

Treatment and Conditioning of Nuclear Wastes



“My uncle’s enthusiasm, always a little more than was required, was now excusable.”

—Henry Lawson in “Journey to the Center of the Earth” by Jules Verne.

Treatment and conditioning

Treatment and conditioning are used to convert radioactive, mixed, and hazardous wastes into inert forms for transportation, storage, and disposal.

Conditioning often means converting solid wastes into a form that is **resistant to leaching by groundwater after disposal.**

Treatment and conditioning

Waste conditioning is accomplished by adding concrete, bitumen, borosilicate glass—and in the future possibly synthetic minerals.

The immobilized wastes are then disposed in metal drums, metal or concrete boxes, or copper and steel canisters.

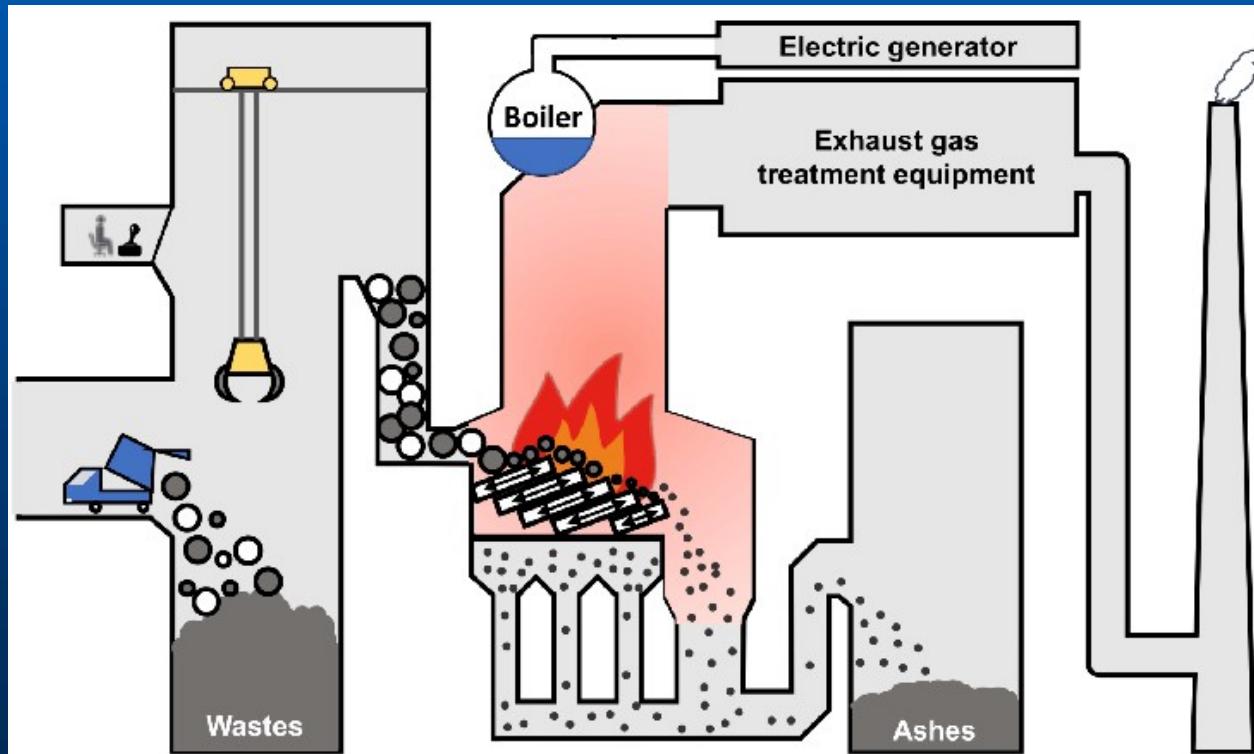
Waste treatment

Incineration

Incinerate wastes at about 1,000° C to reduce volume. Used for low-level radioactive wastes, mixed wastes, and hazardous wastes. Incinerate material like coveralls, protective suits, gloves, hats, bags, adsorbent paper, and wood. Industrial wastes containing volatile organic components such as benzene or hexane. Also medical wastes.

Incineration

Incineration will yield an ash that may need to be conditioned.



Compaction

Volume reduction. Used for Low-Level, TRU, Mixed, and Hazardous Wastes.

A hydraulic or pneumatic press is used to crush a 200-L or 55-gallon drum. Chase Environmental Group, Inc. transports waste drums from the University of Illinois, then crushes them to make “pucks” before turning them over to *EnergySolutions* to transport to Utah.

Drum crusher



Setting a LLRW drum in place



A “puck.”
Reduced volume =
reduced costs



Waste conditioning: Concrete

Concrete is used in fabricating waste-forms (waste immobilization, waste treatment), decommissioning of nuclear facilities, and in the operations of radioactive waste facilities.

Concrete is a mixture of fine- and coarse-grained aggregates bonded together with a cement binder.

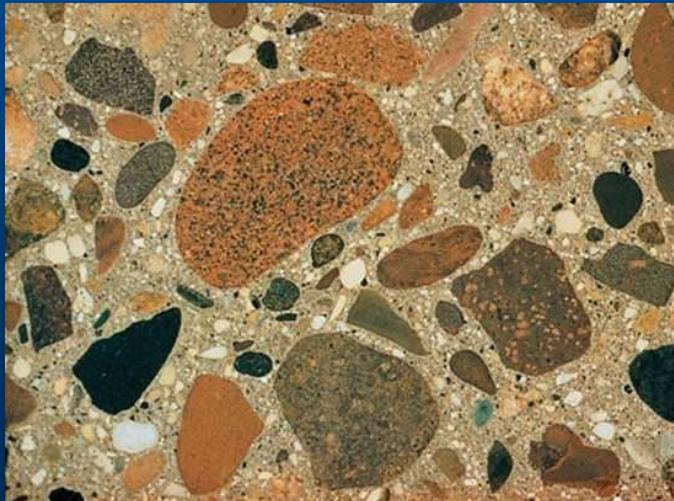




Aggregate

Most of the strength of concrete is from the aggregate: Sand. Coarse gravel.

Crushed limestone, bricks, granite, and demolition debris (recycled concrete).



Cement binder

The most commonly used: Portland cement.

It is a mixture of:

Calcium silicate (Ca_3SiO_5)

Calcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$)

Calcium, aluminum ferrite ($\text{Ca}_4(\text{Al}, \text{Fe})_2\text{O}_7$)

Lime (CaO)

Calcium sulfate (CaSO_4)

Cement hydration

Cement + water →
chemical reactions → hardening

Reaction Products:

Tobermorite gel (amorphous calcium silicate hydrate: $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$)

Portlandite ($\text{Ca}(\text{OH})_2$)

Ettringite and Monosulfate (both hydrous aluminum sulfate).

