NUC/IUC Meeting
21-22 MAY 2008

Enhanced Separation for Nuclear Fuels

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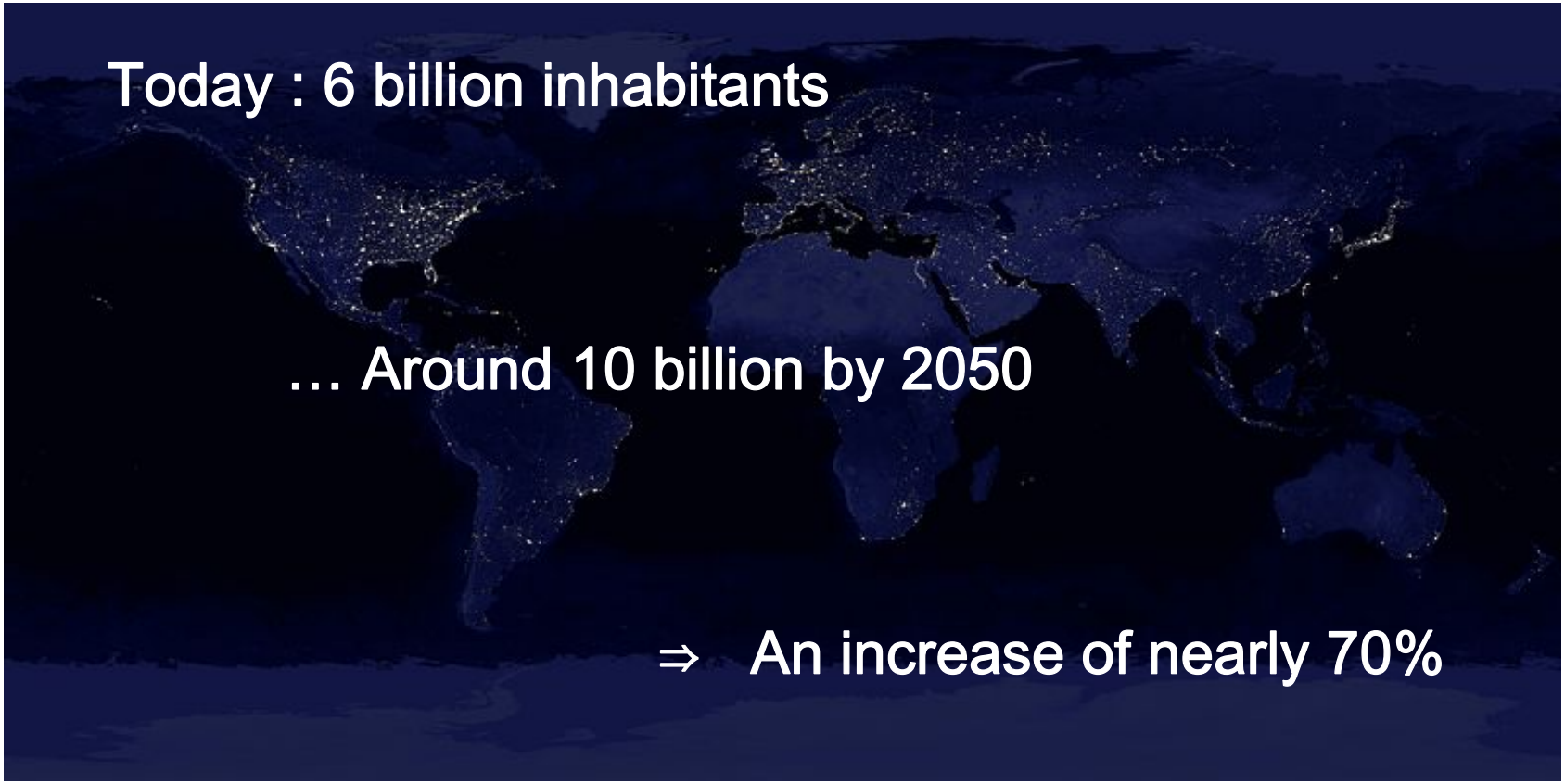
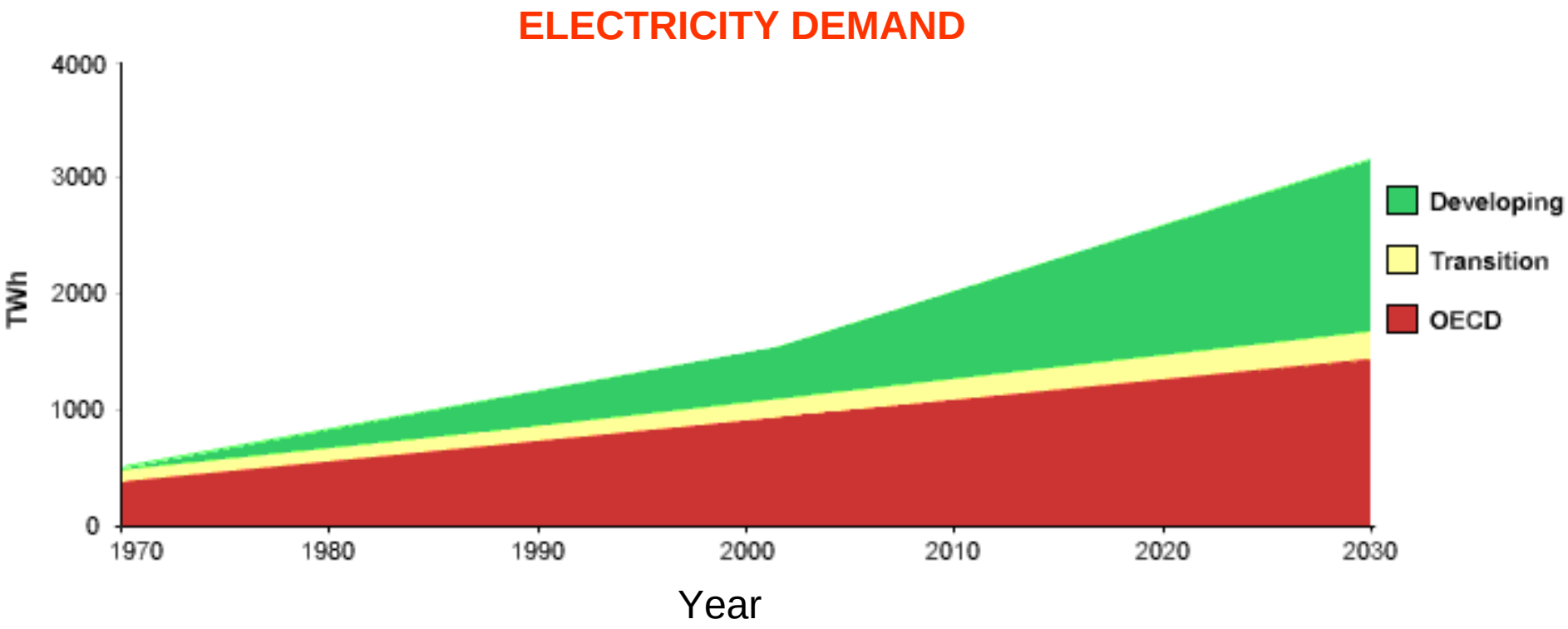
ISU/BSU/INL

Evolution of Population on Earth…



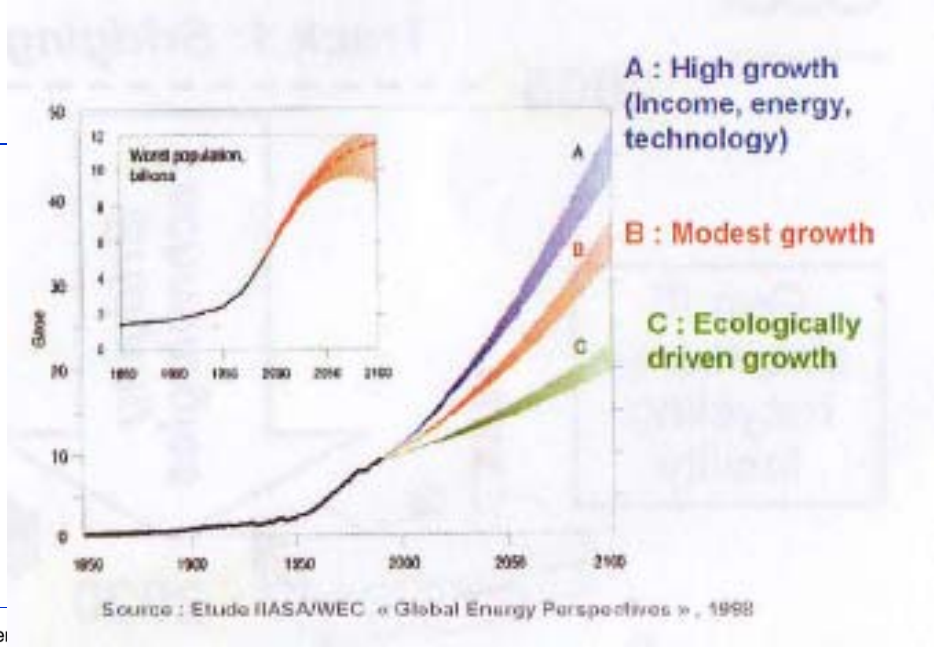
Predicted Global Electricity Demand

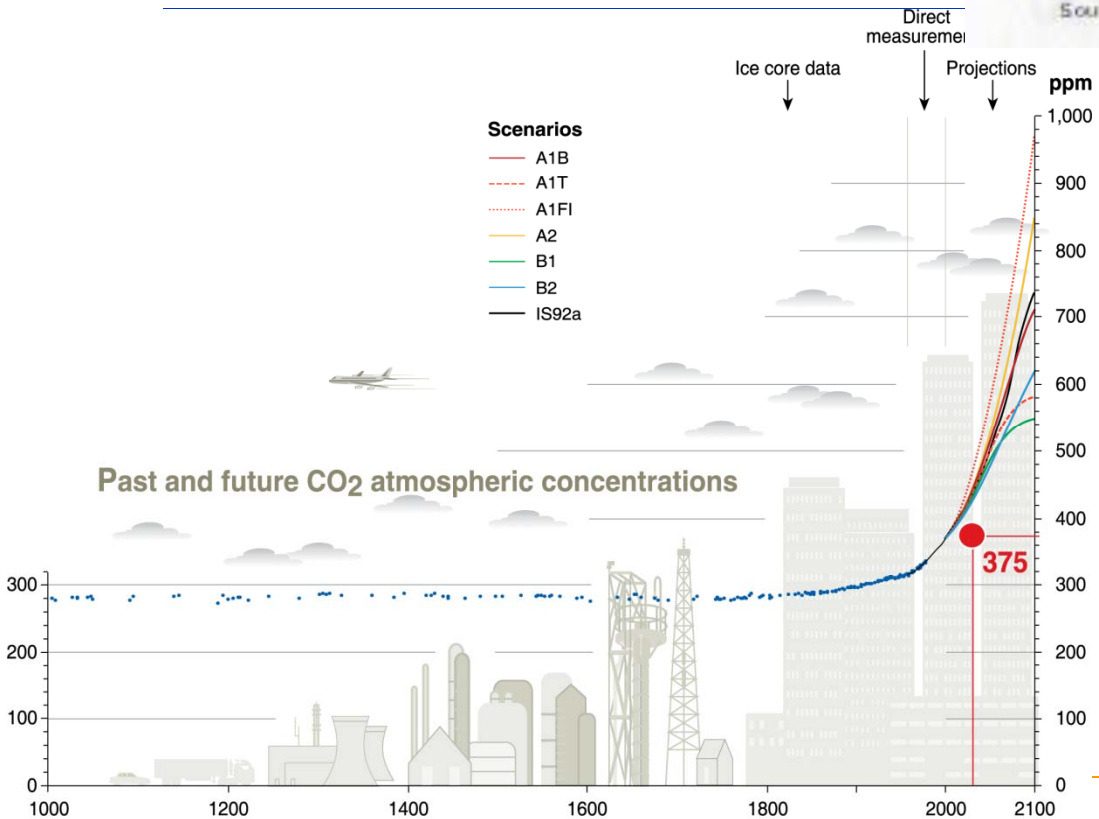


- Growing energy needs

&

- Threat of climate change



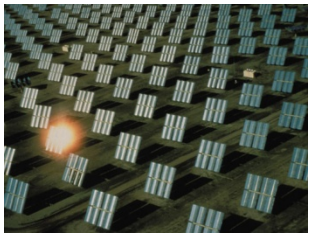


Need for decrease CO_2 release while producing more energy

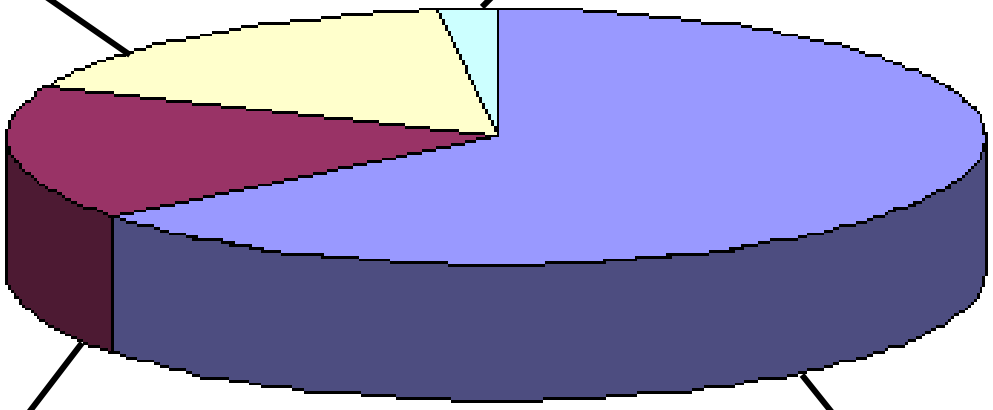
WE need a
CO_2-free energy source such as nuclear energy

