

Advanced Materials and Processes for Energy and Environmental Applications – An Overview

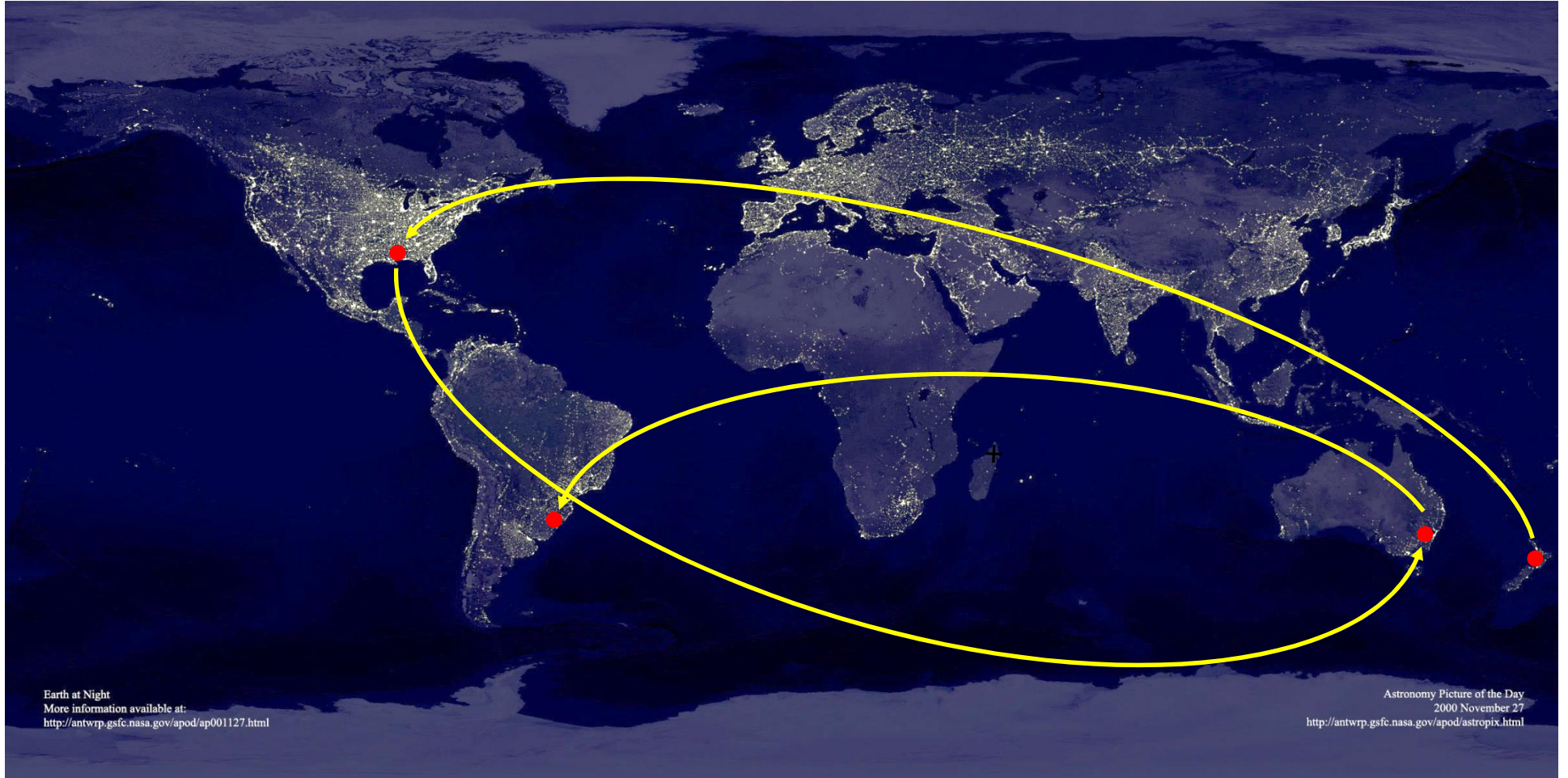


Dr Victor Luca

**Comisión Nacional de Energía Atómica
Buenos Aires, Argentina**



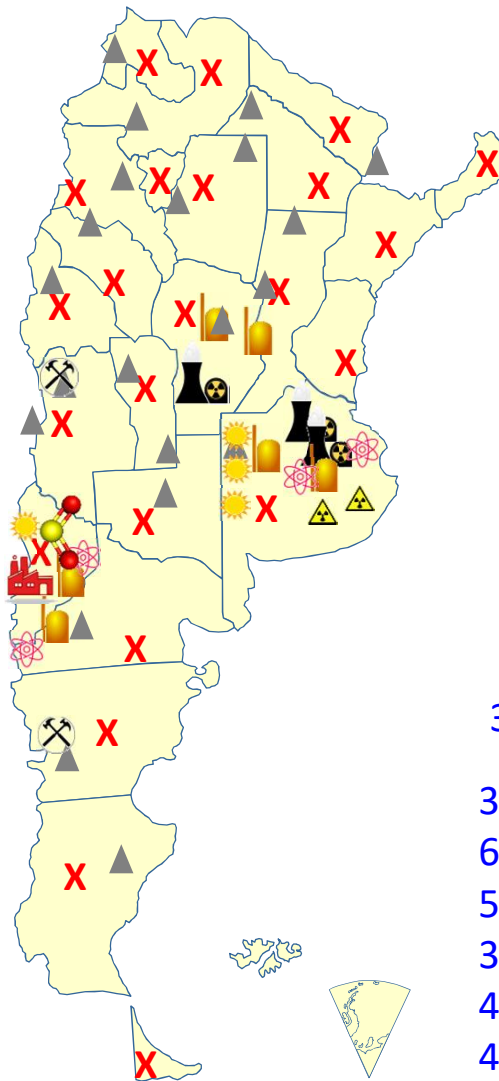
UoA 15 Mar 2019



Earth at Night
More information available at:
<http://antwrp.gsfc.nasa.gov/apod/ap001127.html>

Astronomy Picture of the Day
2000 November 27
<http://antwrp.gsfc.nasa.gov/apod/astropix.html>

ARGENTINA - More than 60 Years of Nuclear Technology Development



3 Nuclear Power Plants

Atucha I 350 MW, Atucha II 700 MW, Embalse 600 MW



6 Research Reactors



4 Accelerators



3 Nuclear Research Centers



1 Technological Center



1 Heavy Water Plant



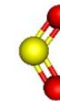
2 Irradiation Plants



2 Uranium Mining Facilities



1 Enrichment Plant



376 Industrial Application Facilities



3 Nuclear Medicine Schools

68 Co Therapy Centers

57 Brachytherapy Centers

309 Nuclear Medicine Centers

45 Medical Accelerators

408 Immunoassay Labs



Reactor: ^{99}Mo , ^{131}I , ^{32}P , ^{153}Sm ,
 ^{51}Cr , ^{177}Lu , ^{192}Ir , ^{60}Co

- Cyclotron: ^{201}Tl , ^{18}F , ^{67}Ga , ^{111}In



ARGENTINE NUCLEAR CAPABILITIES

More than 60 Year Involvement in Nuclear Energy

~2500 Staff Across Three Atomic Centers



CNEA Headquarters



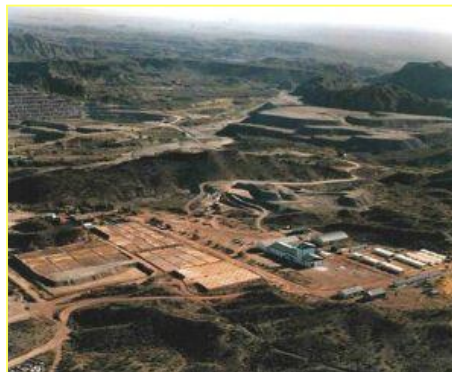
Bariloche Nuclear
Research Center



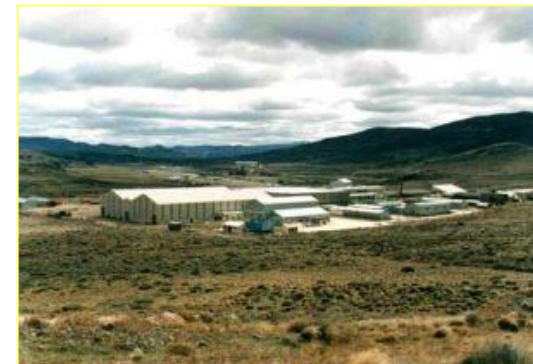
Constituyentes Nuclear
Research Center



Ezeiza Nuclear Research Center



Uranium mining and
milling
(San Rafael - Mendoza)



Pilcaniyeu
Technological Center (Río
Negro)



DIOXITEK
UO₂ Production Plant



FAE Special alloy production



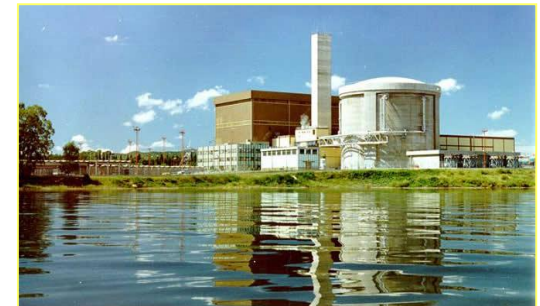
**CONUAR - Fuel element
production**



**ENSI - D₂O Production Plant
(Neuquen)**



**INVAP - Technological
development**



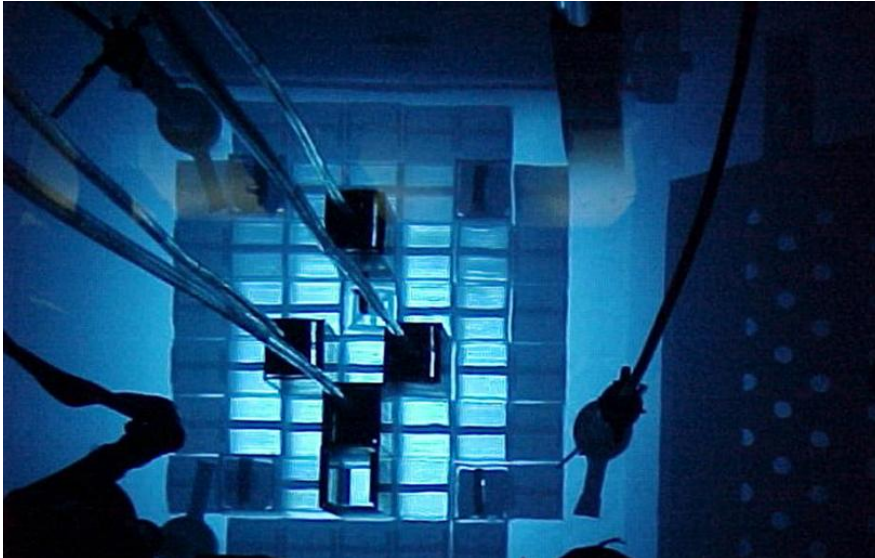
**NA.SA Nuclear Energy
('The Generator')**



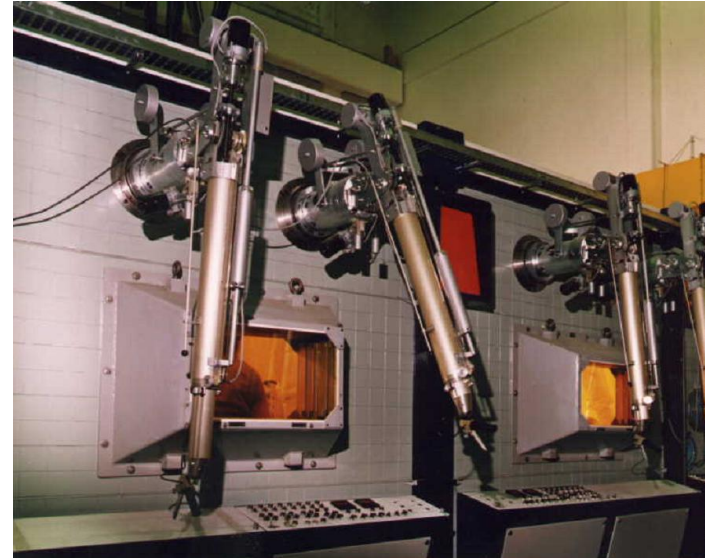
**FUESMEN
Nuclear Medicine**

RA3 – Argentina ^{99}Mo Production Reactor

10 MW Pool Type MTR



Fission ^{99}Mo Production Cells



Thermal flux: $2 \times 10^{14} \text{ n.cm}^{-2}.\text{s}^{-1}$
Fuel: 23x MTR ^{235}U 20%
Moderator & coolant: light water
Control rods: 4x (Ag-Cd-In)
Thermal column: 1 (15 positions)

RA-10 Project

Objetives

1. Structural necessities



https://www.youtube.com/watch?v=qe1jYmStc_4

2. Nuclear technology for national development

3. Radioisotopes for health

^{99}Tc is a daughter of ^{99}Mo which is the most utilized radioisotope in nuclear medicine and is used for the detection of disease and thus contributes saving lives. Globally more than 80.000 procedures utilizing this isotope are undertaken per day. In Argentina more than 2 million patients are processed per year. **The increase in the production of ^{99}Mo will enable Argentina to satisfy national requirements and also help to satisfy an increasing international demand (about 10% of global production). This will enable us to consolidate our leadership position in the provision of radioisotopes for medical applications.**



1-Jan-2013

V13

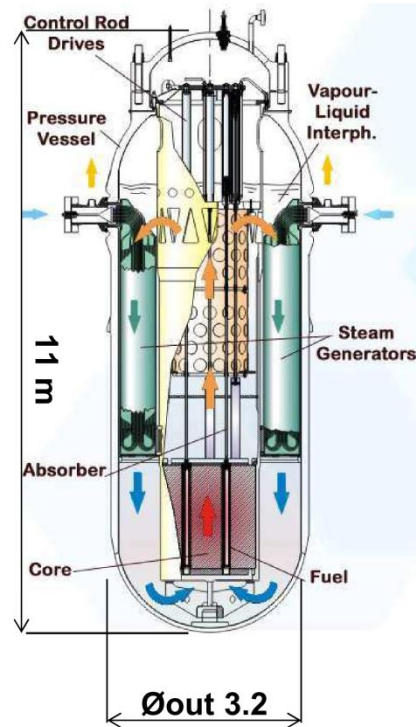
Australian government announces funding for a A\$169 million (\$175 million) plan to develop a new molybdenum-99 production plant and new radwaste facility at the Australian Nuclear Science and Technology Organisation's OPAL reactor site at Lucas Heights.

<http://www.neimagazine.com/features/featurebox-australia-greenlights-mega-moly-project/>

ANSTO Mega Moly plant expected to produce 140,000 6-day curies/yr compared with OECD estimated global demand of 10,000 6-day curies per week (520,000 6-day curies/yr) or 27% of Global demand. V14

New process will be based on the base-side process technology of South African producer NTP, which is ANSTO's international collaboration partner.

Thermal power	100
Electrical power	27
Coolant	Natural circulation 410 kg/s at nominal power
pressurisation	Self-pressurization 12.25 MPa
temperature	326°C / 284 °C
Fuel enrichment	About 3.5%
Core	61 Fuel assemblies Hexagonal cross section Active length 1.40 m
Steam generator type	12 X 8.3 MW helical coil
Steam	Once through Superheated (30°C) 290°C 4.7 MPa



\$685,000,000 spent thus far

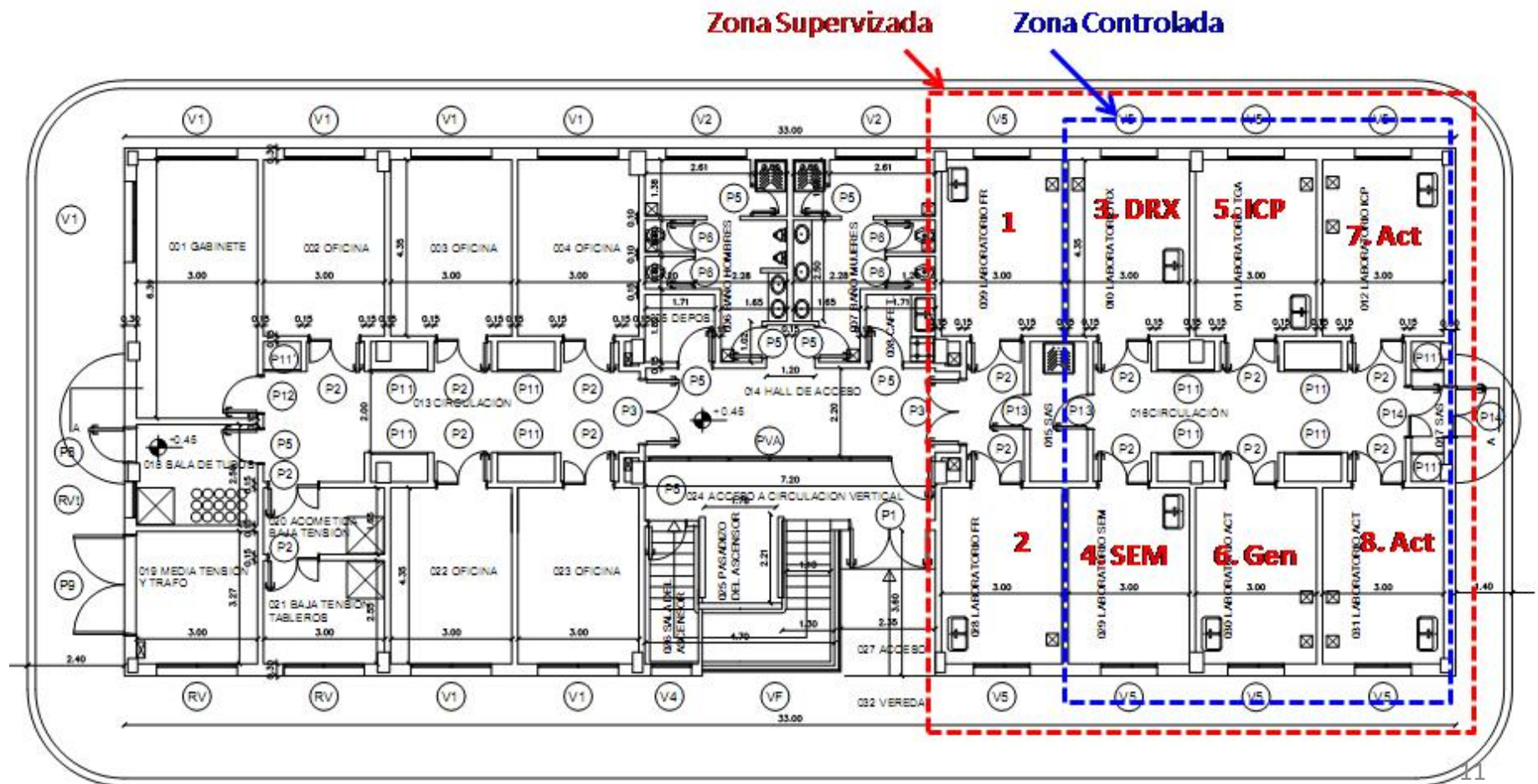
V19



New Installation for R&D Relating to the Treatment and Conditioning of Radioactive Wastes

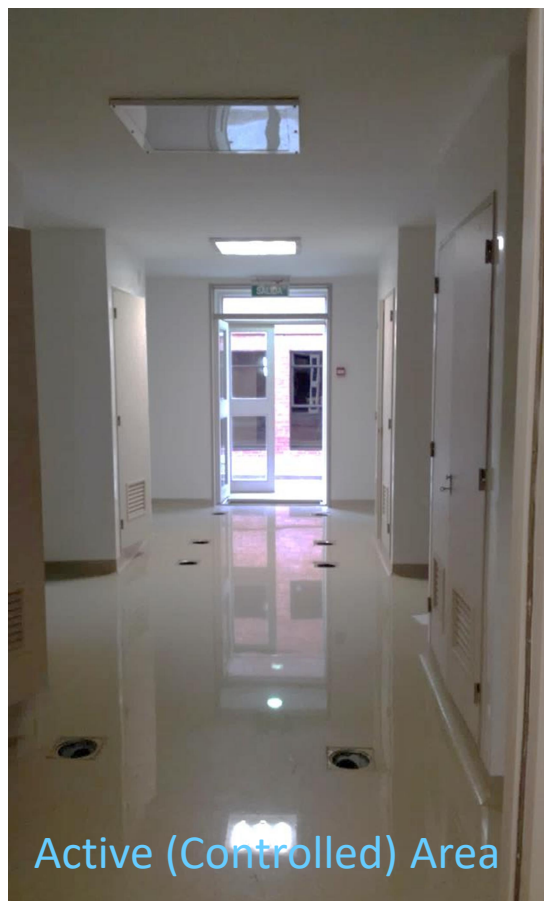
The nature of the work to be undertaken requires the establishment of certain unique research infrastructure that has not previously existed.

Investing in a **New Facilities** - Laboratories for the Characterization (CAE) and for R&D on the treatment and conditioning radioactive wastes (CAC)!



LQMN

Materials and Process Chemistry Laboratory - Centro Atómico Constituyentes



Instrumentation

Perkin-Elmer Wizard² 2480
γ Counter



ICP-HRMS - Thermo Element II



Micromeritics
ASAP 2420 NSP



Autopore IV



Bruker – S8 Tiger XRF



Bruker – S2 Pico FOX TRXRF



Pfeiffer -
Omnistar



TGA-DSC - TA Inst. Q600



Malvern Mastersizer 2000



Panalytical Empyrean



FESEM - FEI Inspect F50



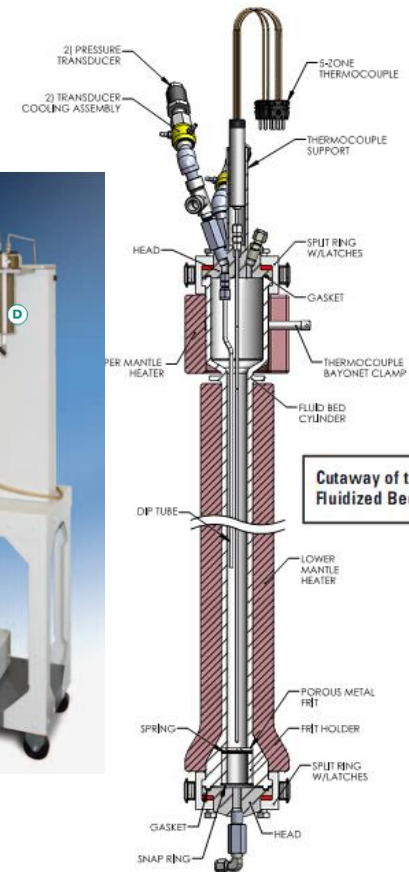
Metkon - Digiprep Accura



Perkin-Elmer Elemental Analyzer (CHON/S)



Fluidized Bed Reactor (FBR) – Parr Inst.



Hot Isostatic Press (AIP)

HIP SYSTEM MODEL #:

AIP6-30H

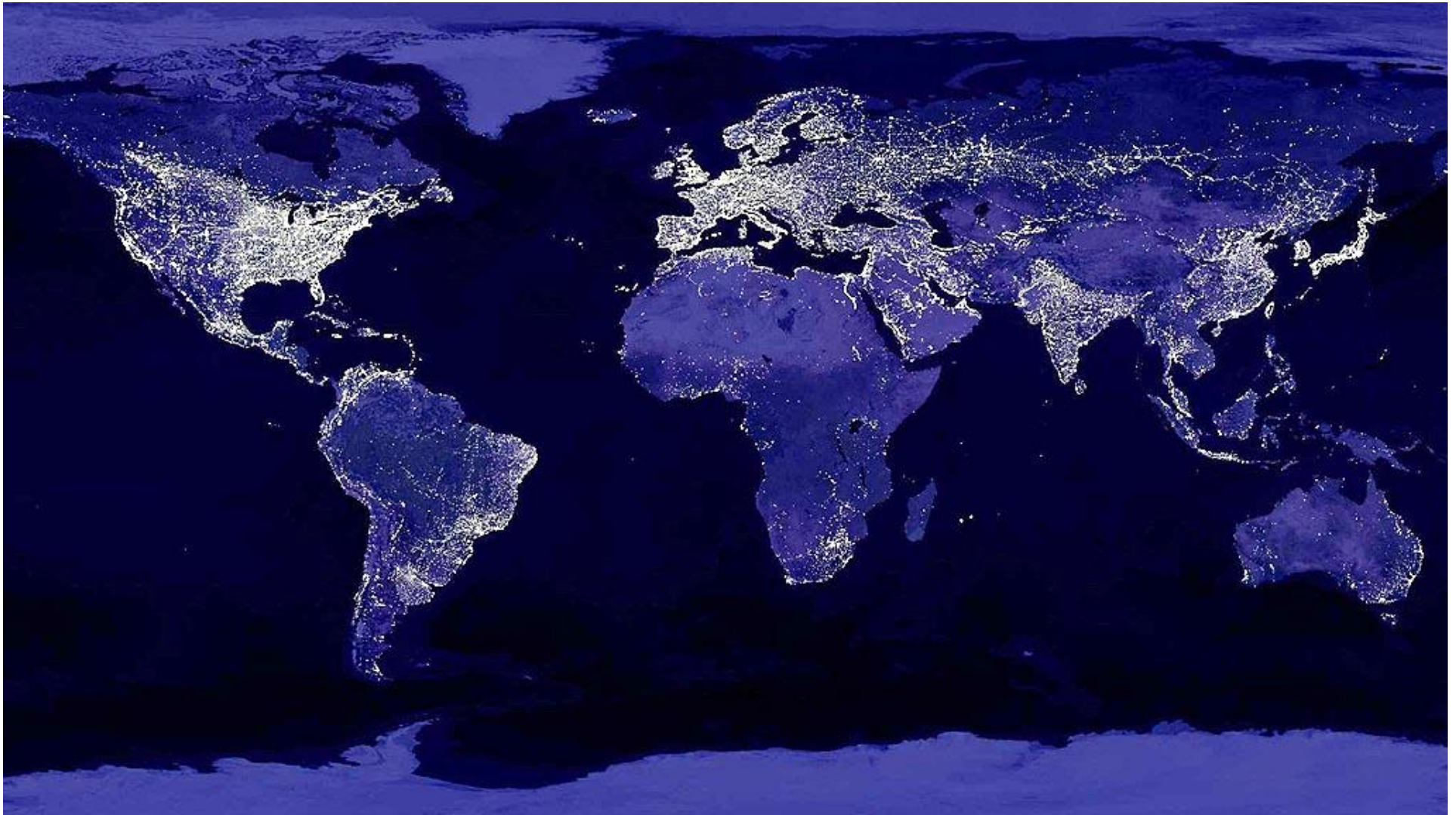


The Big Picture - Worth a Thousand Words



The Blue Marble

The Black Marble



Our Planet".

<https://www.albartlett.org/>

the marketplace will combine to produce vast new energy resources as they are needed. Note the certainty that characterizes this confidence.

(vii) Do not sit back and deplore the lack of "leadership".

Democrats' bizarre bid to 'fix' a booming economy



Leaving Afghanistan and Syria is a mistake we'll regret



Democrats' new 'woke' standards mean hell for 2020 contenders

**OPINION**

The numbers show we just can't get to '100% renewable energy' any decade soon

By Robert Bryce

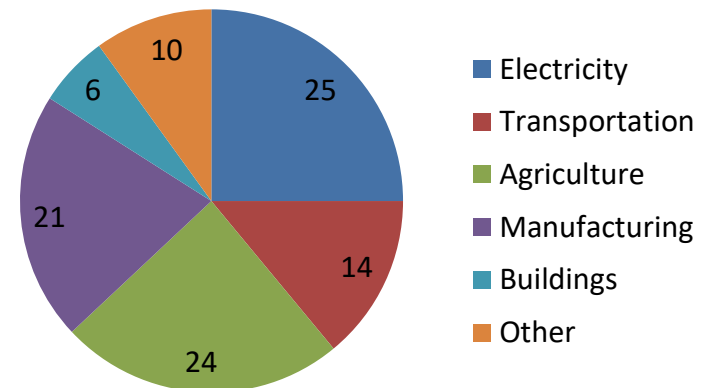
November 16, 2018 | 7:58pm

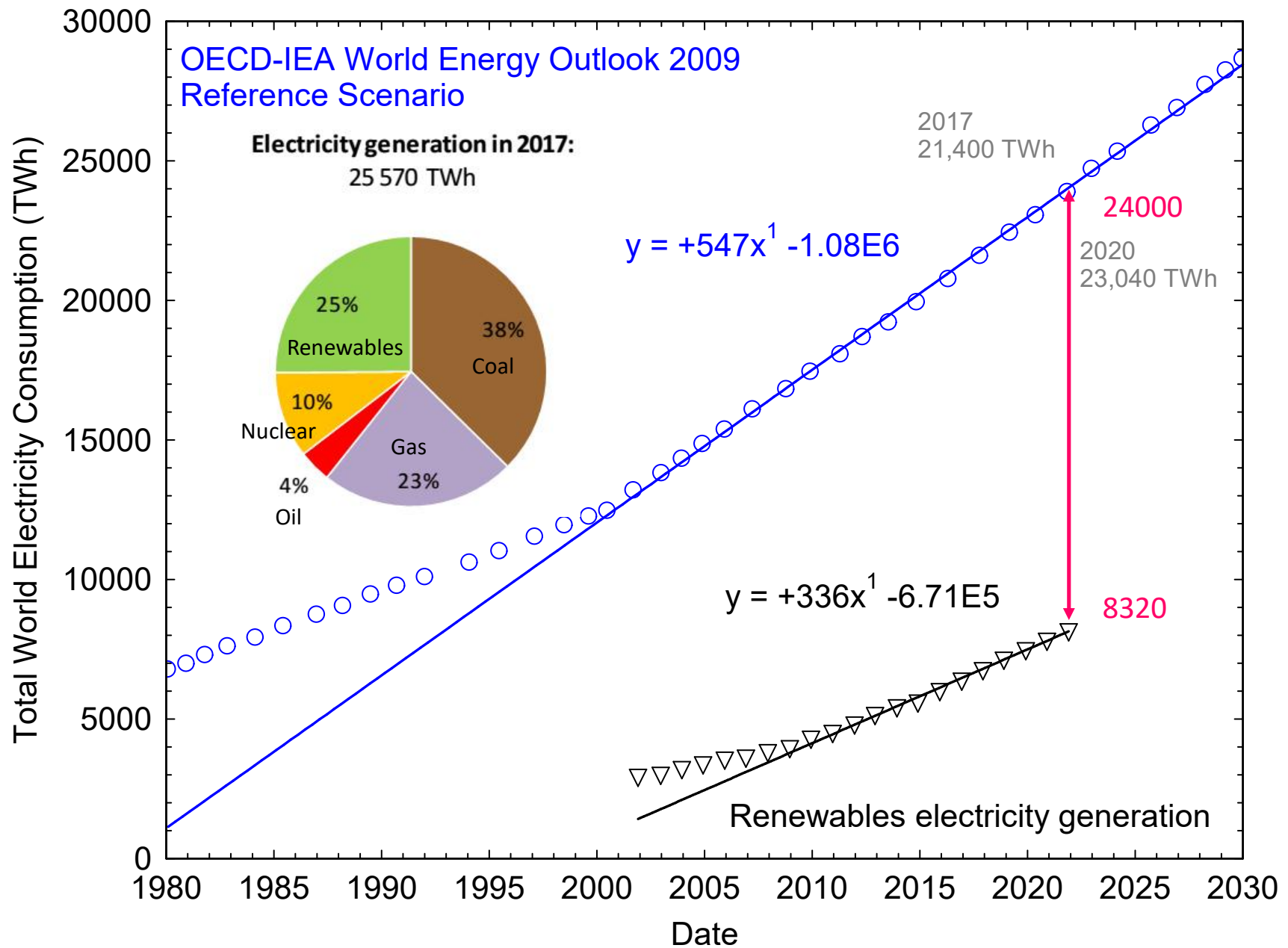


Alexandria Ocasio-Cortez

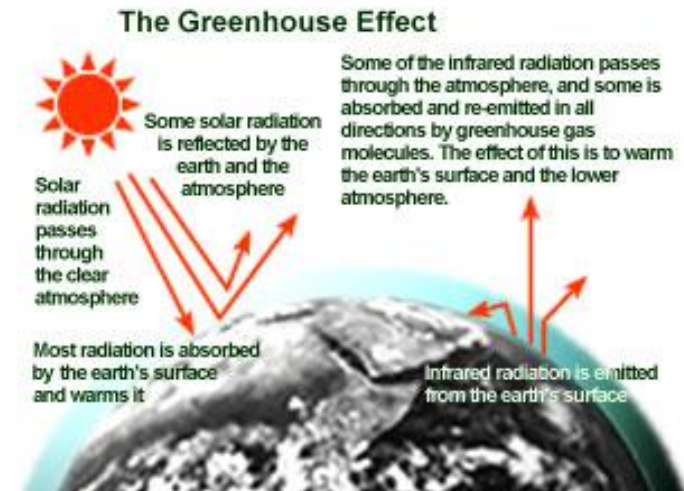
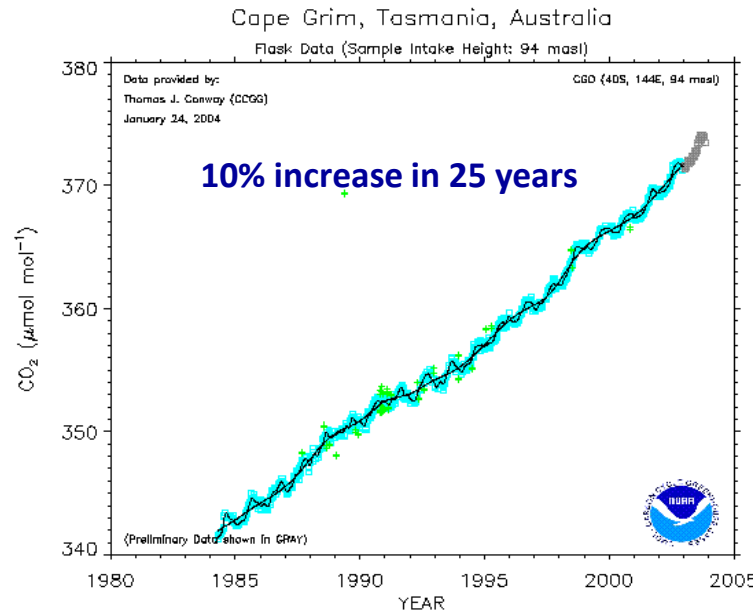
We don't have a choice.
We have to get to 100% renewable energy.
There is no other option!

