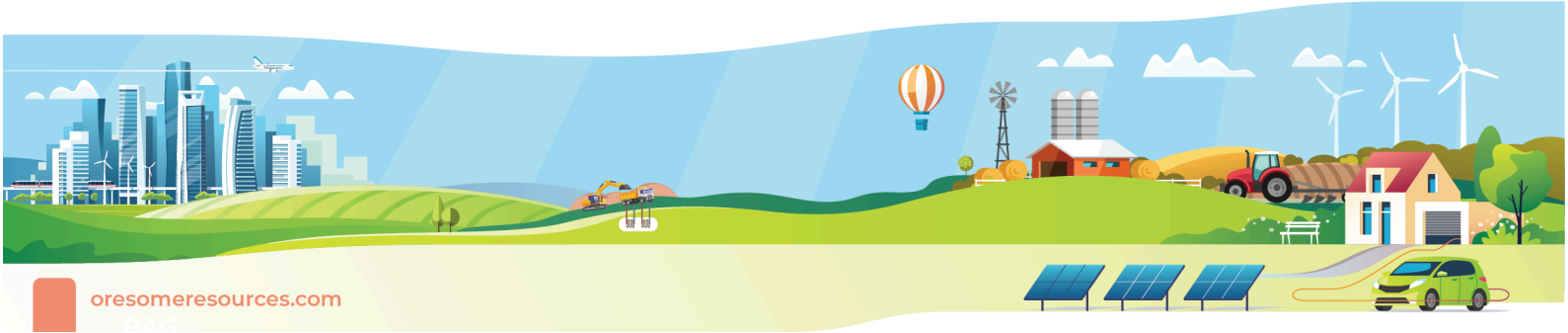
In a pulsed column, uranium and plutonium enters the organic phase while the fission products remain in the aqueous raffinate. In a second pulsed column, uranium is separated from plutonium by reduction with excess U4+ added to the aqueous stream. Plutonium is then transferred to the aqueous phase while the mixture of U4+ and U6+ remains in the organic phase. It is then stripped with dilute nitric acid.

The plutonium nitrate is concentrated by evaporation then subject to an oxalate precipitation process followed by calcination to produce PuO2 in powder form. The uranium nitrate is concentrated by evaporation and calcined to produce UO3 in powder form. It is then converted to UO2 product by reduction in hydrogen.

Recycled plutonium oxide is mixed with depleted uranium to make mixed-oxide fuel. The two oxides are mechanically milled to form a solid solution of U-PuO2, which is then made into fuel pellets and assembled into fuel rods.

Wastes

The high-level liquid wastes from the first extraction cycles are concentrated by evaporation, stored for some years in shielded and cooled tanks, and then calcined to produce solids, which are incorporated into borosilicate glass.

The glass contains about 11% radioactive oxides. It is poured into heavy stainless steel flasks, a lid is welded on and then they are stored pending deep geological disposal.

The World Nuclear Association is acknowledged as a significant source for this information.