Ettringite is: $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$

Major reaction products

Tobermorite



Portlandite

Ettringite



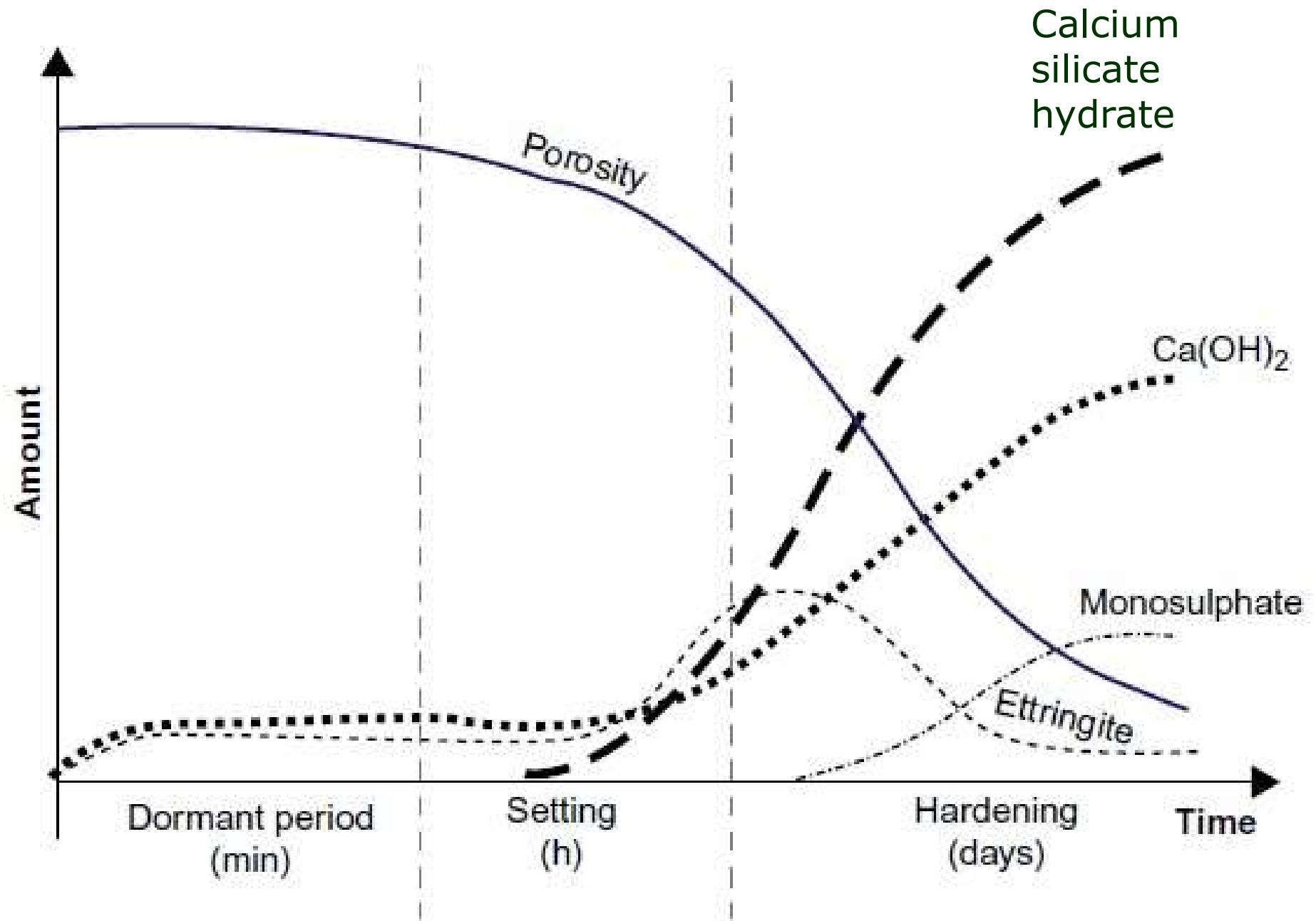


Figure 15.2 Schematic of cement hydration kinetics.

Benefits of concrete

Relatively inexpensive.

Provides a physical barrier between radionuclides and the environment (human exposure and leaching by groundwater) and provides shielding from radiation.

Provides a chemical barrier in terms of reducing diffusion and radionuclide movement from wasteforms.

How long will concrete last?

Natural analogs

Portland cement named after Portland Stone,
a Jurassic-age limestone.

Precursors are limestone, clays, and shales.
Hence, millions of years.

Roman concrete
structures since c. 150 BC.
Conventional concrete:
less than 100 years.



Why does concrete fail?

Internal chemical reactions

Some failure mechanisms are based on products expanding within the concrete microstructure. Because hydrated cement paste is very stiff, and weak in tension, small expansions can result in extensive microcracking and damage.

Alkali aggregate reaction (AAR)

A chemical reaction can occur between certain types of aggregate, alkali hydroxides, normally from the cement, and water that leads to the slow formation of a gel in and around the aggregates.

<https://www.youtube.com/watch?v=qifF89HFLY2A> (7:51)

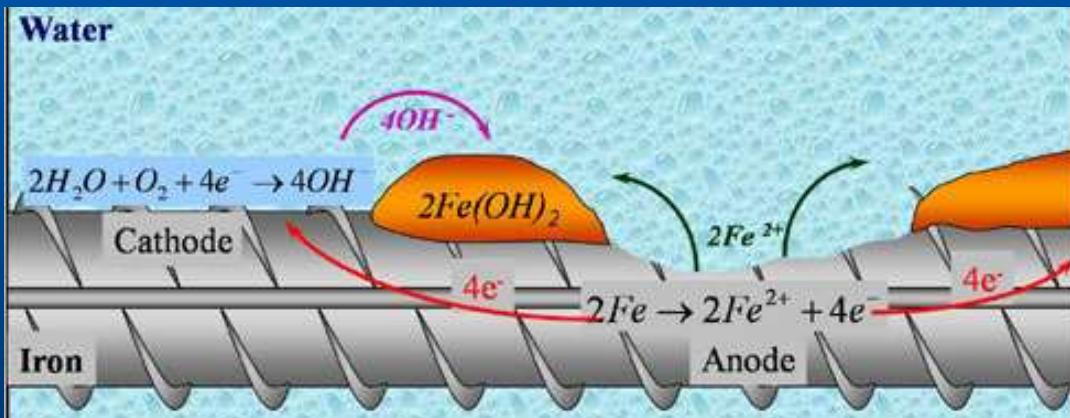
Why does concrete fail?

Overload and Fatigue. Any structural material that is overloaded will likely fail and crack. Likewise, many materials that are repeatedly loaded to a significant proportion of their yield stress will accumulate damage, and eventually fail.



Why does concrete fail?

Steel Corrosion. Iron rebar can expand as much as seven times its original volume when fully oxidized. The pressure breaks the concrete.



Why does concrete fail?

Salt crystallization within the pores and voids of concrete.

Perhaps salt from brine-rich groundwater?



Alternative Cements

Alternative cements/concretes that being studied for radioactive waste conditioning.

Calcium aluminate cement

Made from limestone (CaCO_3) and bauxite (aluminum hydroxide minerals: the major ore of aluminum).

Resulting is a cement more heat resistant than OPC (heat radioactive decay?)



Alternative Cements

Calcium sulphoaluminate cement

Made from limestone + coal fly ash + gypsum.



Uses an industrial waste. Strong compressive strength. More research needed for wastes.

Alternative Cements

Geopolymer concrete

Sources of silica, aluminum, and iron such as industrial wastes (coal fly ash, foundry slags, quartz-rich wastes), obsidian (volcanic glass)

Plus sodium hydroxide → geo (rock) polymer cement.

Can be stronger than OPC. Produces less CO₂.
Research on-going.

Waste conditioning? Maybe.



Alternative Cements

Alternative cements

https://www.youtube.com/watch?v=iFpwgTUV_nk (8:56)

Geopolymers made from “smoke in a bucket”

https://www.youtube.com/watch?v=ci07_52EnBg (4:31)

Long-term applications

In long-term application in a geological repository, how will the efficacy of concrete be impacted by:

1. Contact with groundwater brines?
2. Radioactive decay heat?
3. Earthquakes and tectonic stresses?

Will the concrete last long enough?