But emission are not only about electricity generation!

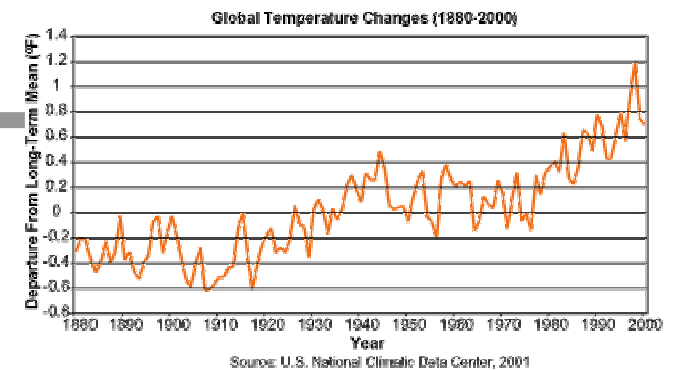




Some of the Major Consequences of Exponential Growth in Population and Consumption



Thomas *et al.*, Extinction risk from climate change.
Nature **2004**, 427, 145-148.



ANSTO - AMEEA Project Objectives

Develop Novel Materials for Environmental and Energy Applications



WORLD SCIENTISTS' WARNING TO HUMANITY

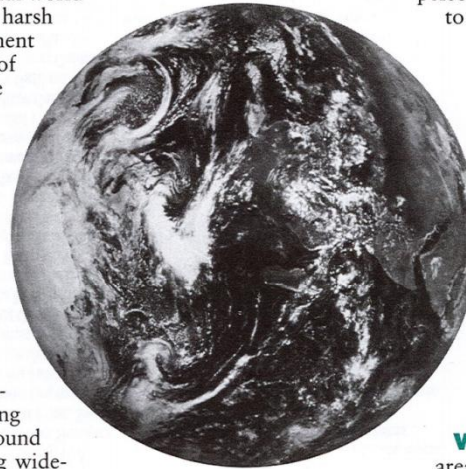
INTRODUCTION Human beings and the natural world are on a collision course. Human activities inflict harsh and often irreversible damage on the environment and on critical resources. If not checked, many of our current practices put at serious risk the future that we wish for human society and the plant and animal kingdoms, and may so alter the living world that it will be unable to sustain life in the manner that we know. Fundamental changes are urgent if we are to avoid the collision our present course will bring about.

THE ENVIRONMENT The environment is suffering critical stress:

The Atmosphere Stratospheric ozone depletion threatens us with enhanced ultraviolet radiation at the earth's surface, which can be damaging or lethal to many life forms. Air pollution near ground level, and acid precipitation, are already causing widespread injury to humans, forests, and crops.

Water Resources Heedless exploitation of depletable groundwater supplies endangers food production and other essential human systems. Heavy demands on the world's surface waters have resulted in serious shortages in some 80 countries, containing 40 percent of the world's population. Pollution of rivers, lakes, and groundwater further limits the supply.

Oceans Destructive pressure on the oceans is severe, particularly in the coastal regions which produce most of the world's food fish. The total marine catch is now at or above the estimated maximum sustain-



person in five lives in absolute poverty without enough to eat, and one in ten suffers serious malnutrition.

No more than one or a few decades remain before the chance to avert the threats we now confront will be lost and the prospects for humanity immeasurably diminished.

WARNING We the undersigned, senior members of the world's scientific community, hereby warn all humanity of what lies ahead. A great change in our stewardship of the earth and the life on it is required, if vast human misery is to be avoided and our global home on this planet is not to be irretrievably mutilated.

WHAT WE MUST DO Five inextricably linked areas must be addressed simultaneously:

1. We must bring environmentally damaging activities under control to restore and protect the integrity of the earth's systems we depend on. We must, for example, move away from fossil fuels to more benign, inexhaustible energy sources to cut greenhouse-gas emissions and the pollution of our air and water. Priority must be given to the development of energy sources matched to Third World needs—small-scale and relatively easy to implement.

We must halt deforestation, injury to and loss of agricultural land, and the loss of terrestrial and marine plant and animal species.

2. We must manage resources crucial to human welfare more

World Scientists' Warning to Humanity: A Second Notice

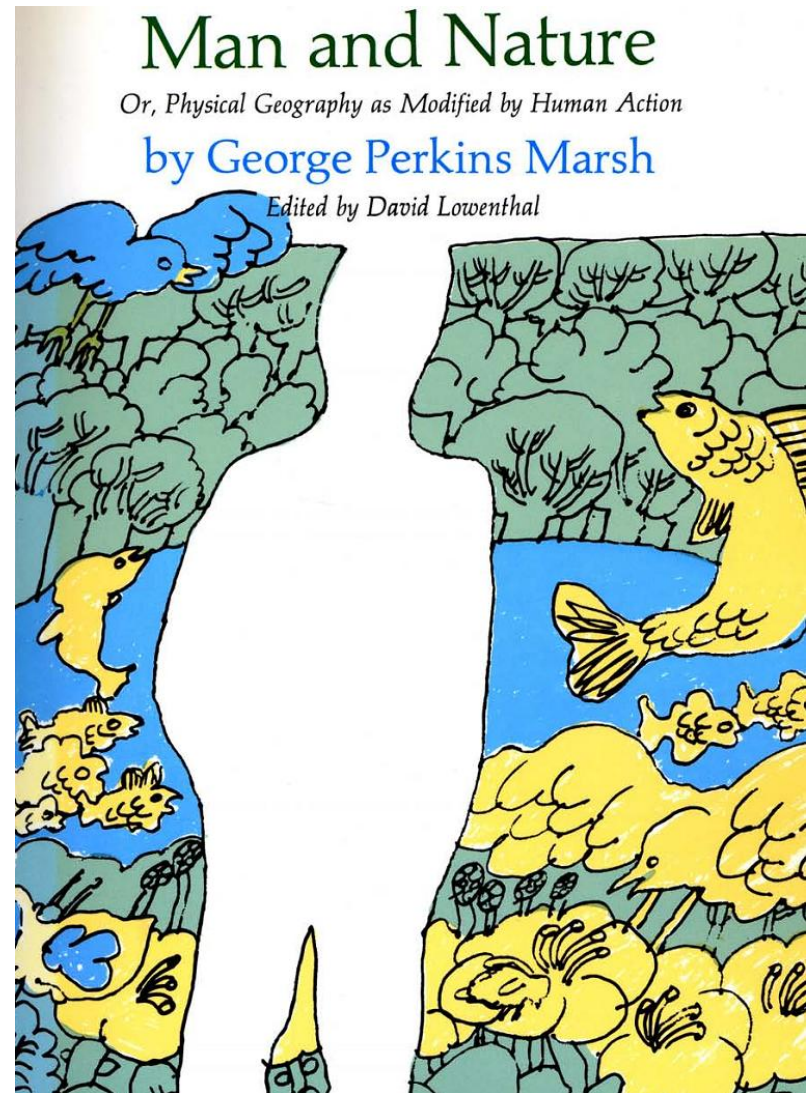
WILLIAM J. RIPPLE, CHRISTOPHER WOLF, THOMAS M. NEWSOME, MAURO GALETTI, MOHAMMED ALAMGIR, EILEEN CRIST, MAHMOUD I. MAHMOUD, WILLIAM F. LAURANCE, and 15,364 scientist signatories from 184 countries

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[FIFTH SERIES.]

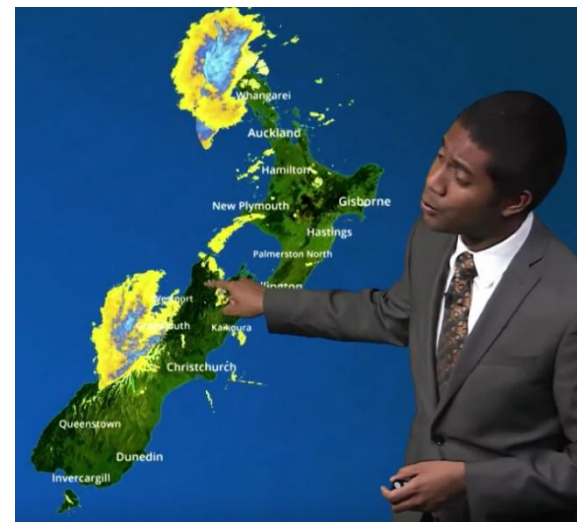
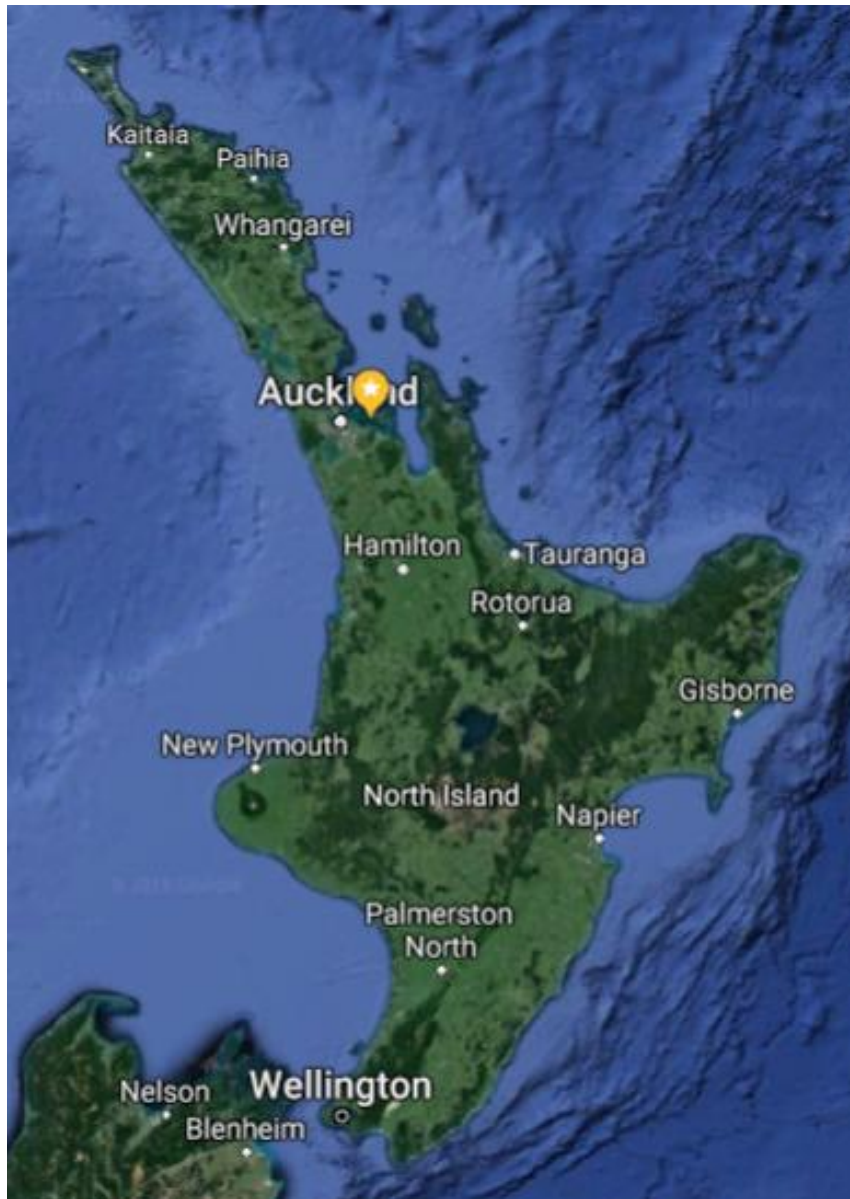
APRIL 1896.

XXXI. *On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground.* By Prof. SVANTE ARRHENIUS *.

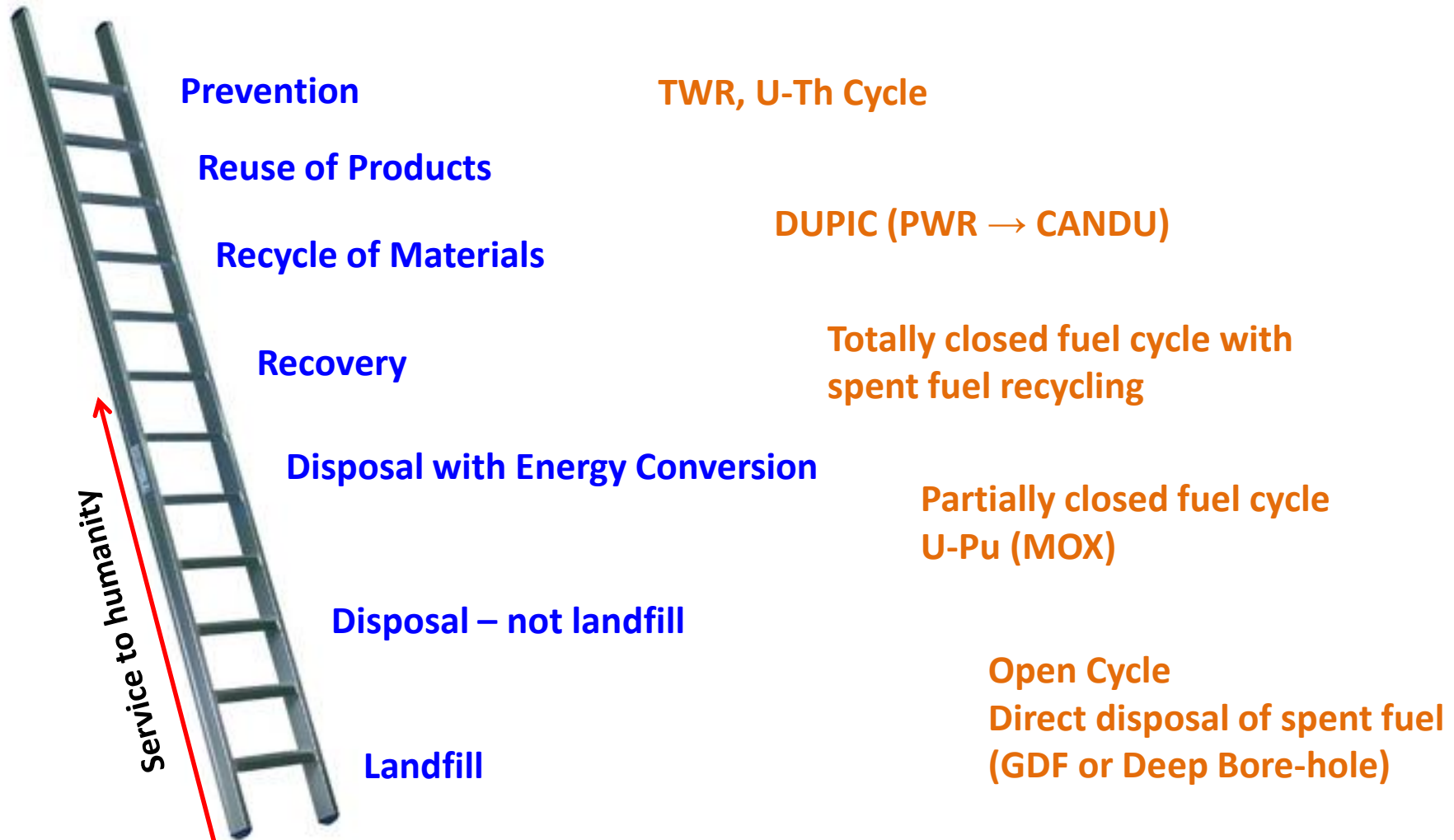


Originally published in 1864

How is NZ doing in terms of Environmental Stewardship?

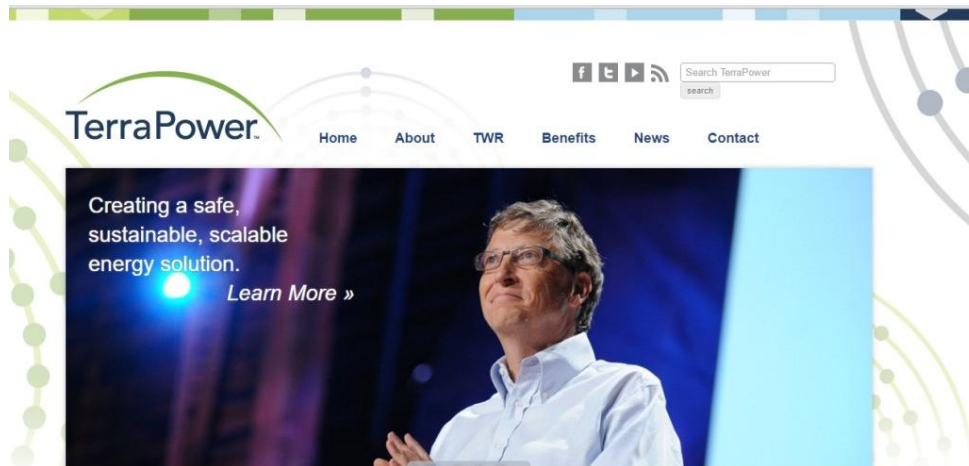


Lansink's Ladder



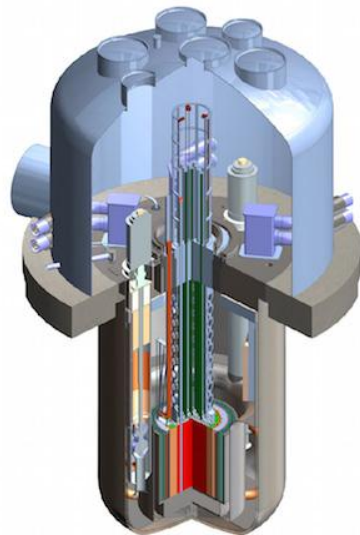
Extended Product Responsibility

Innovating to Zero and the Travelling Wave Reactor



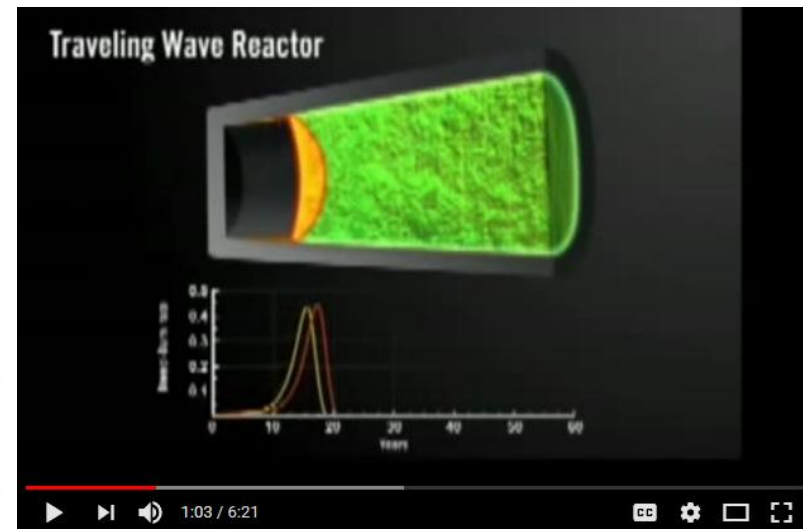
Taylor Swift – Blank Space >2 billion views

Bill Gates explains Terrapower And The Traveling Wave Reactor

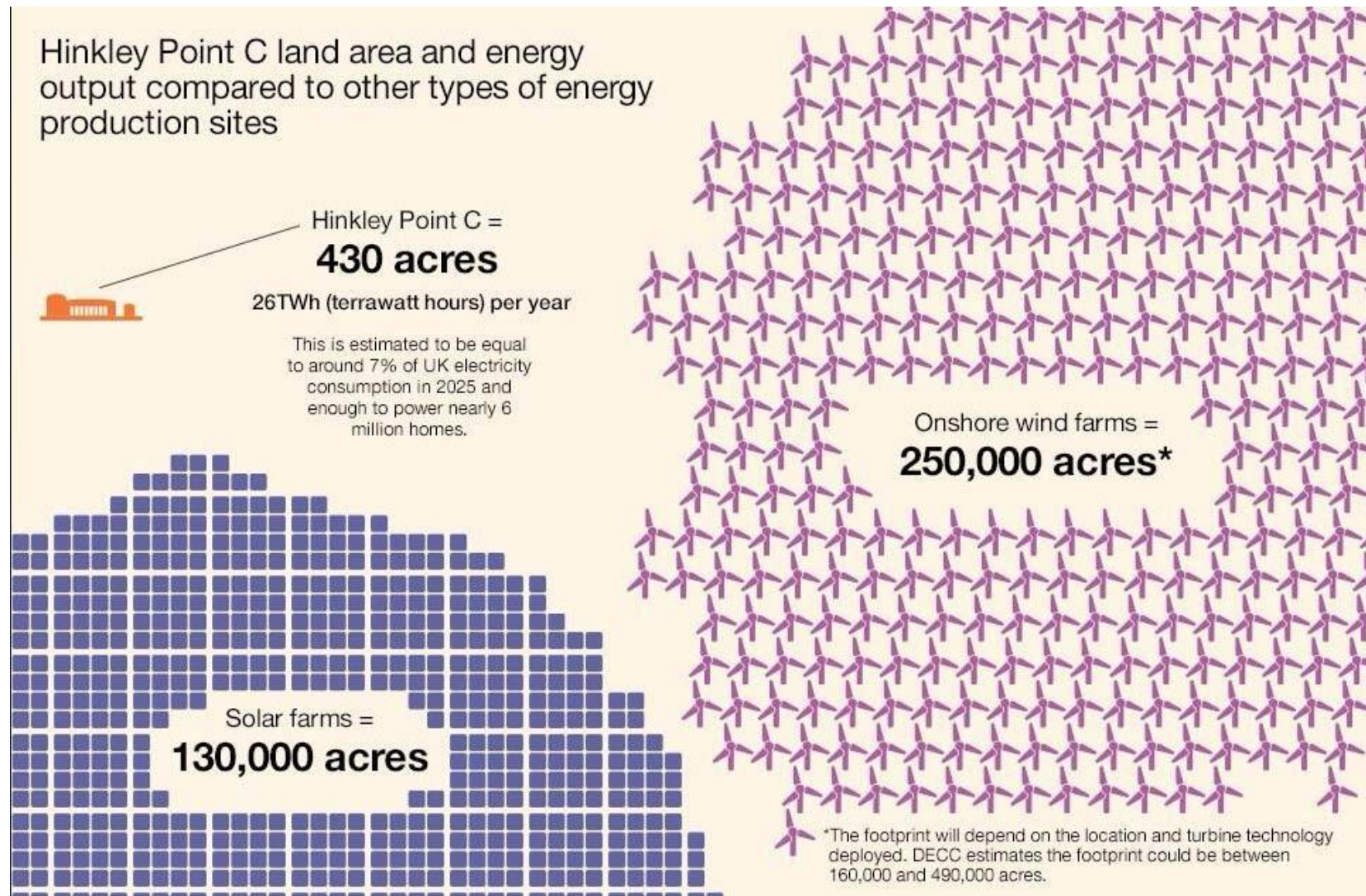


Turns depleted uranium into electricity, using a simple fuel cycle without requiring separations.

SIZE	600 MWe (Prototype Plant) 1150 MWe (Commercial Plant)
TEMPERATURE	510°C
PRESSURE	Low (Atmospheric)
PRIMARY FUEL	Depleted Uranium
COOLANT	Sodium
ENERGY CONVERSION	Steam (Rankine Cycle)
WASTE REPROCESSING	Not Required



Acres required to power 6 million homes



SOURCE ENERGY EQUIVALENTS

1 Uranium Fuel Pellet, without being reprocessed and recycled, has about as much energy available in today's light water reactor AS...
actual size shown below



20 g

3 Barrels of Oil
(42 gal. each)



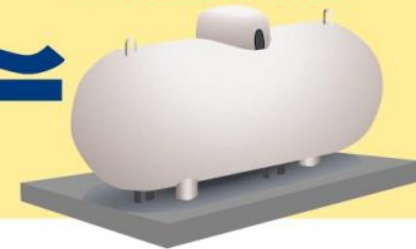
410 L

1 Ton of Coal



400 Kg

**17,000 Cubic Feet
of Natural Gas**



350 L

Once-Through (Open) Fuel Cycle

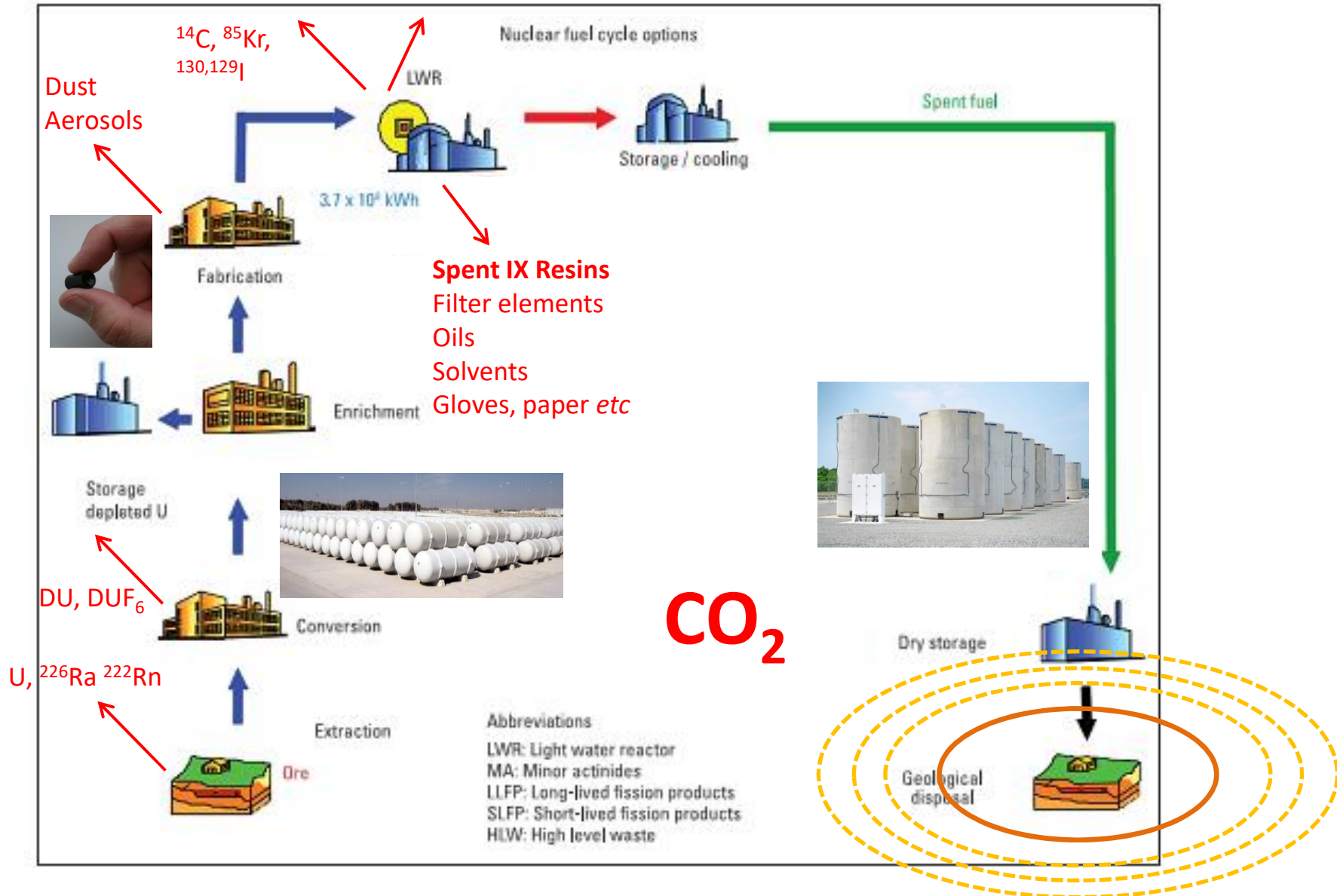
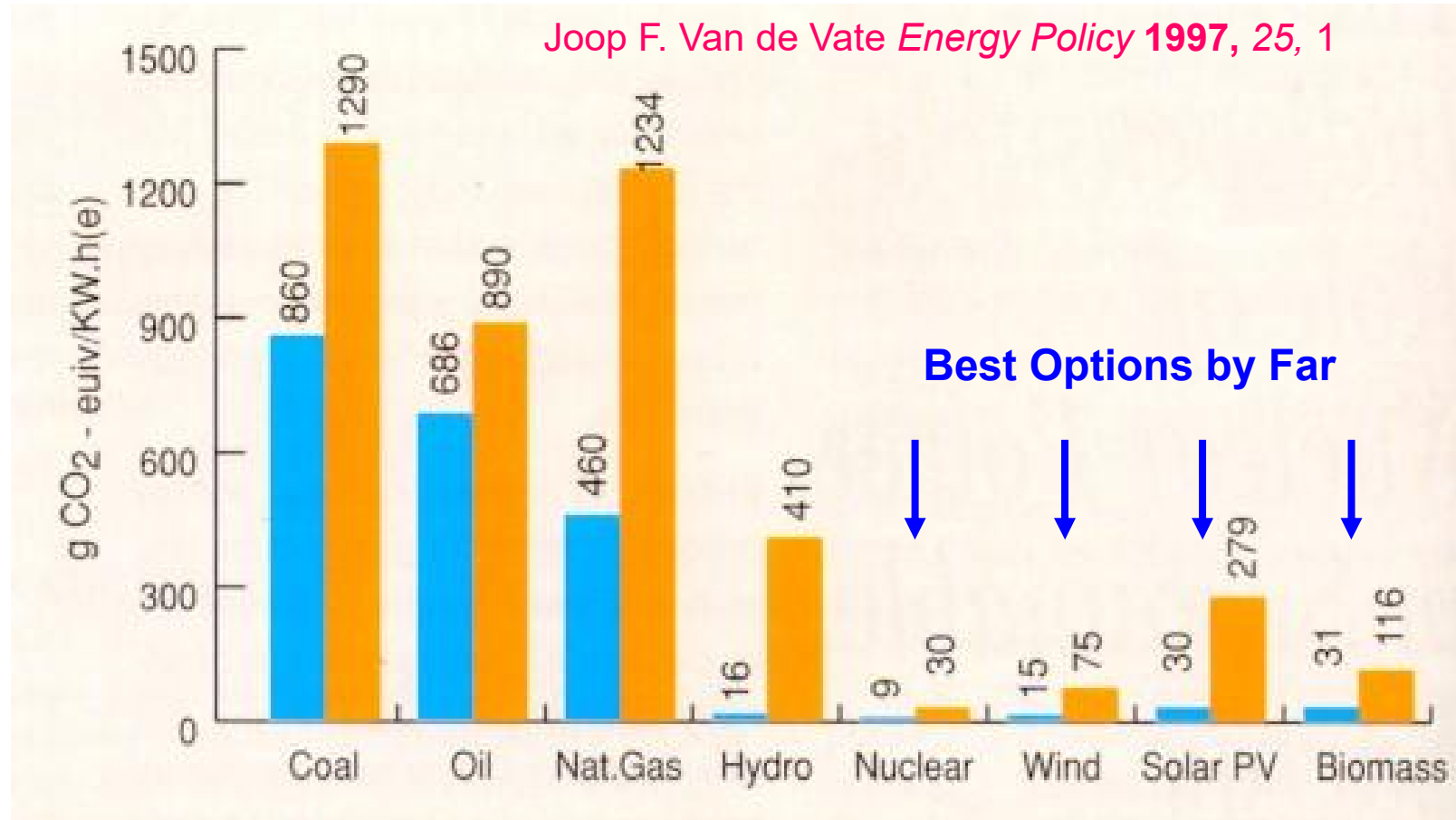


FIGURE 3. Diagram of the nuclear fuel cycle, showing the various options: once-through; conventional closed cycle; advanced closed cycle with partitioning and transmutation. Resultant high-level waste streams are also indicated.