World Electricity Sources

Hydroelectric
17%



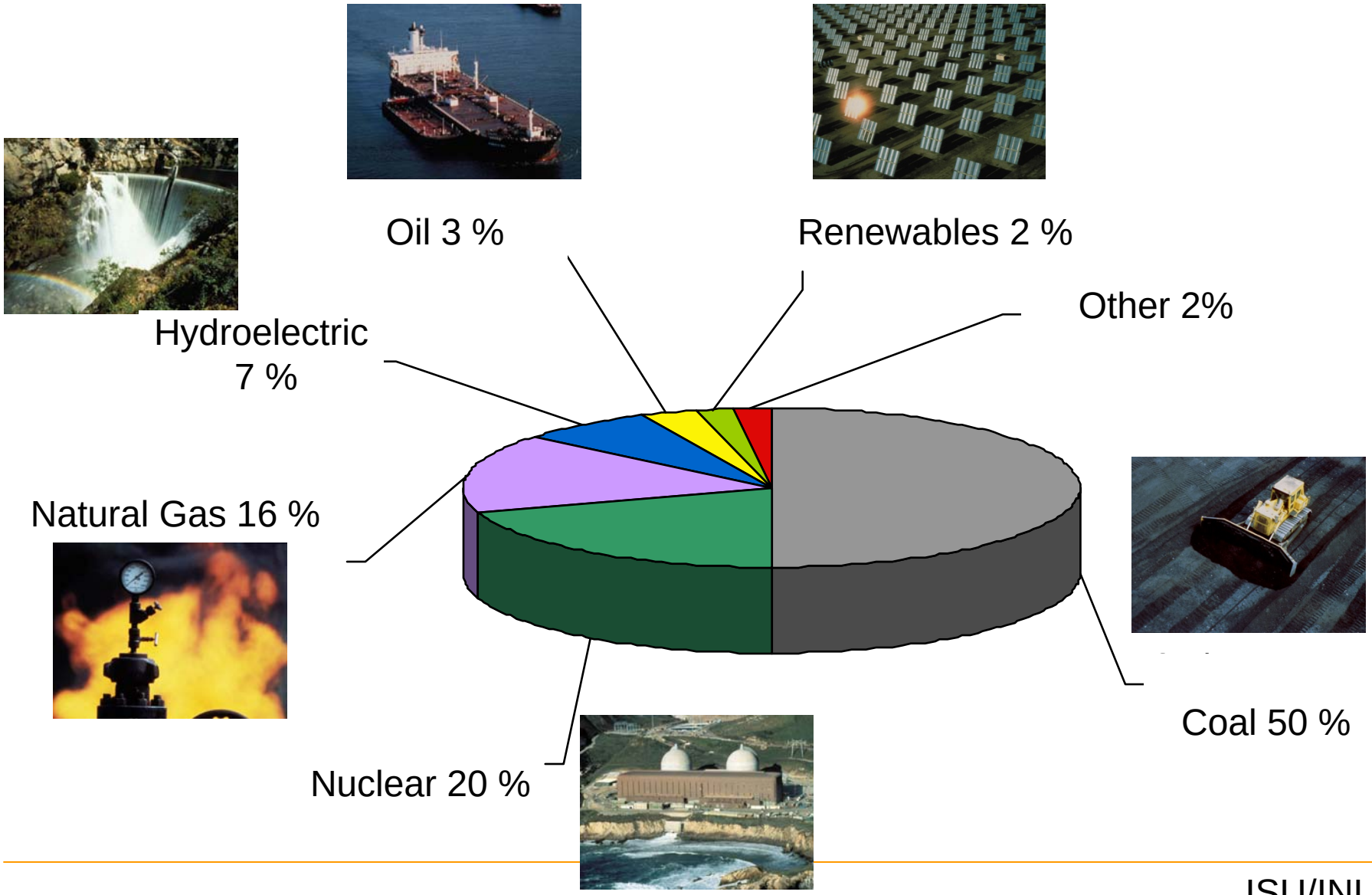
Renewables
2%



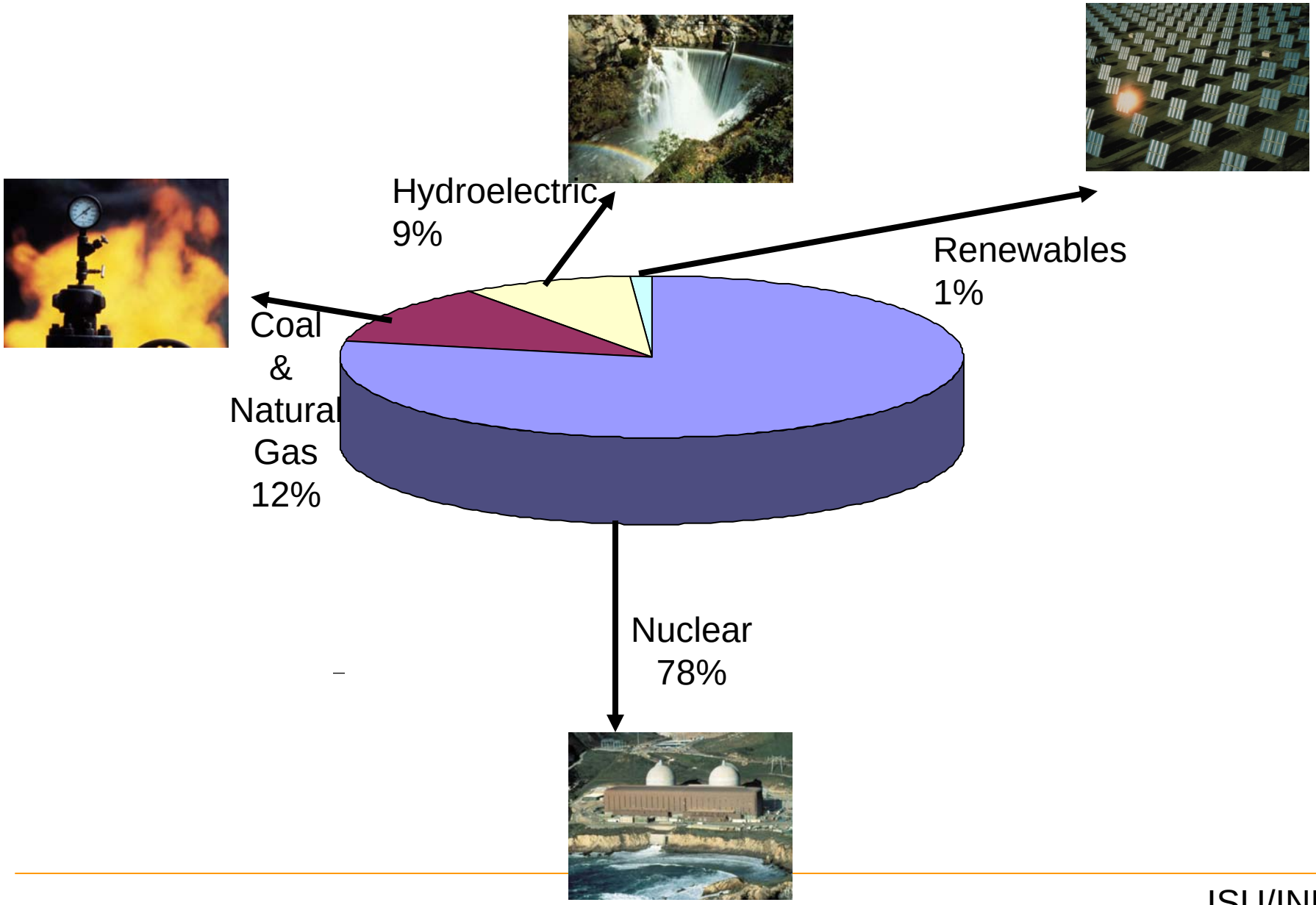
Nuclear
17%

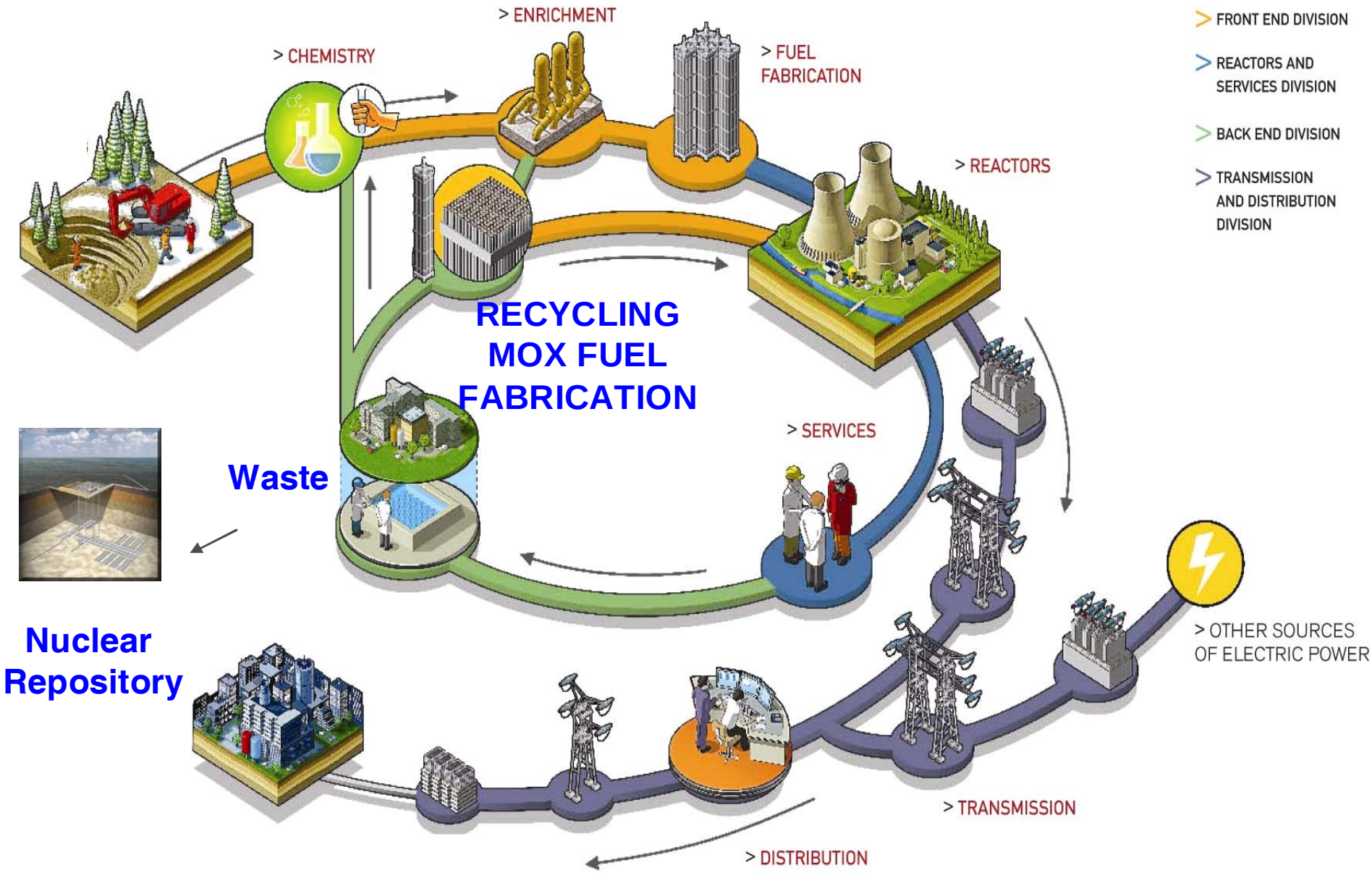
Conventional Thermal
64%

U.S. Electricity Sources



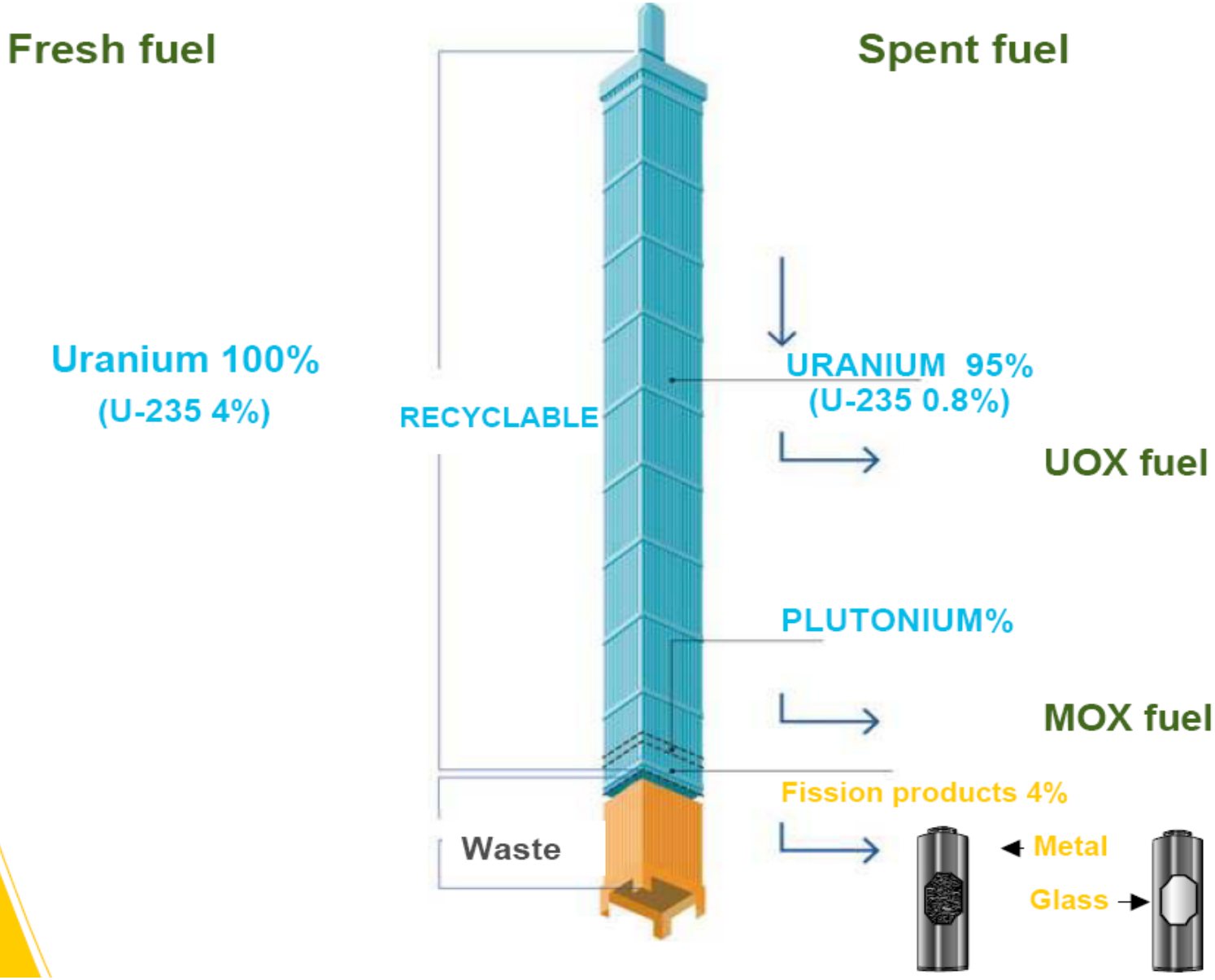
France Electricity Sources

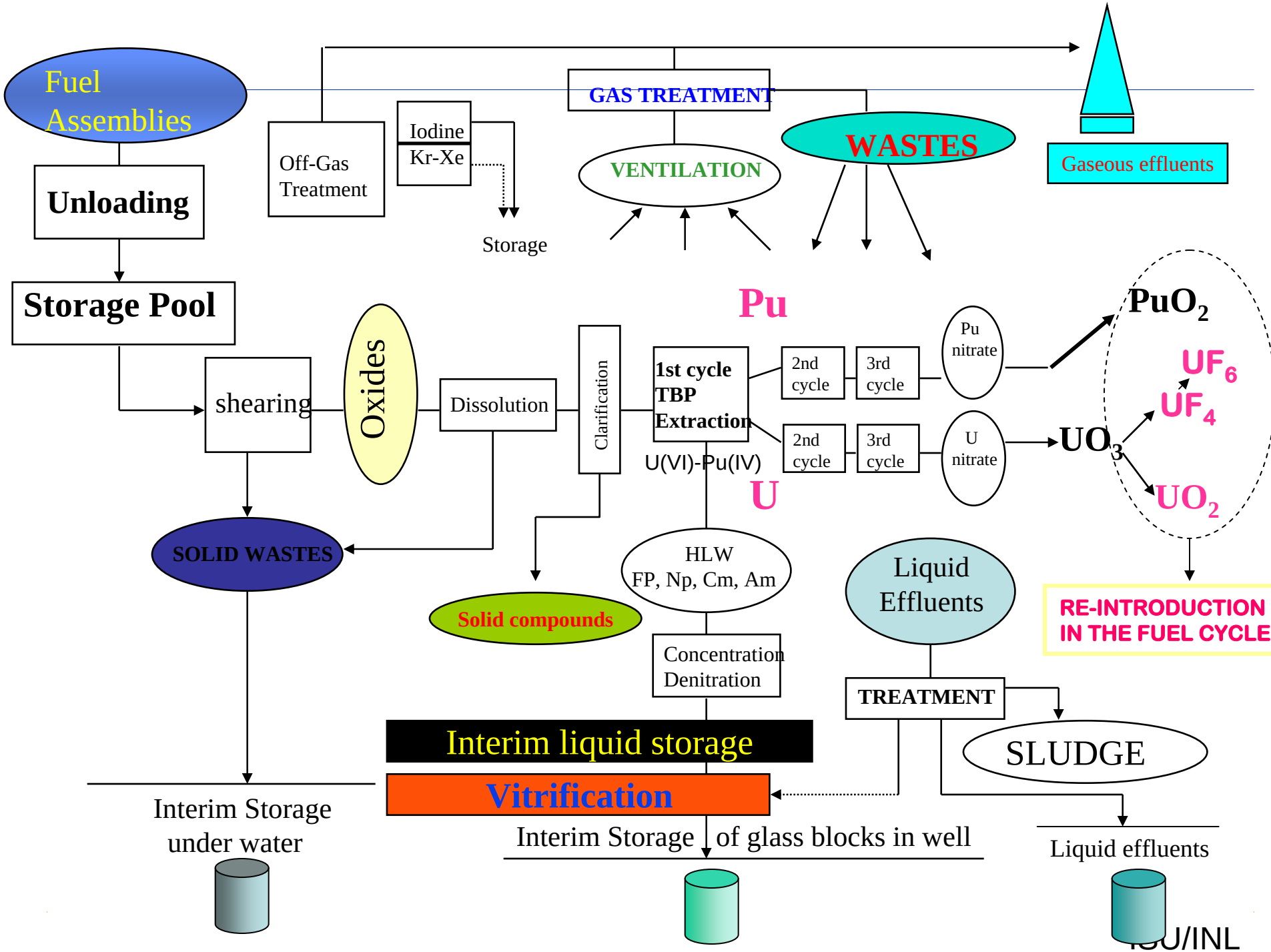



> ENRICHMENT
> CHEMISTRY
> FUEL FABRICATION
> REACTORS
> FRONT END DIVISION
> REACTORS AND SERVICES DIVISION
> BACK END DIVISION
> TRANSMISSION AND DISTRIBUTION DIVISION
RECYCLING
MOX FUEL
FABRICATION
> SERVICES
Waste
Nuclear Repository
> OTHER SOURCES OF ELECTRIC POWER
> TRANSMISSION
> DISTRIBUTION