Waste Conditioning

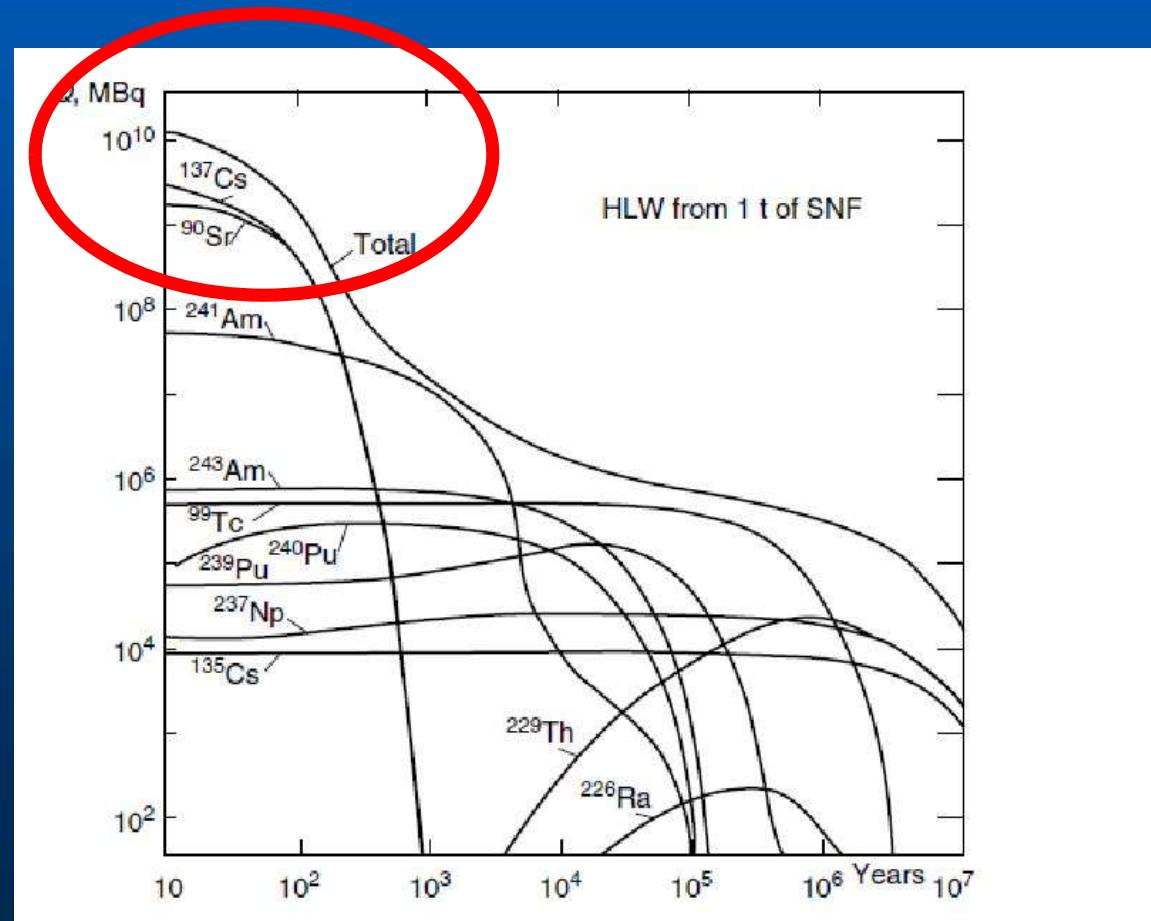
Vitrification and Ceramic Wasteforms.

The goal of these two waste-conditioning approaches is to immobilized the high-level wastes created by reprocessing used nuclear fuel.

Reprocessing wastes

The weight of reprocessing waste is about one-tenth of the weight of UNF.

Sr-90 and Cs-137 are the major problems during the first few centuries of waste storage.

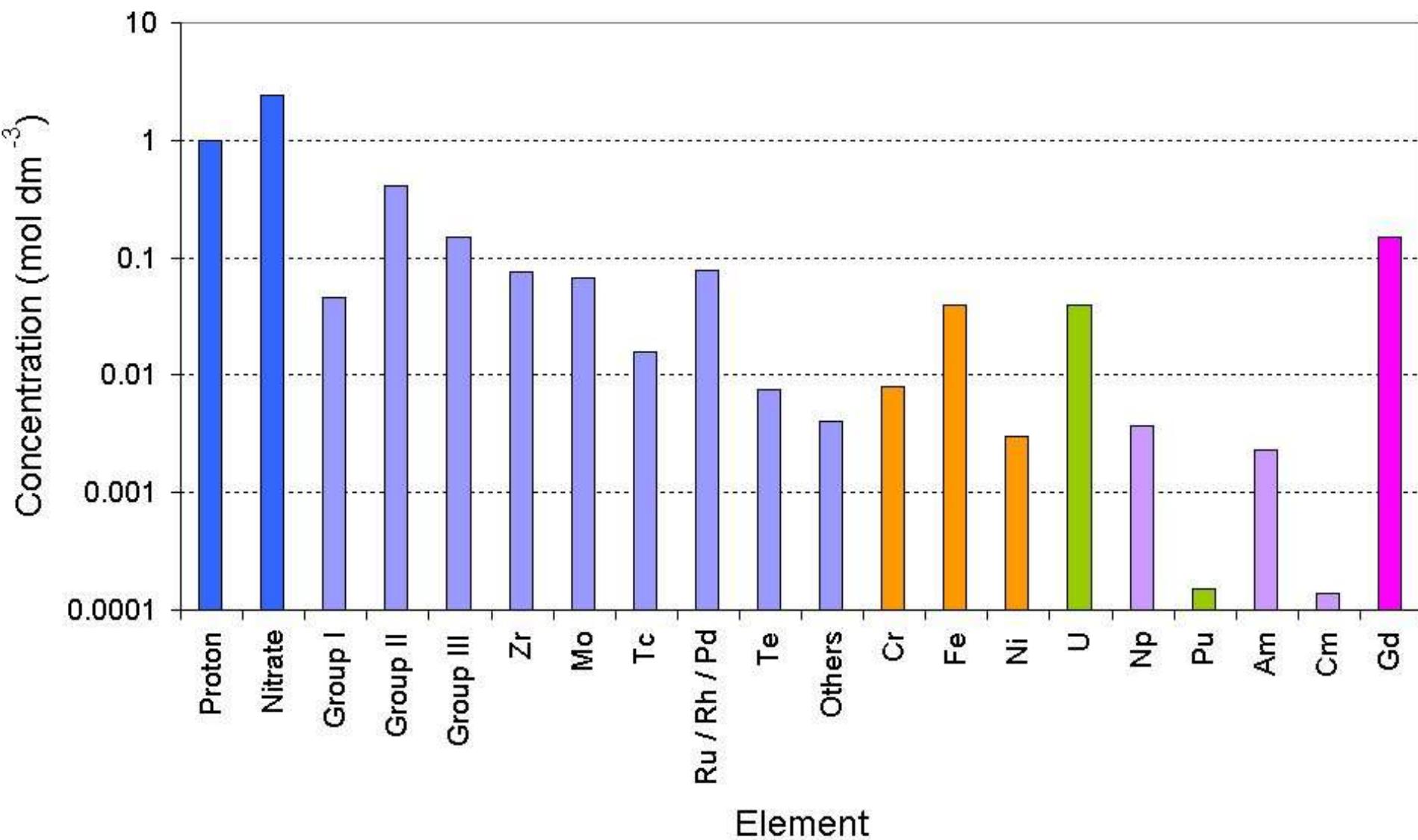


Reprocessing wastes

Aqueous/nitric acid solutions that contain fission products, actinides, corrosion products, and process chemicals (Fe, Na, Cr, N, and P).

Derived from UNF from the Nuclear Weapons Complex in the U.S. Because we do not reprocess UNF, HLW treatment research has not been a major priority in the U.S. In general, these are high-level liquid wastes that are stored in underground tanks.

Typical first-cycle raffinate



Treating High-Level Liquid Wastes

Reduce the volume of waste:

Calcination—heat the liquid to evaporate moisture and volatile constituents without fusing the residue (a granular form is easier to pour).

Fixation, immobilization,—adding some agent to the calcinate to reduce the potential for leaching (waste stabilization) as another safety factor.

