Nuclear decommissioning: Turning waste into Wealth

Radiochemistry and the nuclear fuel cycle

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Overview

Aims

- Introduction to radiochemistry techniques
- Key radionuclide chemistry
- Stages of the nuclear fuel cycle
- Hazards and wastes arising from the fuel cycle
- Basic chemistry of the processing stages

Radiochemistry techniques 1

Radiochemical separations

- Precipitation
- Solvent extraction
- Ion-exchange chromatography
- Extraction chromatography

Radiochemistry techniques 2

Precipitation

- Precipitation involves the creation of a solid during a chemical reaction.
- This could be in solution or within another solid

Radiochemistry techniques 3

Solvent extraction

- Actinides (U/Pu) form complexes with tri-butyl phosphate (TBP) in kerosene, other contaminants do not. E.g.

$Pu^{4+} + 4NO^{3-} + 2TBP \rightleftharpoons Pu(NO_3)_4.2TBP$

- Pu can be extracted with the solvent.

Radiochemistry 1

Ion-exchange chromatography

- Ion-exchange chromatography allows the separation of ions and polar molecules.
- Molecules with +ve charge on one side and -ve on the other – based on their affinity to the ion exchanger.
- Can be used for a wide range of charged molecules.

Radiochemistry 2

Extraction chromatography

- The separation is based on the distribution of radionuclides between organic and aqueous phases.
- A wide variety of extractants: acidic, amines, organic molecules etc.

Key technique: Solvent extraction 1

Advantages

- Rapid, highly efficient and very selective separations.
- Partition coefficients independent of radionuclide concentration.
- Can usually be followed by back-extraction into aqueous solutions.

Key technique: Solvent extraction 2

Advantages

- Wide scope of applications – the composition of the organic phase and the nature of complexing or binding agents can be varied so that the number of practical combinations is virtually unlimited.
- Can be performed with simple equipment, but can also be automated.

Key technique: Solvent extraction 3

Disadvantages

- Often requires toxic or flammable solvents
- Time consuming, especially if the equilibrium is slow.
- Can require costly amounts of organic solvents and generate
- Large volumes of organic waste.
- Can be affected by small impurities in the solvent.
- Multiple extractions might be required, thereby increasing time, consumption of materials, and generation of waste.

Tracers and carriers 1

Carriers

Carriers are chemically identical materials to the radionuclide of interest that have a significant, non-radioactive mass. By adding such a material to the radionuclide of interest the carrier, rather than the radionuclide can saturate loss-sites such as surfaces.

Examples

For ^{90}Sr the stable isotope ^{88}Sr can be used as a carrier.

Radium has no stable isotopes, but barium is in the same chemical group (II) can be used. Both will precipitate together.

Tracers and carriers 2

Tracers

Tracers must exhibit the same chemical behaviour as the analyte – substance of interest – so that the same separations etc. can be performed. The tracer is added in a known quantity and measured at the end, enabling the losses of the processes to be found.