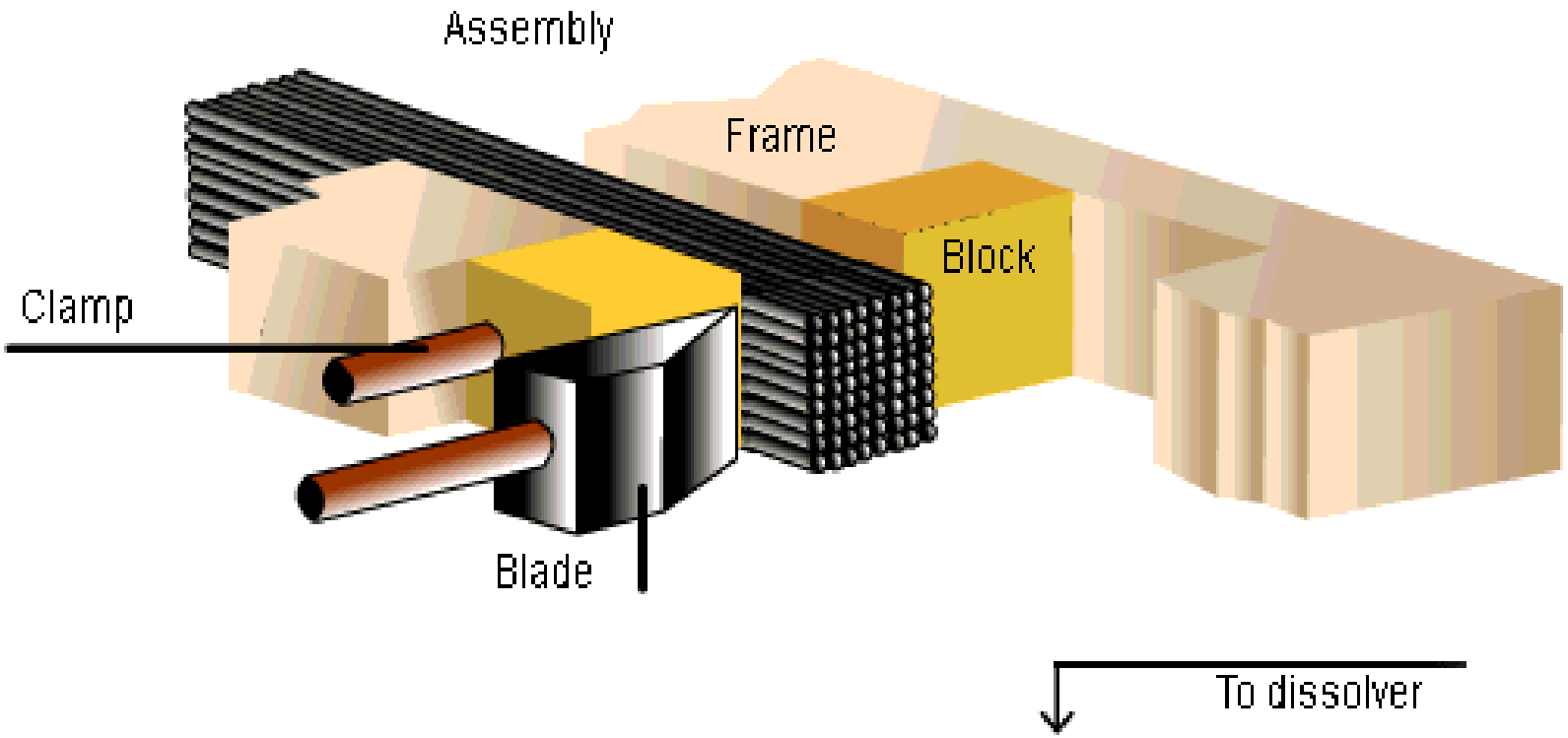
ISU/INL

Spent fuel is 96% recyclable

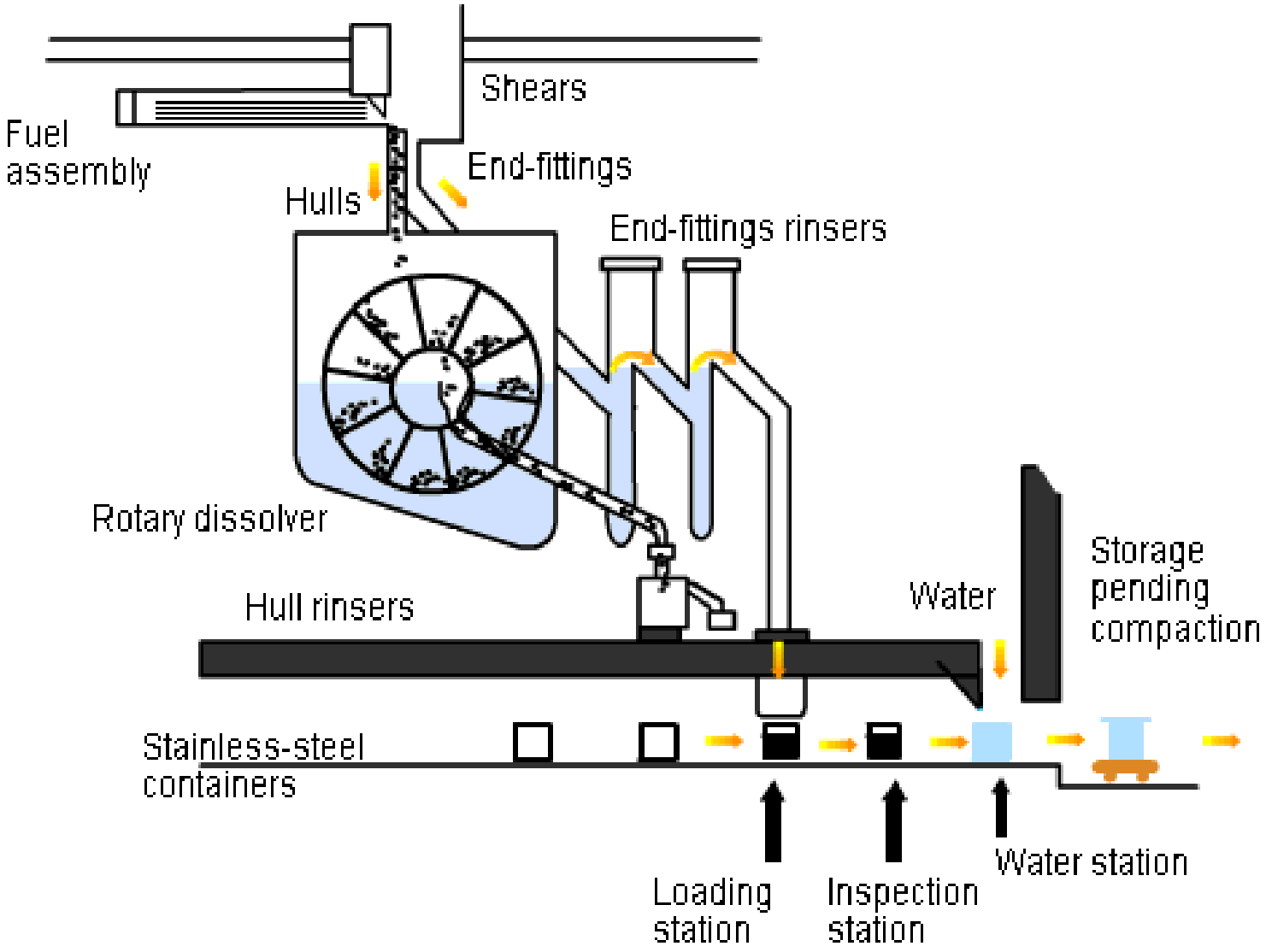



Fuel Assemblies
Unloading
Storage Pool
Off-Gas Treatment
Iodine
Kr-Xe
Storage
GAS TREATMENT
VENTILATION
WASTES
Gaseous effluents
shearing
Oxides
Dissolution
Clarification
1st cycle TBP Extraction
2nd cycle
3rd cycle
Pu nitrate
U nitrate
Pu
U
U(VI)-Pu(IV)
PuO2
UF6
UF4
UO3
UO2
SOLID WASTES
Solid compounds
HLW
FP, Np, Cm, Am
Concentration
Denitration
Liquid Effluents
TREATMENT
SLUDGE
RE-INTRODUCTION IN THE FUEL CYCLE
Interim liquid storage
Vitrification
Interim Storage under water
Interim Storage of glass blocks in well
Liquid effluents