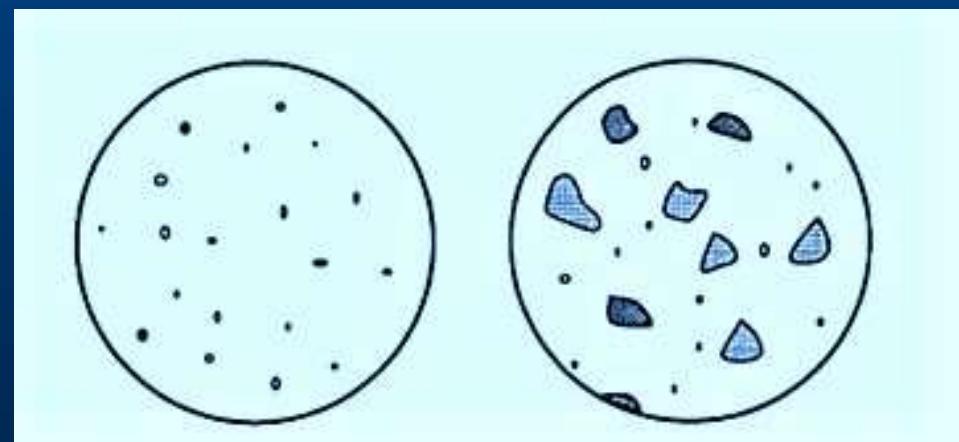
Immobilization of calcinate/HLW

Basic approach is to mix and isolate the calcinate with

- 1. Amorphous glass**
- 2. Ceramic-formation minerals**
- 3. Glass-ceramic combinations**
- 4. Basalt glass-ceramic combinations**

Immobilization of the calcinate (HLW)

Ideally, the goal is to encapsulate solid-waste particles in a glass-like or a ceramic matrix. The glass/ceramic becomes a barrier to leaching by groundwater if the metal contained is compromised.



Immobilization of calcinate

Best understood and widely used additive is borosilicate glass.

70 to 81% SiO_2

7 to 13% B_2O_3

4 to 8% Na_2O

2 to 7% Al_2O_3

Immobilization of calcinate

Borosilicate glass is more resistant to thermal shock such as from the heat from radioactive decay than ordinary glass.

Also called “Pyrex glass” as in lab glassware.

Ultimate goal is to immobilize and make radionuclides unavailable to leach into groundwater.

Immobilization of calcinate

Solid calcinate is mixed with ground borosilicate glass.

The mixture is heated to about 2,012° F.

Molten glass is then poured into a steel container, and allowed to cool.



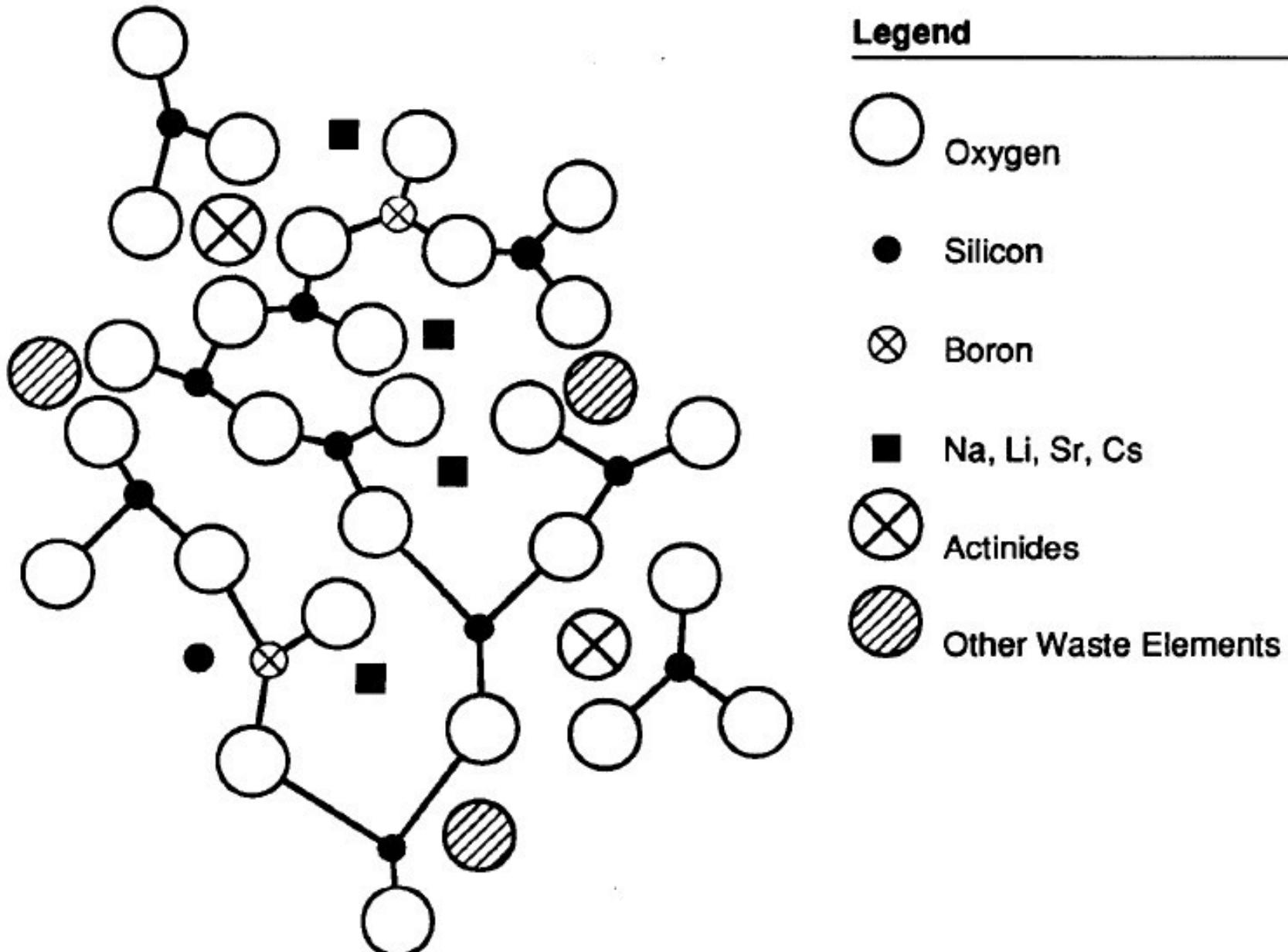
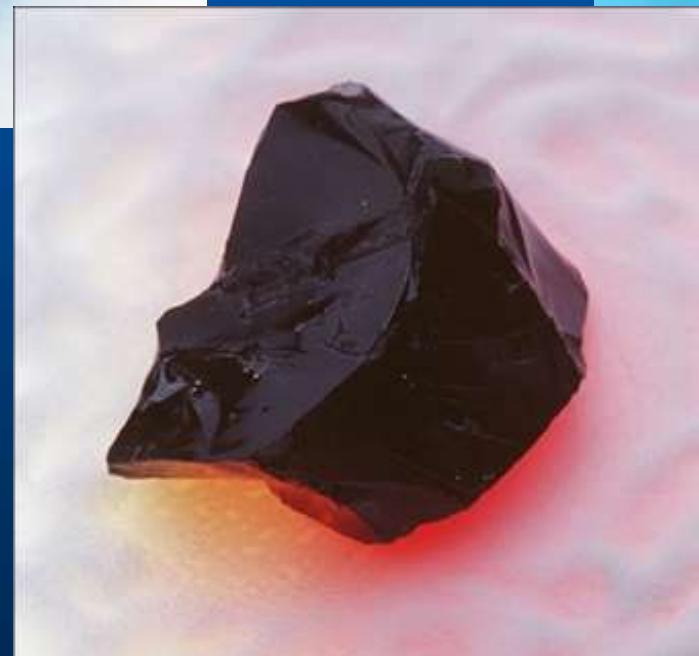