Example

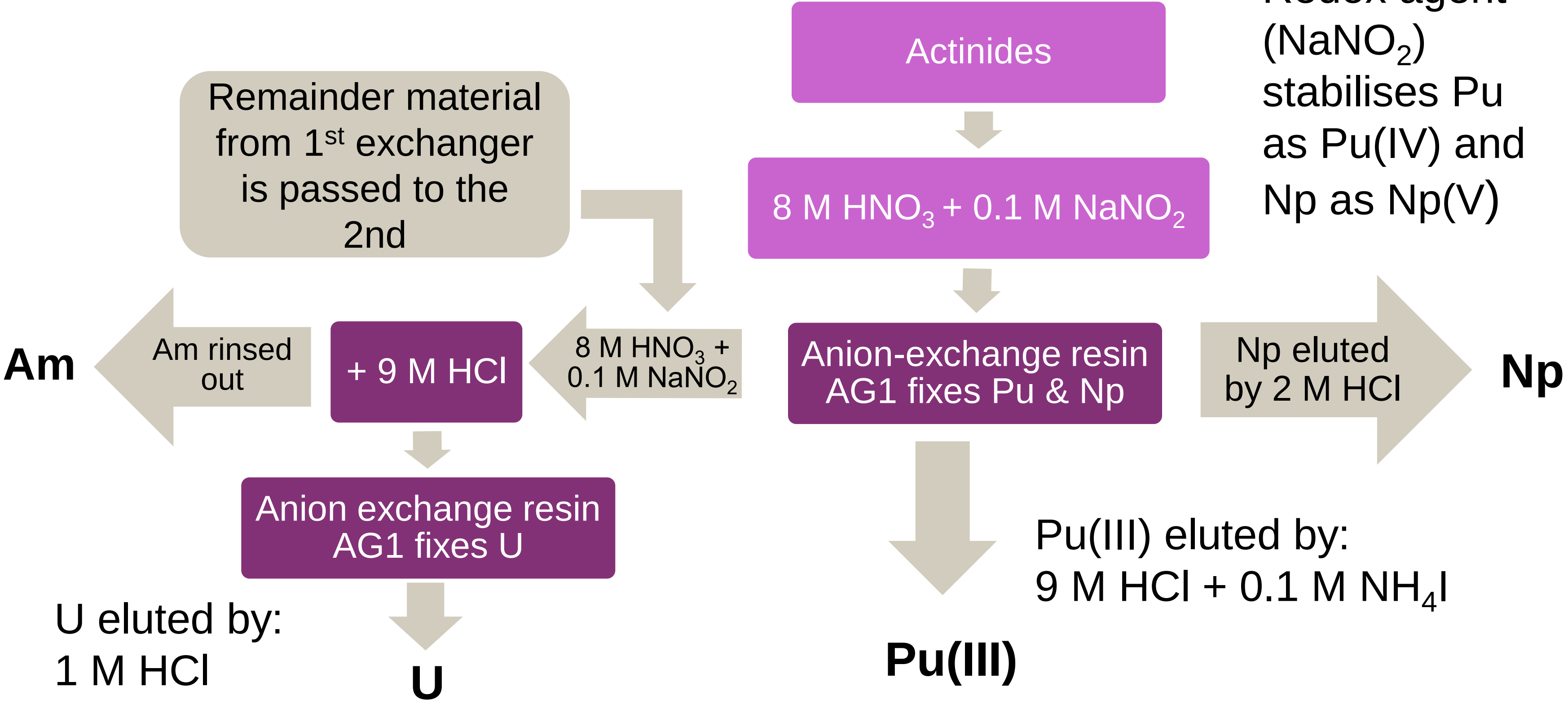
Uranium-236 and 232 are used as tracers for ^{238}U and ^{234}U.

Key radionuclides 1

Ion-exchange separation of actinides:

- Am(III)
- Pu(IV)
- Np(V)
- U(VI).

Key radionuclides 2



Actinides

$8\ M\ HNO_3 + 0.1\ M\ NaNO_2$

Anion-exchange resin AG1 fixes Pu & Np

Np eluted by 2 M HCl

Np

Redox agent ($NaNO_2$) stabilises Pu as Pu(IV) and Np as Np(V)

Pu(III) eluted by: $9\ M\ HCl + 0.1\ M\ NH_4I$

Pu(III)

Remainder material from 1st exchanger is passed to the 2nd

$8\ M\ HNO_3 + 0.1\ M\ NaNO_2$

+ 9 M HCl

Am rinsed out

Am

Anion exchange resin AG1 fixes U

U eluted by: 1 M HCl

U

What is the nuclear fuel cycle? 1

The fuel cycle is a chain of industrial processes to convert the uranium ore into fuel for reactors and, following removal from the core, can also include the steps required to reprocess the spent fuel.

What is the nuclear fuel cycle? 2

Uranium

Uranium is a relatively common element found in the earth's crust. Before uranium can be used as fuel in reactors it must be converted from its natural forms.

What is the nuclear fuel cycle? 3

Uranium ore

Uranium ore consists of impure UO_2, UO_3, U_3O_8 and other material (contaminants).

What is the nuclear fuel cycle? 4

Radioactivity

Much of the radioactivity present with uranium deposits is from the decay products (daughter nuclei) e.g. radon gas, which are removed in the processing.