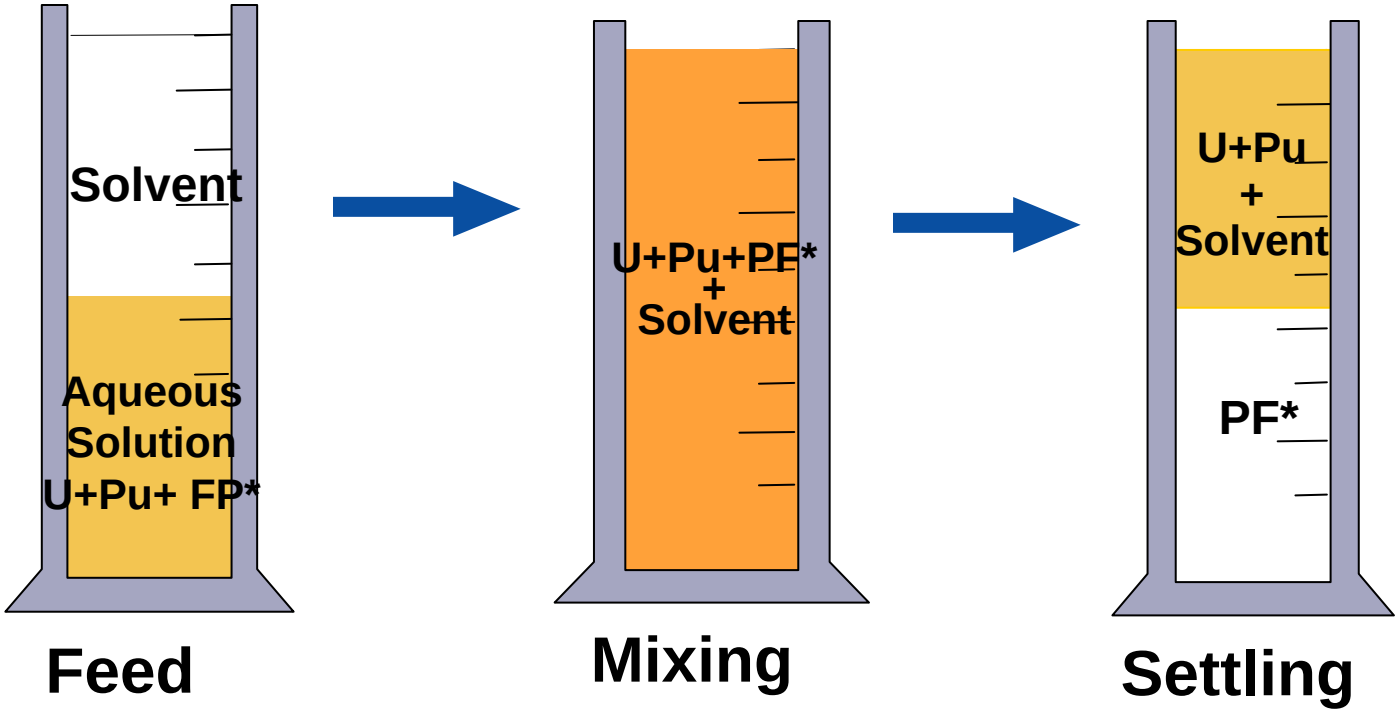
Shearing



Dissolution

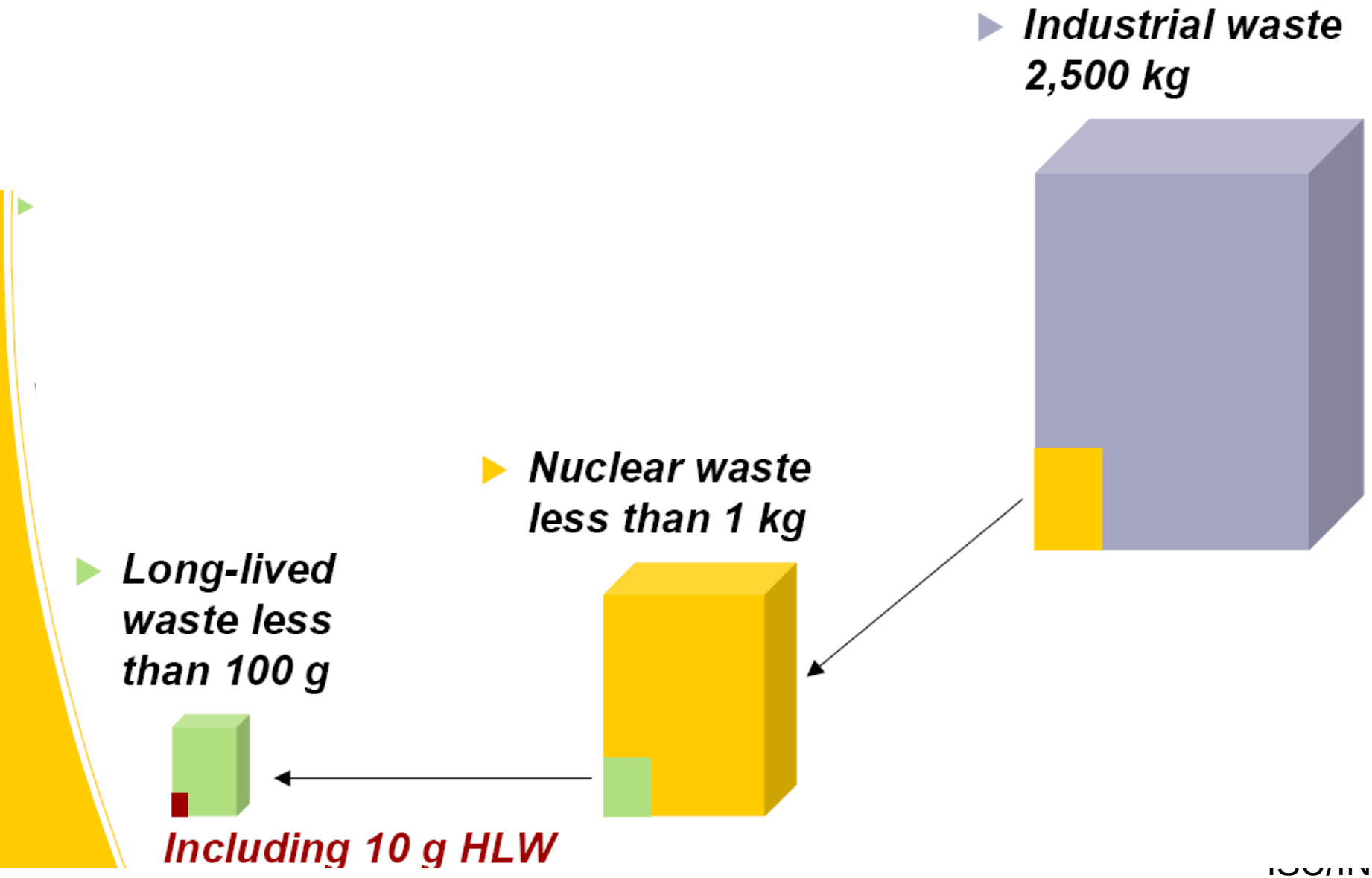


1st extraction cycle

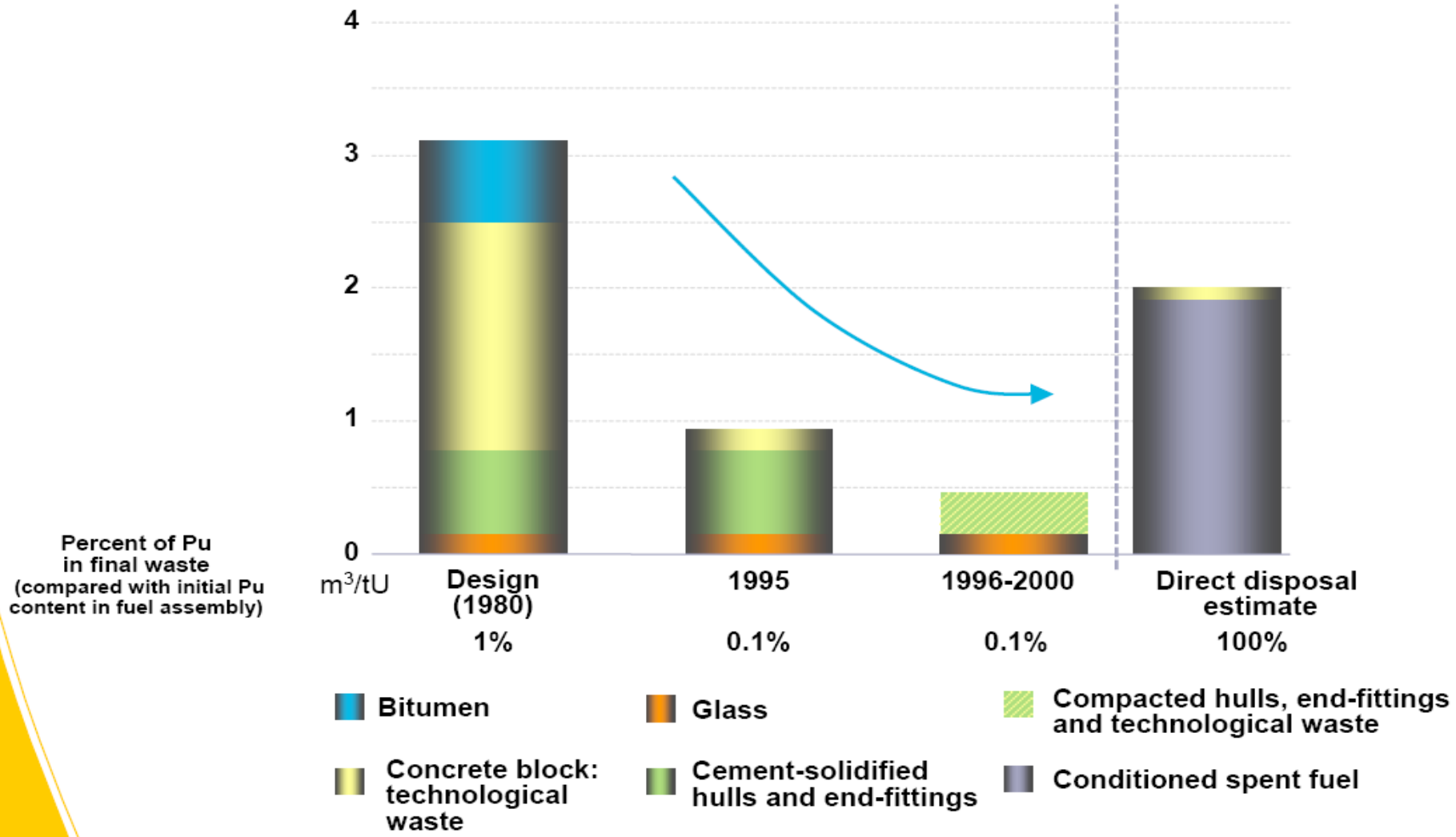


Is waste
the Achilles heel
of nuclear power?

Waste per year per inhabitant in France



Waste volumes conditioned in UP3
(high level long-lived waste after packaging)



Strategies for a flexible management of actinides in Gen IV fast neutron systems

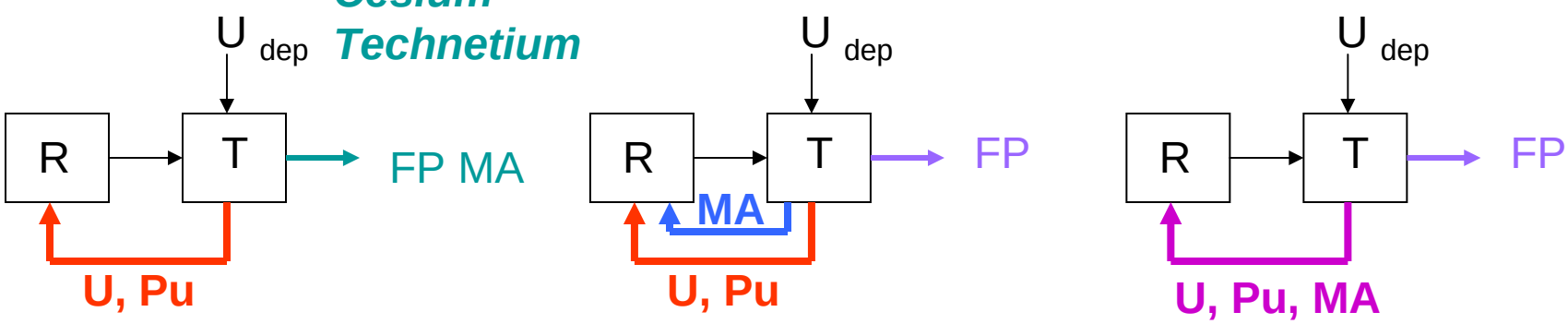
→ Natural resources conservation

→ Waste minimization

→ Proliferation resistance

Minor Actinides:
Americium
Curium

Fission Products:
Strontium
Cesium
Technetium

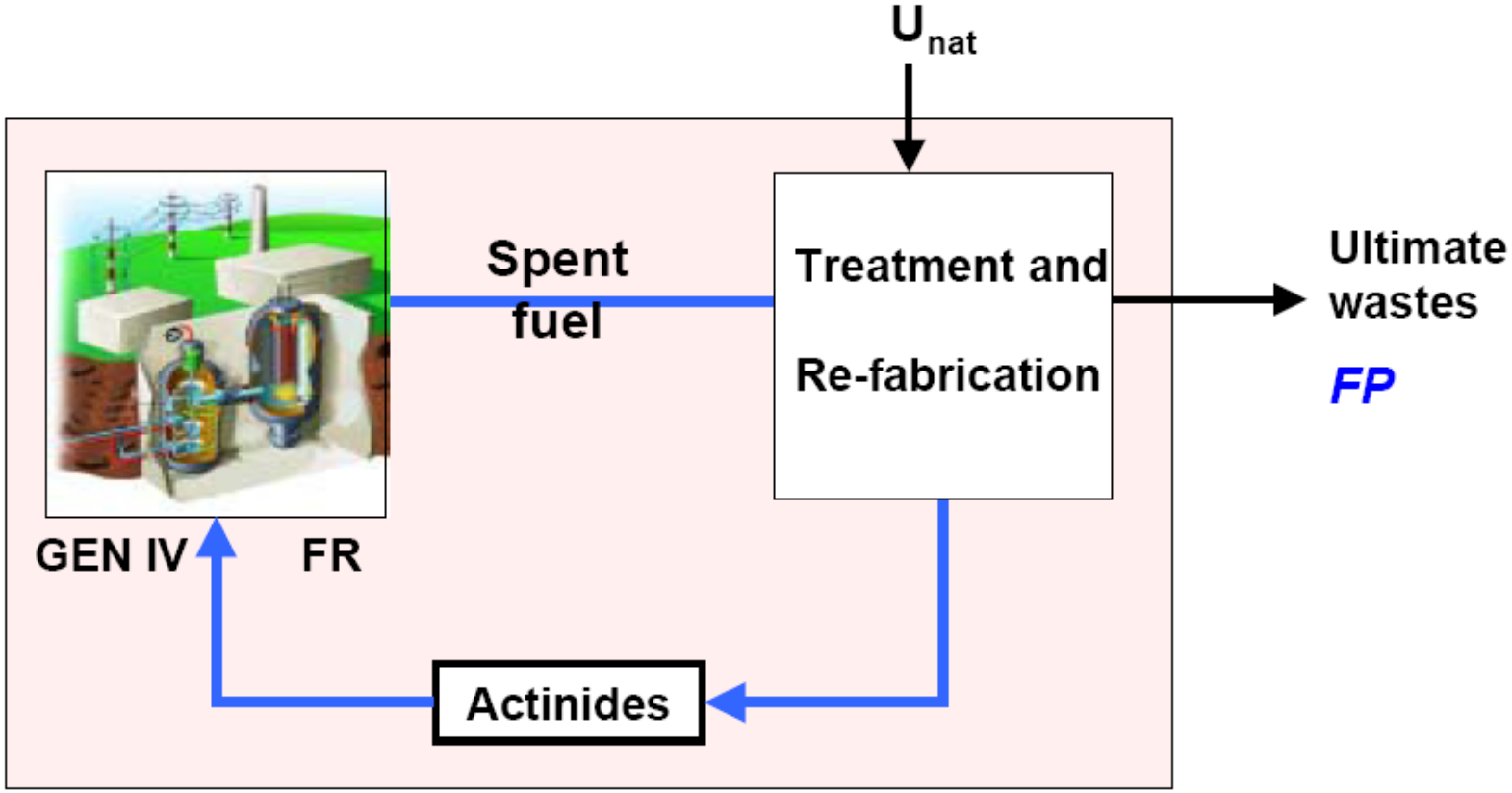


U & Pu Recycling

Heterogeneous Recycling

Homogeneous Recycling

Gen IV systems based on a global actinides recycling



- A drastic minimization of ultimate waste:
  - Very small volumes
  - Heat reduction
- An optimal use of energetic materials
- An increase resistance to proliferation

