

ENVIRONMENTAL EFFECTS OF NUCLEAR FUEL PROCESSING. REFINING: FROM THE YELLOW CAKE TO THE FUEL ELEMENT

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Summary

An analysis of the main steps of the uranium fuel cycle processing and its environmental effects is presented in this article. The analysis covers the treatment of effluents and wastes from the mining and milling of uranium ores, the leach of the uranium from the ore, the uranium concentration, and preparation of the yellowcake, the dissolution of the yellowcake and the uranyl nitrate purification by solvent extraction, scrub and stripping operations, as well as the obtention of the pure solid uranium compounds. Further analysis covers the preparation of several intermediate uranium

compounds, such as the trioxide, dioxide, uranium tetrafluoride, and hexafluoride, enrichment operation, and reversion. Special emphasis is given to the treatment of effluents and to waste disposal. The recovery of uranium from the various steps and recovery of the non-radioactive products is considered. Aspects of health, safety, and radiation and public acceptability are also considered.

1. Refining: From the Yellowcake to the Fuel Element

1.1. Introduction: Living in a Radioactive World

Since the beginning of human history, we have been exposed to natural radiation from the Sun and cosmic space, and from the natural radioactive materials encountered in the soil, foods, water, and the air. Earth is a radioactive planet. The whole place in which we live, the entire environment surrounding us, contains radioactivity. Mankind is subject to cosmic radiation, to terrestrial radiation, and, in the modern era, to artificial radiation.

Cosmic radiation comes from cosmic rays. Radiation from radioisotopes formed in the atmosphere is termed “cosmogenic radiation.” So-called “secondary” cosmic radiation is created in the upper atmosphere by the interaction of protons and alpha particles. It is this cosmic radiation to which we are exposed.

Terrestrial radiation varies greatly depending on the amount of radioactive materials in the environment. Terrestrial radiation is referred to as the naturally occurring radiation originating from primordial radionuclides; in other words, radioactive elements that have always been present on Earth. There are about 70 radioactive isotopes, including those with atomic numbers greater than 83; in other words, those from bismuth to uranium. Populations that live in areas where the presence of radioactive ores is high are submitted to great radiation doses—sometimes 100 to 1000 times higher than in average places.

In the same way, the internal body radiation varies with the environmental and alimentary regime of the individual. For instance, lead-210 and polonium-210, both radioisotopes from the decay chain of natural uranium can be concentrated in fish, tobacco, and some vegetables.

Most of the terrestrial radiation to which we are exposed comes from members of the uranium and thorium decay series, and from singly occurring potassium-40 and rubidium-87.

The natural uranium decay series begins with uranium-238, which has an isotopic abundance of 99.27% and a half-life of 4.468×10^9 years. Uranium-238 is an alpha emitter that undergoes a series of alpha and beta decays before forming the stable lead-206 isotope. The thorium decay series begins with thorium-232, which has a half-life of 1.405×10^{10} years and a relative abundance of essentially 100%. Like uranium-238, thorium-232 is an alpha emitter that undergoes a series of alpha and beta decays before forming the stable lead-208 isotope.

Potassium-40 is also a long-life isotope. It has a relative isotopic abundance of 0.0118% and a half-life of 1.3×10^9 years. It decays by beta emission and by electron capture. This radioisotope is a major contributor to the radiation dose received from natural sources because potassium is one of the ten most surface-abundant elements on Earth.

Rubidium-87 is another natural radioisotope. It has a relative isotopic abundance of 27.8% and a half-life of 4.8×10^{10} years and it is encountered in most soils. It decays by beta emission. Radiorubidium is not an important source of external radiation exposure.

Radon is a radioactive gas present in the air we breathe. Radon is a decay product from radium, which is present in most soils and rocks: ${}_{88}\text{Ra}^{226} \rightarrow {}_{86}\text{Rn}^{222} + \alpha$.

There are other radon isotopes, but radon-222 is the most common and has the longest half-life (3.8 days). As a gas it is quite easy for radon to migrate through the soil and enter buildings and houses through the floors, cracks in concrete floors, and walls. Radon in buildings can also originate from construction materials. Building materials such as gypsum and calcium silicate slag, stone used in buildings, and cement can have small amounts of natural uranium, and so are a possible source of radon.

Most of the radon that we breathe in is subsequently exhaled. The most serious problem with radon lies in the fact that it decays to radioactive solid daughters, which may become trapped in the lungs. It is these decayed products, mainly isotopes of polonium and lead, that make a large contribution to the radiation dose received by man.