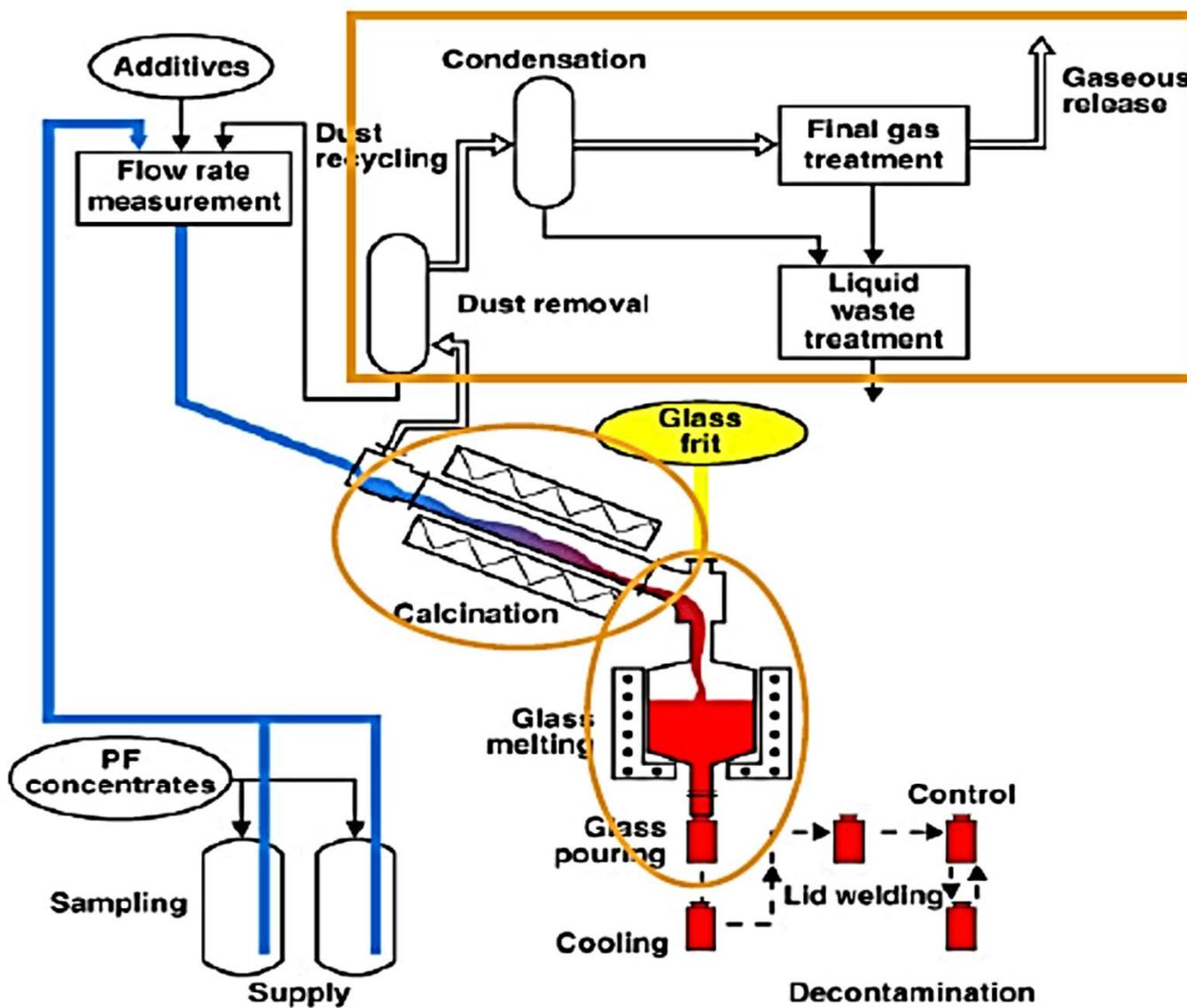
Figure 3-3. Schematic of Alkali Borosilicate Glass Structure Containing Dissolved Nuclear Wastes (adapted from Hench et al., 1986)

Examples of vitrified HLW



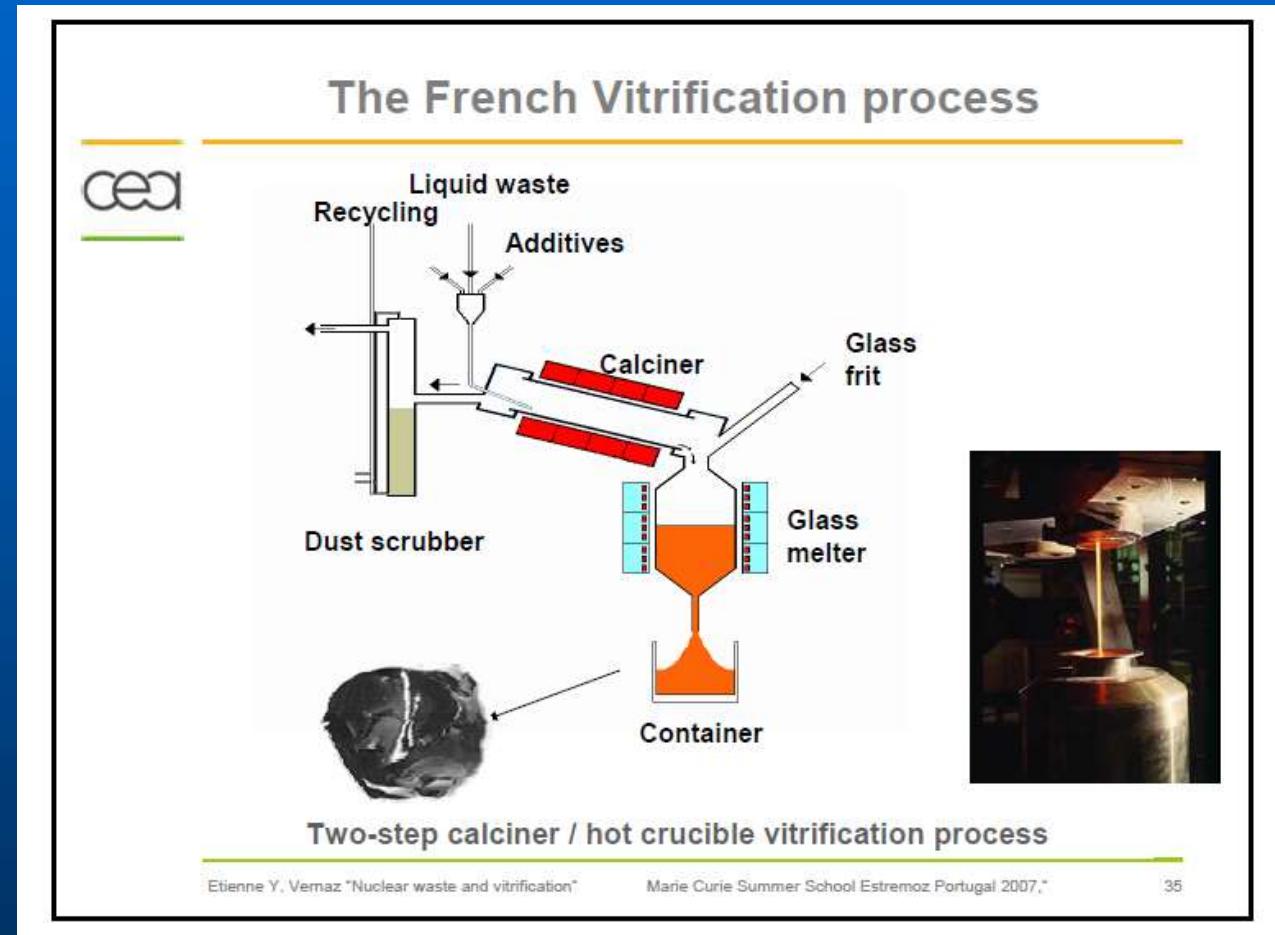
French Industrial HLW Vitrification Plants Process Principles

► Principle of the French vitrification facilities



Commercial treatment

Calcination and vitrification are coupled (two-stage process).



Storage of high-level vitrified waste



Ceramic Wastefoms

Synroc: “Synthetic rock”

Invented in 1978 at the Australian National University.