The Global Nuclear Energy Partnership

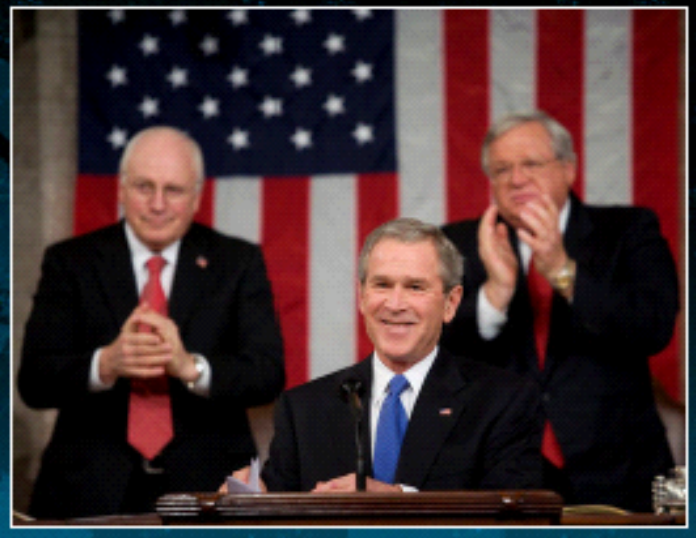
Global Nuclear Energy Partnership

Greater Energy Security in a Safer, Cleaner World

February 6, 2006

The Initiative

- Expand Nuclear Energy
  - Build reactors at home and abroad for energy, to reduce carbon, and achieve development
- Recycle Nuclear Fuel & Reduce Nuclear Waste
- Enhance Nonproliferation Arrangements

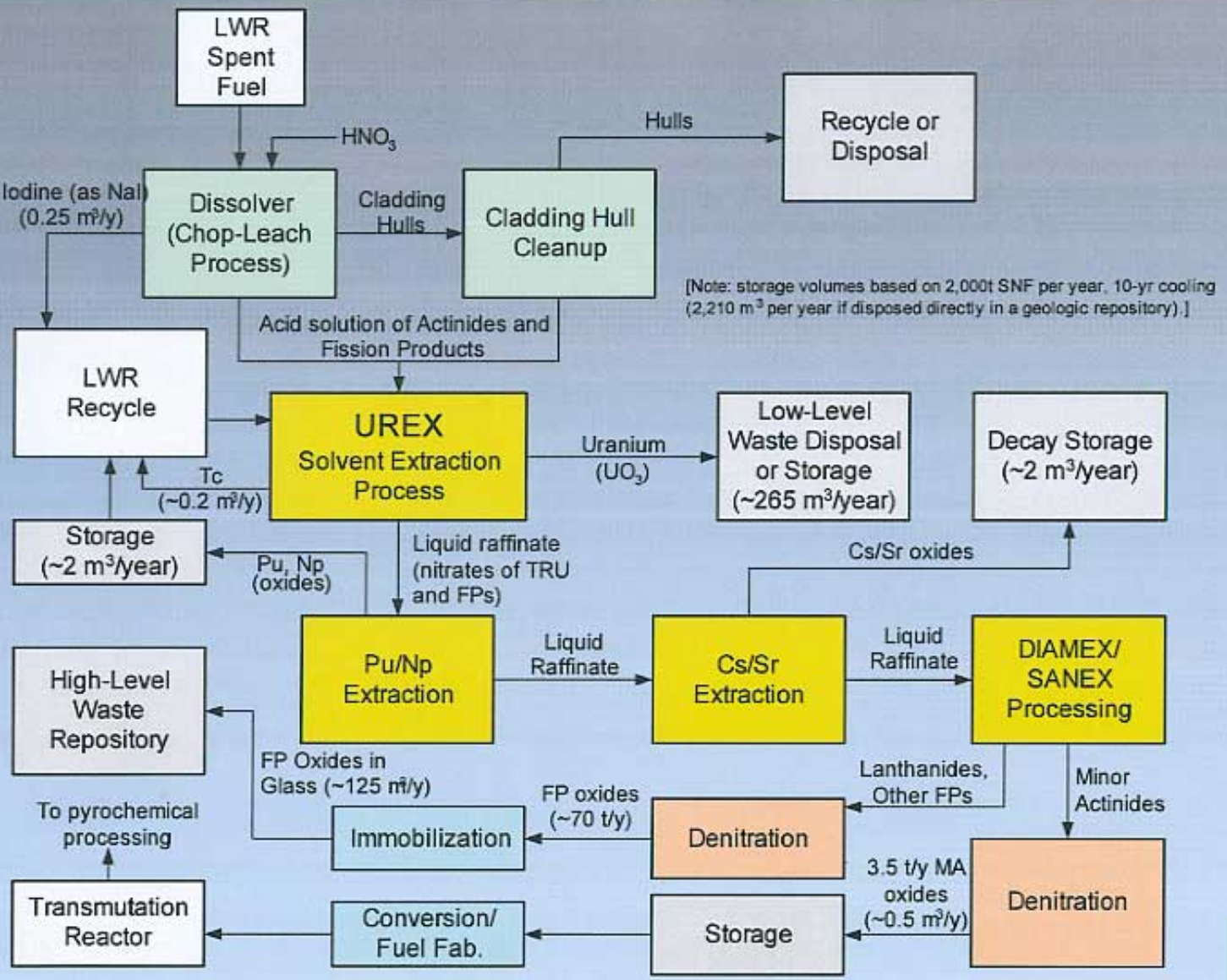


"So tonight I announce the Advanced Energy Initiative… We will invest more in… clean, safe nuclear energy."

President Bush, 01/2006

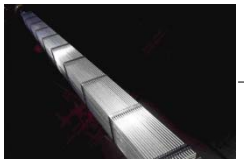
Global Nuclear Energy Partnership

UREX+ Process for LWR Spent Fuel



The Global Nuclear Energy partnership (GNEP)

Spent Nuclear Fuel



Uranium – 94%
Plutonium – 0.9%
Neptunium – 0.1%
Americium – 0.1%
Curium – 0.015%
Fission Products = 4.9%

High Radiation Level
High Radiotoxicity
High Level of Decay Heat

UREX+1a Process

- Pure Uranium → *Storage for future recycle*
- Long-Lived Fission Products → *Technetium and iodine in durable waste form for geologic disposal*
- Cesium and Strontium → *Near surface decay storage*
- Transuranic Elements → *Recycle fuel*
- Residual Fission Products → *Geologic disposal (with fuel cladding and assembly hardware)*

Extraction of Tc-99

Motivation for the Extraction of Tc-99

The research goal remains the adaptation of processes to the evolution in fuels while optimizing the back-end of fuel cycle costs and guaranteeing a very high level of safety.

The back-end of the fuel cycle is guided by three lines of research:

- separation and transmutation of long-lived radionuclides
- studies of the possibilities of reversible or irreversible deep geological storage
- studies of conditioning and long term surface interim storage.

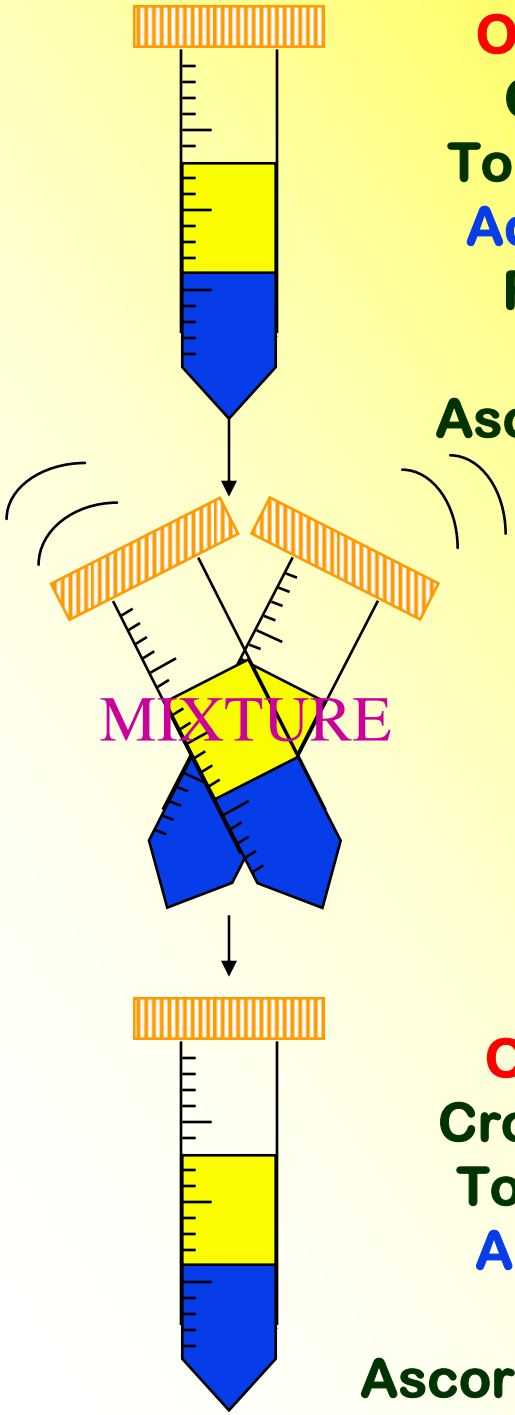
Importance of Determining ^{99}Tc in Radioactive Liquid Wastes

Long Half Life Time
$t_{1/2} = 2.1.10^5$ years

Pure Beta-Emitter

Chemical separation prior to any measurement in complex media

Liquid-liquid Extraction of ^{99}Tc with Crown-Ether

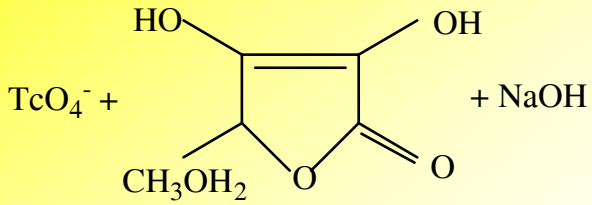


Organic Phase
Crown Ether
Toluene/Acetone
Aqueous Phase
Real Effluent
^{99}Tc
Ascorbic acid, 4M NaOH

Organic Phase
Crown Ether - ^{99}Tc
Toluene/Acetone
Aqueous Phase
Real Effluent
Ascorbic acid, 4M NaOH

Principal Reactions

Aqueous Phase



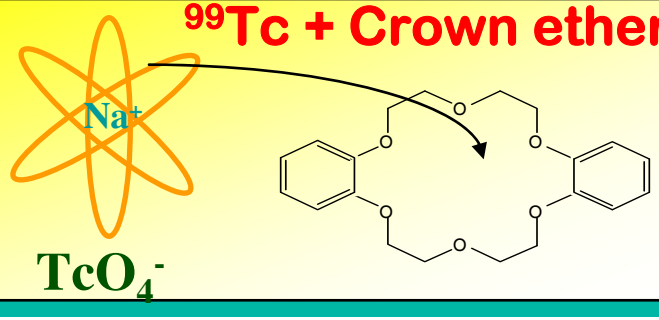
Mixture

$$TcO_4^- + xCE + \overline{y\ Na^+} \longrightarrow \overline{TcO_4^-\ .\ xCE\ .\ yNa^+}$$