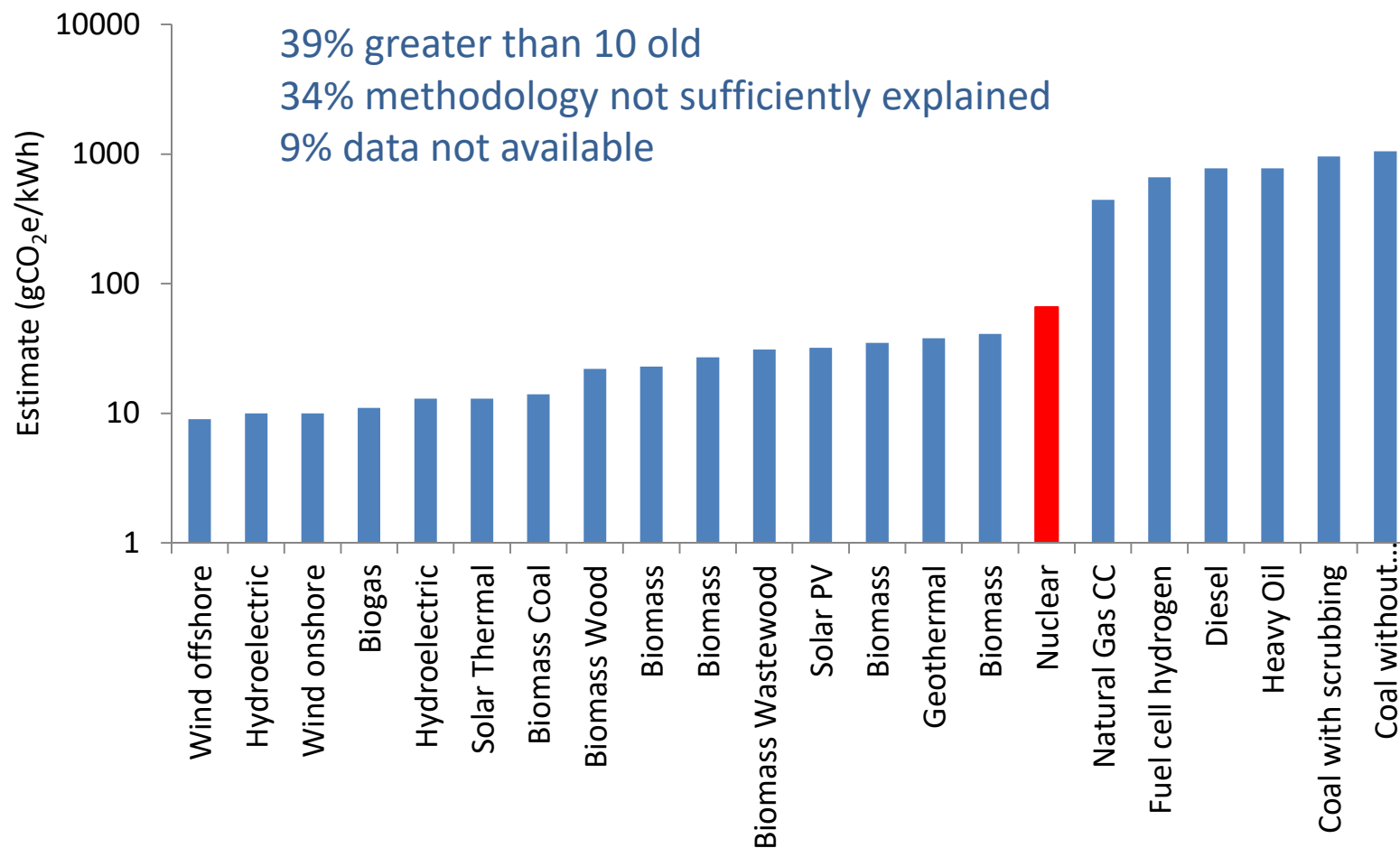
Life Cycle Emissions from Different Sources



Sovacool, Valuing the greenhouse gas emissions from nuclear power: A critical survey. *Energy Policy* 2008, 36, 2950

Screening of 103 lifecycle studies of GHG equivalent emissions for NPPs to identify a subset of the most current, original, and transparent studies.

Basis for Rejection of Life Cycle Analysis Studies



The New York Times

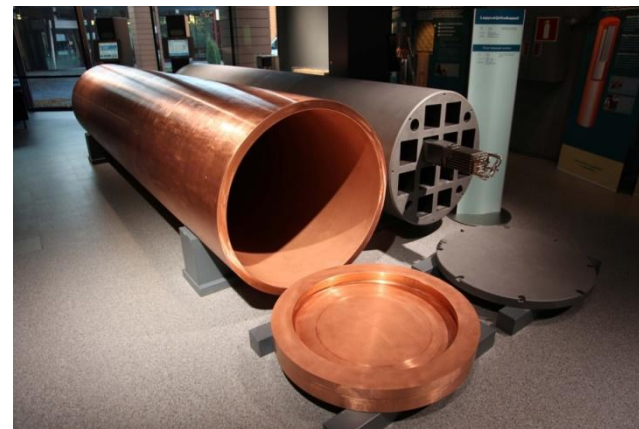
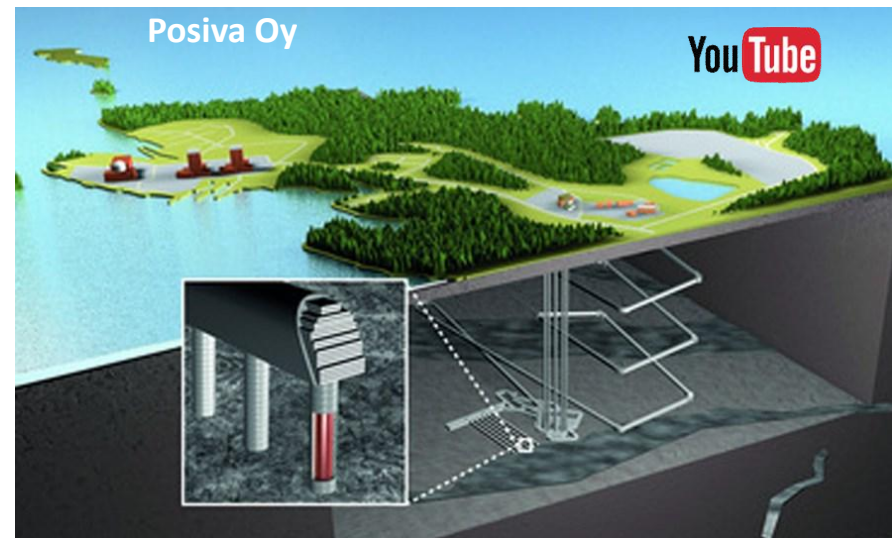
Fortum and Teollisuuden Voima (TVO)
Nuclear Waste Is Allowed Above Ground Indefinitely

By [MATTHEW L. WALD](#) AUG. 29, 2014

http://www.nytimes.com/2014/08/30/us/spent-nuclear-fuel-is-allowed-to-be-stored-above-ground.html?_r=0



McGuire Station dry cask storage stores spent fuel on site



Closed Fuel Cycle

p21

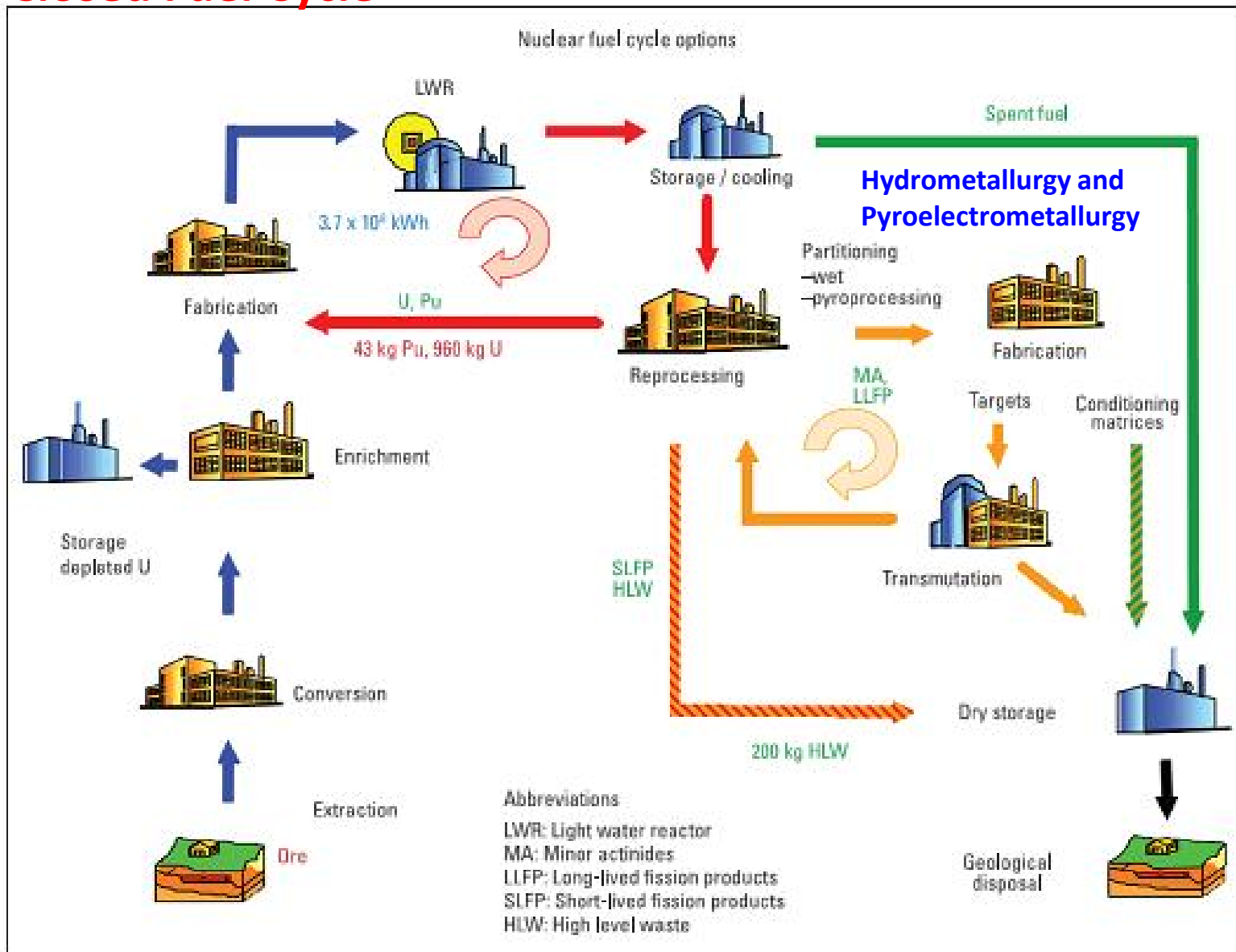


FIGURE 3. Diagram of the nuclear fuel cycle, showing the various options: once-through; conventional closed cycle; advanced closed cycle with partitioning and transmutation. Resultant high-level waste streams are also indicated.

f-element Separations – Major Objectives

1. Separate 5f-actinides from 4f-trivalent lanthanides
2. Separate trivalent minor actinides from trivalent lanthanides
3. Intra-lanthanide separations

Spin Off

57 La Lanthanum 138.9055	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
89 Ac Actinium (227)	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

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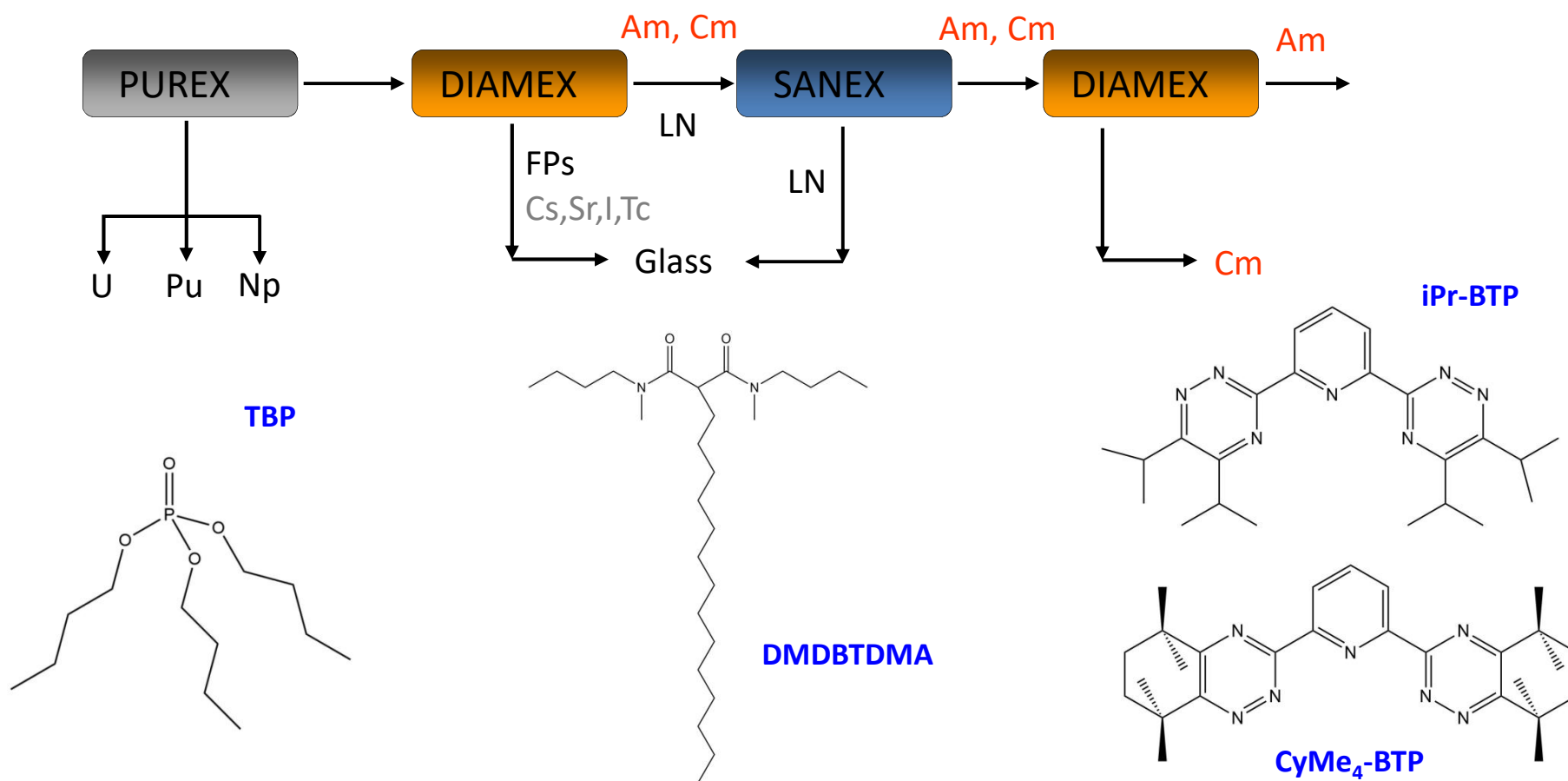
95 Am Americium (243)

96 Cm Curium (247)

The European Approach to Spent Fuel Recycling using SX

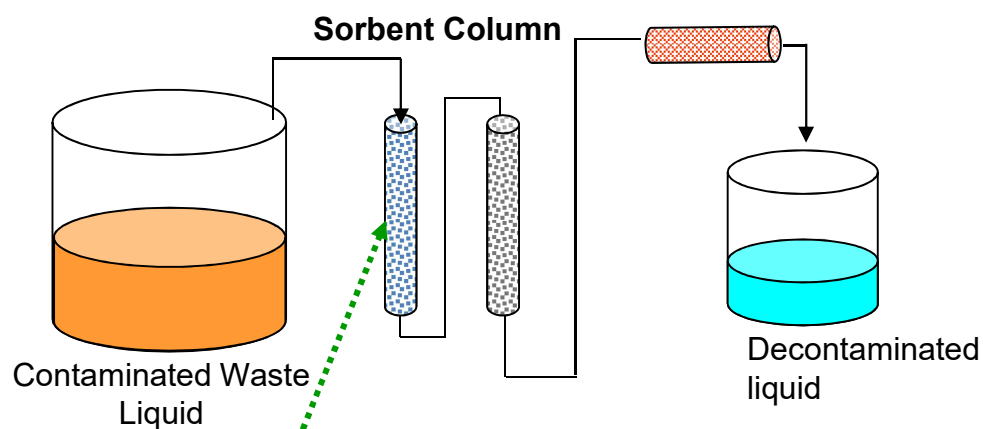
57 La Lanthanum (138.9055)	58 Ce Cerium (140.116)	59 Pr Praseodymium (140.90765)	60 Nd Neodymium (144.24)	61 Pm Promethium (145)	62 Sm Samarium (150.36)	63 Eu Europium (151.964)	64 Gd Gadolinium (157.25)	65 Tb Terbium (158.92534)	66 Dy Dysprosium (162.50)	67 Ho Holmium (164.93032)	68 Er Erbium (167.26)	69 Tm Thulium (168.93421)	70 Yb Ytterbium (173.04)	71 Lu Lutetium (174.967)
89 Ac Actinium (227)	90 Th Thorium (232.0381)	91 Pa Protactinium (231.03588)	92 U Uranium (238.0289)	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

Chemical similarity of LN and AN elements makes their separation non-trivial



Solid-Liquid Extraction (Ion Exchange)

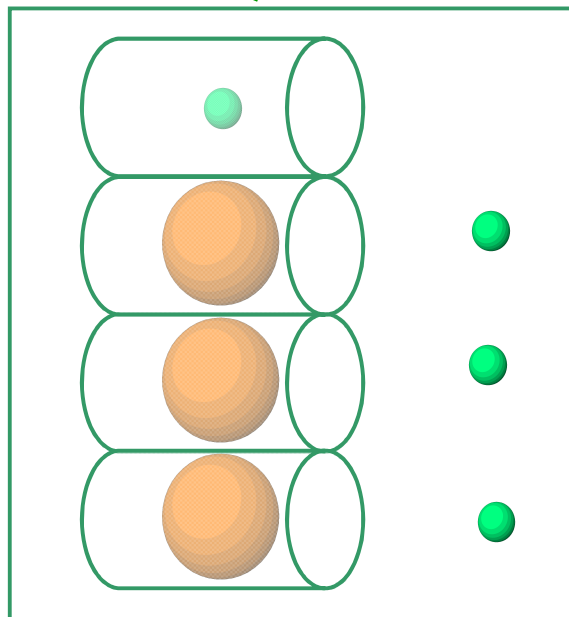
A Simple and Robust Separation Process For Extraction of Radioactive (Fuel Cycle) and Non-radioactive Heavy Metals



$$K_d = \frac{(A_i - A_f)}{A_f} \times \frac{V}{m} \frac{1}{F}$$

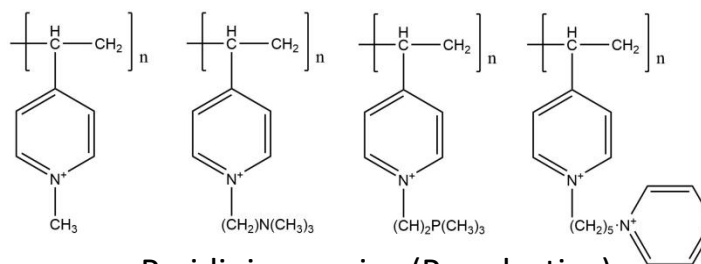
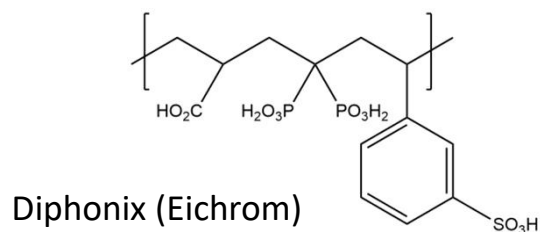
Ion Exchange Desiderata

- High **selectivity** (for *e.g.* $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$)
- High **capacity**
- **Fast** sorption kinetics
- High chemical and radiation **stability**
- Available in suitable morphology
- Can be converted to a form suitable for **safe disposal (EOL management)**
- Active over **pH range** of interest
- **Elutable?**

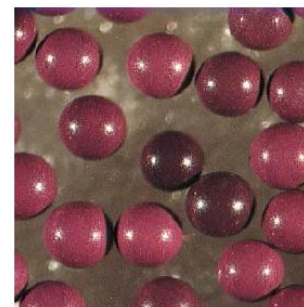


The Tool Kit of Open Framework Materials

1. Organic (polymeric) ion-exchange resins



Pyridinium resins (Pu selective)



Phenolics (Cs selective)

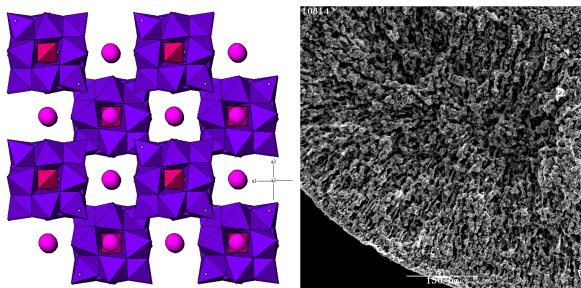
2. Metal Oxide Nanoparticles

Insulating - Conducting

e.g. TiO_2 , ZrO_2 , WO_3 , Fe_2O_3 ...

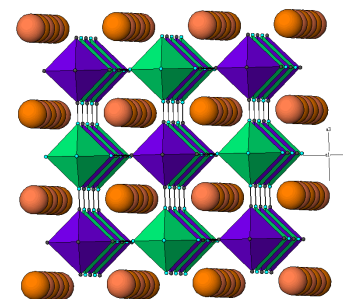
3. Heteropolyacids

e.g. Ammonium Molybdophosphate on PAN



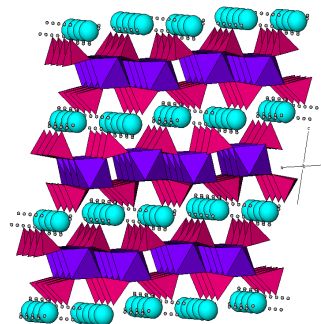
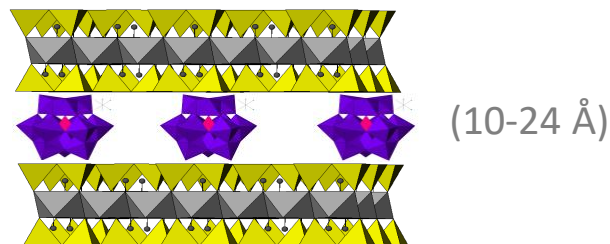
Selective against alkali
ACIDIC – Cs
BASIC – Na

4. Hexacyano Metallates (Ni,Co,Fe)



Extremely selective against alkali
Limited pH range
ACIDIC – Cs
BASIC – Cs

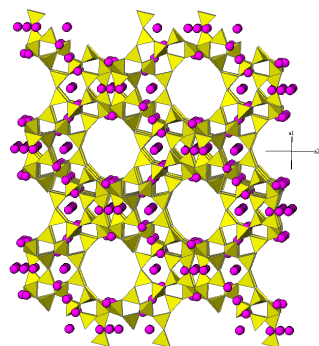
5. Layered Oxides



6. Microporous

(e.g. Zeolites, AlPO's)
 $2 < d < 20 \text{ Å}$

Single molecule template
 for synthesis

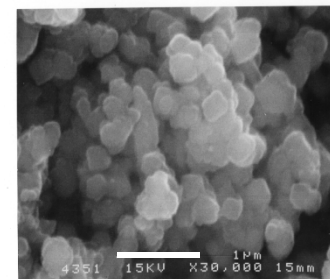
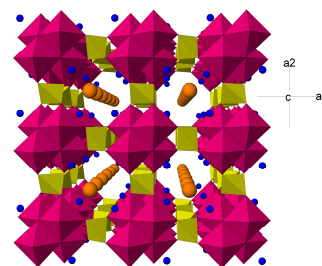


7. Mixed Framework Tunnel Structures

Crystalline Silicotitanate (CST)
 (e.g. ETS-10)
 $2 < d < 20 \text{ Å}$



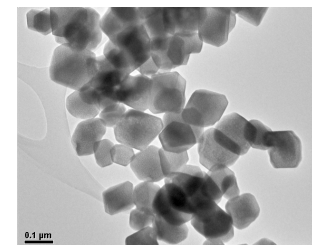
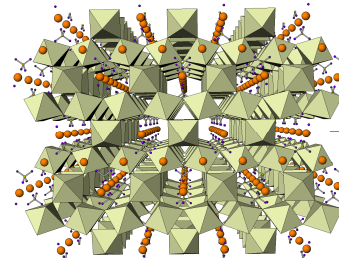
Engineered Crystalline Silicotitanate



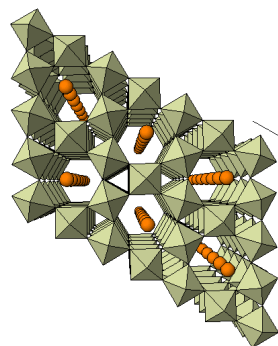
8. Si-doped Antimony Pyrochlore (Si-Sb-pyro)

Only Sr-selective materials in acid
 Good stability
 ACIDIC – Sr
 BASIC – na

Luca *et al.* *J. Mater. Chem.* **2005**, *15*, 564

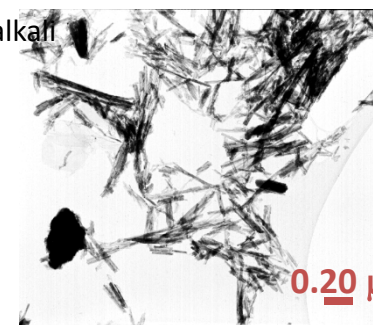


9. Mo-doped Hexagonal Tungsten Bronze (MoW-HTB)

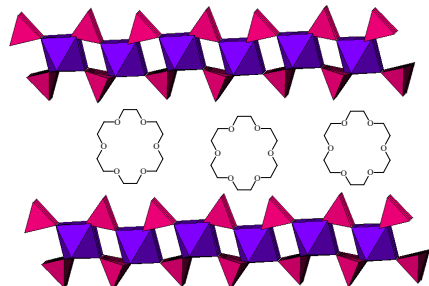


Moderate selectivity against alkali
 Good stability
 ACIDIC – Cs/Sr
 BASIC – na

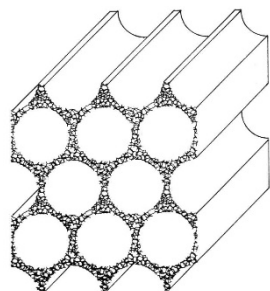
Selective against alkali
 Questionable stability
 ACIDIC – Cs
 BASIC – Cs/Sr