Radon is a decay product of naturally occurring uranium and represents one step in the 14-step chain that ultimately produces stable lead. This series, known also as the uranium decay chain originates from U^{238} , which is widespread in geologic formations. A series of decays leads to Ra^{226} (1.6×10^3 years), then the gas, Rn^{222} (3.82 d). Radon decays to Po^{218} (3.05 min), then to Pb^{214} (26.8 min) and Bi^{214} (19.7 min), the latter two radionuclides being gamma emitters. Several more steps ultimately produce stable Pb^{206} .

Naturally occurring radioactive ore owes its activity to uranium and/or thorium.

Radon gas in uranium mine atmospheres is a serious question, especially when the uranium mines are underground.

In the modern age, man is subject to several artificial radiation sources, i.e. television, radar, microwaves, X-rays used for medical applications, fallout from the A-bomb explosions, radioisotopes used in nuclear medicine, and other radioisotopes liberated from uranium ores worked out for the nuclear fuel cycle. We may voluntarily choose to receive some radiation exposure during the course of medical diagnosis and medical treatments.

Although nuclear weapons testing has ceased, the explosions made in the open-air atmosphere from the middle of 1940 to 1980 contribute today to several fission products like cesium-137, strontium-89,90 and artificial radionuclides like plutonium-239 and

carbon-14. The dispersed radionuclides and their fallout contributed to the background radiation dose.

1.2. Carbon-14, Potassium-40, Tritium, Rubidium-87, and Radon

There are some radionuclides formed by the interaction of cosmic rays with atoms in the atmosphere. They are termed “cosmogenic radionuclides.” Cosmic rays interacting with gases in the upper atmosphere cause the release of protons and neutrons from the nucleus of an atom. These secondary particles form the cosmogenic radionuclides via nuclear reactions. Carbon-14 is the most significant of the cosmogenic radionuclides. Carbon-14 is a radioactive isotope of carbon; its half-life is 5730 years and decays by beta emission: ${}^6\text{C}^{14} \rightarrow {}^7\text{N}^{14} + \beta^-$

In the atmosphere, carbon-14 is present as carbon dioxide. When it reaches Earth, it becomes part of the carbon cycle. Since we continuously eat and breathe carbon-containing matter, we will always have some carbon-14 in our bodies. Besides this substance, tritium (hydrogen-3), beryllium-7, and sodium-22 are cosmogenic radionuclides that make minor contributions to our radiations exposure. Although these cosmogenic radioisotopes have relatively short half-lives, they are always present in the environment because they are continuously being produced. Tritium is a radioactive isotope of hydrogen with a half-life of 12.3 years. It is a beta emitter: ${}^1\text{H}^3 \rightarrow {}^2\text{He}^3 + \beta^-$. Tritium is predominantly found in the atmosphere as water vapor. Eventually, it falls to earth in rain or snow. We are continuously ingesting foods and drinks containing hydrogen and for this reason we will always have trace amounts of tritium in our bodies. The radiation dose received from tritium is extremely small.

Unfortunately, nuclear accidents have occurred. The Chernobyl accident occurred in 1986 and contributed to the increase in background radiation. For this reason, the Earth will continue to be radioactive and nuclear power and radioactive waste disposal will remain environmentally controversial topics. However, a basic understanding of radiation, made in simple terms, may be useful to the population. The term “nuclear” or “atomic” does not have to have a negative connotation.

1.3. Radioactive Products in the Soil and in the Atmosphere

In a country like Brazil, some zones are characterized by frequent occurrences of sand deposits of heavy minerals with ilmenite and magnetite, and zircon and monazite (rare earth phosphates with a 4% to 6% admixture of thorium) as chief components. There are deposit concentrations along many beaches. The region of Poços de Caldas, MG, Brazil, constitutes an outstanding example of such radioactive regions. The Morro do Ferro (Iron Hill), in the same region, is another area where intense mineralization took place, yielding a great variety of rare earth oxidation compounds (up to 20%) with a strong percentage of thorium oxide (0.5% to 1.8%) and traces of uranium.

1.4. Radiation Types and Radiation Dose

Alpha particles are nuclei positively charged (two protons and two neutrons together) and emitted by natural and artificial radioactive elements. Beta particles (electrons) are

negatively charged. Gamma-radiation is a heavily electromagnetic radiation. X-ray radiation has the same nature as gamma rays but is produced by X-rays machines and not by radioactive materials.