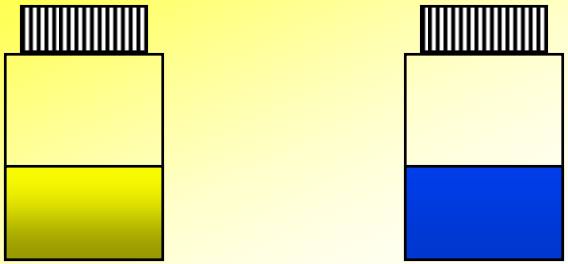
Organic Phase

$$\overline{TcO_4^-\ .\ xCE\ .\ yNa^+}$$

^{99}Tc + Crown ether



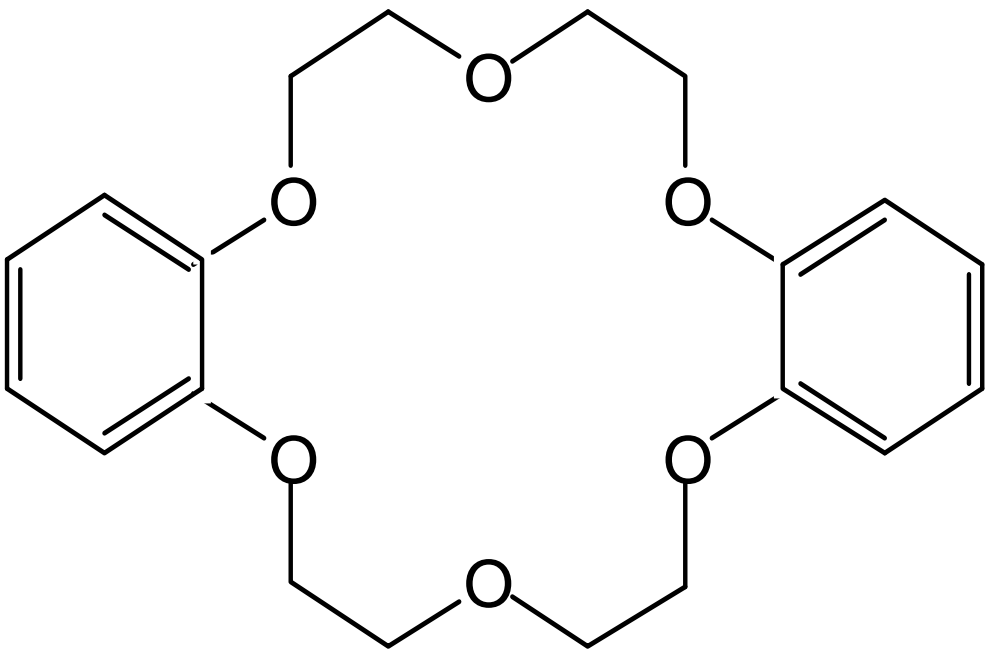
Liquid Scintillation



Modifying Factors of the Crown Ether for the Complex Stability

- Cation Size
- Donor Atoms
- Oxygen Atom Numbers
- Flexibility
- Solubility

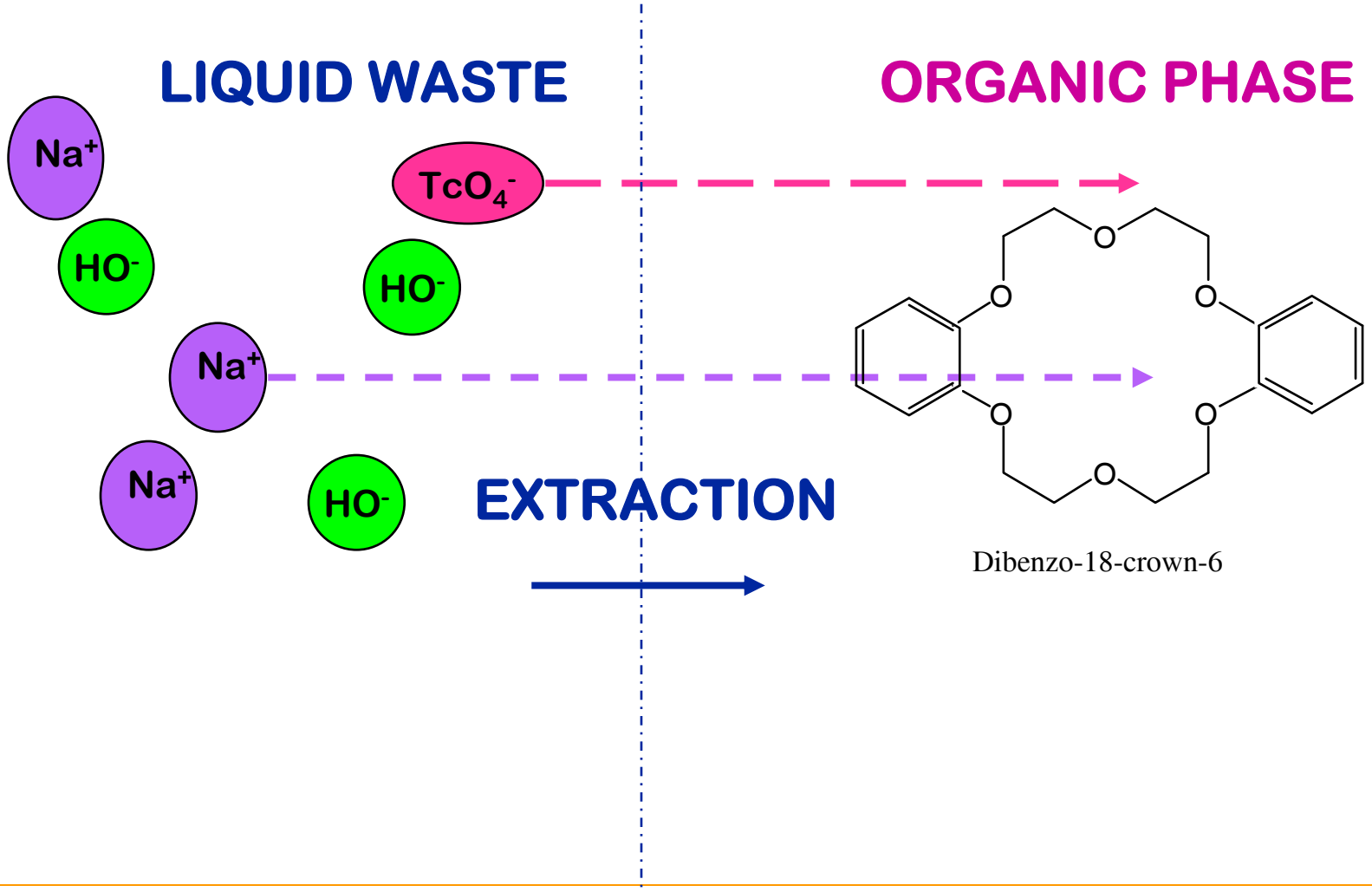
Dibenzo-18-Crown-6 (DB18C6)



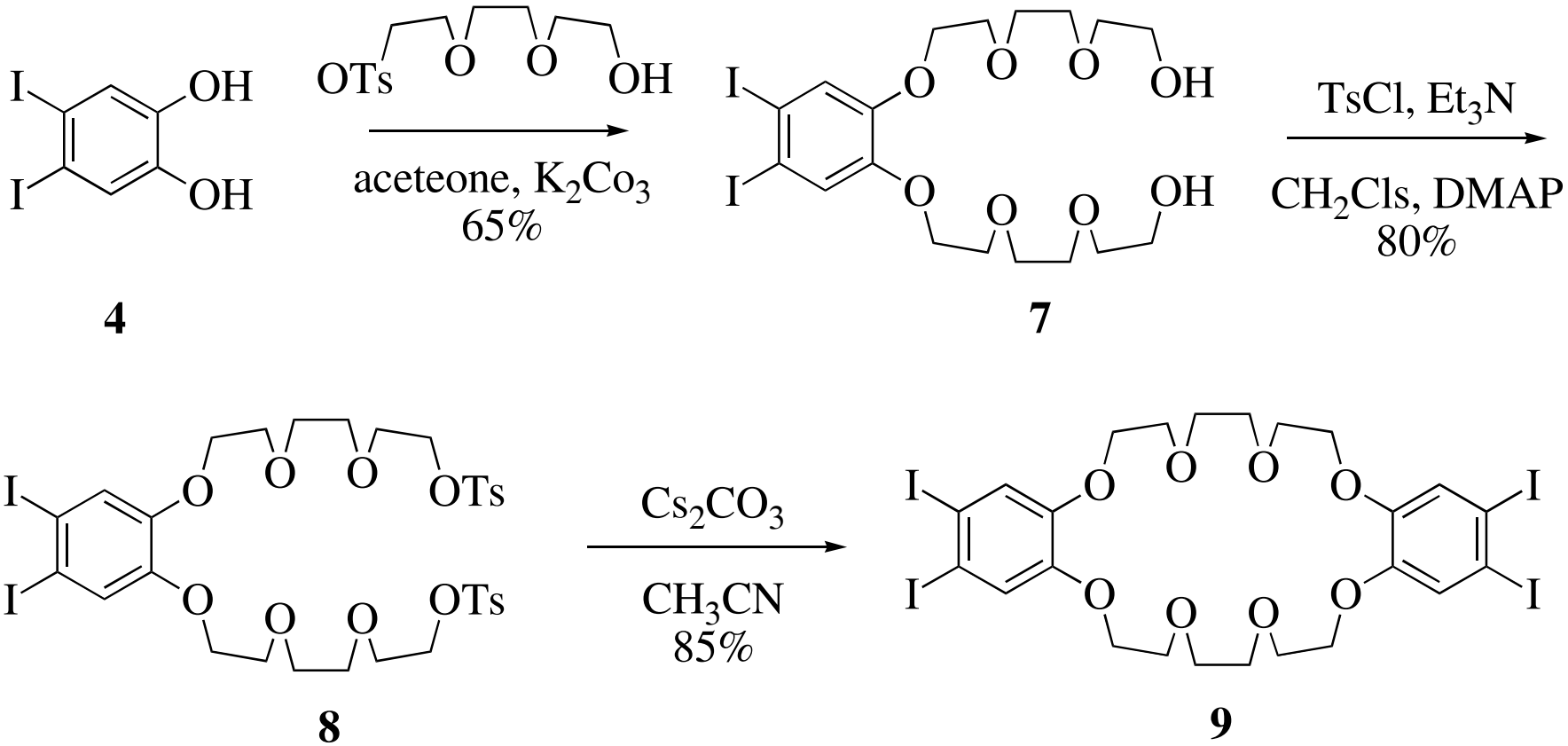
Size of crown ethers

12C4	15C5	18C6	21C7	24C8
1.2-2.5 Å	1.7-2.2 Å	2.6-3.2 Å	3.4-4.3 Å	4.5-5.6 Å

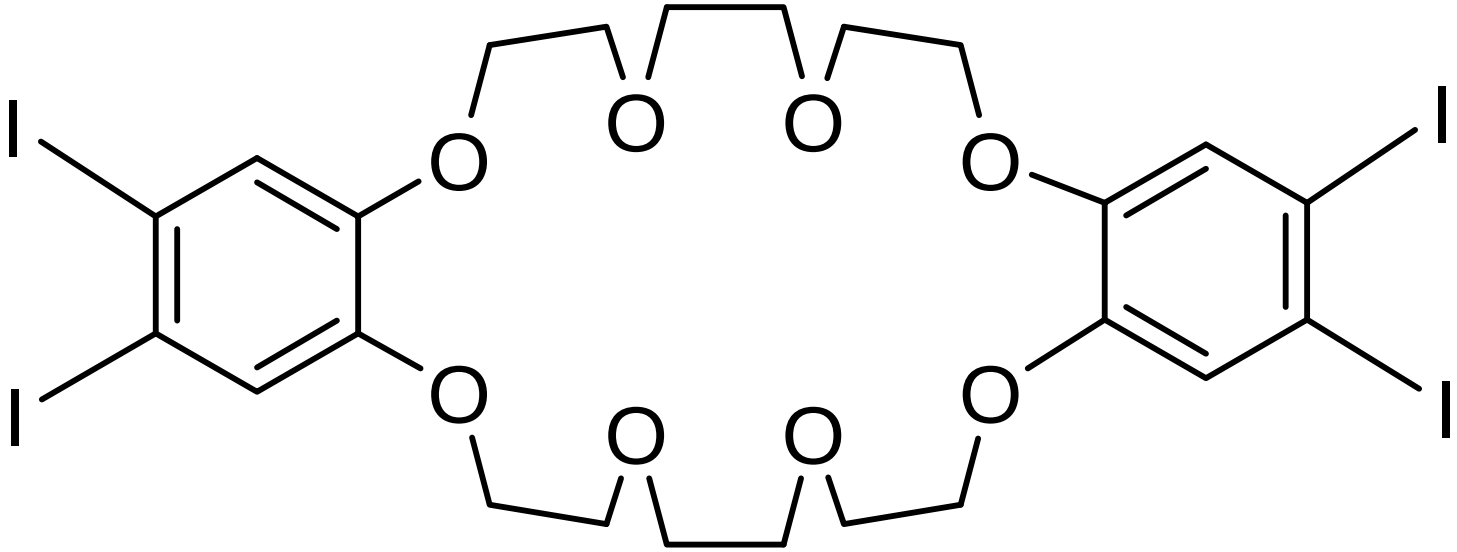
Extraction Mechanism



4,4',5,5'-Tetraiododibenzo-24-crown-8 ether



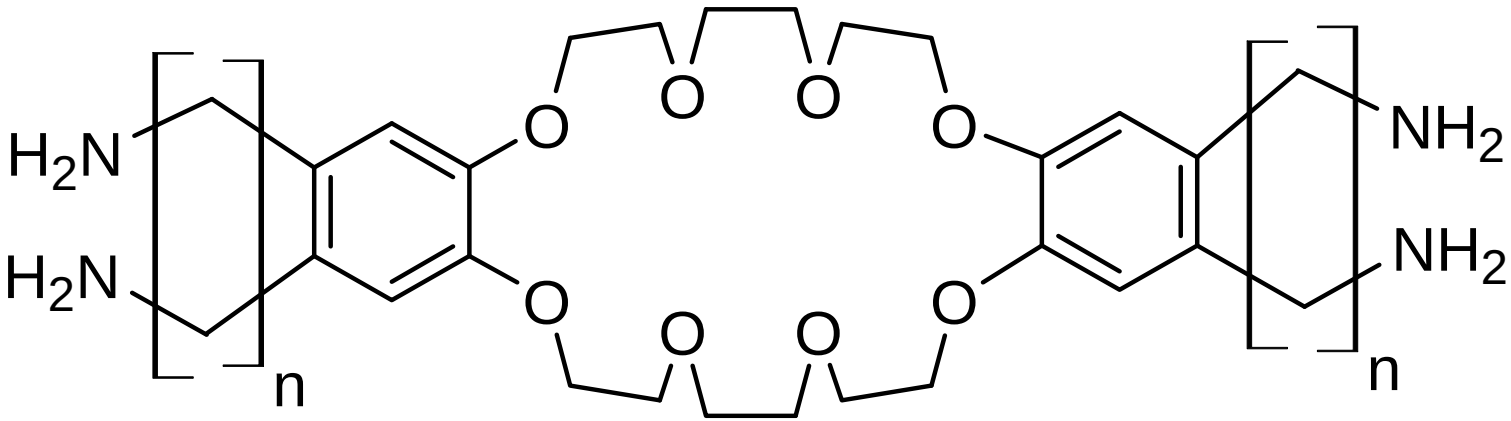
4,4’,5,5’-Tetraiododibenzo-24-Crown-8 Ether

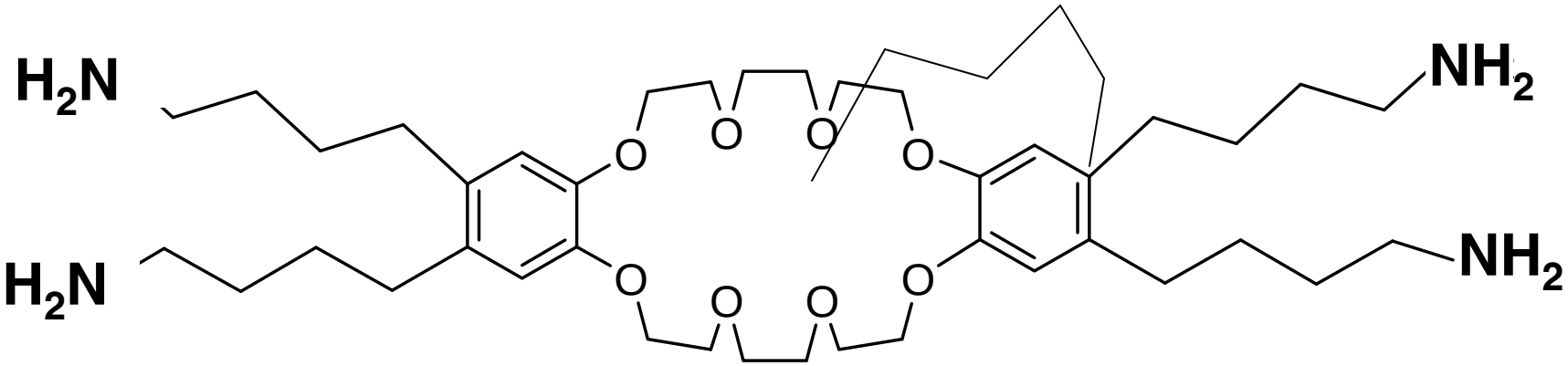


ReO_4^- Extraction with Iodo Crown Ether

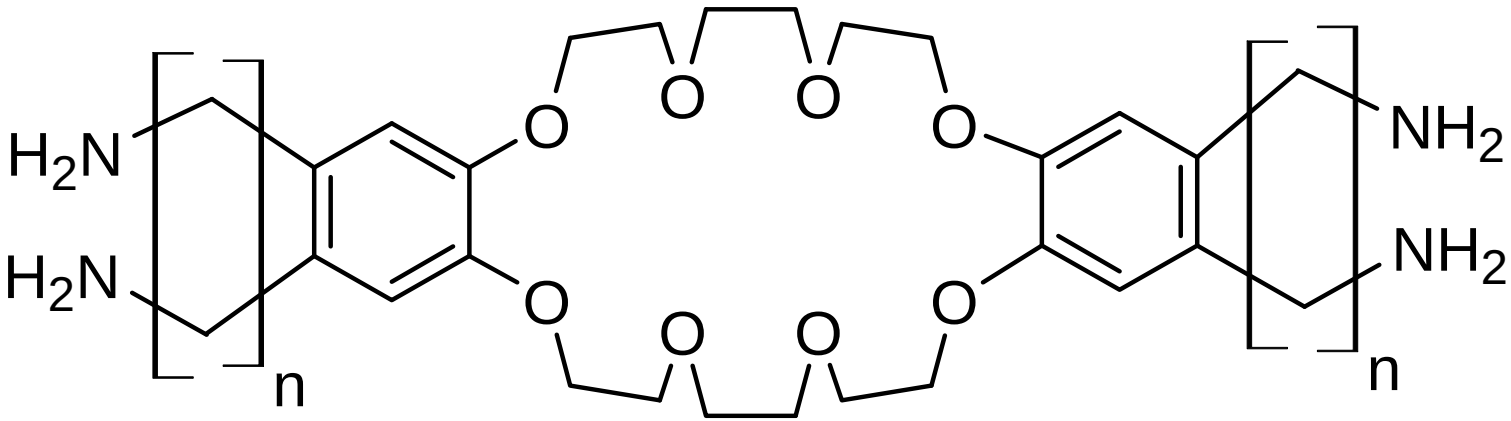
Diluent	Aqueous Phase	% Extraction
Cyclohexanone	0.1M HNO_3	92%
Nitrobenzene	0.1M HNO_3	5.6%
Nitrobenzene /Acetone 1:1	0.1M HNO_3	50%
Nitrobenzene /methyl isobutyl ketone 1:1	0.1M HNO_3	21%
Benzene/Acetone 4:1	4M NaOH	42.2%
Toluene	4M KOH	28.5%
Toluene	4M NaOH	26.6%