Overview of the fuel cycle

Mining and milling

Tailings

Conversion

UF_6 production

Enrichment

3.5 – 5% ^{235}U

Natural U fuel

Fuel fabrication

Power plant (electricity production)

Recycling

Reprocessing of spent fuel

High-level waste storage

Disposal

Image credit: United States Department of Energy via Wikicommons

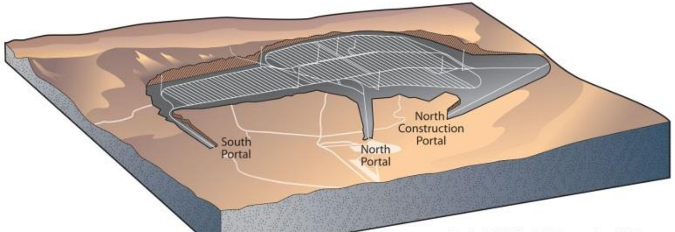


Image credit: LANL/LANS under US Department of Energy via Wikicommons

Key steps in the fuel cycle 1

Mining

The ore is extracted by either excavation or in situ leaching (ISL) with oxygenated water. Depending on conditions of the ore, weak acid or alkali solutions may be used in leaching.

Key steps in the fuel cycle 2

Milling

Milling is generally performed close to the mine. This refers to the process of producing yellowcake. The ore is crushed and purified to extract U_3O_8 triuranium octoxide also known as yellowcake. See handout 'The chemistry of cake' for details.

Image credit: Geomartin via Wikicommons (CC BY-SA 3.0)

Key steps in the fuel cycle 3

Conversion

Conversion refinement to UO_2 uranium dioxide. This can be used directly as a natural fuel for reactors needing no enrichment (0.7% ^{235}U), or converted to UF_6 uranium hexafluoride gas for enrichment.

Key steps in the fuel cycle 4

Enrichment

Enrichment is the process by which the % of ^{235}U is increased. The UF_6 is allowed to solidify (melting point 64 °C) in metal containers for transport to the enrichment facility. Gaseous diffusion or centrifuges are used to perform the enrichment.

Image credit: A billet of highly enriched uranium (via Wikipedia) or Uranium Enrichment Plant (U.S. Department of Energy via Wiki Commons)

Key steps in the fuel cycle 5

Fuel fabrication

Fuel for most reactor types is in ceramic pellets formed by pressed UO_2 held at high temperatures. Lots of pellets are typically placed into tubes – fuel rods – which are combined together into groups, called stringers, ready to be placed into the reactor.

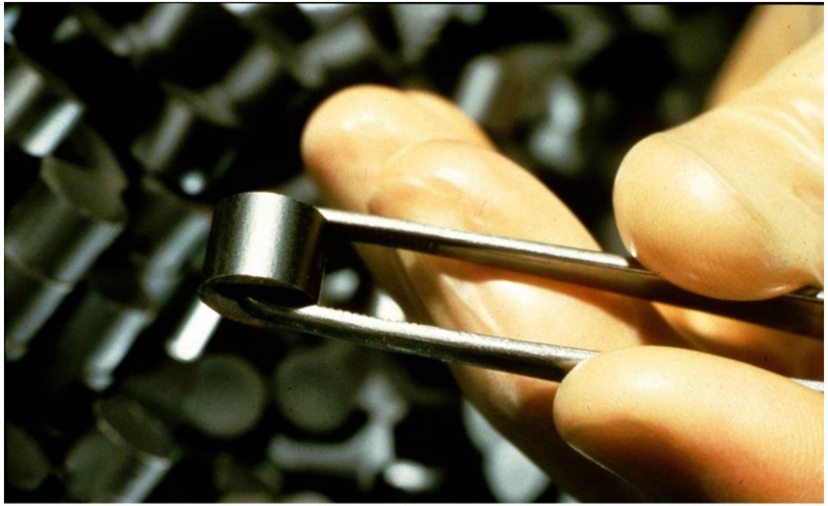


Image credit: Uranium fuel pellet (Nuclear Regulatory Commission via Wiki Commons)

Key steps in the fuel cycle 6

Reprocessing

Reprocessing is the process by which fissile material (e.g. Pu) is separated out from the fission products. This material can be used as new reactor fuel.