10. Group(IV) Metal Phosphate Intercalation Compounds



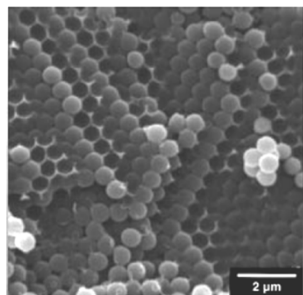
11. Mesoporous Materials



Mesoporous
 $30 < d < 100 \text{ \AA}$
 Supramolecular
 templates

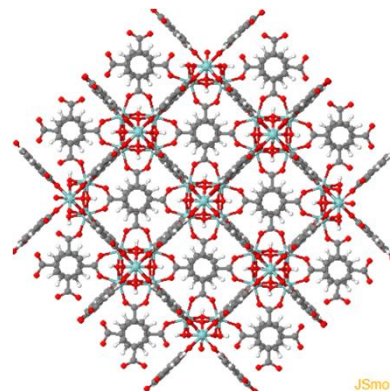
12. Macroporous Assemblies

$100 < d < 1000 \text{ \AA}$

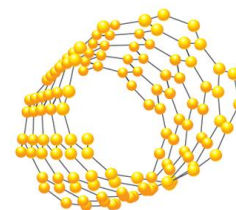
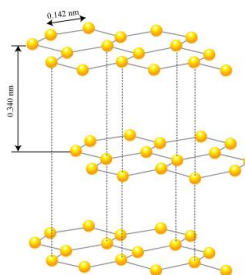


**Microemulsions or Infiltration polymer
 Networks/microspheres**
Holland et al. Chem. Mater. 1999, 11, 795

13. Coordination Polymers



14. Carbons



15. Biomass

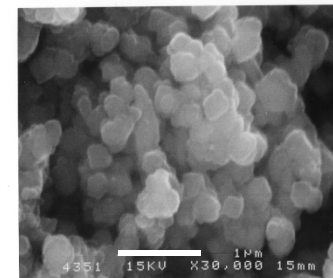
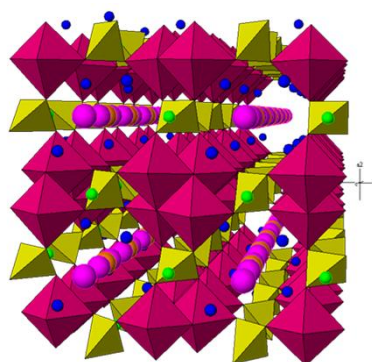
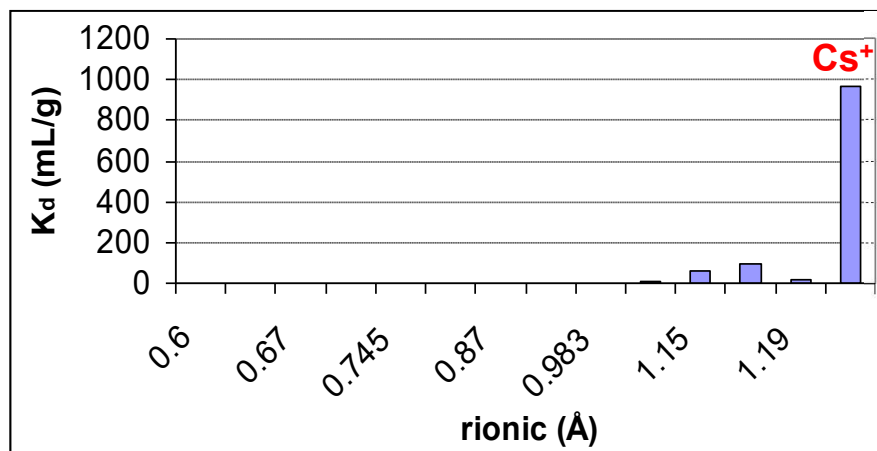


Sugar Cane Bagasse

Spectrum of Selectivity – Selected Examples

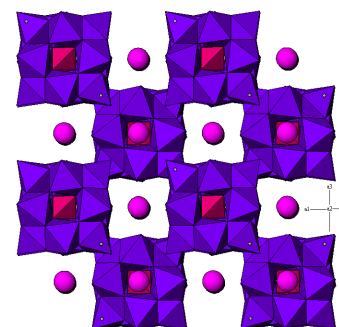
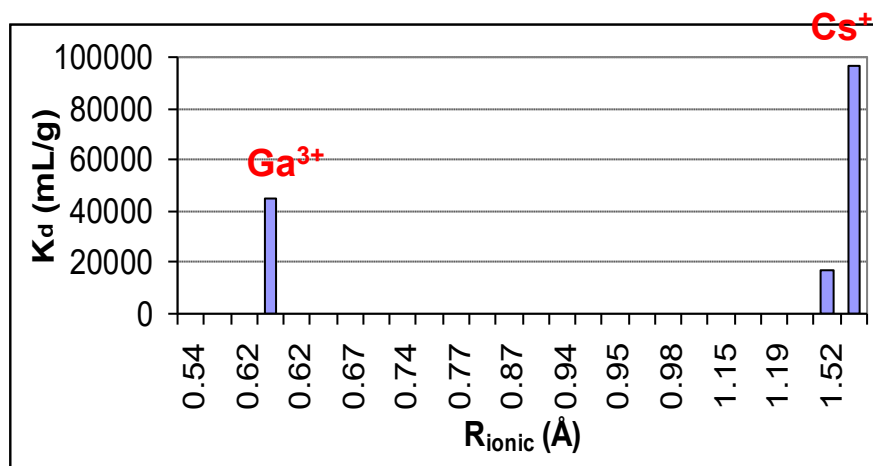
- There are thousands of inorganic materials with channel structures some of which are hydrated and can be prepared very easily.
- The adsorption properties of only a small number have ever been investigated in any detail.

Examples



Titanosilicate
(sitinakite)

Developed as part of a
collaboration between US DOE &
Texas A&M



Polyoxometallate
(dodecatungstophosphate)

Cradle-to-Grave Concept for Radioactive Waste Management

Step 1

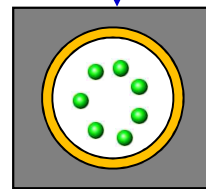
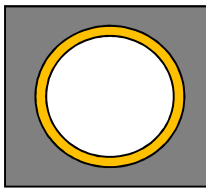
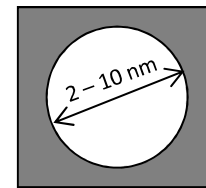
Utilization and/or development of predominantly inorganic & hybrid adsorbents with tailorable porosity and composition (*e.g.* $\text{Zr}_x\text{Ti}_{1-x}\text{O}_2$).

Step 2

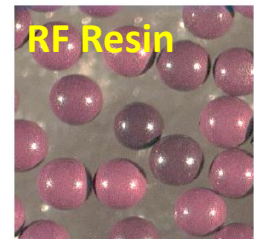
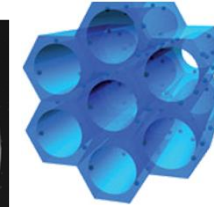
Functionalization of adsorbent surfaces to enhanced selectivity for target species (*e.g.* Polyphosphonic acids).

Step 3

Selective extraction of target species.

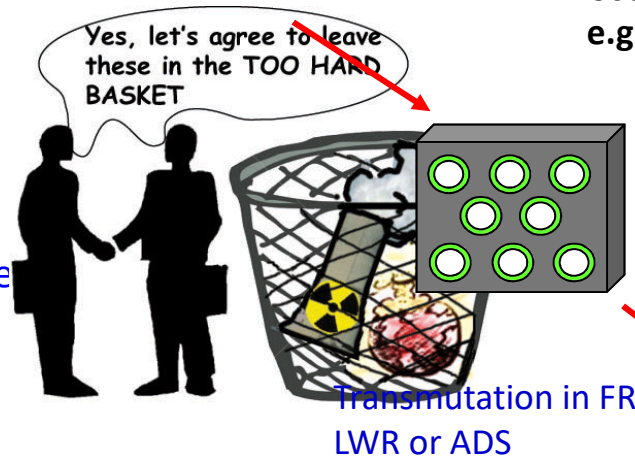


Ceramic with hierarchical porosity



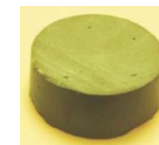
Option 1: Cradle-to-Grave Requirements

- Transparent to neutrons
- High melting point
- Stable in very high radiation field
- Good chemical stability
- High thermal conductivity
- No phase changes
- Recyclable/reprocessable (i.e. soluble in HNO_3)



Option 2

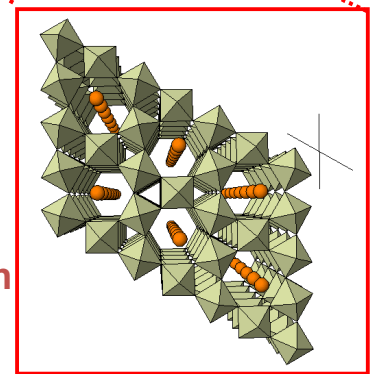
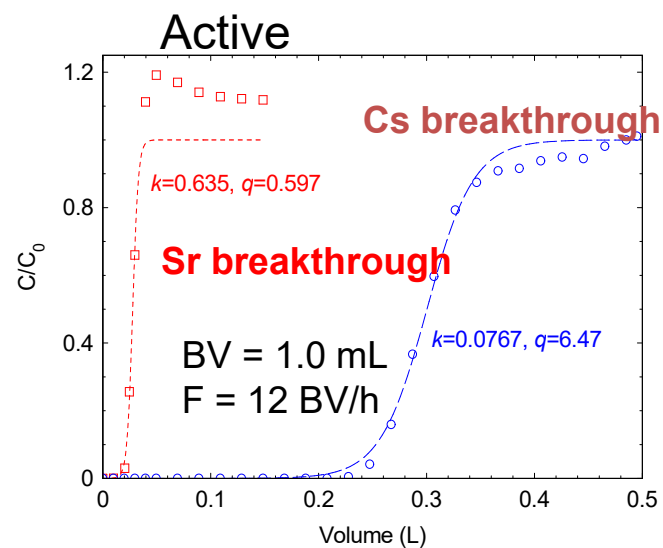
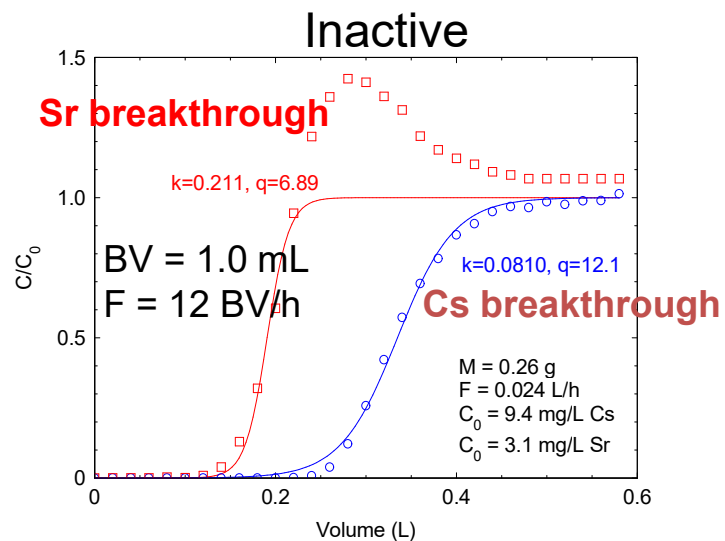
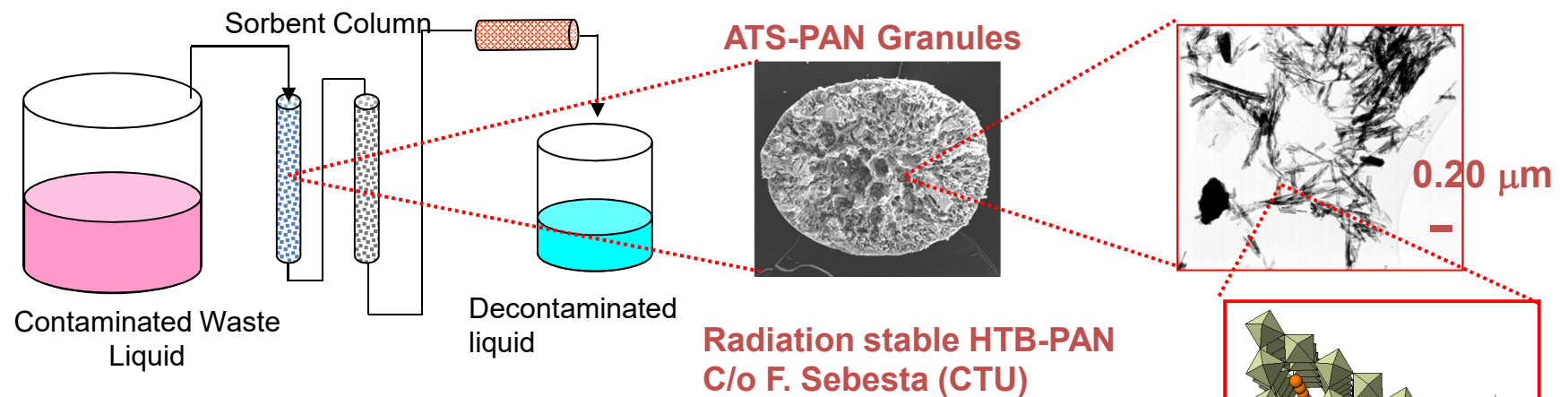
Use as recyclable inert matrix *e.g.* ZrC , SiC , ZrO_2 , Al_2O_3 ...



5 mm Porous Monolith



Demonstration of Radioactive Waste Pretreatment

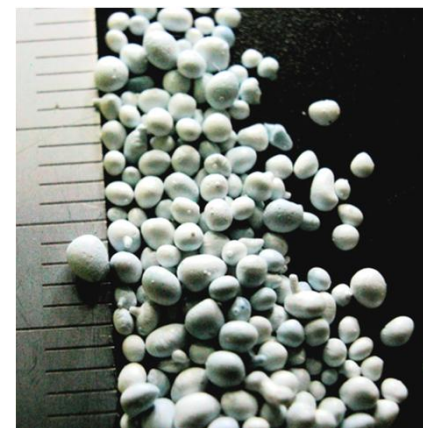
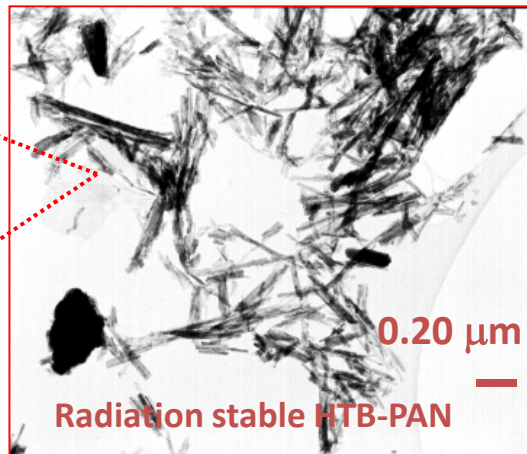
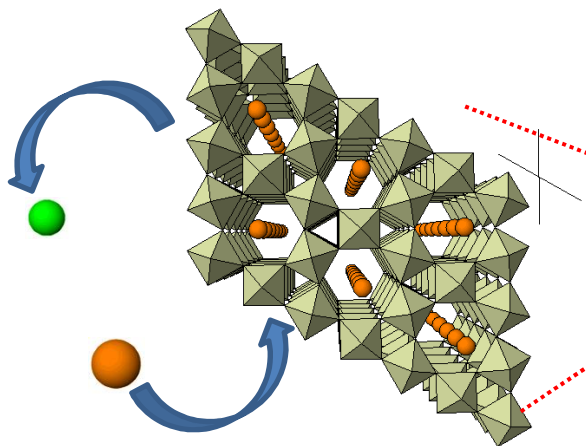


ATS Adsorbent

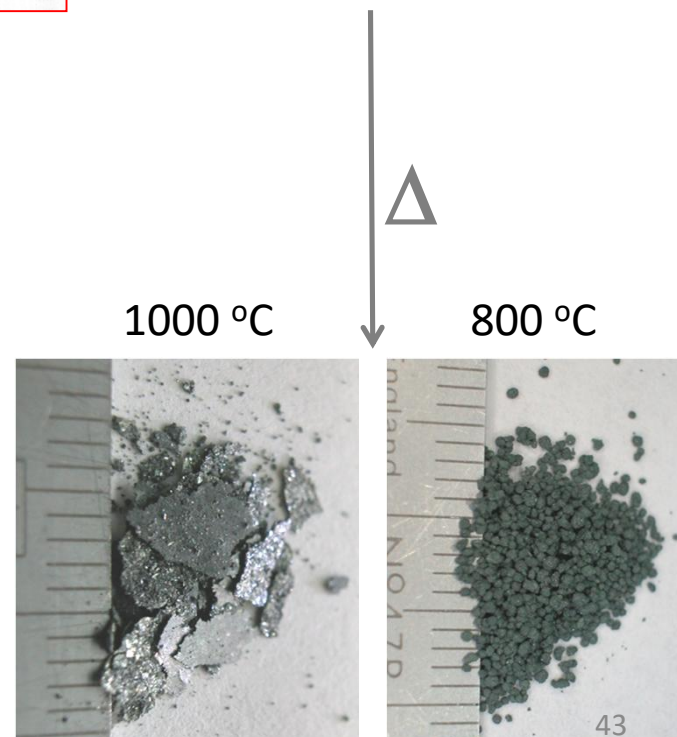
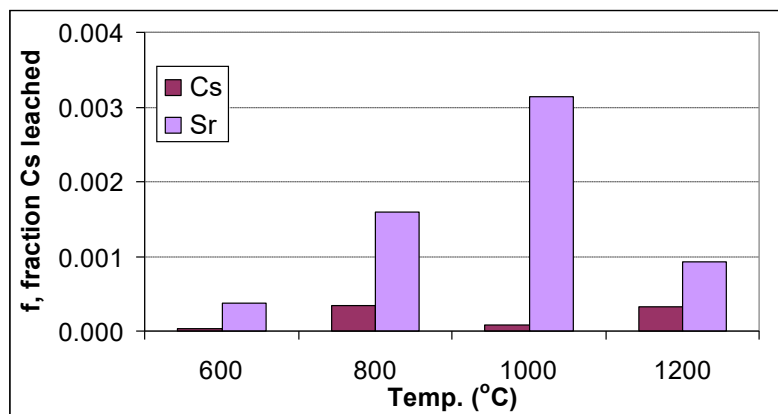
Causes of early breakthrough not clarified

Luca et al. *MRS Proceedings* **2004**, 807, 309
Griffith & Luca *Chem. Mater.* **2004**, 14, 4992
Griffith et al. *Sep. Sci. Technol.* **2005**, 40, 1781

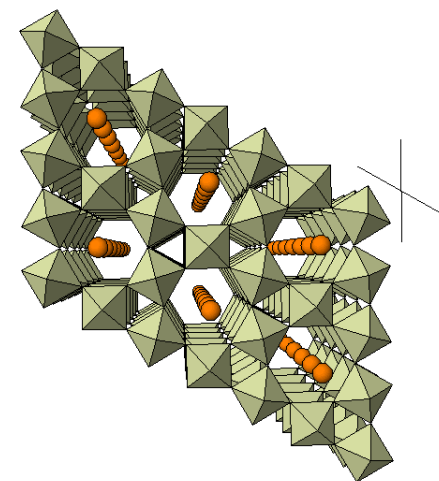
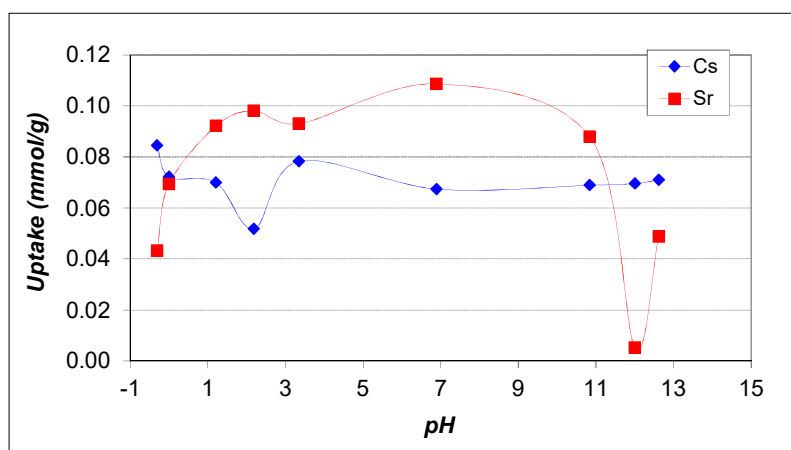
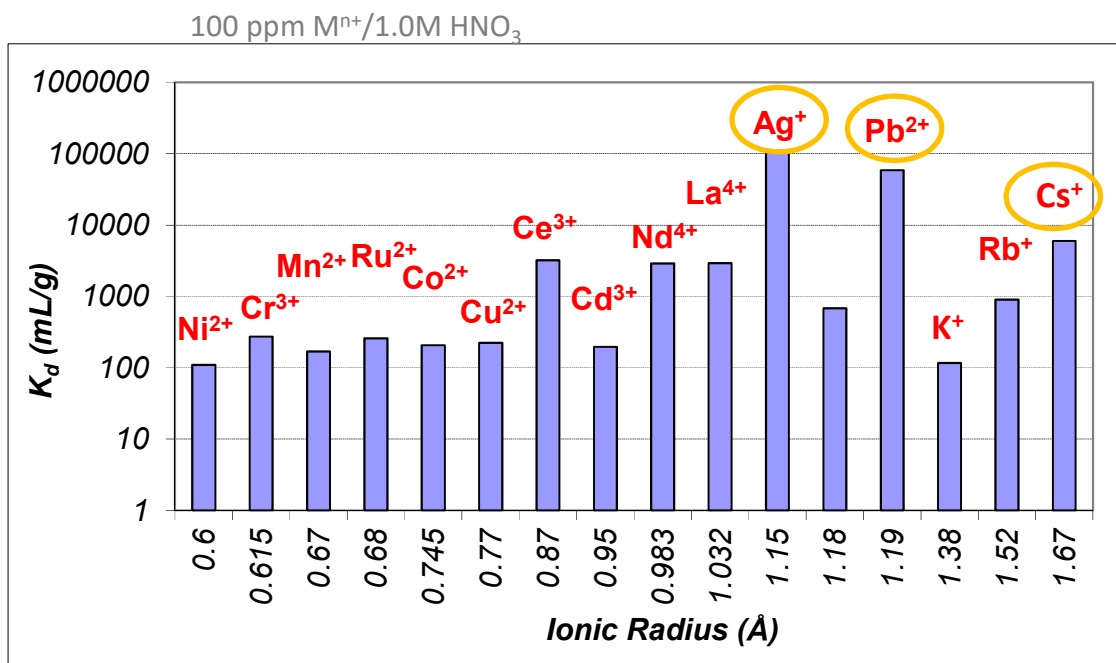
The Cradle-to-Grave Approach to Radwaste Treatment and Conditioning



Griffith & Luca *Chem. Mater.* **2004**, 14, 4992
 Griffith et al. *Sep. Sci. Technol.* **2005**, 40, 1781
 Luca et al. *MRS Proceedings* **2004**, 807, 303
 Luca et al. *J.Nucl. Mater.* **2006**, 358, 139
 Griffith et al. *J.Nucl. Mater.* **2006**, 358, 151
 Luca et al. *J.Nucl. Mater.* **2006**, 358, 164
 Drabarek et al. *J.Nucl. Mater.* **2008**, 384, 119
 Griffith, C.S. et al. *Inorg. Chem.* **2009**, 48, 5648
 Luca et al. *Inorg. Chem.* **2009**, 48, 5663



Selectivity Profile for Tungsten Bronze $\text{Mo}_{0.10}\text{W}_{0.90}\text{-HTB}$



(19) **United States**
 (12) **Patent Application Publication** (10) Pub. No.: **US 2006/0249461 A1**
 Luca (43) Pub. Date: **Nov. 9, 2006**

(54) **INORGANIC ION EXCHANGERS FOR REMOVING CONTAMINANT METAL IONS FROM LIQUID STREAMS**

(52) U.S. CL. 210/688

(75) Inventor: **Vittorio Luca, Narellan Vale (AU)**

(57) **ABSTRACT**

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Medlen & Carroll
 Suite 350
 101 Howard Street
 San Francisco, CA 94105 (US)

(73) Assignee: **Australian Nuclear Science & Technology Organisation, Lucas Heights, NSW (AU)**

(21) Appl. No.: **10/479,540**

(22) PCT Filed: **May 31, 2001**

(86) PCT No.: **PCT/AU01/00645**

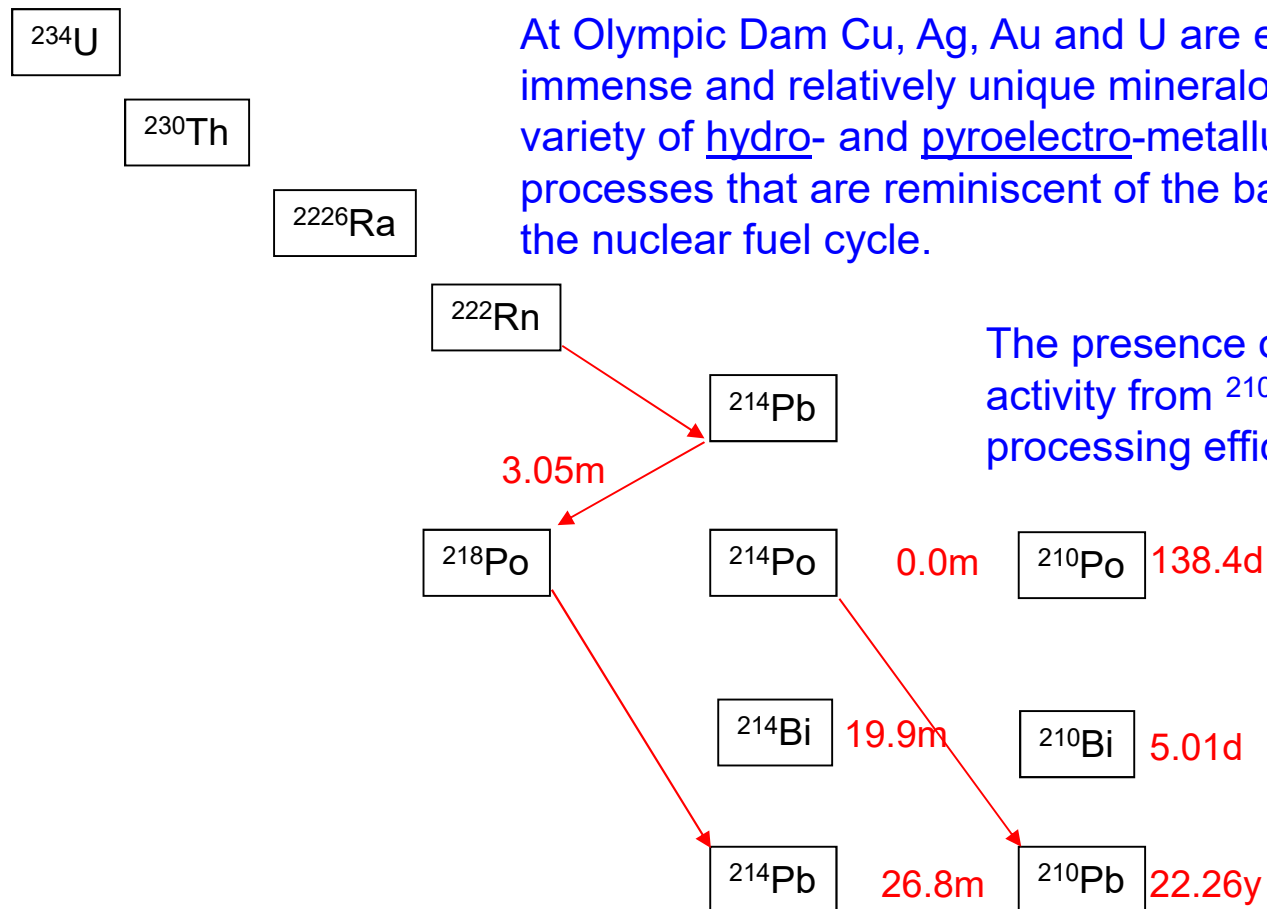
Publication Classification

(51) Int. Cl. **C02F 1/42** (2006.01)

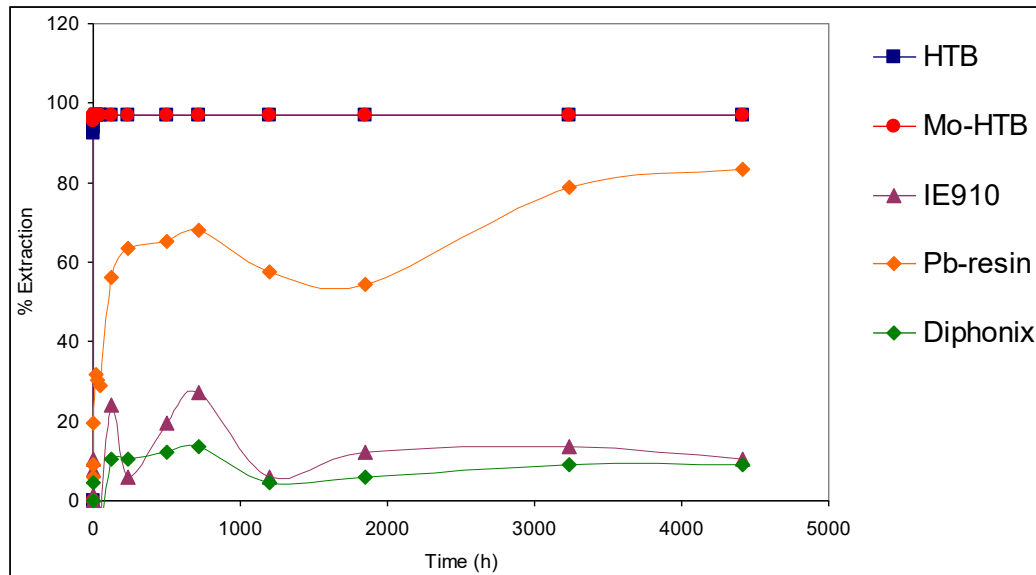
The invention relates to processes and compositions for at least partially removing cations of one or more metals selected from the group consisting of caesium, strontium, lead, silver, transition metals, lanthanides and actinides from a liquid containing the cations. The process comprises contacting the liquid with a sorbent material in an amount and for a time sufficient to at least reduce the concentration of the cations, wherein the sorbent material is a metal oxide composition having the empirical formula $\text{A}_{x-y}[\text{B}_y\text{M}_{1-x}\text{O}_{3+x}] \cdot \text{Z} \cdot \text{H}_2\text{O}$ where M is one or more metals of Group Vb or Vlb of the Periodic Table; A is a cation selected from the group consisting of alkali metals, alkaline earth metals, silver, ammonium, hydrogen and mixtures thereof; n is the charge on the cation A; B is one or more elements selected from the group consisting of W, Zr, Mo, V, Ti, Fe, Ce, Sb, Nb, Mn, Co, Cr, Fe, Ta, Sn and Cu, provided that M and B are different; x represents the quantity of framework charge; y is a number in the range of 0 to about 0.5; Z is a number in the range 0 to 3; and 3+x indicates the oxygen stoichiometry. Preferably, y is greater than zero.