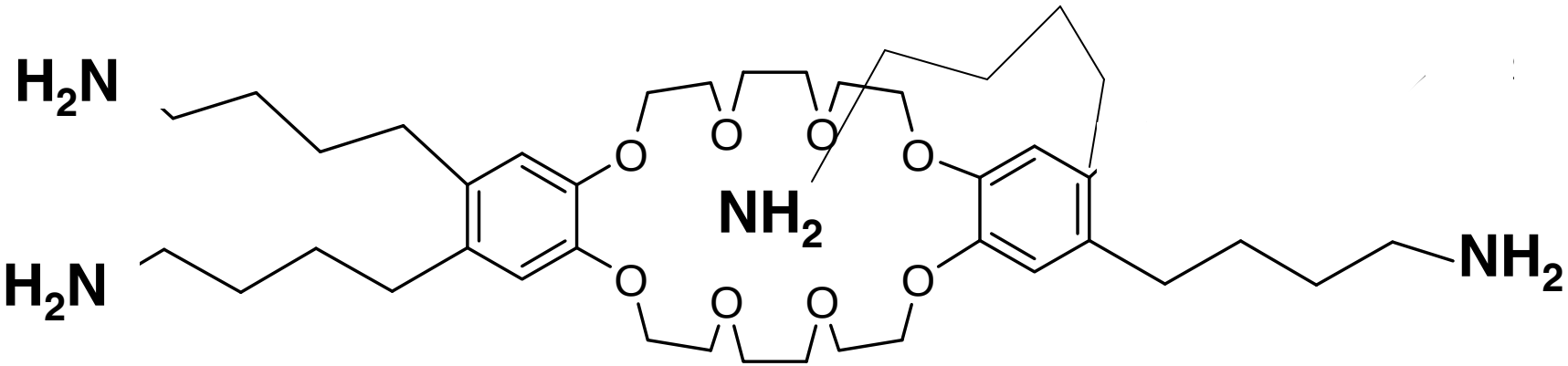
Tetra-Ammonium-Dibenzo-24-Crown-8 Ether



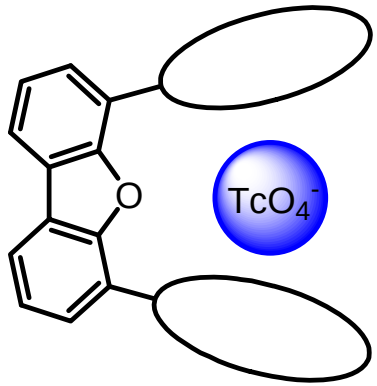


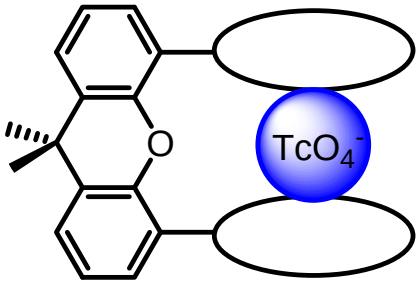
Tetra-Ammonium-Dibenzo-24-Crown-8 Ether

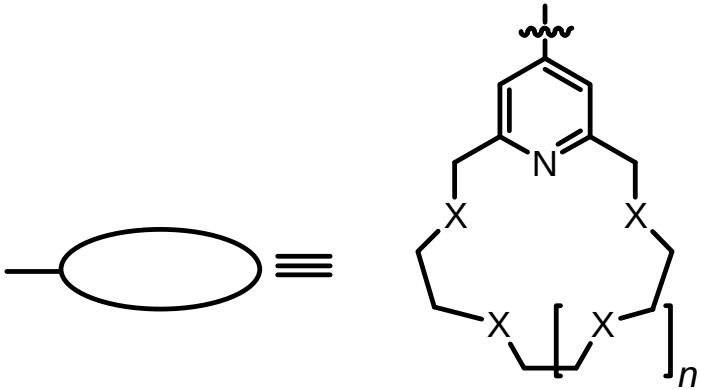




New Macrocompounds Design





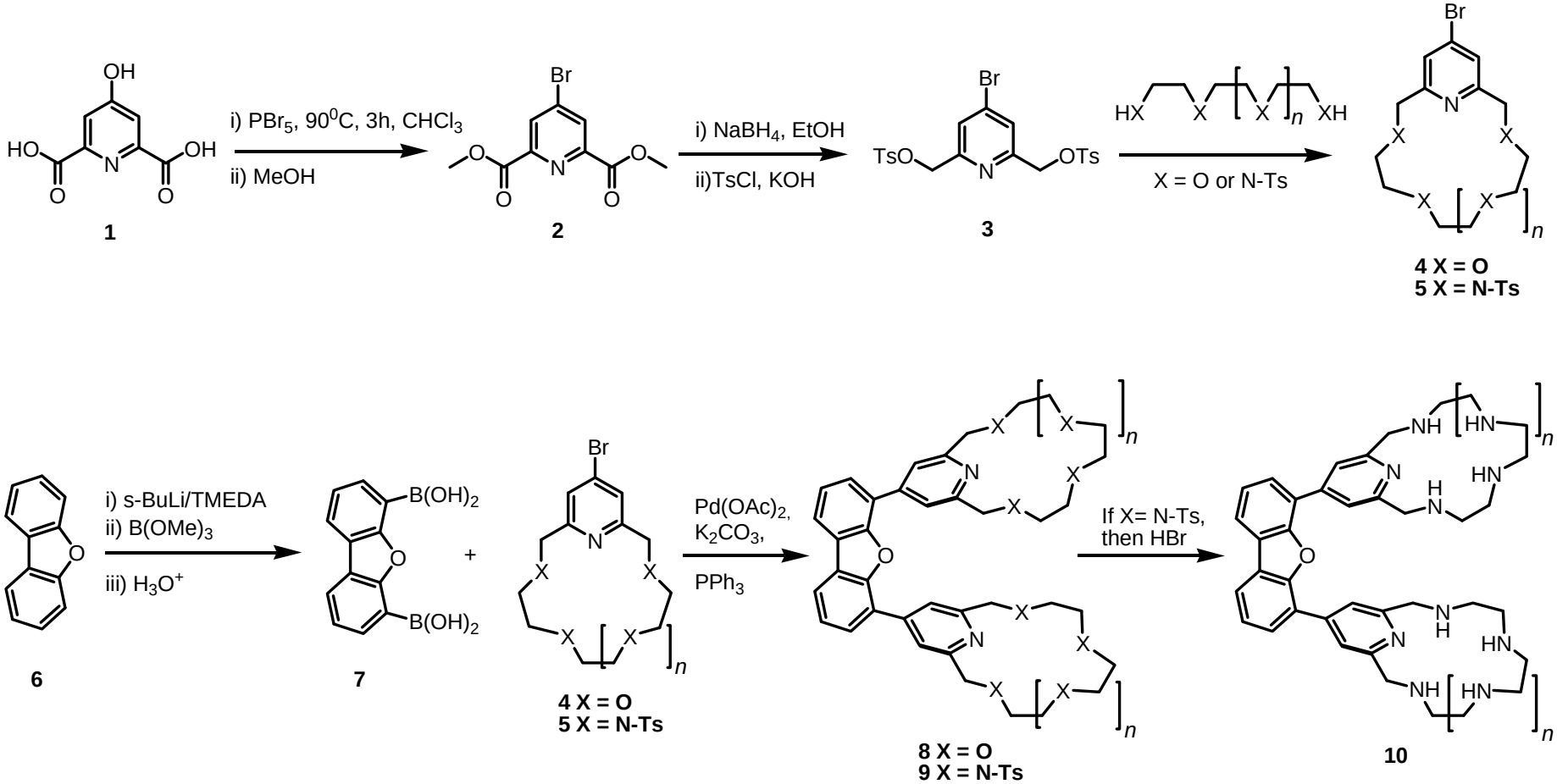


X = O or NH

Anion Encapsulation Receptors for TcO_4^- Extraction:

- Dibenzofuran and xanthene will be used as scaffolds to construct anion encapsulated receptors that contain different cavity size dimensions.
- The cavity between created by the two cofacial rings is intended to encapsulate and desolvate TcO_4^-.
- Rings containing hydrogen bonding groups (when X = NH compared to X = O) are expected to result in an increased affinity for TcO_4^- .

Anion Encapsulation Ligand



Separation Trivalent Actinides from Trivalent Lanthanides

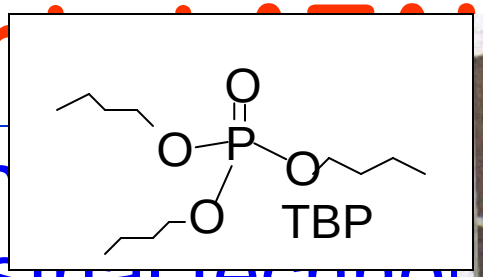
Motivation

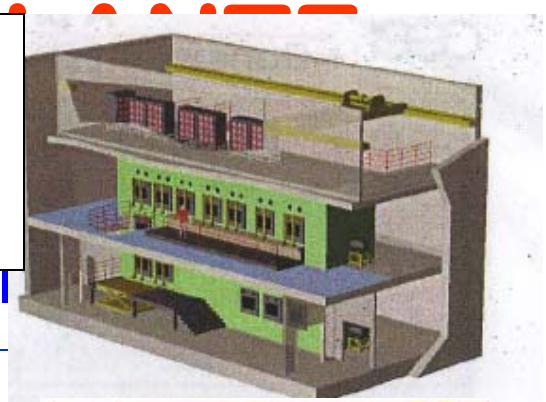
- The separation of trivalent actinides from fission product lanthanide ions represents one of the most challenging aspect of advanced nuclear fuel partitioning schemes.
- A considerable amount of effort has been dedicated to the development of effective methods for accomplishing this separation, essential for transmutation of the actinides heavier than Pu.
- Among the methods currently considered to be ready for technological deployment is the TALSPEAK (Trivalent Actinide - Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes) Process, developed in the late 1960s at Oak Ridge National Laboratory, as well as the Ganex (Grouped Actinides Extraction) Process developed in France.

Advanced Separation Achievemen

Used Fuel

D stration test in
fuel with industrial technol

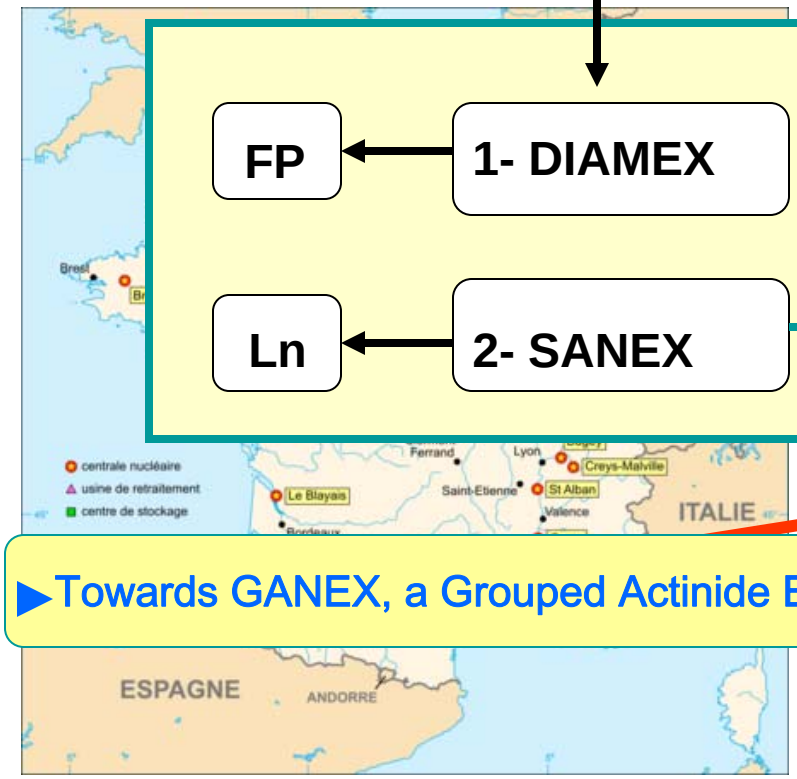




U, Pu

PUREX

Np



FP

1- DIAMEX

Ln

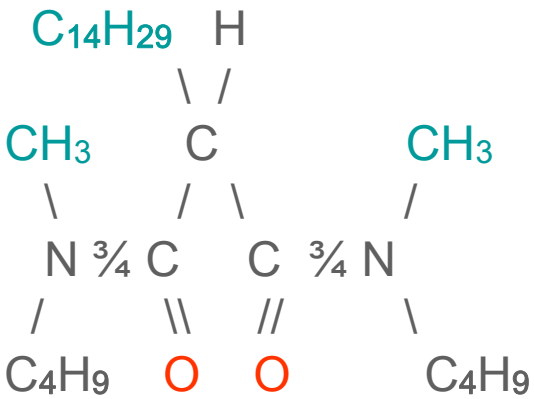
2- SANEX

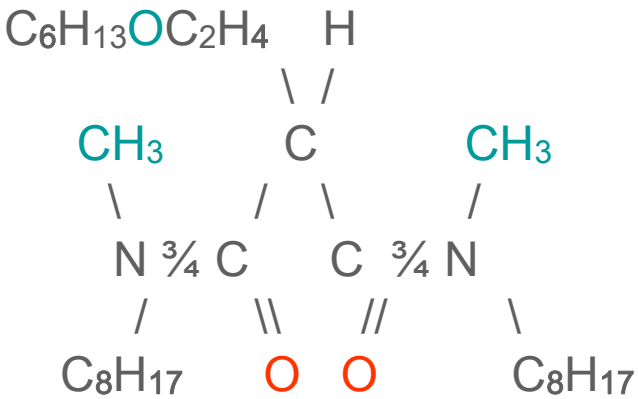
Am, Cm

▶Towards GANEX, a Grouped Actinide Extraction Process

DIAMEX PROCESS: Malonamide

DIAmide Extraction
co-extration of Am, Cm, Ln from PUREX raffinate solution





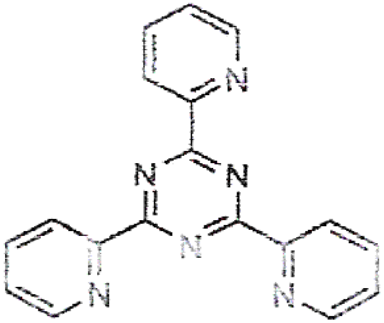
(DMDBTDMA) (27C)
N,N'-dimethyldibutyltetradecyl malonamide