Three terms are used to describe radiation dose: the roentgen(R), the rad, and the rem. The roentgen is a unit of exposure and is only used to define an external exposure from X-rays and gamma rays. A roentgen is sufficient radiation to produce 2.58×10^{-4} coulombs of charge per kilogram of air.

The rad is the abbreviation of Radiation Absorbed Dose and is used to describe the amount of any type of radiation energy deposited in any medium. In air, one rad equals approximately 0.87 roentgens but, in soft tissue, one rad of X-ray or gamma radiation is essentially equivalent to one roentgen. Nowadays the rad is being replaced by an international (SI) unity termed the gray (Gy). One gray is equivalent to 100 rads.

The rem, an acronym for Roentgen Equivalent Man, is the rad multiplied by a quality factor. This quality factor is based on the biological effects or damage received from the different types of radiation relative to those caused by gamma rays or X-rays. Gamma rays, X-rays, and beta particles have a quality factor of one; neutrons have a quality factor of ten, and alpha particles, 20. Thus, for a given amount of energy, alpha particles will be twenty times more harmful to humans than the same amount of energy received from gamma rays. The SI equivalent for the rem is the sievert (Sv), which is equal to 100 rems.

Different types of radiation will cause different biological effects for the same amount of energy deposited within our bodies, so the rem was introduced to take this effect into account.

1.5. The Curie (Ci) and the Becquerel (Bq)

The Geiger counter and scintillation counters can be used to count the particles given off from radioactive materials. The rate of nuclear disintegrations occurring in a radioactive material is the activity of the material. A curie is an activity unity equal to 3.7×10^{10} disintegrations per second. The becquerel, which is the SI unity comparable to the curie, equals one disintegration per second.

Summarizing the above: typical units of radioactive decay are the Curie (Ci) and the Becquerel (Bq). One Curie is equal to 3.7×10^{10} disintegrations per second, and a Becquerel is one disintegration per second. The unity of dosage for X- and gamma radiations is the Röntgen (R).

2. Nuclear Power

2.1. Is Nuclear Power Necessary?

In the beginning of 1986 the prospects for nuclear power in the US looked quite promising, with reform of nuclear power plant licensing and reauthorization. In April, however, the reactor accident at Chernobyl set nuclear power back. The public must, however, be assured that nuclear power plants can be and are operated safely. The

average citizen invariably associates nuclear power plants with nuclear arms, A-bombs, H-bombs, and, until the nuclear power industry gains the confidence of the public in general, it will continue to be discredited by its opponents.

In the US nuclear power is the second largest source of electrical power, saving the country almost two million barrels of oil each day. In France, nucleoelectricity today is over 75% of the total. England and various other countries are also using electricity generated by fission.

To have the reactors in operation, it is necessary to supply the fuel elements. The overall beginning of this is in uranium resources.

The difference in the scale of supply operations reflects the difference in energy content between conventional and atomic fuels. One cubic foot of uranium has the same energy content as 1.7 million tons of coal, 7.2 million barrels of oil, or 32 billion cubic feet of natural gas. In today's atomic power plants only a very small fraction of the potential energy value of the fuel is extracted in a single cycle of operation, but even so a truck-load of atomic fuel substitutes for many train loads of coal. For every gram of atomic fuel actually consumed (i.e. that undergo nuclear fission), approximately one "megawatt-day" of heat is released.

2.2. Fertile and Fissile Material

Nuclear fuel essentially consists of "fissile" and "fertile" material. In a nuclear reactor, heat is produced by fission reactions following neutron absorption in fissile material. Each neutron absorption in fissile material destroys a fissile atom, and produces on the average some neutrons, and usually two fission product atoms. To maintain the chain reaction, one of the neutrons produced must be absorbed to result in another fission.

Only two nuclides existing in the earth's crust can play the role of fertile nuclides: thorium-232 and uranium-238. These nuclides can be transformed into fissile nuclides by simple neutron capture and spontaneous beta-decay. With these two nuclei uranium-233 and plutonium-239, both fissile nuclides, are produced, respectively.

2.3. Uranium, Radioactive, and Depleted Uranium

Uranium can be safely fabricated and used with very few special precautions. Education of potential users is needed to remove the fear and the stigma created by the words "uranium" and "radioactive." Precautions regarding safety hazards should be presented in the same manner as those for materials such as lead, silver, mercury, cadmium, and arsenic.