High Selectivity of HTB materials for Pb^{2+} , Ag^{+} suggests other potential applications

BHPB's Olympic Dam Operations – The World's Largest Uranium Mine



Kinetics of Pb Extraction from Copper Electrolyte



Electrolyte Composition

H ₂ SO ₄	1.8 mol/L	Ti	2.2 mg/L
Cu	33 g/L	Al	200 mg/L
Pb	0.66 mg/L	Ca	50 mg/L
Po-210	3.6 Bq/L	Na	154 mg/L
Pb-210	5.3 Bq/L	Zn	290 mg/L
U	17 mg/L	Mg	58 mg/L
Fe	1500 mg/L	Co	70 mg/L
Th	0.3 mg/L	Sn	2.1 mg/L
Ni	0.8 mg/L	As	0.12 mg/L

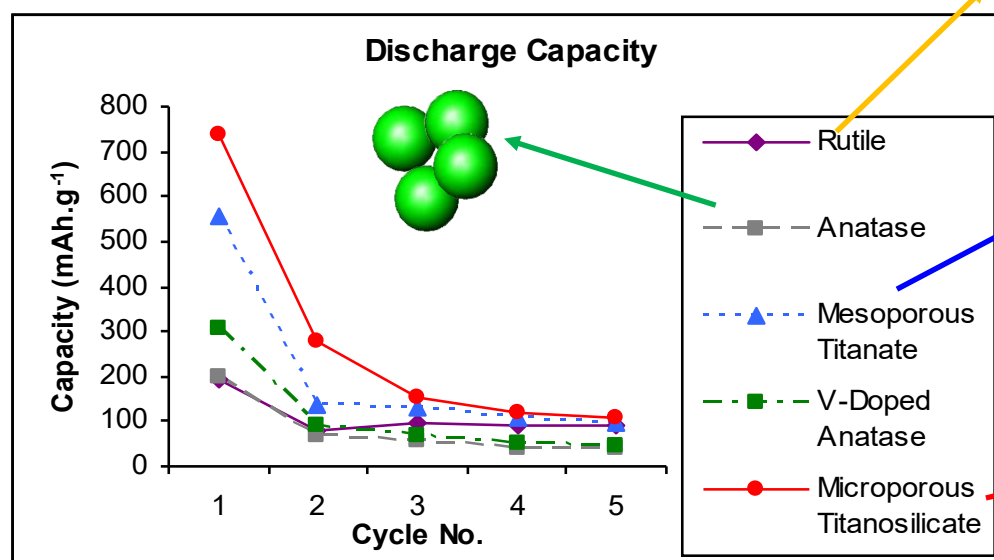
- ²¹⁰Pb ($t_{1/2} = 22.3\text{y}$) & ²¹⁰Po ($t_{1/2} = 138.4\text{d}$) uptake parallels that of inactive Pb
- >95% Pb extraction for tungstate sorbents throughout 6 month experiment
- Tungstate sorbents are stable in electrolyte solution
- Mo-HTB extract >95% Pb after only 15 mins - fast kinetics

Secomb et al. *Radiochimica Acta* 2007, 95, 727

Nanostructured Titanates Investigated as Anode Materials in Li-ion Batteries

Crystalline and nano-particulate anatase

Luca et al., NMR and X-ray Absorption Study of Lithium Intercalation in Micro- and Nanocrystalline Anatase. *Chem. Mater.* **1999**, 11, 2089.

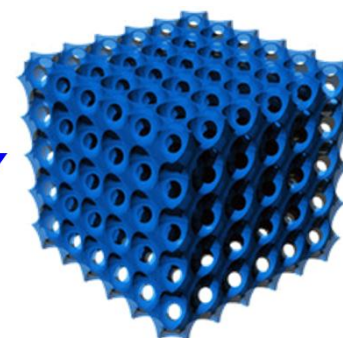


Rutile nanoparticles

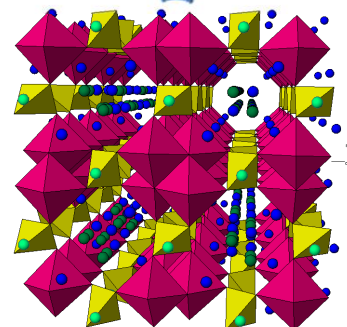
Milne et al., Crystallite Size Dependence of Lithium Intercalation in Nanocrystalline Rutile. *J. Phys. Chem. C* **2009**, 113, 12983.



Mesoporous Titanates



Microporous Titanosilicates



Milne et al., Lithium Intercalation into the Titanosilicate Sitinakite. *Chem. Mater.* **2006**, 18, 3192.

From Cs-selective ion-exchanger to Li-ion battery electrode materials



Current CNEA Projects

Álvarez, Reibel

Thermal treatment of polymeric
spent IX resins

Banchi, Castro, Rodriguez

Induction plasma treatment of pyrolysis gases

Civitate

Materials for adsorption of $^{14}\text{CO}_2$, ^{129}I ...

Curi ...

Materials for ^{137}Cs & ^{90}Sr selective
extraction

*Microporous titanium & zirconium
silicates*

Tejada ...

Materials for *f*-element separations
($\text{LN}^{3+}/\text{AN}^{3+}$)

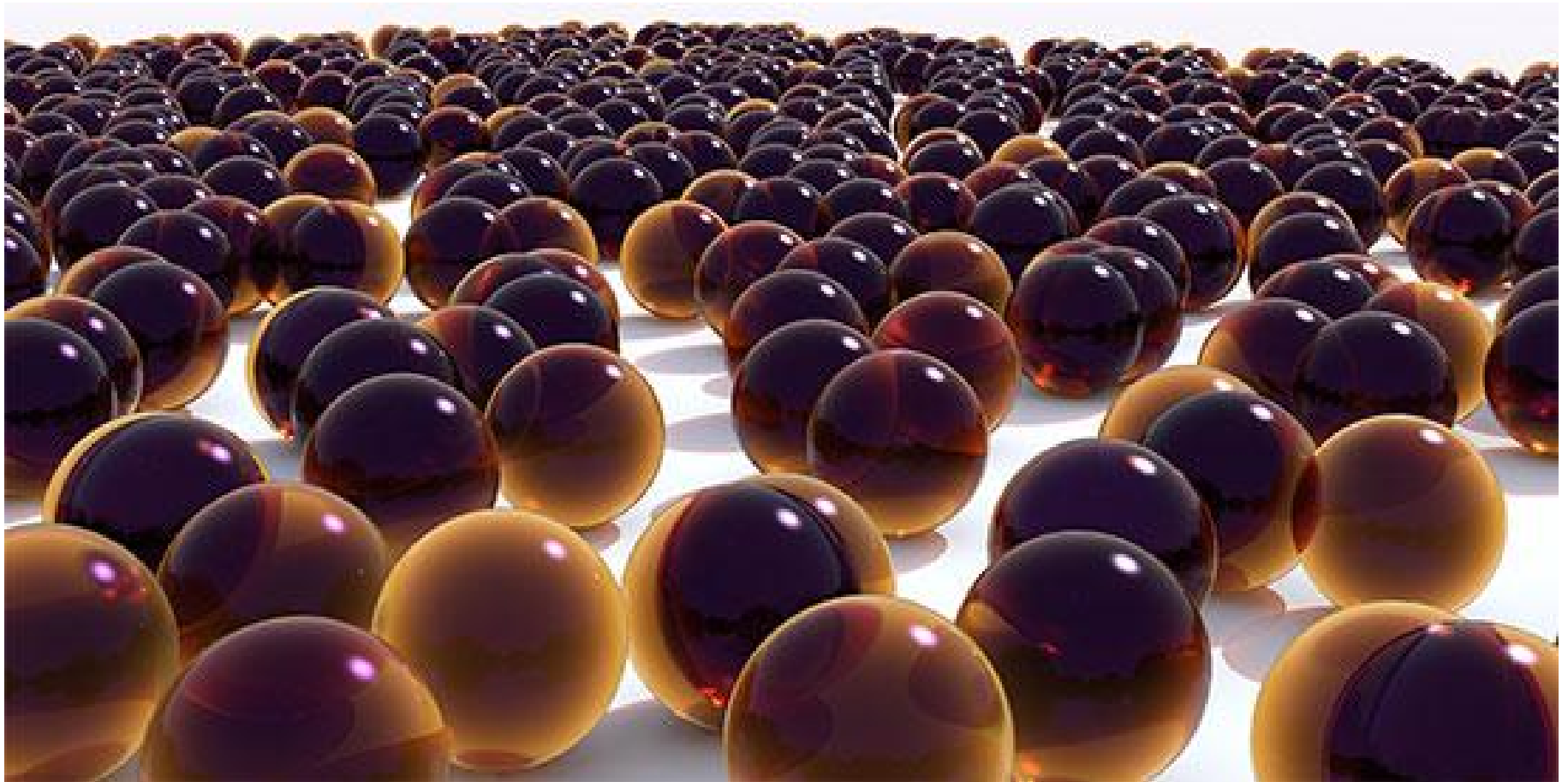
*Coordination polymers, carbons,
lignocellulosic biomass*

Dos Santos, Manzini, Telleria, Ramos

New target materials for clean production of ^{99}Mo .

Carbons, carbides, oxides ...

Treatment and Conditioning of Spent Resins



Processes Considered

Direct Immobilization

Polymer (*e.g.* Socodei, France) ★
Cement (OPC-based, Geopolymer) ★
Bitumen (*e.g.* Sweden) ★
Ceramicrete, Duralith, SiAl, Cast Stone



Pyrolysis (300 ± 50 °C)

- Simple process
- Volume reduction
- Flameless
- Versatile
- Ultra stable products
- Minimal 2^o wastes

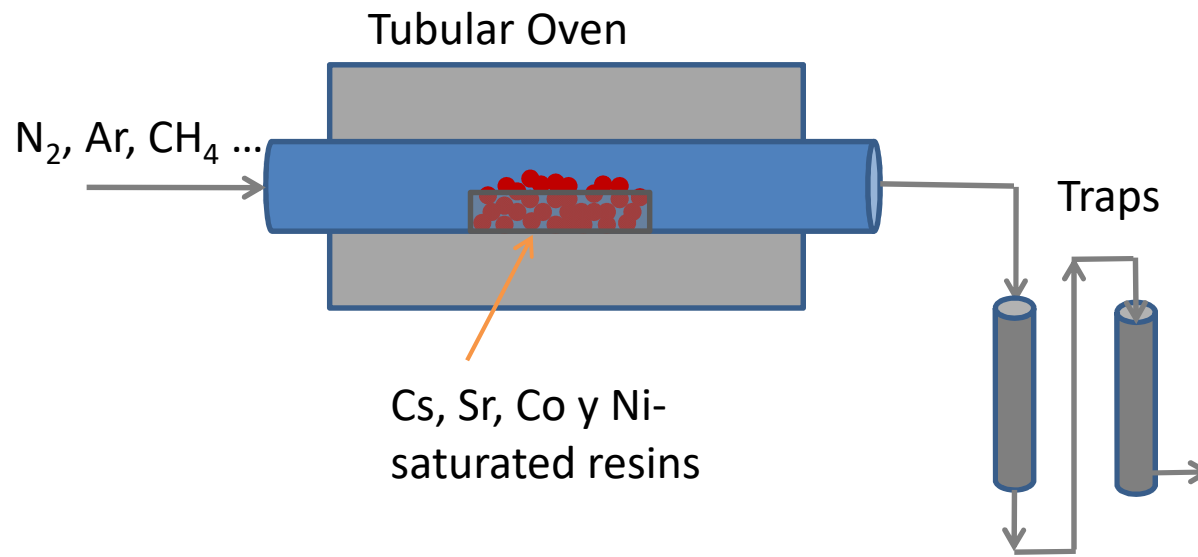
Destructive Treatment

Pyrolysis (*e.g.* Belgoprocess) ★
FBSR (*e.g.* THOR, USA) ★
Incineration
Vitrification
Thermal Plasma
Microbiological
Wet Oxidation
Acid Digestion
Molten salt
Catalytic oxidation
Supercritical Water Oxidation
Electrochemical Oxidation
Thermochemical methods
HIP

Treatment and Conditioning of Spent IX Resinas

- Is it possible to develop a low temperature pyrolysis process (<350 °C) that results in a volume reduction and at the same time confines that entire radionuclide inventory within the matrix that is generated?
- What are the relations between processing parameters and the structure microstructure and the chemical properties of the products generated?

Experimental Setup

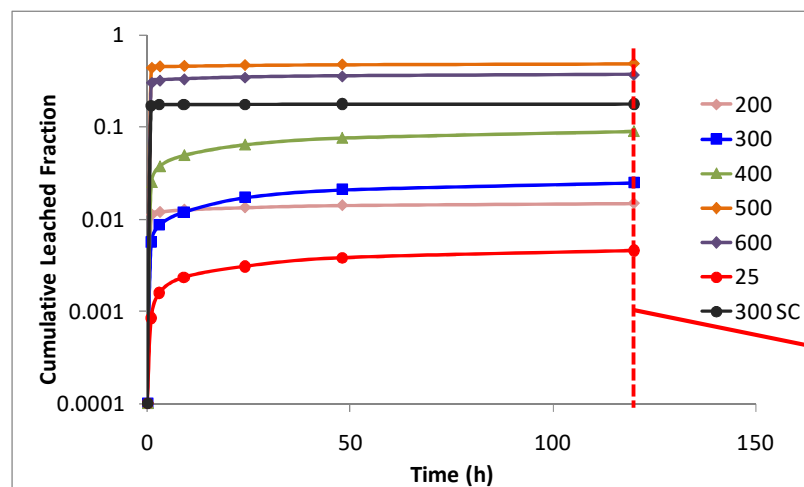
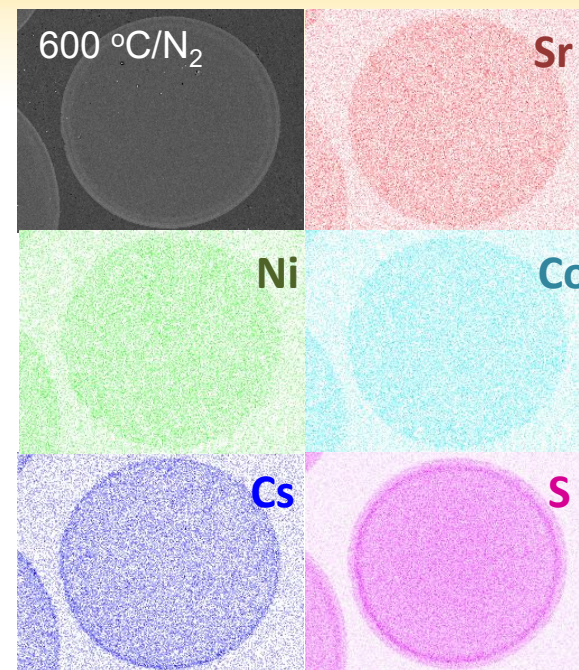
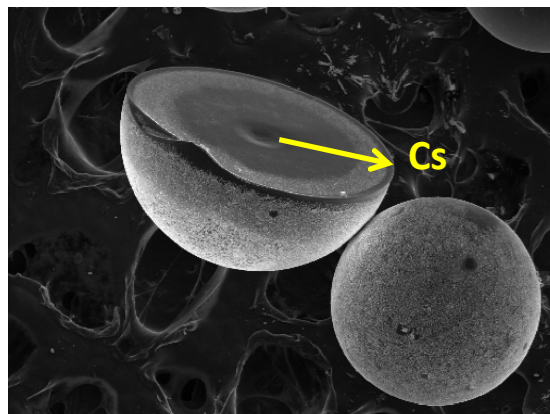


Thermal Treatment of Cation Exchange Resins

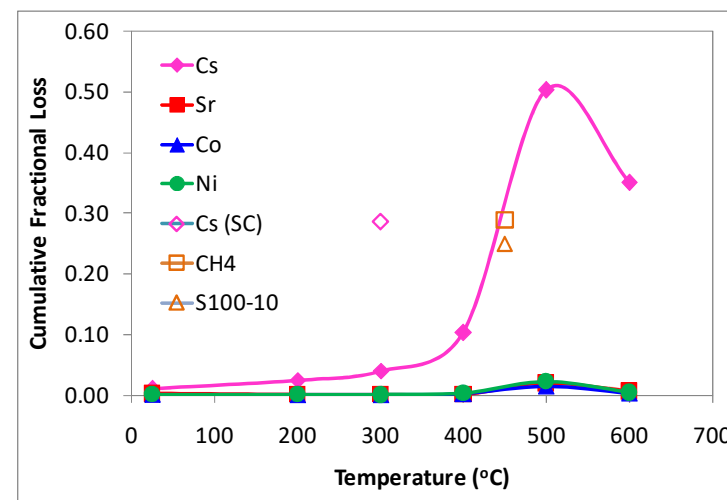
Cation Exchange Resin (Lewatit® MonoPlus S100H)



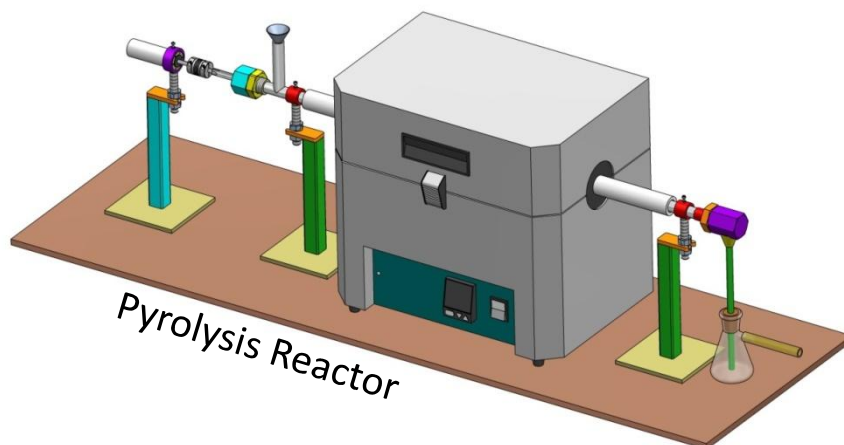
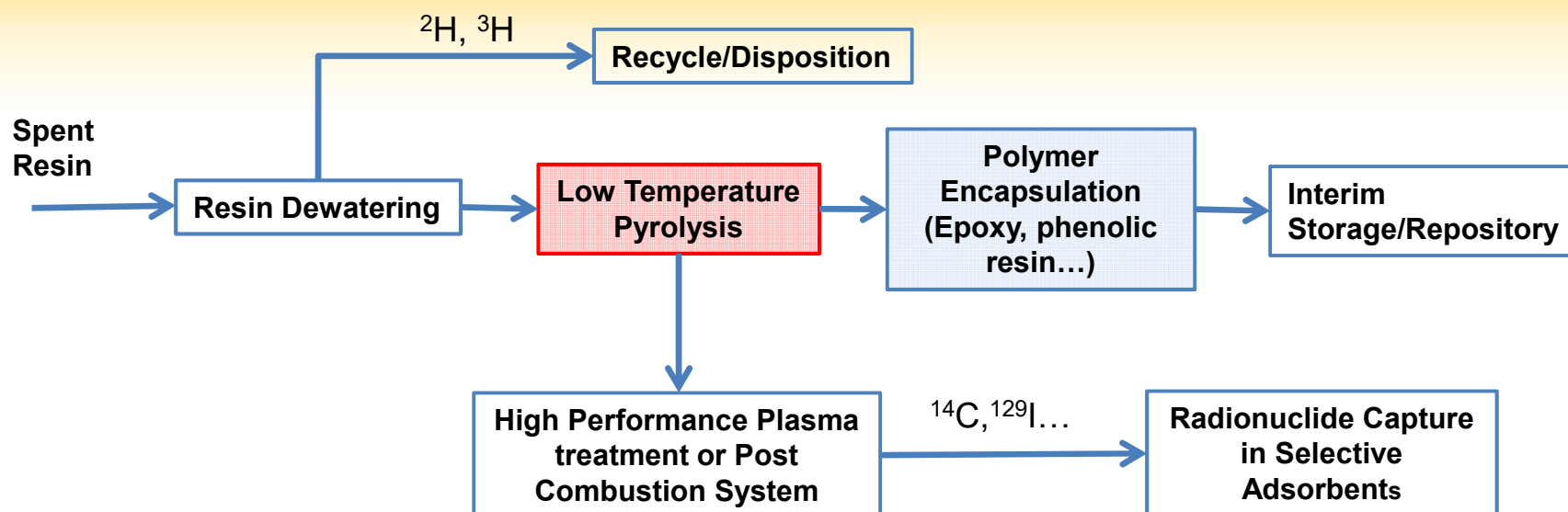
Δ, N_2
 $\xrightarrow{10\text{ }^\circ\text{C/min}}$



Luca et al. J. Nucl. Mater. 2012, 424, 1



Simplified Process Flow Sheet



Induction Plasma System

Bench-Scale Demo → Pilot Scale at Kg/h Throughput (cold and then hot)

Luca et al., Low temperature pyrolysis of simulated spent anion exchange resins. *J. Env. Chem. Eng.* **2017**, 5, 4165

Closed Fuel Cycle - Fuel Recycling

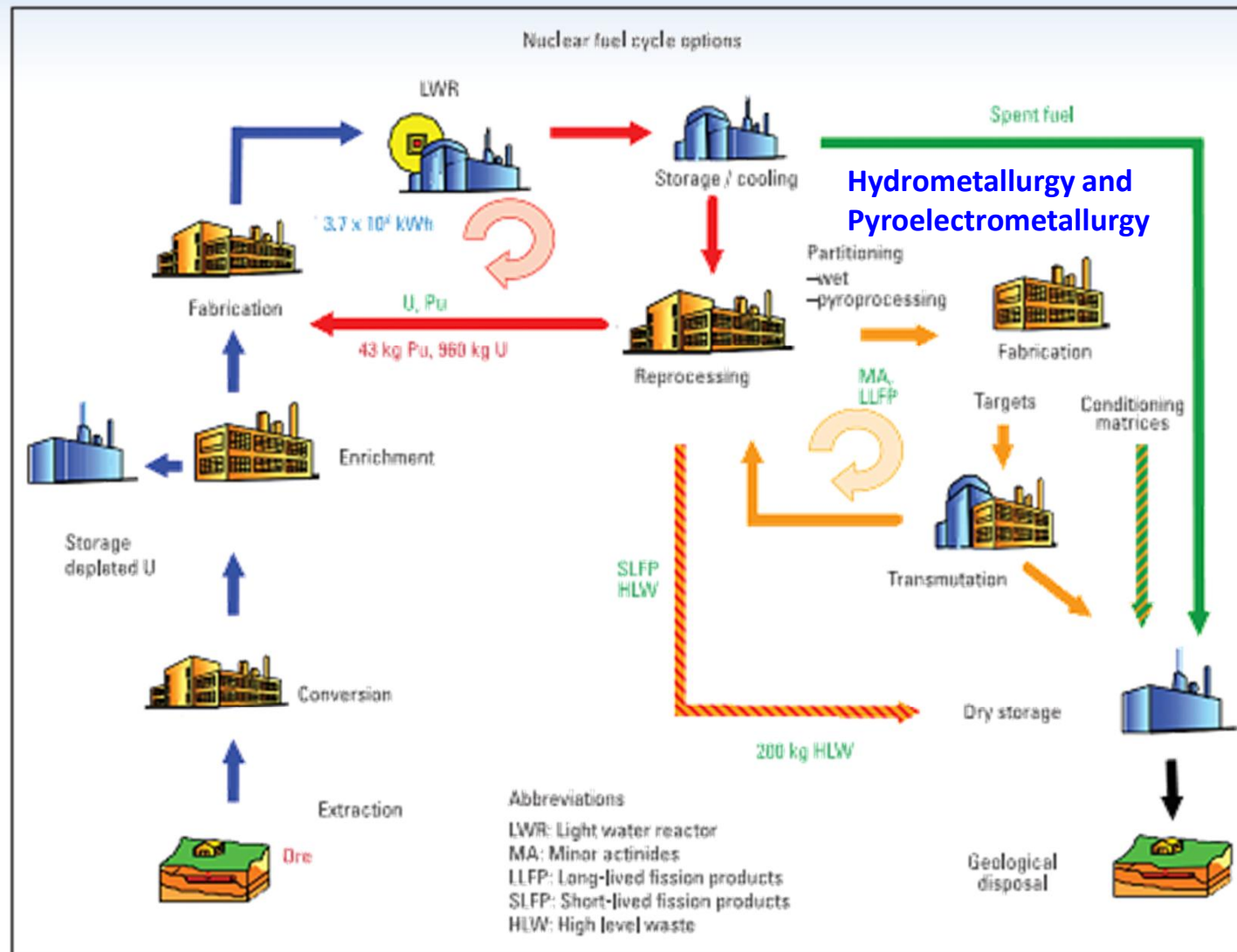


FIGURE 3. Diagram of the nuclear fuel cycle, showing the various options: once-through; conventional closed cycle; advanced closed cycle with partitioning and transmutation. Resultant high-level waste streams are also indicated.

f-element Separations – Major Objectives

1. Separate 5f-actinides from 4f-trivalent lanthanides
2. Separate trivalent minor actinides from trivalent lanthanides
3. Intra-lanthanide separations

Spin Off

57 La Lanthanum 138.9055	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
89 Ac Actinium (227)	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

57 La Lanthanum 138.9055	58 Ce Cerium 140.116	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
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89 Ac Actinium (227)	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)
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92 U Uranium 238.0289	93 Np Neptunium (237)	94 Pu Plutonium (244)
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95 Am Americium (243)	96 Cm Curium (247)
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92 U Uranium 238.0289

93 Np Neptunium (237)

94 Pu Plutonium (244)

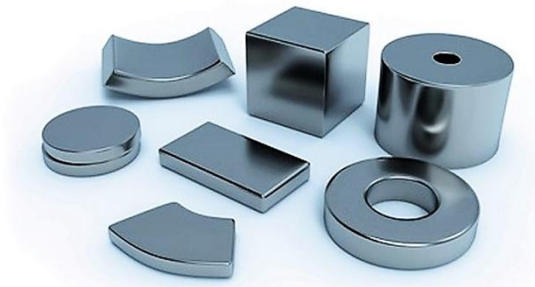
95 Am Americium (243)

96 Cm Curium (247)

Possible Spin-off: Rare-Earth Element Separations for Clean Energy Applications

V15

- Investigate adsorption or lanthanides (rare-earth elements) as surrogates of the trivalent actinides.
- REE elements are of interest in their own right because of the potential use in renewable energy technologies.
- Move to major actinides and then minor actinides if the systems allow to investigate lanthanide-minor actinide separation



Cradle-to-Grave Concept for Radioactive Waste Management

Step 1

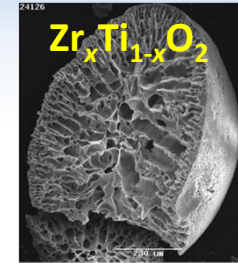
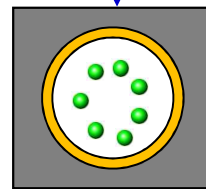
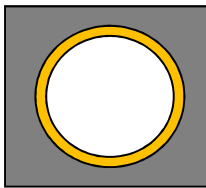
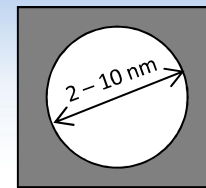
Utilization and/or development of predominantly inorganic & hybrid adsorbents with tailorable porosity and composition (e.g. $Zr_xTi_{1-x}O_2$).

Step 2

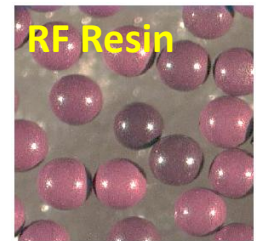
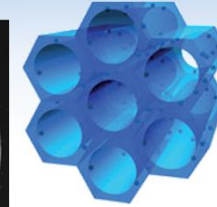
Functionalization of adsorbent surfaces to enhanced selectivity for target species (e.g. Polyphosphonic acids).

Step 3

Selective extraction of target species.

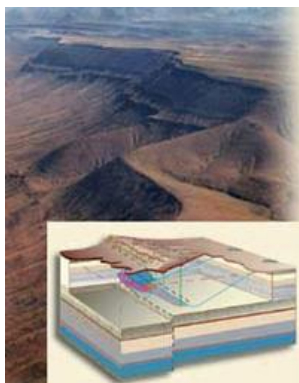


Ceramic with hierarchical porosity

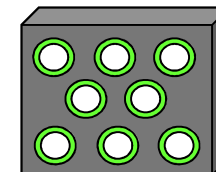
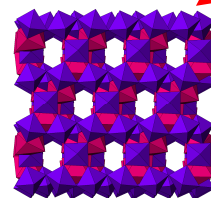


Option 1: Cradle-to-Grave

Simple conversion to dense highly insoluble ceramic, glass or other

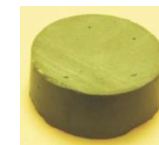


Deep underground repository disposal



Transmutation in FR, LWR or ADS

Option 2
Use as recyclable inert matrix
e.g. ZrC , SiC , ZrO_2 , Al_2O_3 ...



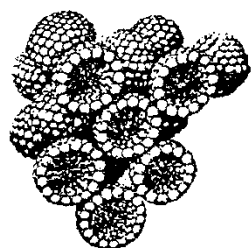
5 mm Porous Monolith



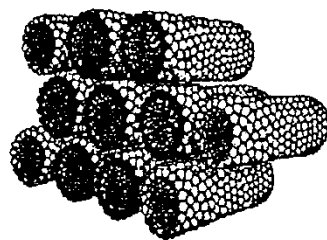
Mesoporous Materials

A Platform for Designing Materials
for Metal Ion Separation
Sequestration/Immobilization

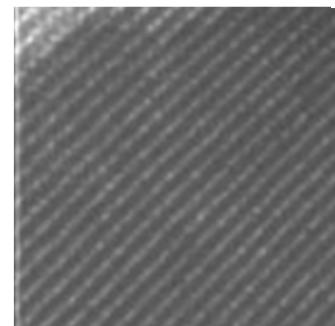
Advantages:



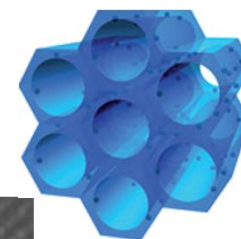
**Supramolecular
templates**



Versatility
Ready Deployability
Stability?