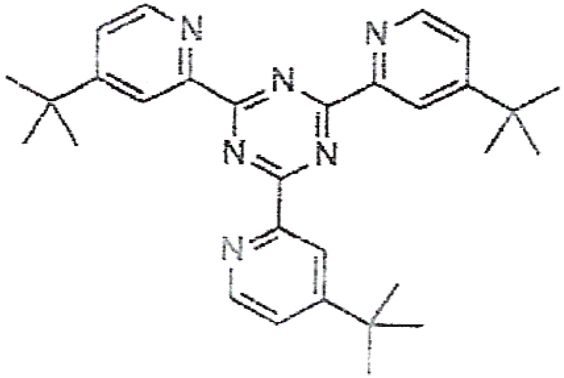
(DMDOHEMA) (29 C)
N,N'-dimethyldioctyltetradecyl hexyloxyethyl malonamide

SANEX

Selective ActiNides(III) Extraction extraction of Am, and Cm over Ln directly from DIAMEX product solution.

Nitrogen donors: TPTZ and substituted TPTZ

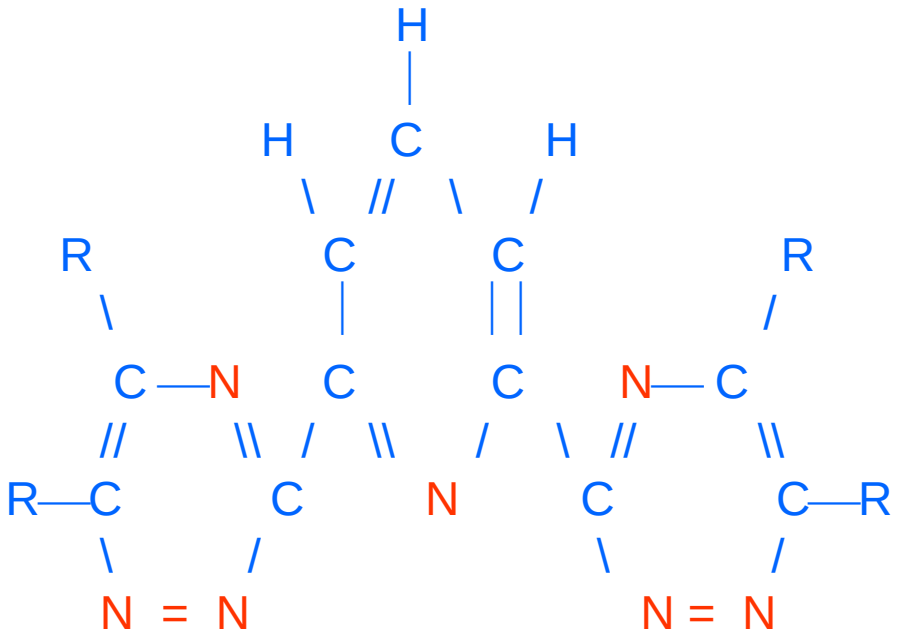




SANEX (2)

BTP (bis triazines pyridines) and substituted BTP

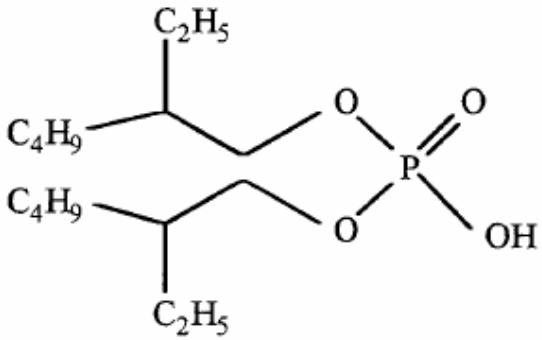
These nitrogen donors were the surprise of the last years . They have the formula



pK_a BTP < pK_a TPTZ

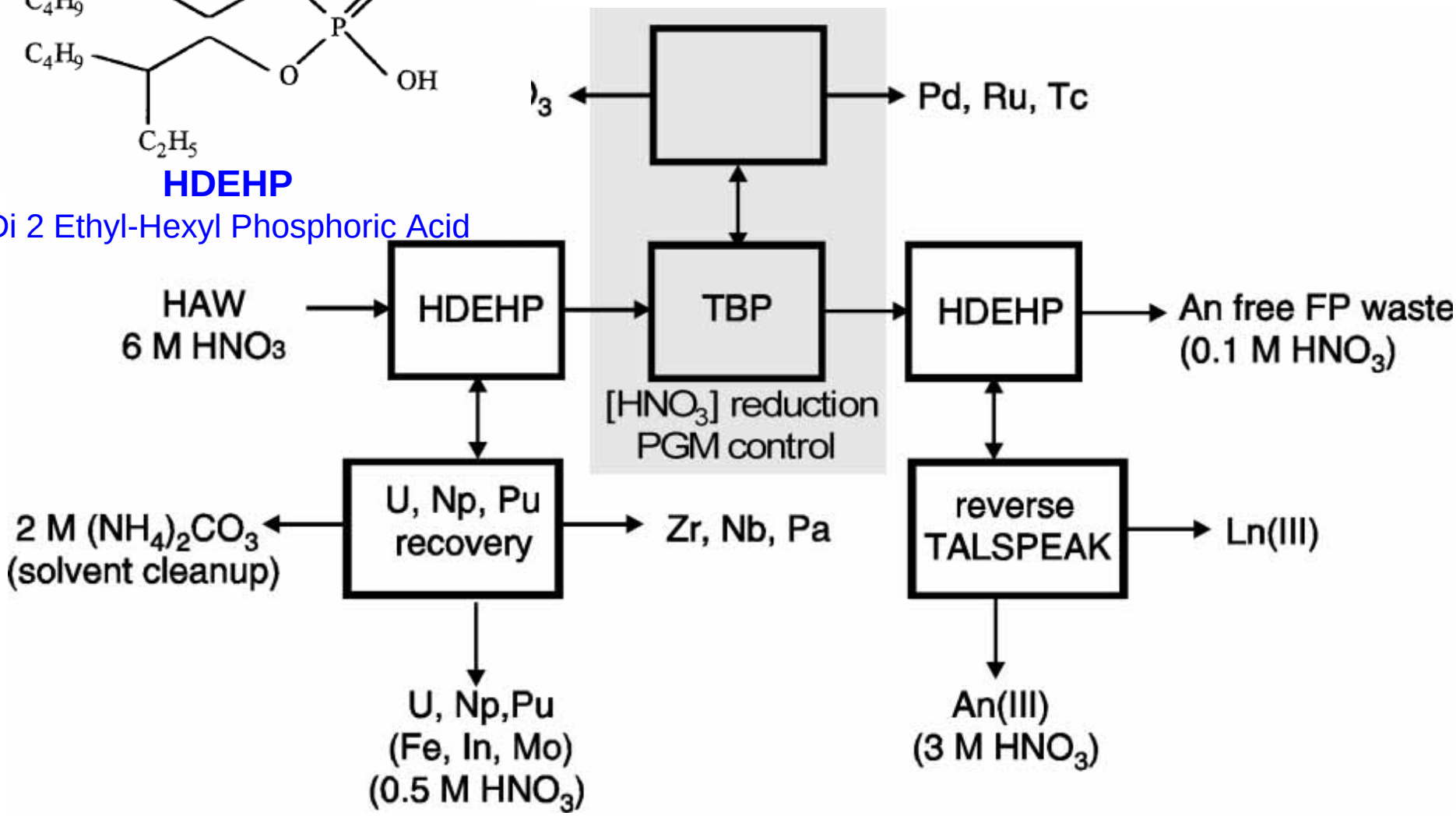
- These ligands are able to extract Am(III) and Cm(III) from 1N nitric acid as nitrates without the addition of a second acidic extractant and that for 10^{-2} M solutions

The TALSPEAK Process

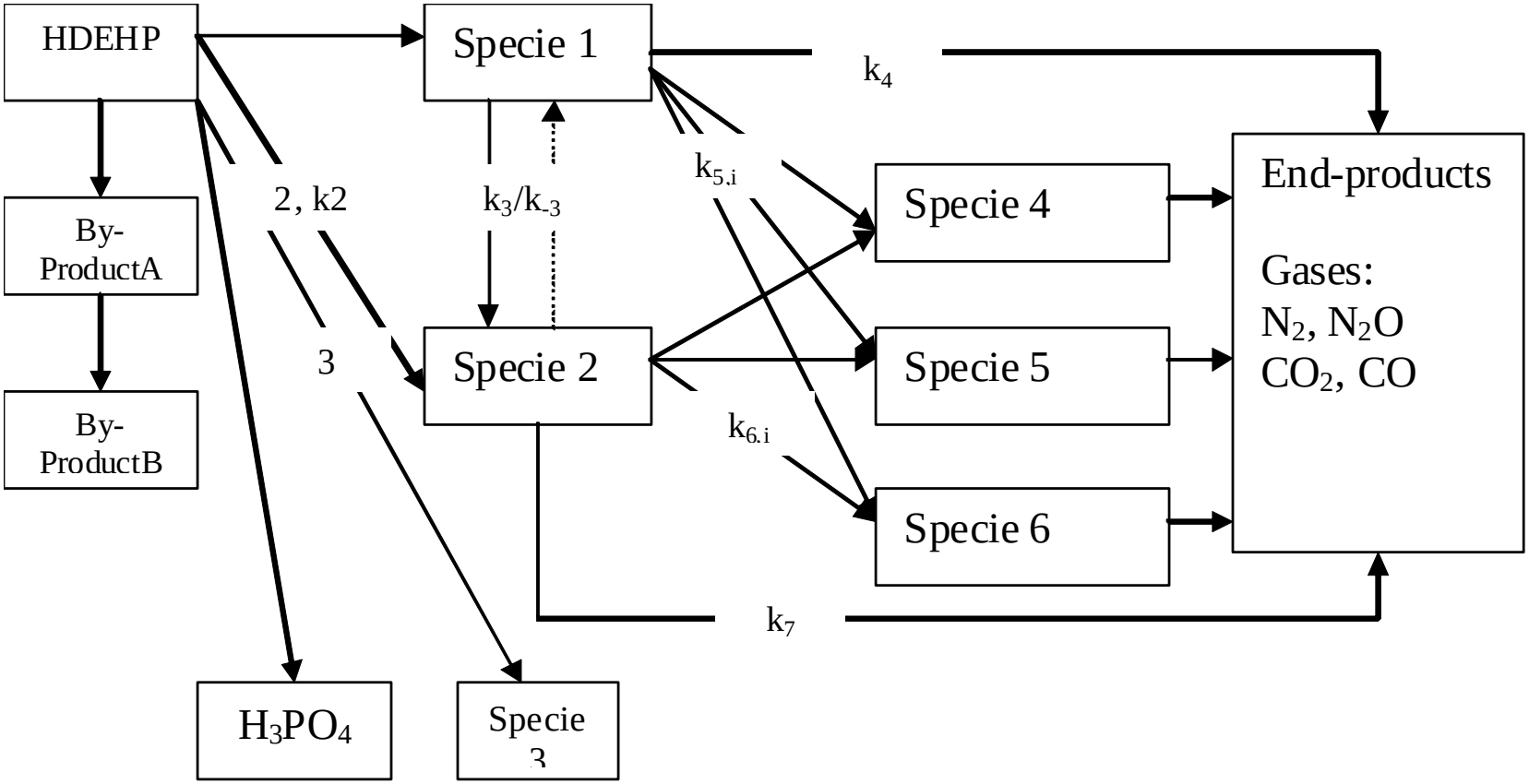


HDEHP

Di 2 Ethyl-Hexyl Phosphoric Acid



Potential reaction scheme of HDEHP degradation in contact with nitric acid solution



HDEHP Chemical Degradation

- *Hydrolysis* (acid catalyzed): the reaction of HDEHP with H_2O/H^+ may yield to an ethyl-hexanol specie, and ethyl-hexyl-phosphoric acid. The ethyl-hexanol specie may then react to form an ethyl-hexyl nitrate, carboxylic acids and gases.
- *Dealkylation*: the reaction of HDEHP with nitric acid may yield to the formation of an ethyl-hexyl nitrate and ethyl-hexyl-phosphoric acid. Ethyl-hexyl nitrate may then react to form carboxylic acids and gases (the reaction may also lead to ethyl-hexanol specie).
- *Pyrolysis:* HDEHP can be decomposed into ethyl hexene, phosphoric esters and phosphoric acid.
- *Oxidation*: the reaction of HDEHP with nitric acid yields gases

Experiments under way at ISU

- Determine the extraction mechanisms that take place between HNO_3 and HDEHP
- Determine the complexes and/or degradation products formed between HNO_3 and HDEHP in the organic phase

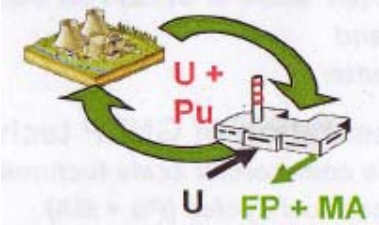
Vision of the Nuclear Energy for the 21st Century

- **Renaissance**
  - ⇒ Avoid spent fuel pilling up!

Gen III Reactors with advanced recycling proven technologies

Nuclear energy for the 21st century

- **Sustainability**



Gen IV Reactors with fuel cycle options

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