Key steps in the fuel cycle 7

Storage

High-level waste requires cooling to remove the heat generated by radioactive decay. This waste is stored near the surface for at least 50 years in order to enable monitoring.

Image credit: Centre for Land Use Interpretation (CC BY-NC-SA 3.0)

Site in Utah constructed for uranium mill tailings and debris from a mill site.

Wastes and hazards 1

Tailings

These wastes from the mining process are not classified as radioactive waste, as they originated from naturally occurring ores and generally retained near the mine site.

Wastes and hazards 2

Low-level waste

Produced from all stages in the fuel cycle

Intermediate-level waste

Largely produced from reactor operation and processing

High-level waste

Produced in the form of actinide nuclei and fission products separated from the fuel during reprocessing

Depleted uranium (DU)

Depleted uranium (DU) is a by-product of the enrichment process. It refers to predominantly ^{238}U in which the % of ^{235}U is less than 0.7% – the uranium is thus depleted in ^{235}U. Due to its high density, depleted uranium has applications in shielding and trim weights in aircraft as well as military uses. Thus, not all DU is waste.

Chemistry of conversion 1

Dry process

The triuranium octoxide is heated to drive off impurities, then collected together and crushed. This is known as the dry process.

$U_3O_8 + 2H_2 \rightarrow 3UO_2 + 2H_2O$

The oxide is reduced in a kiln with hydrogen gas.

Chemistry of conversion 2

Wet process

Involves:

- Dissolving U_3O_8 in nitric acid to form uranyl nitrate $UO_2(NO_3)_2.6H_2O$.
- Fed into a solvent extraction process using tributyl phosphate dissolved in kerosene or dodecane (long-chain hydrocarbons used as organic solvents).

Chemistry of conversion 3

Wet process

Involves:

- The uranium is collected and washed out of the solvent.
- The product is concentrated by evaporation.
- The solution is heated yielding UO_3 or UO_2 (under extreme heating).

$UO_3 + H_2 \rightarrow UO_2 + H_2O$ (Again, a reduction using hydrogen)

Chemistry of conversion 4

Production of uranium hexafluoride

Step 1

Uranium dioxide heated in kiln with HF

$UO_2 + 4HF \rightarrow \mathbf{UF_4} + 2H_2O$

Occasionally, HF is reacted in aqueous solution (wet process)

Chemistry of conversion 5

Production of uranium hexafluoride

Step 2

Finally, UF_4 reacted with $F_{2(g)}$ in a fluidised bed (flame tower) at 800 – 1200 °C

$UF_4 + F_2 \rightarrow UF_6$

The UF_6 is condensed in thick-walled steel shipping containers, as a white crystalline solid.

The PUREX process 1

- PUREX – Plutonium Uranium Redox Extraction process
- Same solvent extraction process as wet process for producing UO_2
- Specifically, PUREX refers to the process used in reprocessing.
- Aim of reprocessing: To extract U and Pu from spent fuel.
- When combined these form what is known as MOX – mixed oxide fuel.

The PUREX process 2

Separation

- In the solvent extraction the Pu and U are separated from fission products, which remain in the aqueous phase.
- Transuranium elements americium and curium also remain in the aqueous phase rather than forming complexes with nitrate etc.

Objectives

After this workshop you should be able to:

- Describe the principles behind radiochemical separation
- Appraise the technique of solvent extraction
- Draw the separation method used for actinides/radionuclides
- Sequence the key steps in the nuclear fuel cycle
- Explain chemical process used in conversion and reprocessing.

Bibliography 1

Sources/further reading

World Nuclear Association: an organisation for the nuclear profession.

http://www.world-nuclear.org/

International Atomic Energy Agency

https://www.iaea.org/

Bibliography 2

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Gregory Choppin, Jan-Olov Liljenzin and Jan Rydberg, Radiochemistry and Nuclear Chemistry, Third Edition (2001).

Gerhart Friedlander and Joseph W. Kennedy, Introduction to Radiochemistry, (John Wiley and Sons,1949).

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