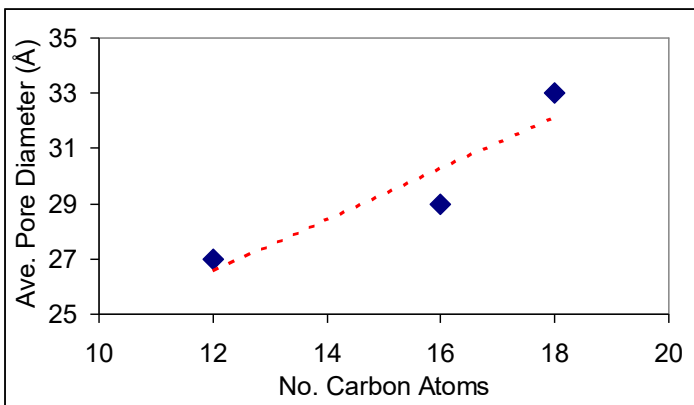
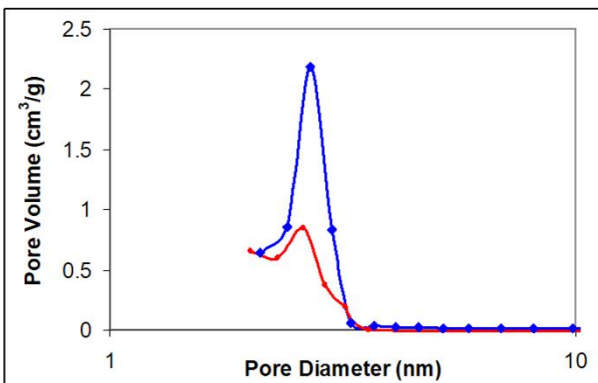
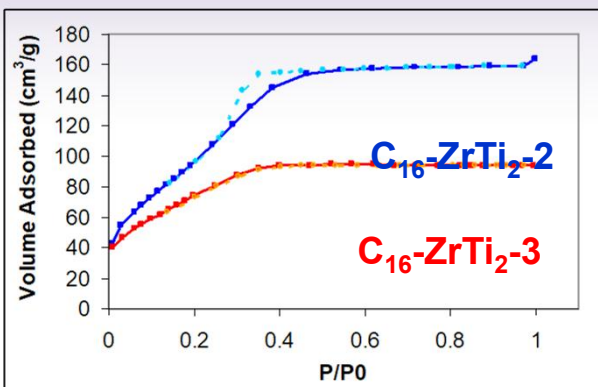


Mesoporous Metal Oxides
 $30 < d < 100 \text{ \AA}$

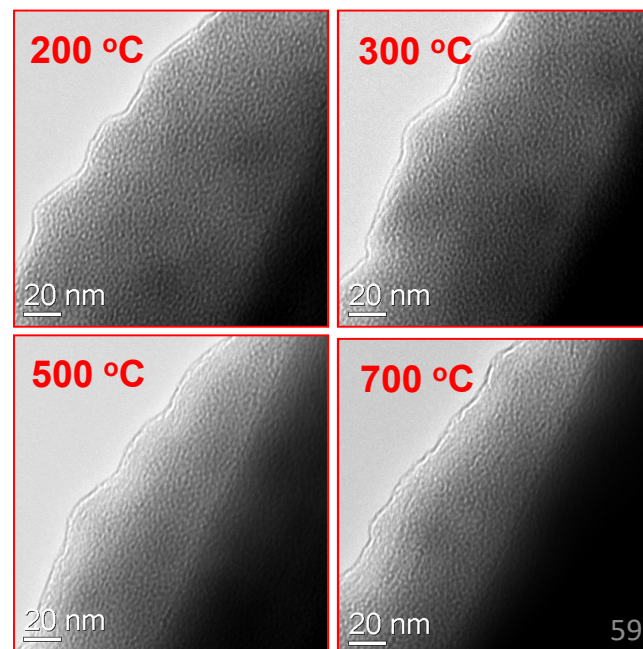
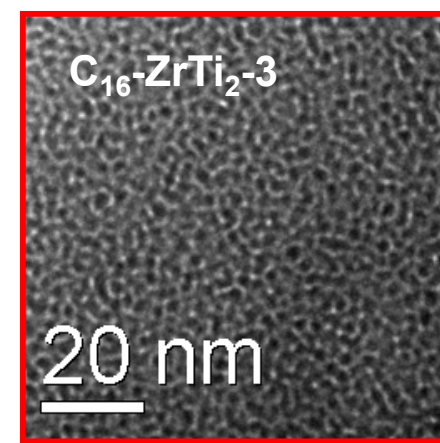
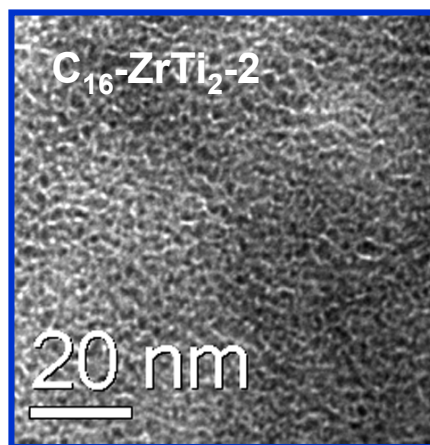


Objective: To produce via simple, scalable, synthetic methodologies, a robust and tailorable (porosity, selectivity, capacity, composition) semiconductor adsorbent (ion exchange) platform that is suitable for nuclear and other applications and which offers prospects for ultimate disposal or recycle.

$\text{Zr}_{0.33}\text{Ti}_{0.66}\text{O}_2$ - Carboxylate Mesophase Xerogels



Luca et al. *Micro Meso. Mater.* **2007**, 103, 123



Features of Mesoporous $\text{Zr}_{0.33}\text{Ti}_{0.66}\text{O}_2$ system

- Uniform porosity (monomodal)
- Homogenous distribution of Zr and Ti
 - Very high thermal stability
- Conversion to zirconolite possible
- Able to be produced directly in column-ready bead form

Luca et al. *Micro. Meso. Mater.* **2007**, 103, 123

Griffith et al. *Langmuir* **2008**, 24, 12312

Sizgek et al. *Langmuir* **2008**, 24, 12323

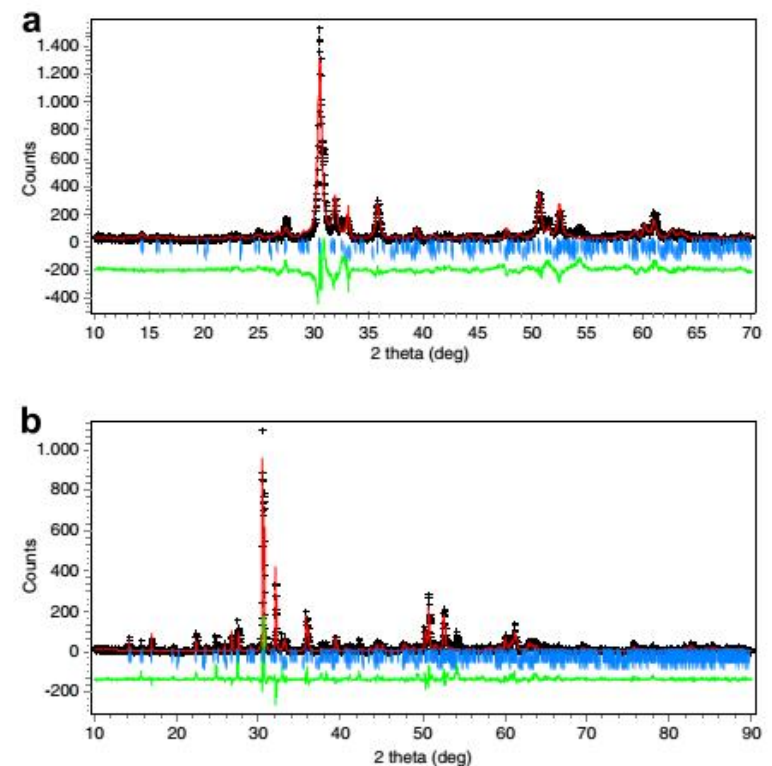
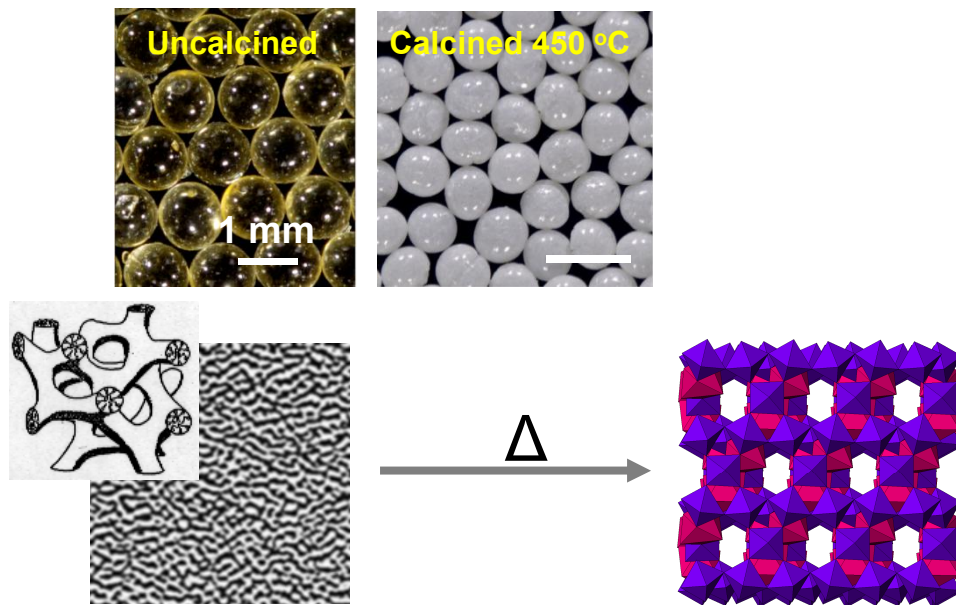
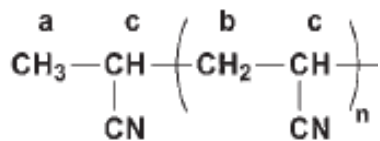


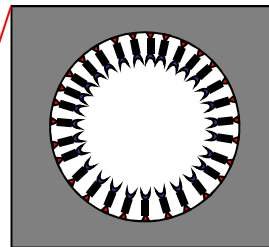
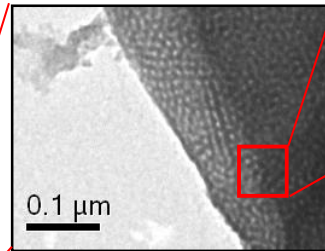
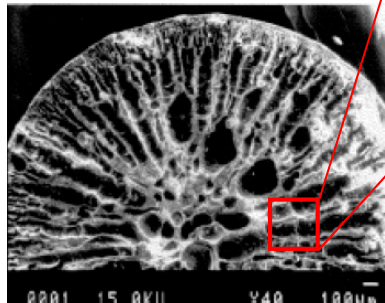
Fig. 11. Refined X-ray diffraction pattern of Ca^{2+} -impregnated $\text{C}_{16}\text{-ZrTi}_2\text{-2}$ mesophase calcined at (a) 900 °C and (b) 1300 °C.

Strategies for Engineering Hierarchical Porous Beads

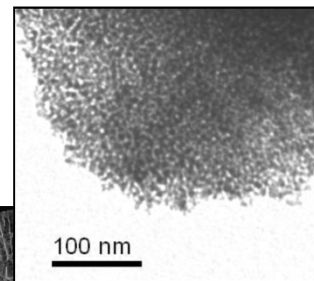
1. Hard template – infiltration of pre-formed polymer bead having suitable macroreticular structure with metal oxide precursor solution under controlled conditions and including additional mesopore forming porogen.
2. One pot – all chemistry at one time in an engineering friendly scalable process.



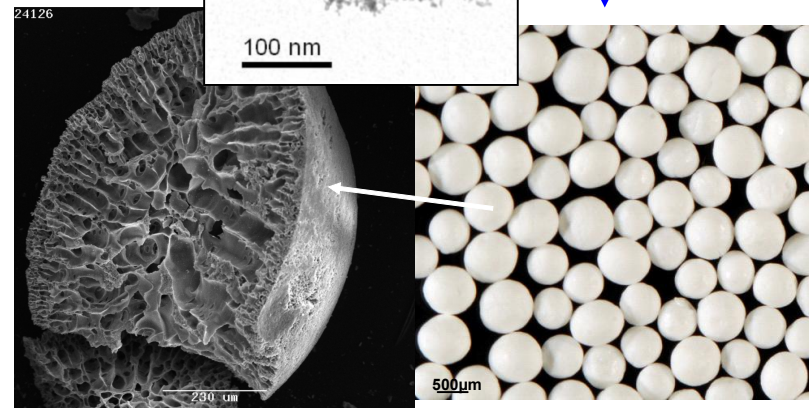
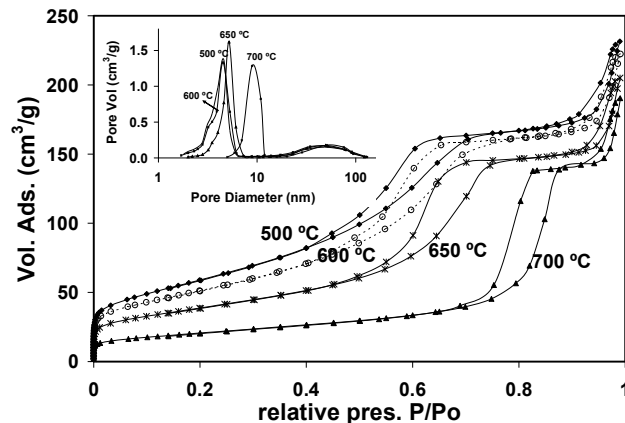
Preformed PAN Bead



Sizgek et al. *Langmuir* 2009, 25, 11874



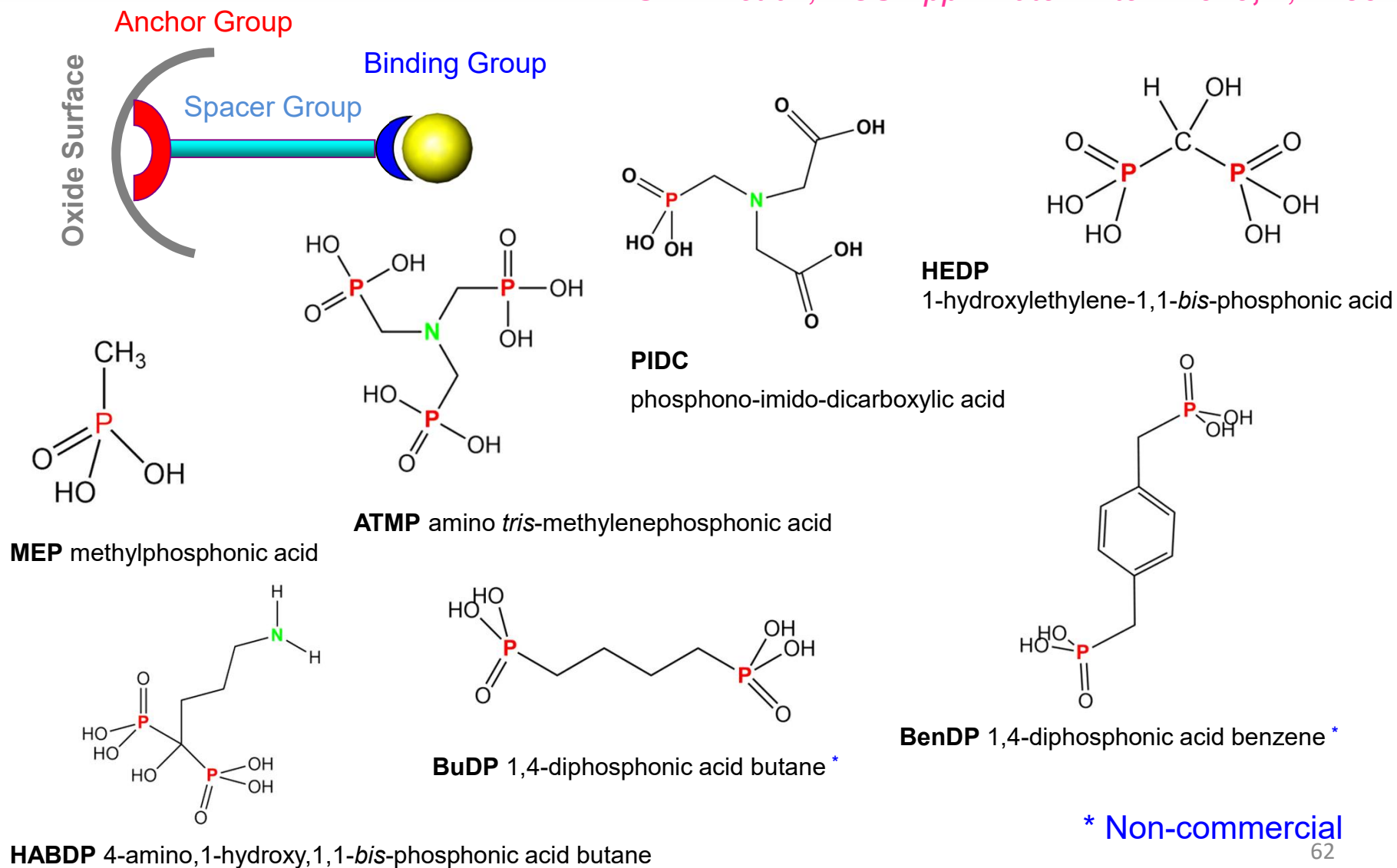
Moon et al. *J. Rad. Nucl. Chem.* 2000, 246, 299



Robust hierarchical ZrTi₂ beads having radial macroporosity and disordered mesoporosity

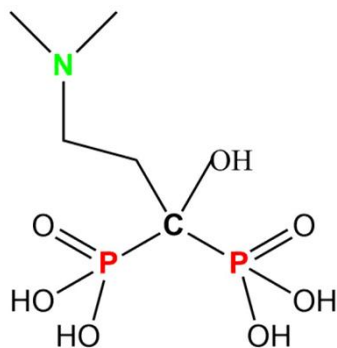
Functionalization and Hydrolytic Stability of Mono and Poly-Phosphonate Functionalized Mesoporous $\text{Zr}_{0.33}\text{Ti}_{0.66}\text{O}_2$ Xerogel Powders and Beads

Griffith *et al.*, *ACS Appl. Mater. Inter.* **2010**, 2, 2436

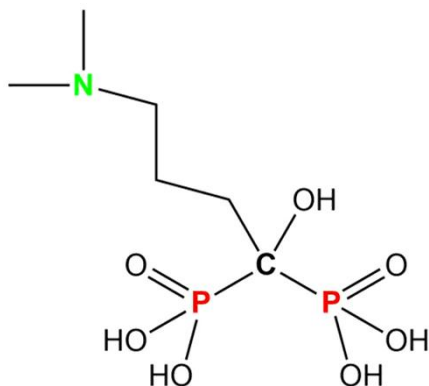


Bisphosphonic Acids

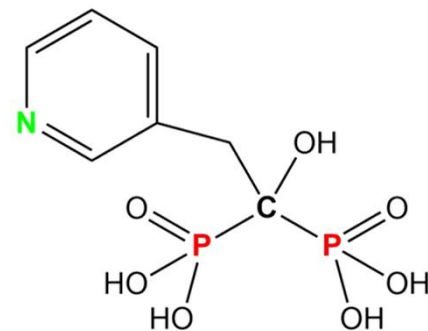
Pamidronic Acid



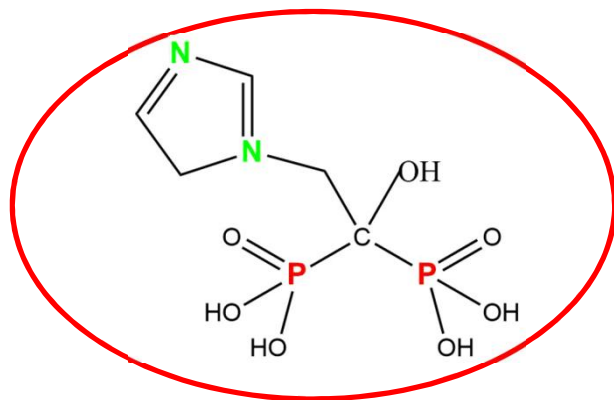
Aledronic Acid



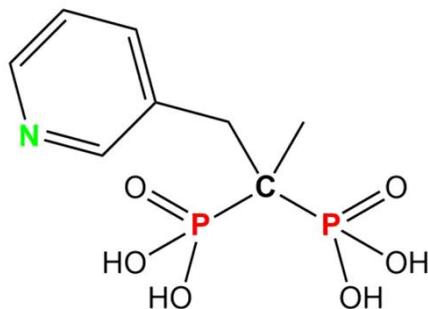
Risedronic Acid



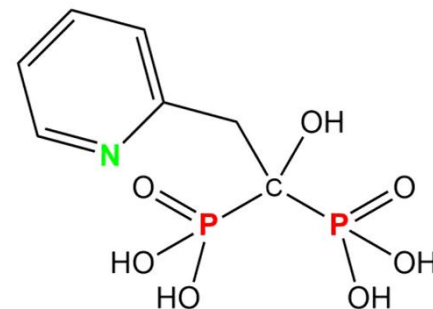
Zoledronic Acid



Deoxyrisedronic Acid



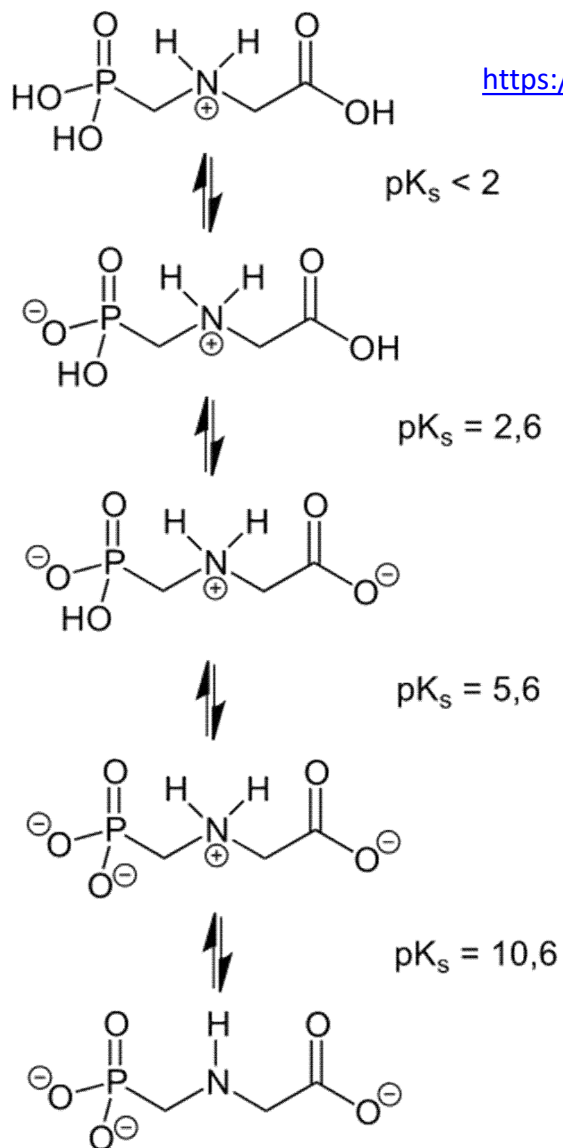
Ortho-risedronic acid



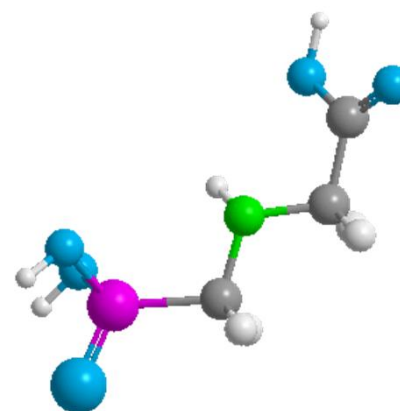
NMR Investigations of the Static and Dynamic Structures of Bisphosphonates on Human Bone: a Molecular Model

Sujoy Mukherjee,[†] Yongcheng Song,[‡] and Eric Oldfield^{*,†,‡}

Glyphosate – A Multifunctional Ligand



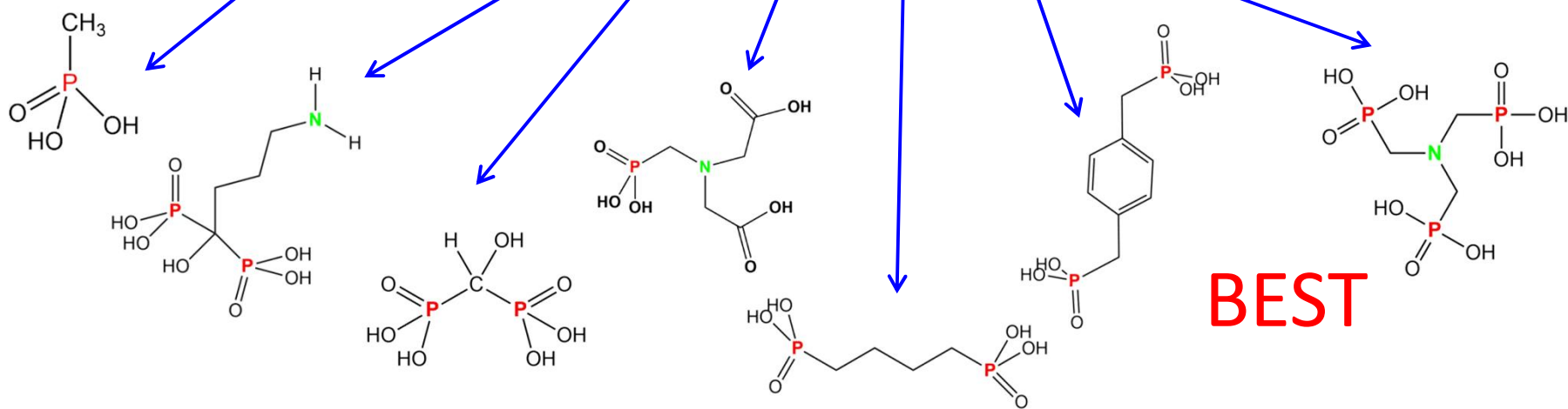
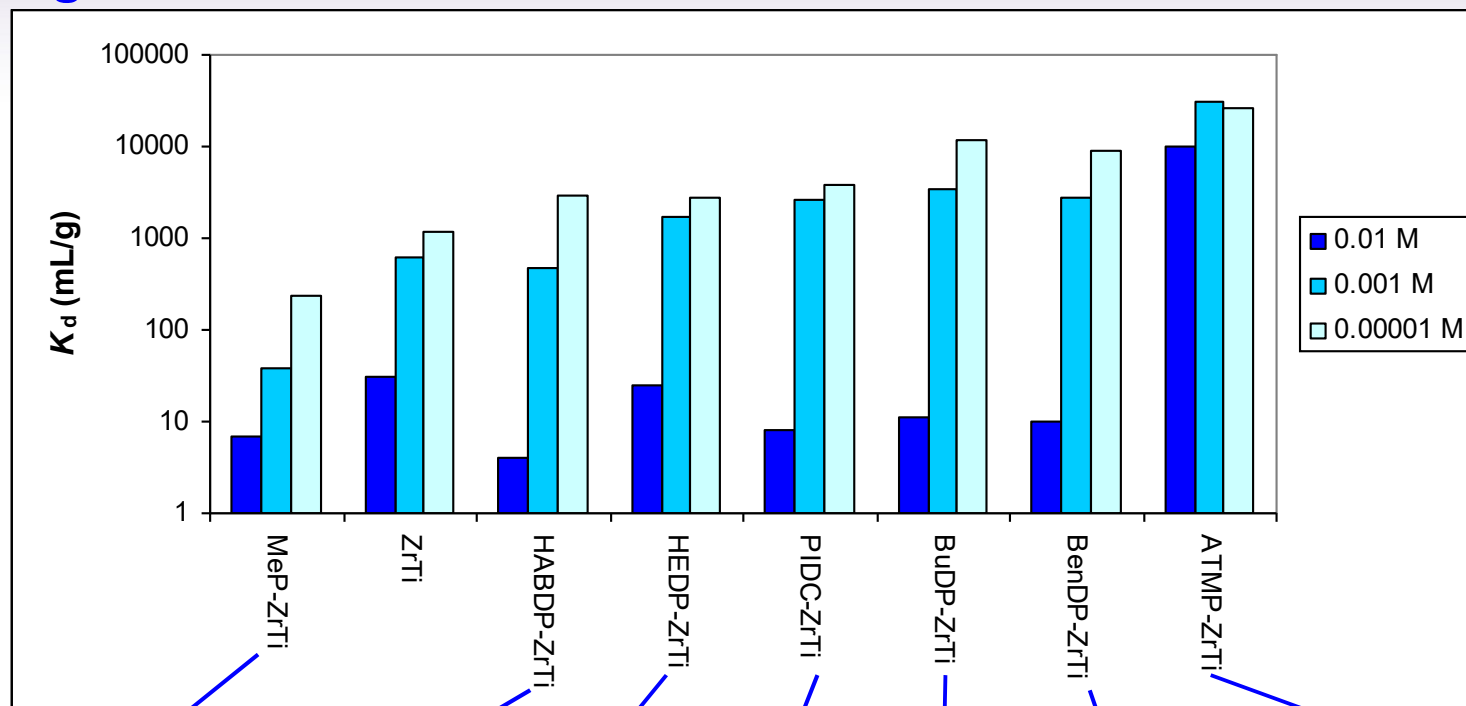
<https://en.wikipedia.org/wiki/Glyphosate>