Basic premise: to imitate geological storage of radionuclides by using a mixture of titanium minerals and heat to create a ceramic wastefom.

Dr. Alfred E. Ringwood

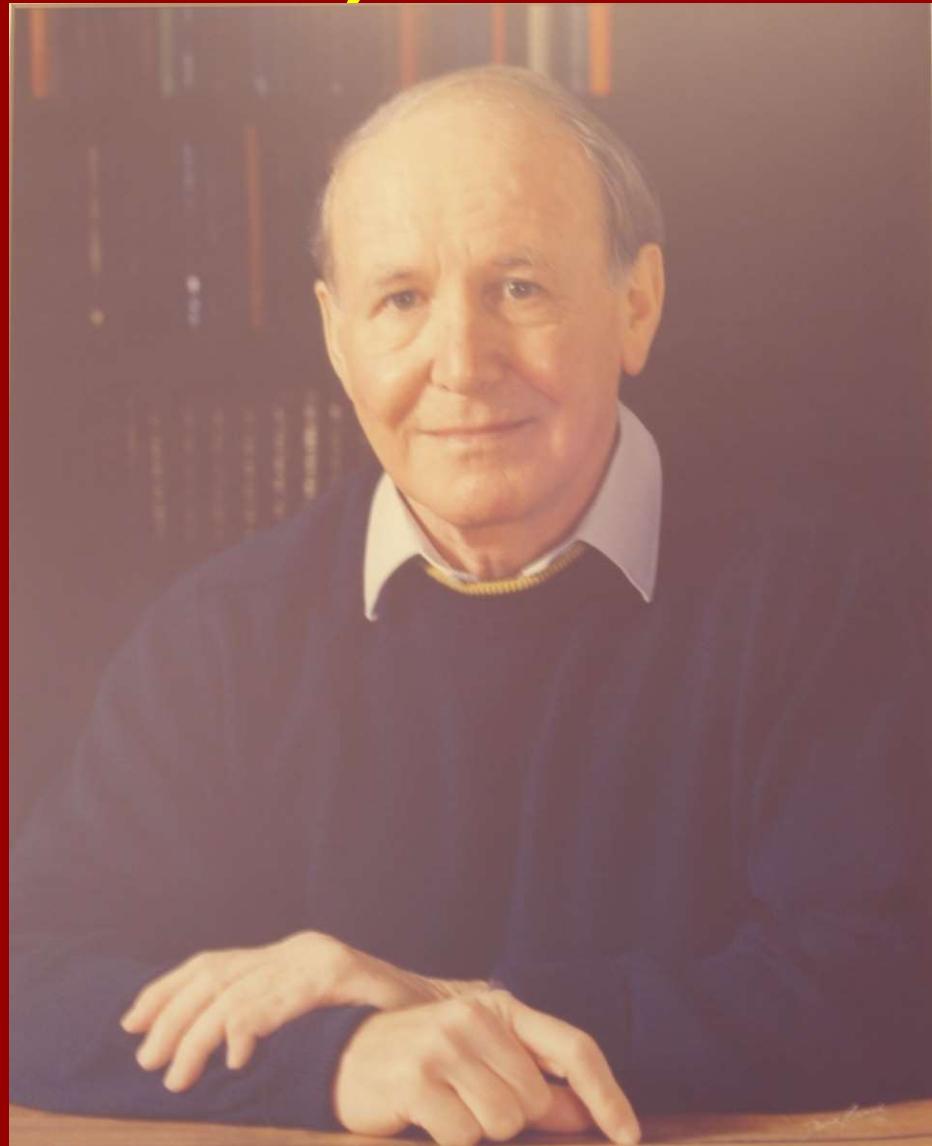
(1930-1993)

Australian Geochemist

**Fellow, Australian
Academy of Science,**

**Fellow, American
Geophysical Union,**

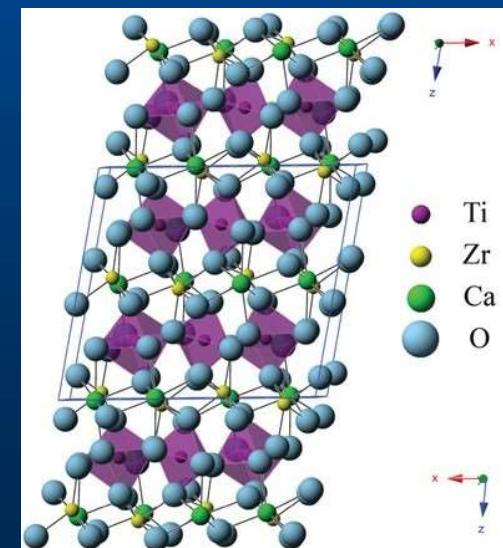
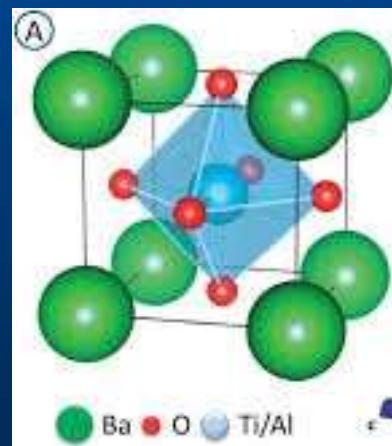
**Fellow, Royal Society of
London**



Synroc

Use titanium oxide minerals that have stored U, Th, and other rare earth elements (REE) for millions of years.

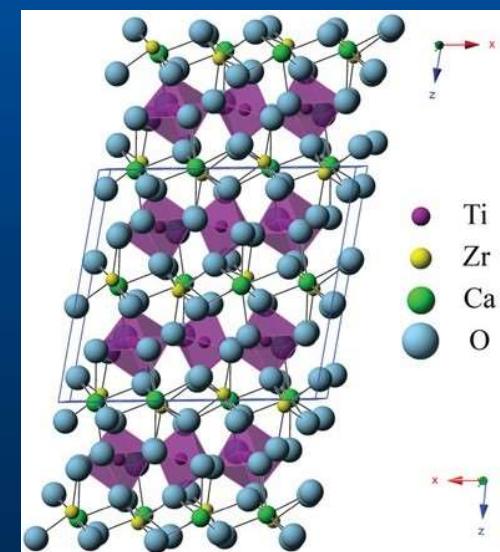
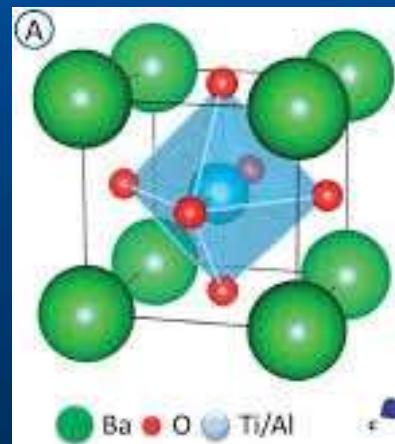
Hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$): Rh (rodium), Ru (ruthium), can replace Al and Ti