Uranium, as it occurs in nature, is largely the isotope uranium-238 (99.27%) with a small fraction of uranium-235 (0.711%) and a very minor amount of a third isotope (U^{234}). The isotopic composition of this normal uranium is generally referred to as 99.3% U^{238} and 0.7% U^{235} . Depleted uranium is uranium that contains less of the U^{235} isotope than normal uranium.

Although uranium ingested or inhaled in small quantities is listed as chemically toxic, normal laboratory operating procedures that might be used with experimental quantities of many other heavy metals and their compounds are appropriate for uranium as well.

Larger-scale operations, however, require the use of safety measures similar to those considered proper for eliminating chemical toxicity hazards in corresponding operations involving materials such as lead, silver, mercury, cadmium and arsenic dusts.

Control of health hazards in large-scale uranium production has been reported in the literature. Uranium is mildly radioactive; however, uranium metal is a good shield to radioactivity.

2.4. Uranium in Nature

Uranium occurs widely in nature chiefly as oxide which may be in combination with other metal or nonmetal oxides. Major steps in the processing of uranium-bearing ores to obtain high-purity compounds include ore beneficiation, chemical treatment to yield an impure compound, and a liquid-liquid extraction to purify the compound. The purified compound, which is usually uranyl nitrate, may be treated to form other uranium compounds, including those from which the metal is subsequently extracted.

Uranium in river water: Japan 0.34 to 1.23 $\mu\text{g L}^{-1}$, USA 0.01 to 1.22 $\mu\text{g L}^{-1}$ and Brazil 0.29 to 1.61 $\mu\text{g L}^{-1}$. Uranium in drinking water: 0.42 $\mu\text{g L}^{-1}$ (Brazil) and 0.11 to 649 $\mu\text{g L}^{-1}$ (USA).

Uranium in seawater is reported to be 3.34 $\mu\text{g L}^{-1}$. The uranium concentration in seawater is probably stationary: a large amount, estimated at 27 000 tons annually, contributed by rivers, appears to be balanced by an equal amount carried down with the bottom deposits.

The uranium concentration is remarkably constant. A very interesting feature is that the uranium occurs in true solution as the tricarbonato complex, $\text{UO}_2(\text{CO}_3)_3^{4-}$. Thus, the ocean is virtually a limitless reservoir of uranium in solution in a well-defined chemical environment.

Uranium is present in coal in a form that is easily soluble in aqueous solutions of Na_2CO_3 - NaHCO_3 but with the increase of the temperature of coal combustion, the solubility of uranium decreases drastically.

Almost all phosphate deposits contain small quantities of uranium and the increase in the price of uranium together with the need to ensure availability of uranium has increased the incentive for recovery of uranium from phosphatic sources. Some 85% of the world's supply of phosphate is from marine phosphorites with the remaining 15% from apatite veins. Some 85% of all phosphate rock produced world wide is used in the manufacture of fertilizers and more than half of the world's production of phosphatic fertilizers is via the production of phosphoric acid as an intermediate. In general, phosphate rocks contain significant quantities of uranium such as 50 to 200 $\mu\text{g g}^{-1}$.

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Biographical Sketch

Alcídio Abrão. Nationality: Brazilian, S.José Bela Vista, S.Paulo State (b. 1925).

Academic degrees: Baccalaureate in Chemistry (1951), licentiate (chemistry teacher, 1954), and Ph.D. in Analytical Chemistry (1971) at the Chemistry Institute of S.Paulo State University; researcher at the IPEN, from 1957 to 1991. Today: adviser and consultant for the nuclear fuel cycle chemistry and processes applied to the environmental remediation at IPEN, S.Paulo. Lecturer of two pos-graduation courses: 1) Nuclear Materials Chemistry and 2) Ion Exchange Technology. Active as guide for post-graduation students. Adviser for the Gallium Project, Polytechnic Engineering School, São Paulo State University

Specialization: Nuclear science and technology; inorganic and analytical chemistry of the materials of nuclear interest as uranium, thorium, rare earth elements, zirconium, hafnium, beryllium and gallium.

Pos-Graduation Guidance: Under his orientation 52 thesis (master and doctor) had been presented and approved.

Publications: Author of several papers dealing with analytical chemistry, radiochemistry, spectrochemical analysis, trace analysis, uranium and thorium fuel cycle, rare earth elements and gallium.