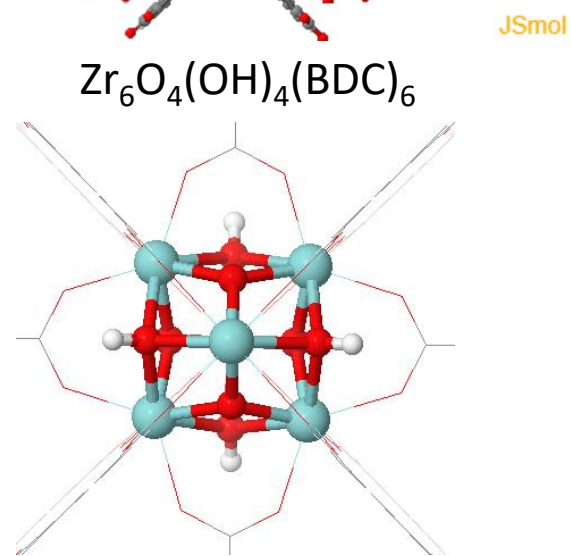
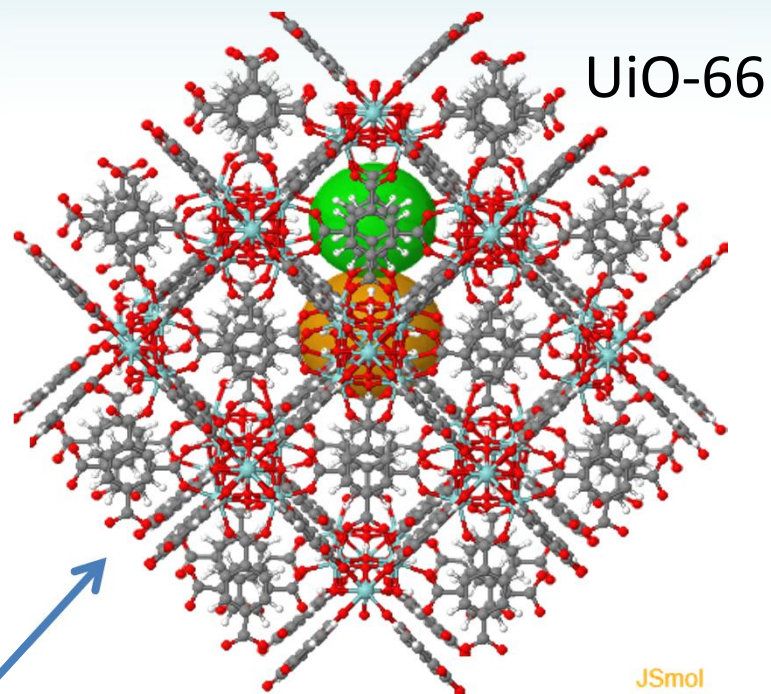
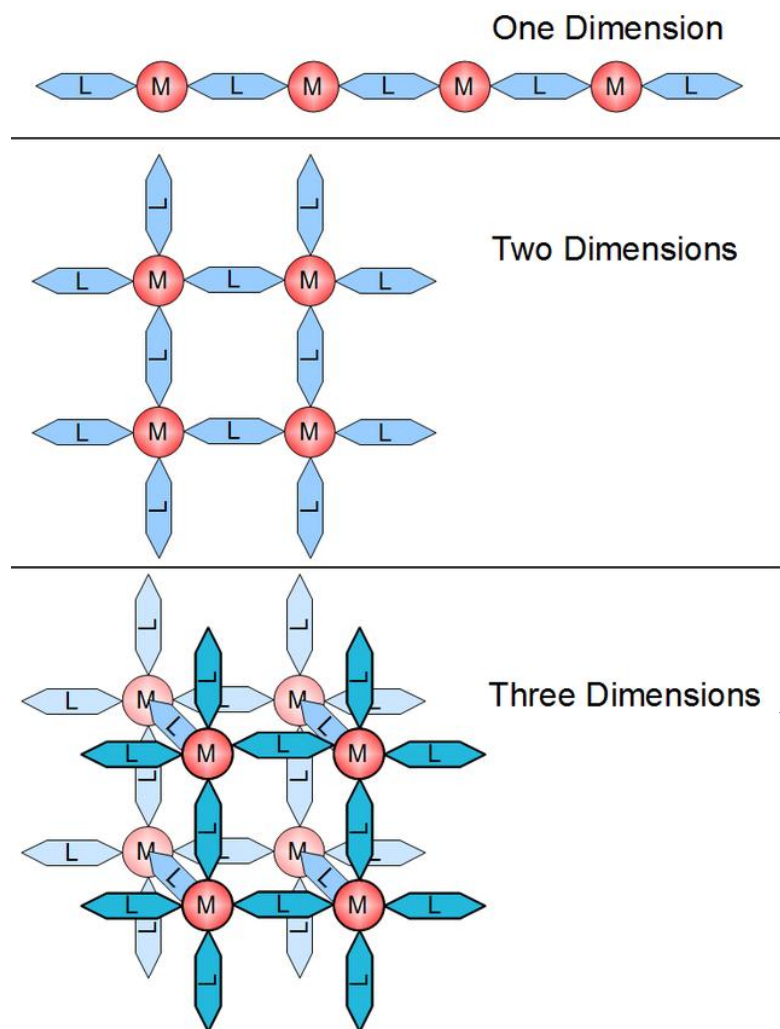
N-(phosphonomethyl)glycine



Carrier-free K_d ($^{153}\text{Gd}^{3+}$) (mL/g) on Mesoporous $\text{Zr}_{0.33}\text{Ti}_{0.66}\text{O}_2$ Xerogels

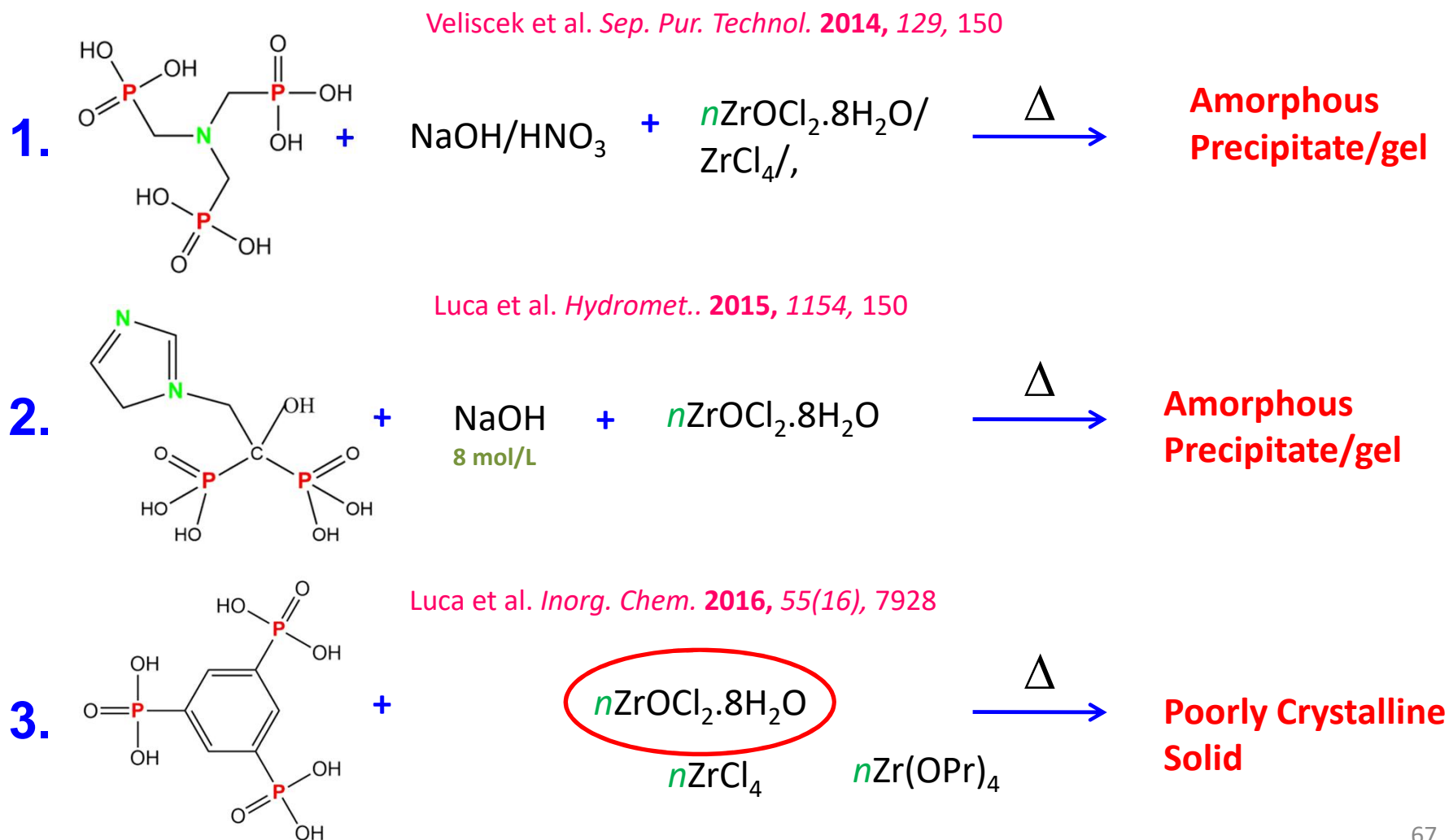


Coordination Polymers for f-element Separations

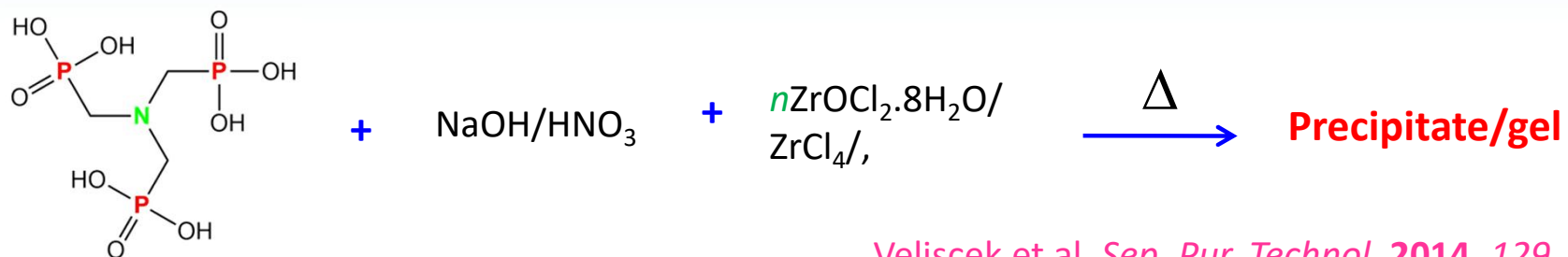


Preparation and Adsorption Properties of Zirconium (IV) – Polyphosphonate Coordination Polymers

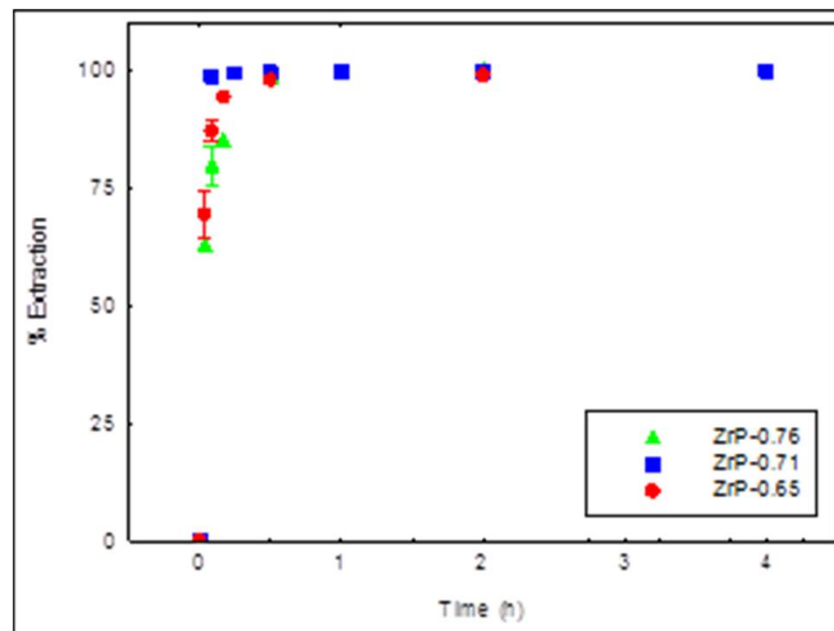
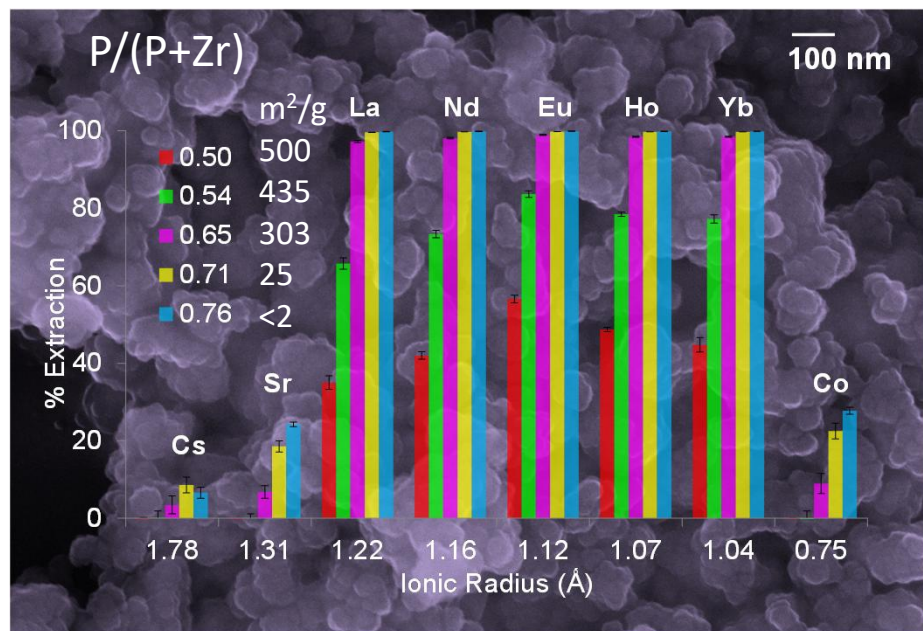
Zr(IV)-based MOFs are expected to be highly insoluble



1. Preparation and Adsorption Properties of Zirconium (IV) – ATMP



Veliscek et al. *Sep. Pur. Technol.* **2014**, 129, 150



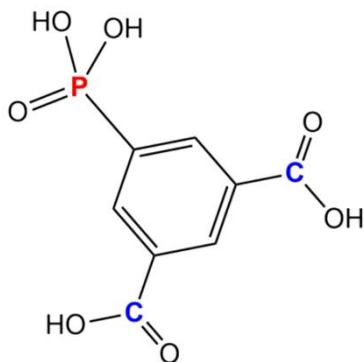
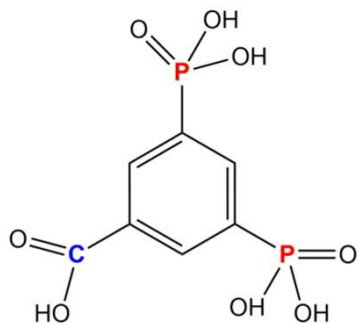
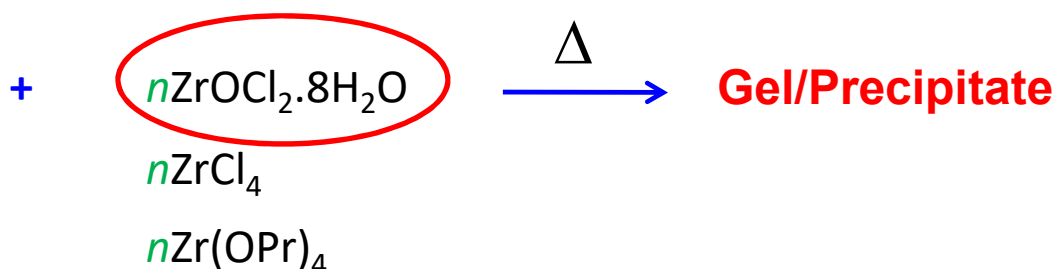
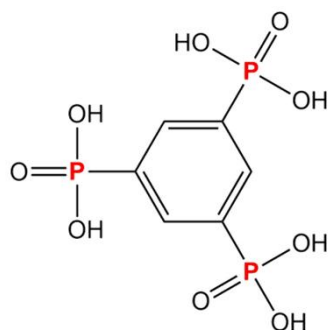
ZrP-0.65 37 mg Eu/g
 ZrP-0.71 56
 ZrP-0.76 60

Capacities measured from the isotherms are very high!

3. Preparation and Adsorption Properties of Zirconium (IV) – BTP Coordination Polymers

Collaboration with Guilhem Arrachart, ICSM-CEA

Synthesis

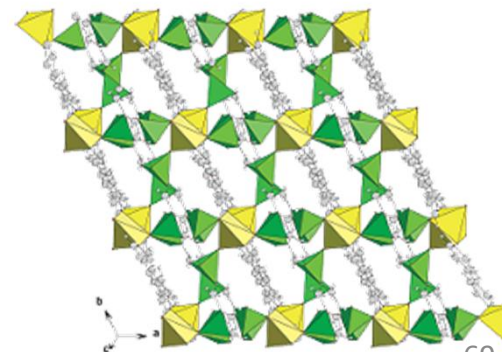


Rational Design and Synthesis of Porous Organic–Inorganic Hybrid Frameworks Constructed by 1,3,5-Benzenetriphosphonic Acid and Pyridine Synthons

Deyuan Kong,[†] Jerzy Zoln,[‡] Jennifer McBee,[§] and Abraham Clearfield^{*†}

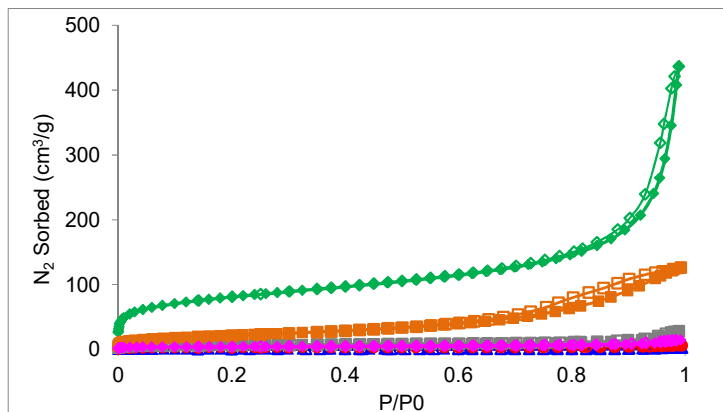
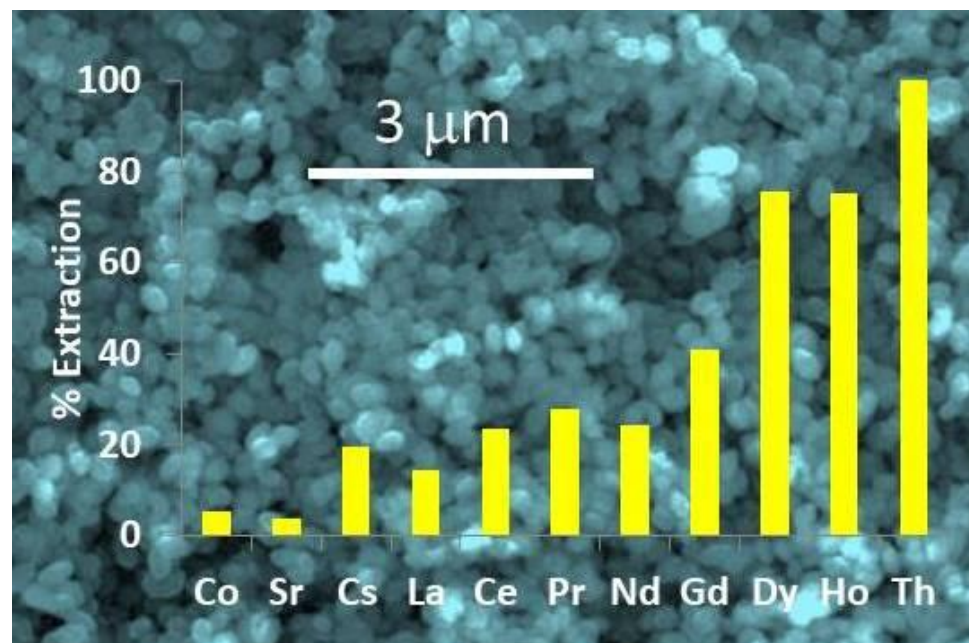
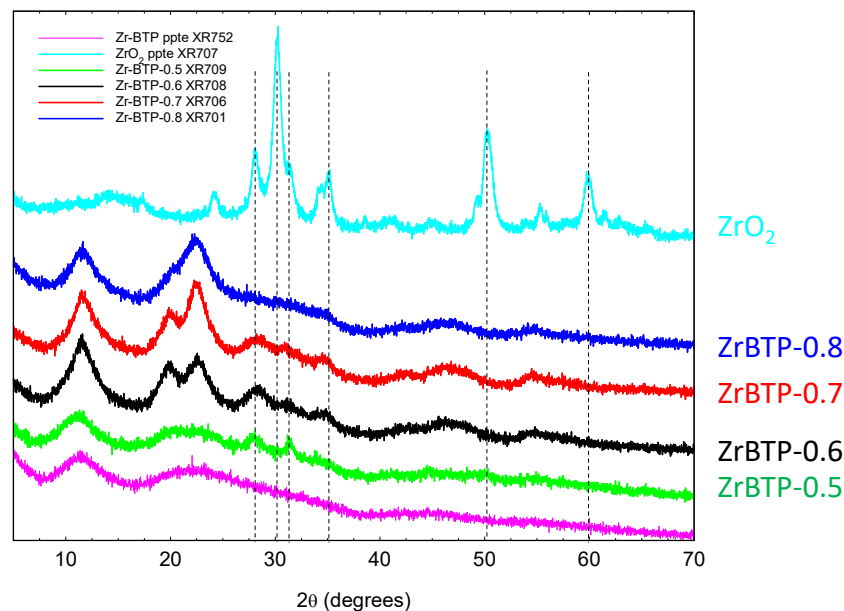
Department of Chemistry, Texas A&M University, College Station, Texas 77843, and Faculty of Chemistry, Department of Organic Chemistry, Wrocław University of Technology, 50–370 Wrocław, Poland

Received June 9, 2005



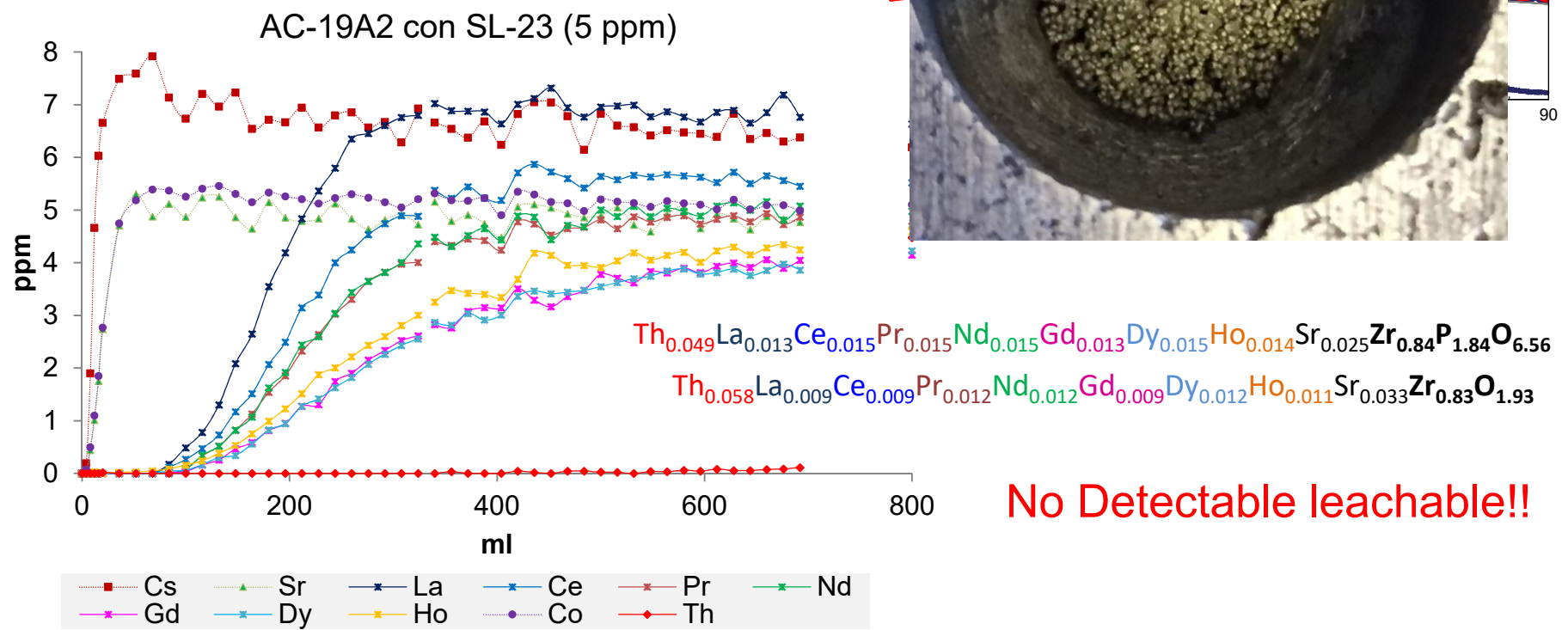
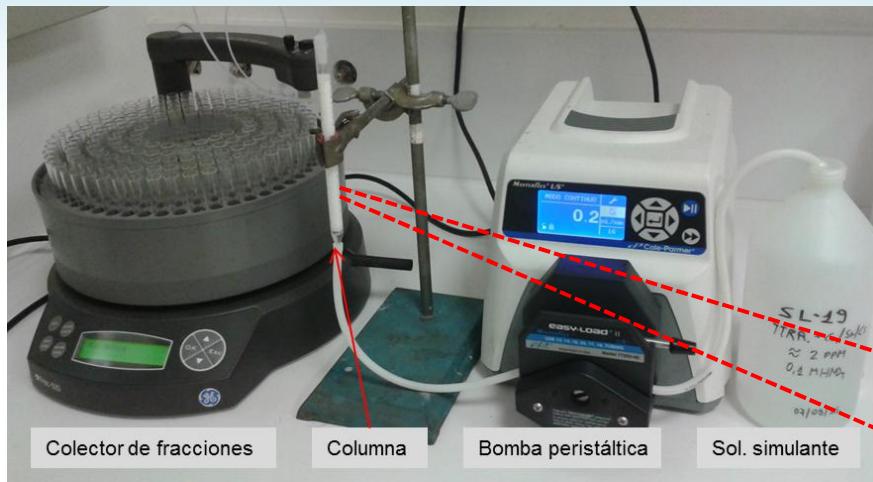
Zr-BTP System

Precipitate formed in absence of BTP comprises nanocrystalline mono- and tetragonal-ZrO₂.



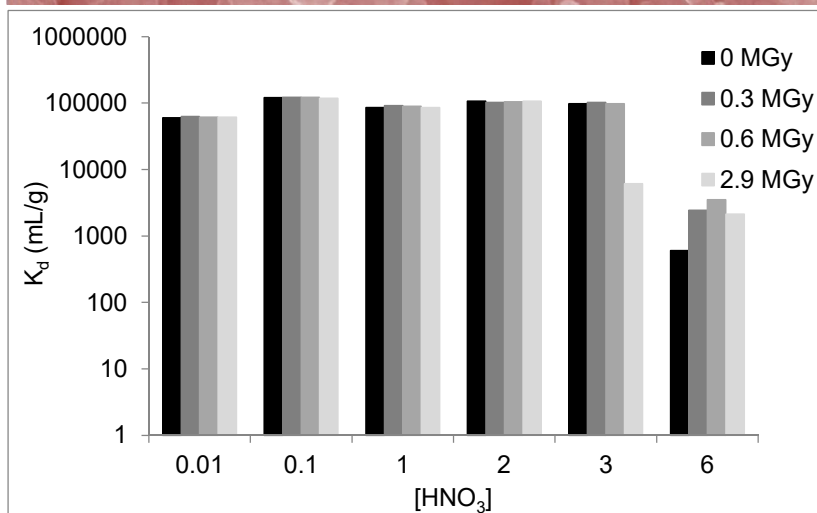
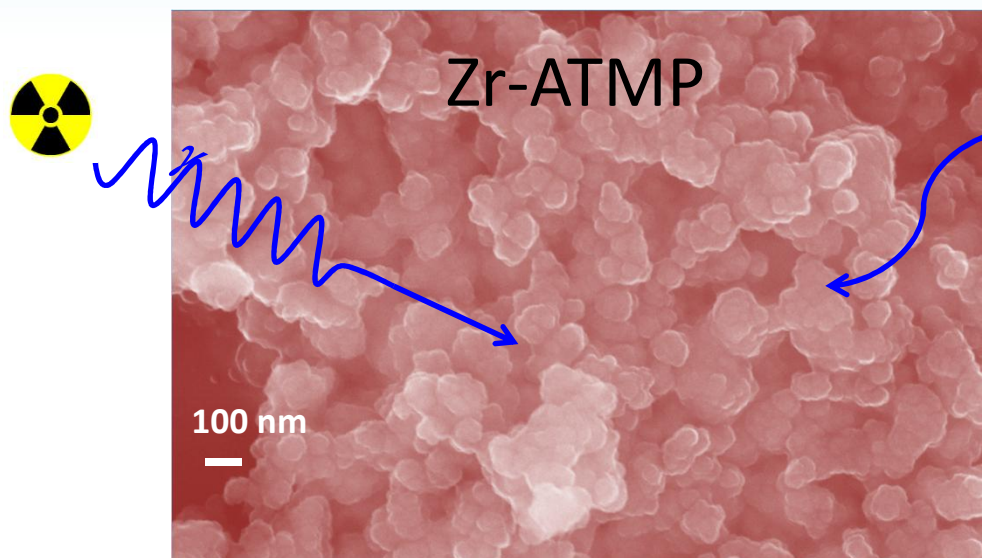
	S_{BET} (m ² /g)
Zr-BTP-0	79.3
Zr-BTP-0.5	281.2
Zr-BTP-0.6	708.6
Zr-BTP-0.7	249.1
Zr-BTP-0.8	22.3
Zr-BTP-0.6	313.0

Addition of 0.5 M ZrOCl₂ solution to an aqueous solution of BTP instantly forms precipitate with some structure without the need for hydrothermal treatment.

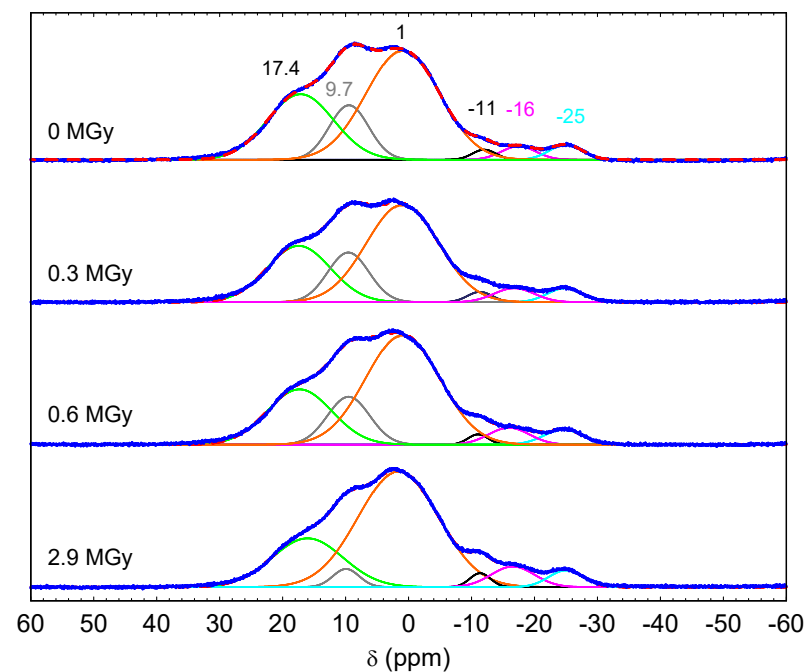


No Detectable leachable!!