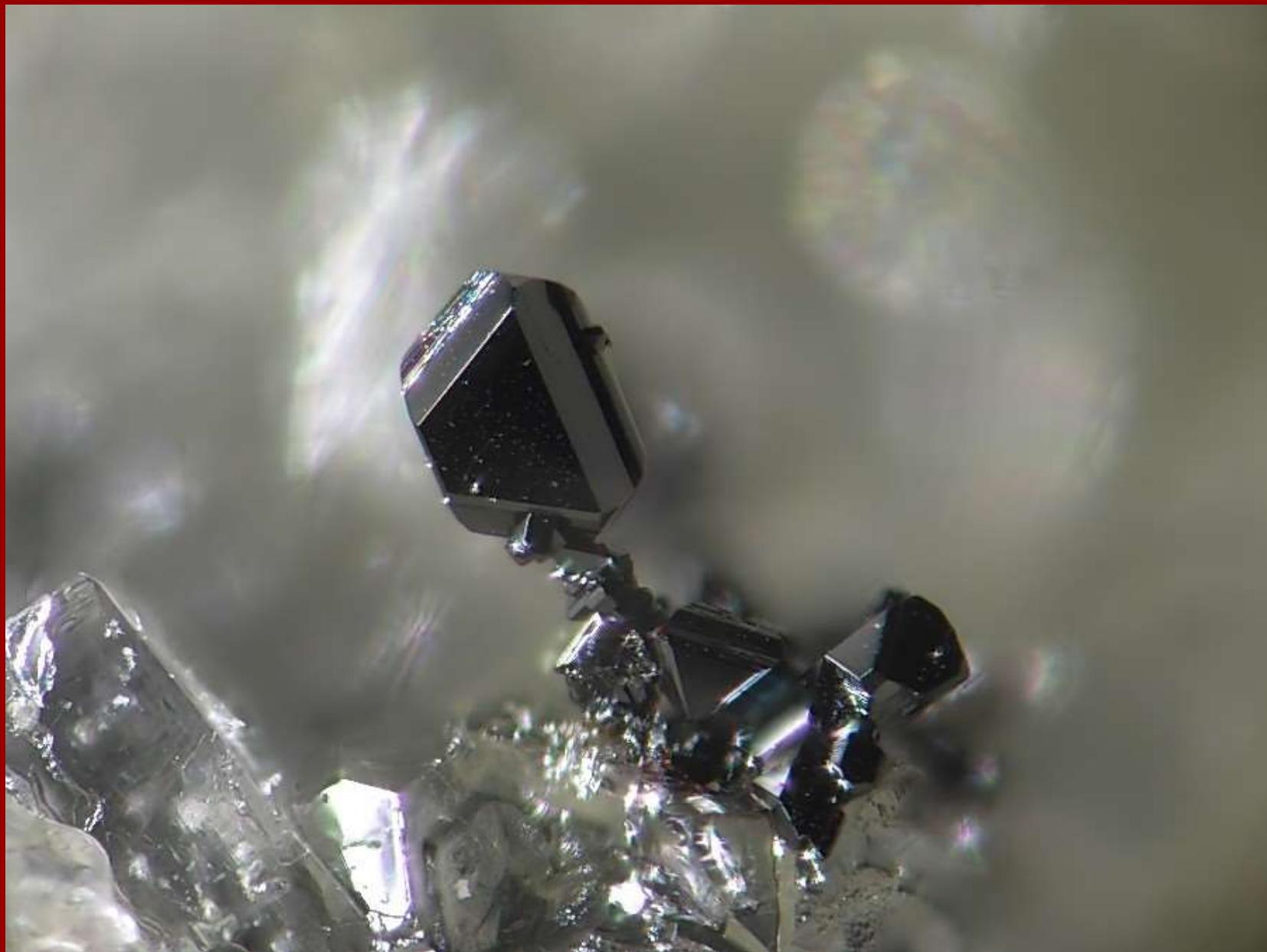
Synroc

Zirconolite ($\text{CaZrTi}_2\text{O}_7$): Sr, REE, and others can replace Ca.

Perovskite (CaTiO_3): Sr, Cm, Am, Pu, and others can replace Ca or Ti



Zirconolite



Perovskite



Process

- 1. About 10% calcinate is added to a mixture of ground hollandite, perovskite, and zirconolite.**
- 2. Hot press at 1,100 to 1,350° C. Radionuclides become part of mineral structures.**
- 3. Allow to cool and recrystallize in sealed containers.**
- 4. Containers then are to be disposed in a geological repository.**

ANSTO update (2018)

Australian Nuclear Science and Technology Organisation (ANSTO)

Their mission: “To undertake research that will advance the application of nuclear science and technology.”

https://www.youtube.com/watch?v=0h1g0A70P_w (2:51)

Pyrochlore-rich ceramics

Pyrochlore: an oxide of niobium

$(\text{Na}, \text{Ca})_2\text{Nb}_2\text{O}_6(\text{OH}, \text{F})$. Very rare

in nature, there are however, more

than 500 synthetic combinations with a pyrochlore structure. The composition can be written as $\text{A}_2\text{B}_2\text{X}_6\text{Y}$

Where A = lanthanides and actinides

B = Ti, Zr, Nb, Sn (tin), and W (tungsten).

X = an anion (typically O) and Y = anion.



Pyrochlore-rich ceramics

Pyrochlores are similar to Synroc.

The primary host for actinides in Synroc is zirconolite ($\text{CaZrTi}_2\text{O}_7$)

Synroc-F contains 85 wt% pyrochlore-like CaUTi_2O_7 + 5 wt% of rutile (TiO_2), hollandite, and perovskite.

Most research has focused on pyrochlore titanates because of its chemical stability.

Pyrochlore-titanates ceramics

Range in composition (examples)

pyrochlore	70 to 80 wt %
rutile	10 to 14 wt %
hollandite	2 to 10 wt %
perovskite	0 to 12 wt %
brannerite (U, Ca, Ce) (Ti, Fe)₂O₆	1 wt %

Pyrochlore-titanates ceramics

At the experimental stage, primarily in Australia. Thus far, most ceramics are made by sintering rather than melting.

A current area of research is radiation damage from alpha particles, and alpha-recoils by the nucleus, which results in self-heating. This occurs naturally in minerals containing alpha sources.

Leaching of wasteforms

Whether glass or polyphase ceramic forms are used then placed in canisters what happens if the canister is comprised?

Groundwater could flow through the disposal area.

Can radionuclides leach from these immobilized HLW forms?

Leaching Behavior

Everything is soluble in water at some level.

Extent of leaching depends on

- 1. pH and chemical composition of the water.**
- 2. glass/ceramic composition.**
- 3. surface chemistry and area.,**
- 4. flow rate (static vs dynamic conditions).**
- 5. time.**
- 6. radiation damage.**

Standardized tests used.

Transmutation of Radioactive Waste



Basic concepts

Transmutation. Transformation of one isotope into another by neutron absorption.

Products: Next heavier isotope or two or more fission products.

Fissile: Fissionable by thermal neutrons.

^{235}U is fissile whereas ^{238}U is not.

Transmutation as a curse or a cure?

Transmutation creates waste management issues with respect to either once-through UNF or in reprocessing UNF.

Can transmutation be applied to UNF and wastes to reduce their radiotoxicity by converting radionuclides with long half-lives to ones that decay more quickly?

The Roy Process

Some people think so. Several transmutation processes have been proposed. Take for example “The Roy Process.”

In 1979, the late Dr. Radha Roy announced he “had invented a new method to render all radioactive waste elements, including plutonium, into non-radioactive elements.”

Dr. Radha R. Roy Ph.D.
Professor Emeritus
Nuclear Physics
Arizona State University

[BRIEF BIO](#)



[VIDEO](#)

The Roy Process

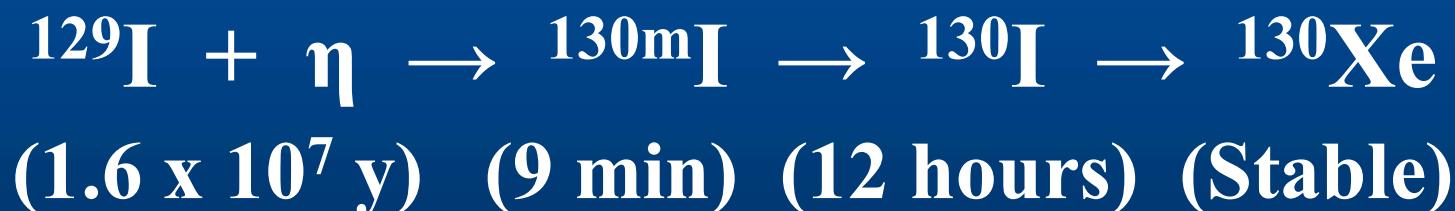
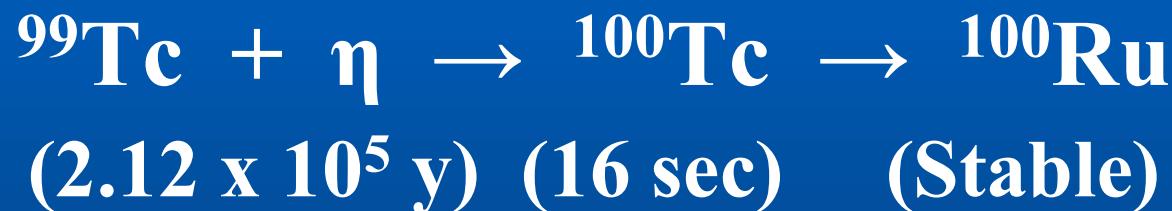
“With the Roy Process, high level nuclear waste can be neutralized and totally eliminated at each reactor site, where the waste is now stored in cooling ponds. When treated with the Roy Process, these unstable radioactive isotopes rapidly decay into stable, non-radioactive elements . . .”

From:

<http://www.lightparty.com/Energy/RoyProcess.html>

Realities of Transmutation as a Waste-Treatment Technology

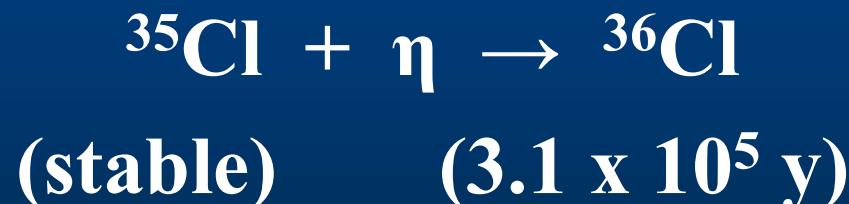
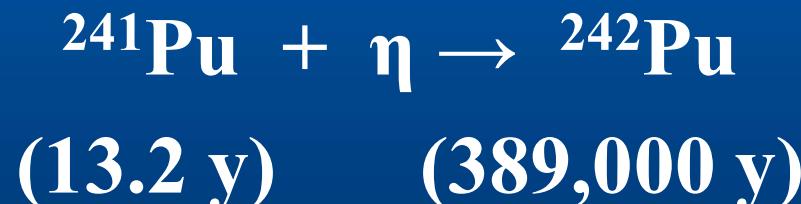
Transmutation of persistent fission products:



These are examples of desirable reactions.

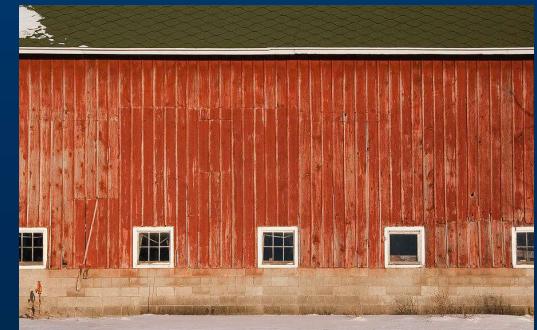
Realities of Transmutation

The process of transmutation can also initiate undesirable side reactions that produce new radionuclides with long half-lives. For example,



Realities of Transmutation

Some fission and activation products do not transmute significantly because their cross sections for capturing thermal neutrons are too small. The term “cross section” is the probability of a nuclear reaction resulting in transmutation. Some of these products include ^{79}Se , ^{126}Sn , ^{36}Cl , and ^{14}C . This also includes ^{90}Sr (1.34 barns) and ^{137}Cs (0.176 barns). One barn = 10^{-28} m^2 .



Realities of Transmutation

Transmutation cannot be applied to solid UNF. Because UNF contains ^{235}U and ^{238}U , the addition of thermal or fast neutrons would produce more plutonium which is not the goal.

Transmutation must be coupled with chemical separation of the radionuclides into different wastes streams.

Barriers to Separation and Transmutation

Separation requirements for transmutation:

U and Pu must be separated (Purex).

Cs and Sr must be separated (under study).

**Methods for separating Am, Cm, Np, and
turning them into targets for transmutation
still at the experimental stage.**

**All extractions need to be optimized to extract
nearly all of each radionuclide.**

Separation and Transmutation

Under study:

Aqueous chemical separation (Purex, UREX, TRUEX, and many others) followed by transmutation in light water reactors or fast breeder reactors.

Pyroprocessing separation followed by transmutation in light water reactors or fast breeder reactors.

Barriers to Separation and Transmutation

Any separation-transmutation approach would increase the volume of LLRW.

What is the best source of neutrons for separation-transmutation? Light-water reactors? Fast reactors breeder? Coupled with accelerators? (Accelerator Transmutation of Waste)? Generation IV reactors?

Pyroprocessing

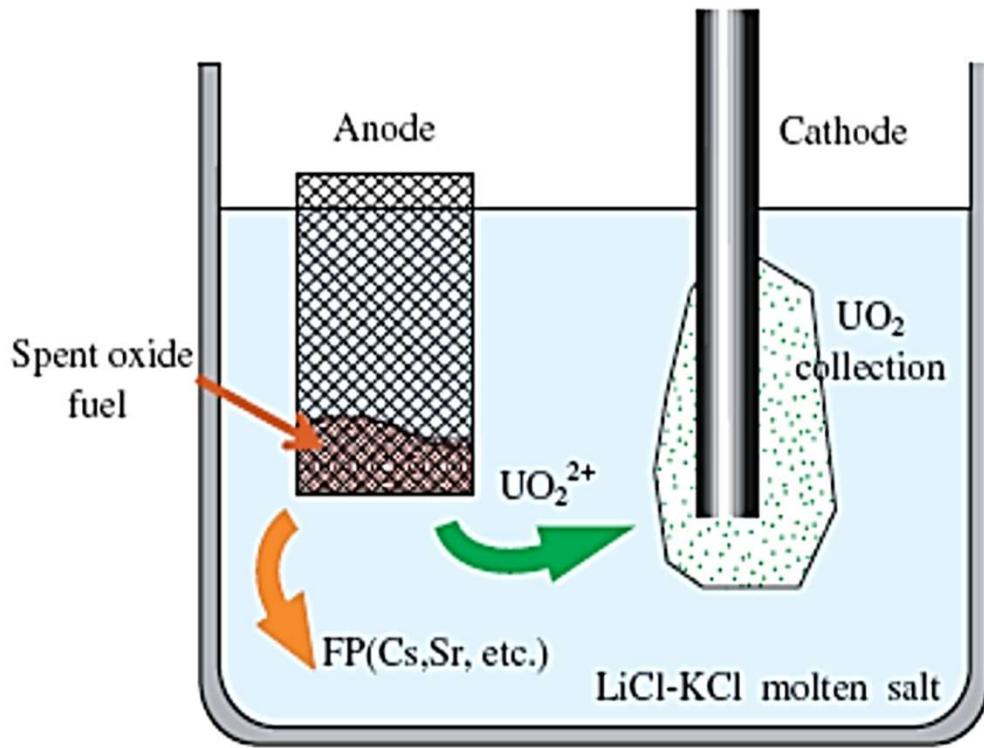


Fig.1 Schematic image of
UO₂-electrolysis process

(Spent oxide fuels are set on an anode and UO₂ is selectively dissolved by electrolysis. Some FP is dissolved in molten salt. High purified UO₂ is collected on a cathode.)

Still have waste issues . . .

The accumulation of these alkali and alkaline earth fission products in the salt will require periodic disposal of the salt into a waste form that can be safely stored for approximately 300 years to allow decay of the ^{137}Cs and ^{90}Sr .

Still have waste issues . . .

The salt can be simply removed from the process once it reaches a contamination limit, blended with zeolite (adsorbent clay), and formed into a ceramic waste.

Questions?