Radiolytic Stability of Polyphosphonate Group (IV) Metal Oxide Hybrids



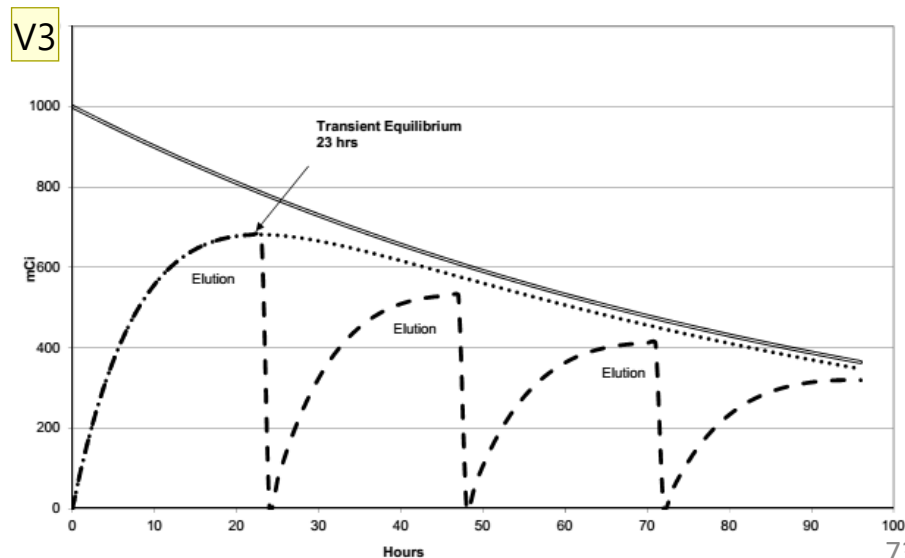
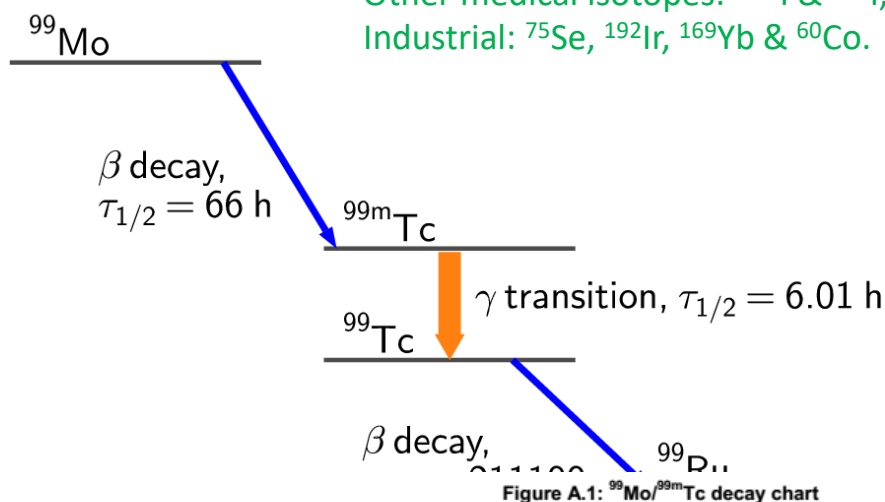
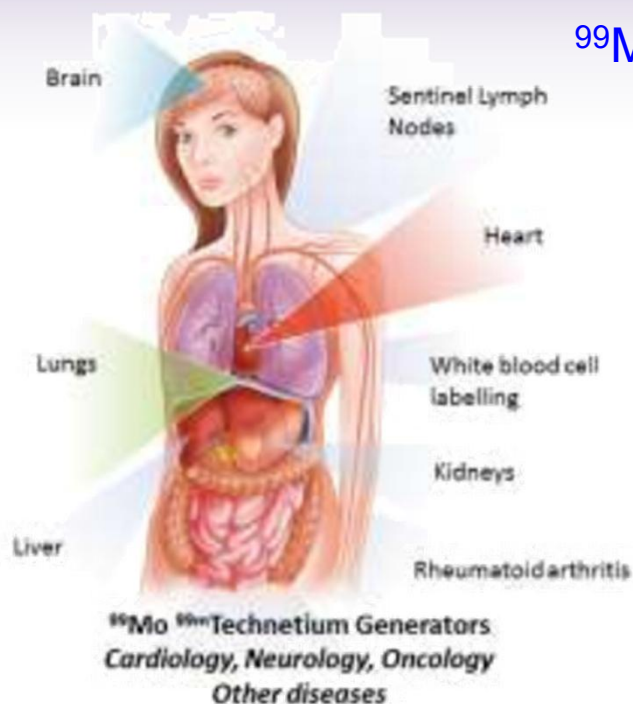
^{31}P MAS-NMR

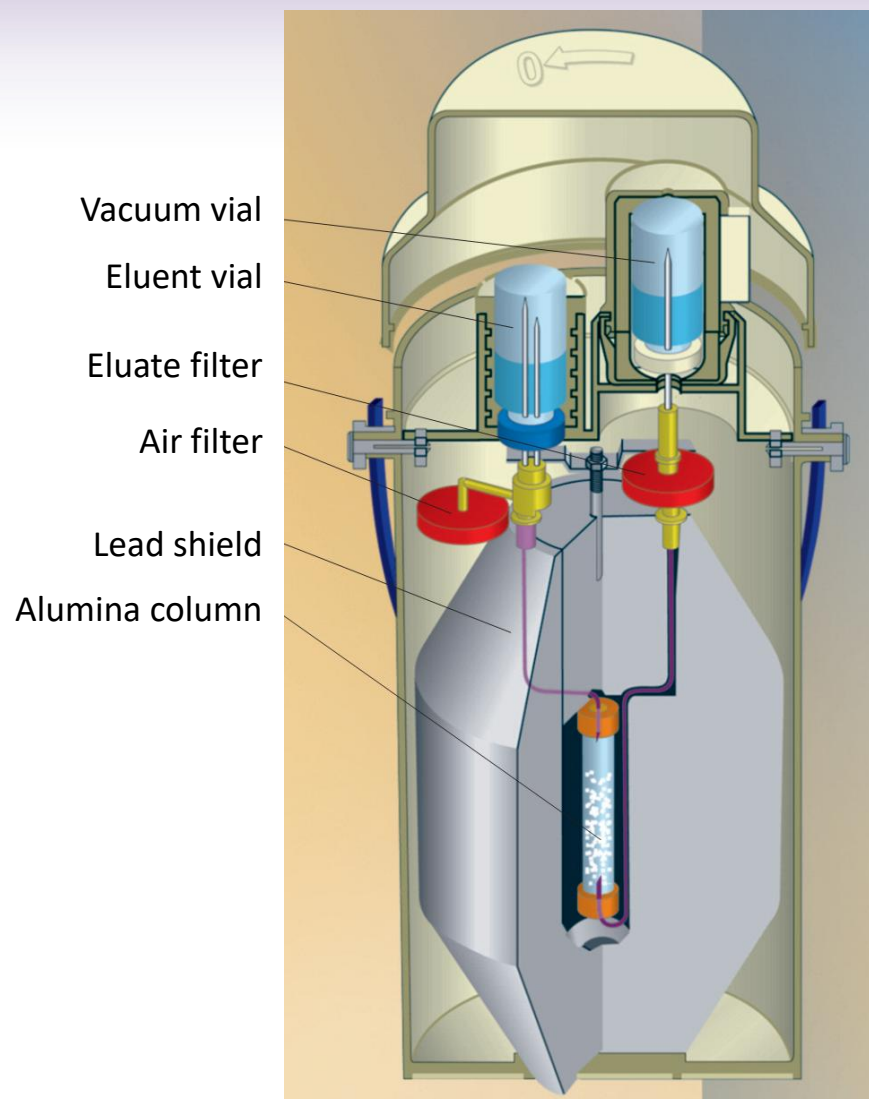


⁹⁹Mo – A Key Isotope in Nuclear Medicine V4

⁹⁹Mo accounts for 30 million diagnostic procedures annually

Other medical isotopes: ¹²⁵I & ¹³¹I, ¹³³Xe & ⁸⁹Sr
Industrial: ⁷⁵Se, ¹⁹²Ir, ¹⁶⁹Yb & ⁶⁰Co.





A



B

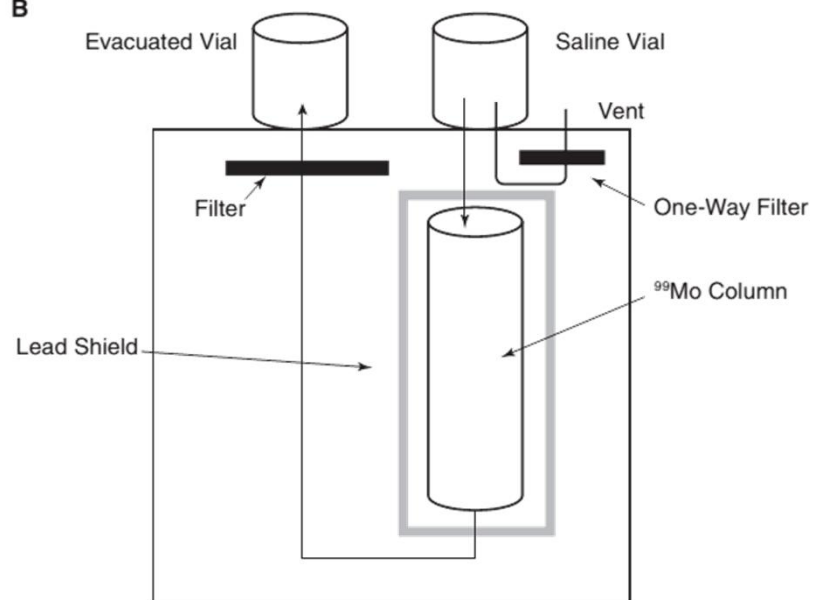
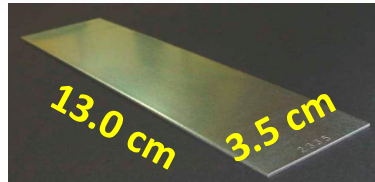


FIGURE 2.1 (a) External view of a technetium generator produced by the Australian Nuclear Science and Technology Organisation (ANSTO). SOURCE: Courtesy of ANSTO. (b) Schematic diagram showing the internal structure of a typical technetium generator.

⁹⁹Mo Production - Traditional versus New Approaches

Improve process from the head-end?



UAl_x dispersion Target

Nordion (Canada)
IRE (Belgica)
IPPE (Russia)
ANSTO (Australia)

Target Fabrication

Irradiation

Dissolution

CNEA (Argentina)
NECSA-NTP (S. Africa)
MALLINCKRODT (Holland)
ANSTO (Australia)

Acid

Alkaline

Recovery

Recovery ²³⁵U

Improve recovery step?

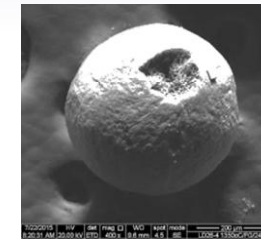
Precipitation

IX or SX

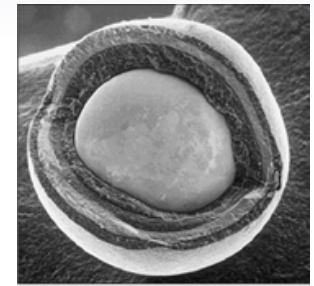
LLW/ILW

LLW/ILW

?



Sublimation
o
Leaching



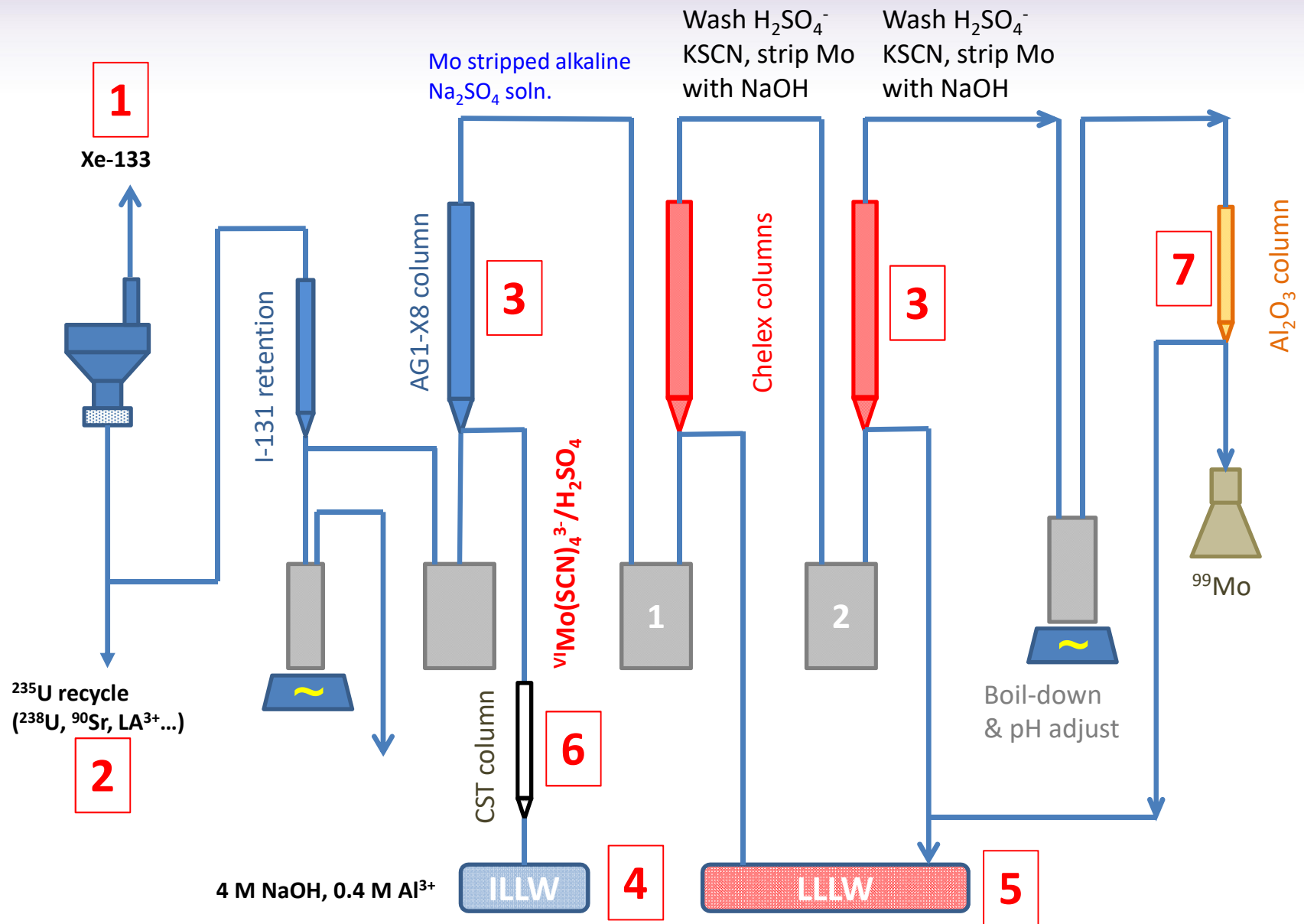
< 1000 μm



~500 L/y

75

Current CNEA LEU-based Process



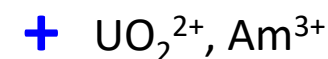
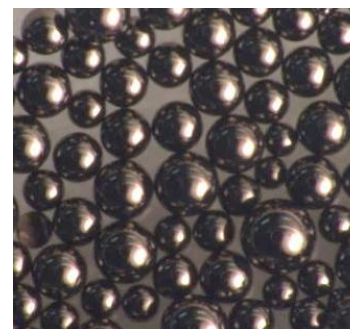
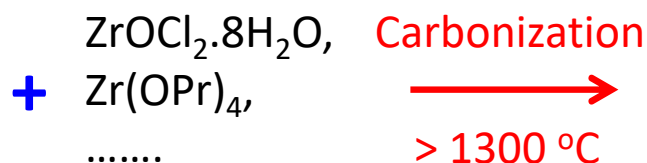
V5

Synthesis of Porous Microspheres through Polymer Templating

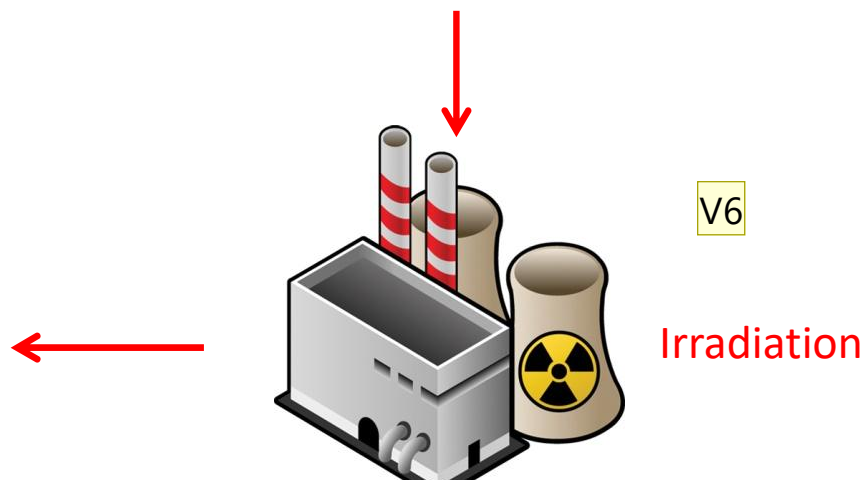
Incorporate inorganic precursors into polymer microspheres and use carbothermic reduction to generate carbon Zr-carbide, nitride and oxycarbonitride composites:



Macroporous Polymeric Resins
PAN, XAD7, XAD4, XAD16, Chelex 100



Mo-recovery (reprocessing)



Candidate IMF Materials and their Properties

Material	Structure	MP (K)	Thermal Conductivity (W/m-K) @ RT	Radiation Resistance	Moh's Hardness	Linear Thermal Expansion Coefficient (°C ⁻¹)
Al				excellent	2-2.9	23.1x10 ⁻⁶
Zr			27.0	excellent		
Si		1412	130.0	good	7	2.6x10 ⁻⁶
SiC	cubic (3C, 4H, 6H)	2973	14.2	good	9.3	2.77x10 ⁻⁶
ZrC	cubic	3800	20.5	good		22.4x10 ⁻⁶
ZrN	cubic	3228	20.5	good		
Si ₃ N ₄	hexagonal	2151	29.0		9	3.4x10 ⁻⁶
ZrO ₂	mono, tet, cubic	2988	2.7	excellent	6.5	10.5x10 ⁻⁶
Mg ₂ Al ₂ O ₄ (spinel)	cubic	2408	15.0		8	
MgO	cubic	3100	37.7		5.5	
Al ₂ O ₃	hexagonal	2327	35.0		9	
ZrSiO ₄	tetragonal	>1700	2.6		7.5	
CeO ₂	cubic	2670	6.0		5	
Graphite	hexagonal	4300 *	24.0	excellent	0.5-1	

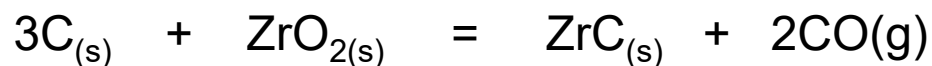


ZrO₂

ZrC



Traditional Synthesis



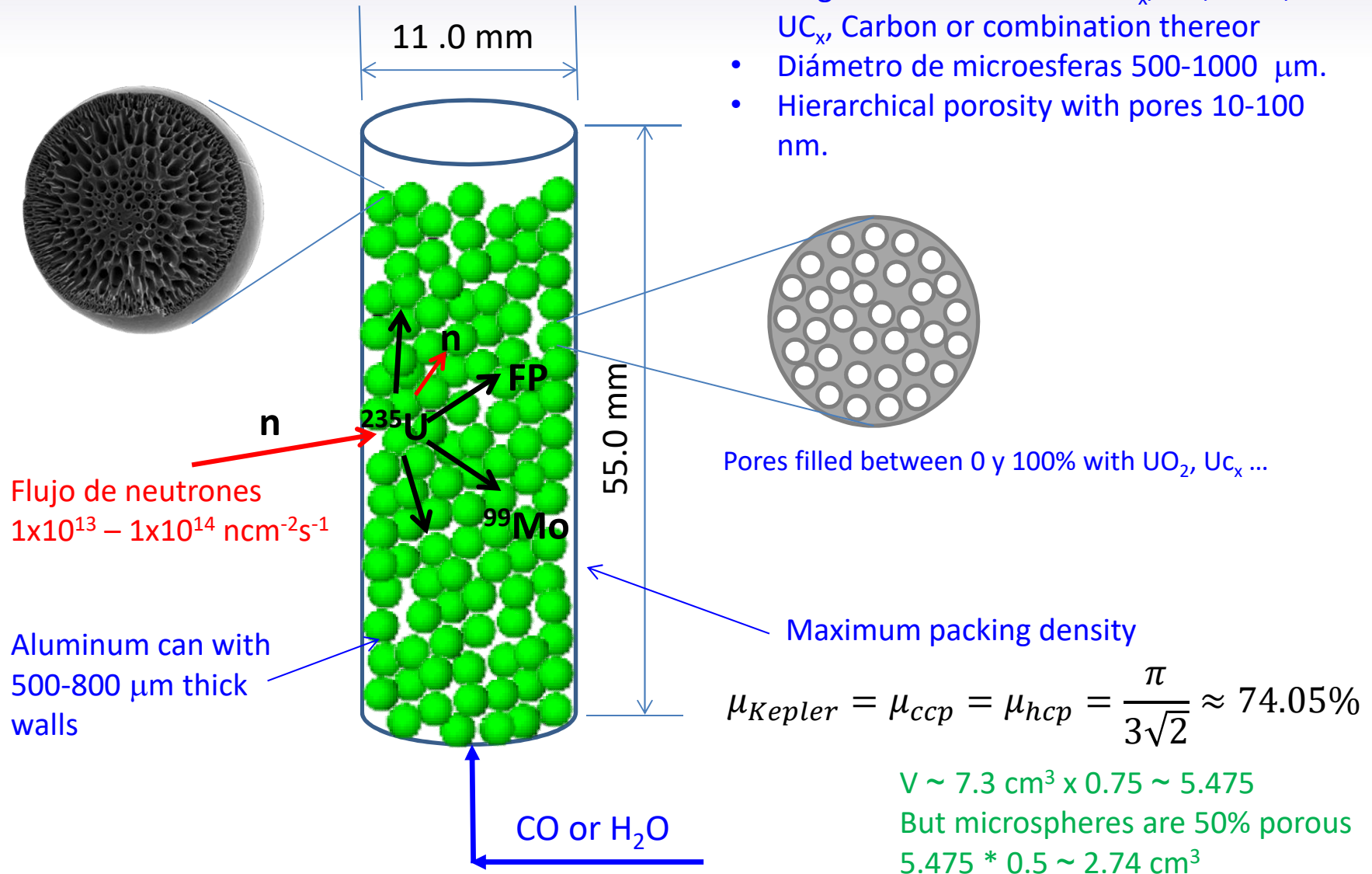
Burghartz et al. *JNM* **2001**, 288, 233

- Compatible with sodium coolant
- Soluble in HNO₃

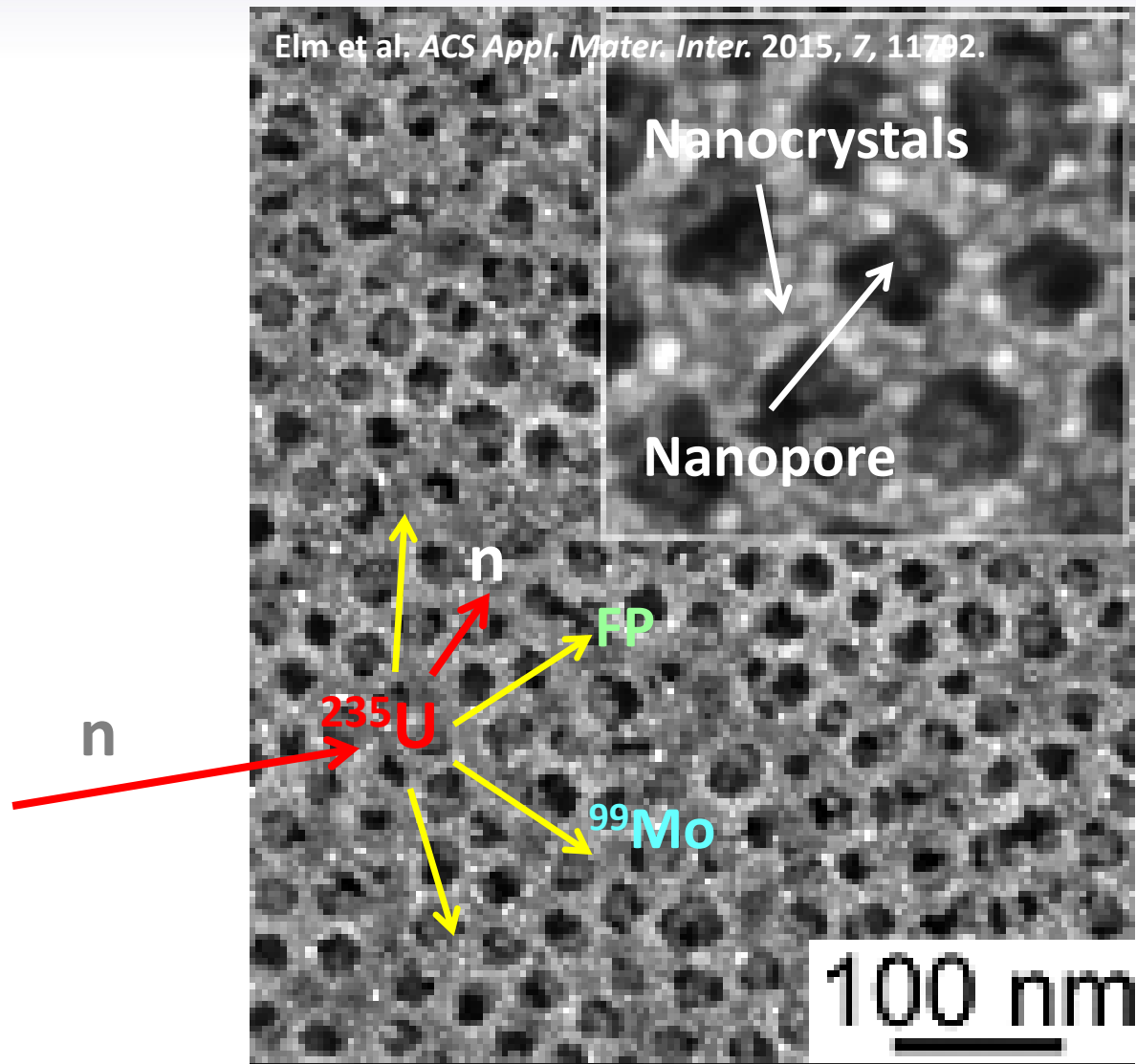
Hania et al. *JNM* **2015**, 466, 597.

Pu_{0.3}Zr_{0.7}N fuels tested to 33 MWd/Kg and found to perform well.

Hypothetical Target



High Resolution SEM of Y-stabilized ZrO₂



V18

$$R = n \times \sigma \times \phi$$

R = reaction rate

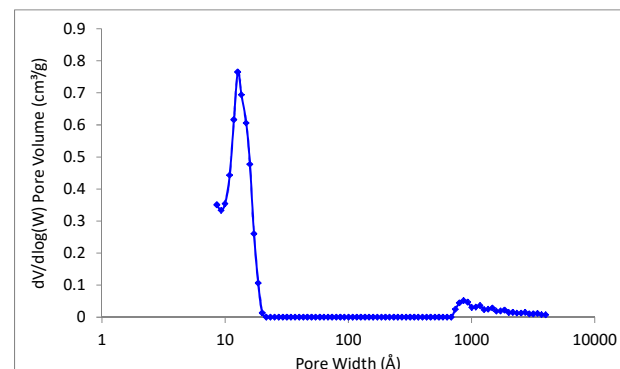
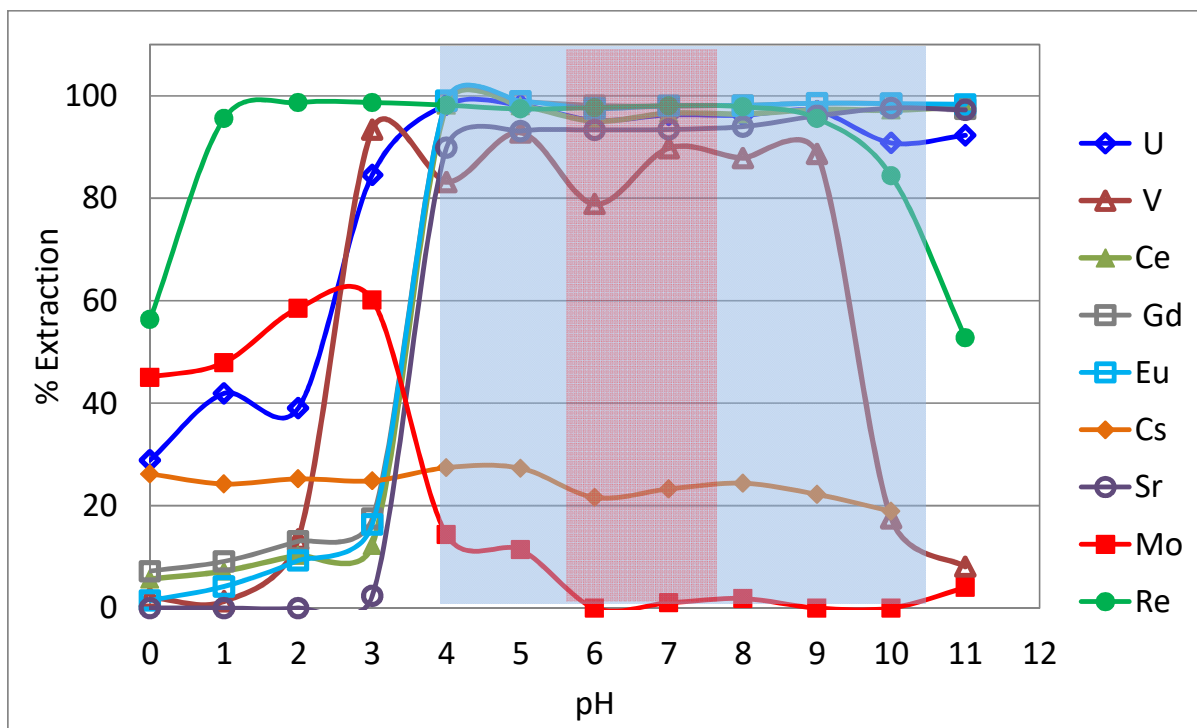
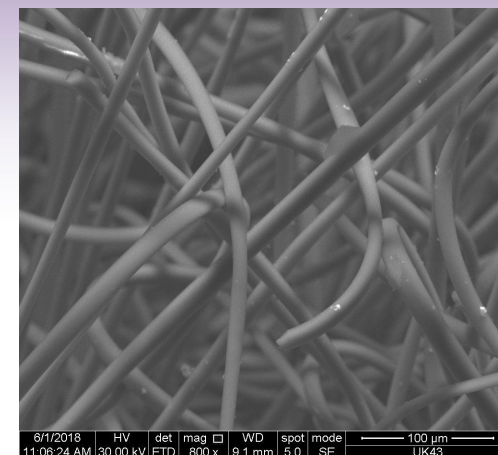
n = no. target nuclei

ϕ = neutron flux ($\text{n.s}^{-1}\text{cm}^{-2}$)

σ = cross section (barns)

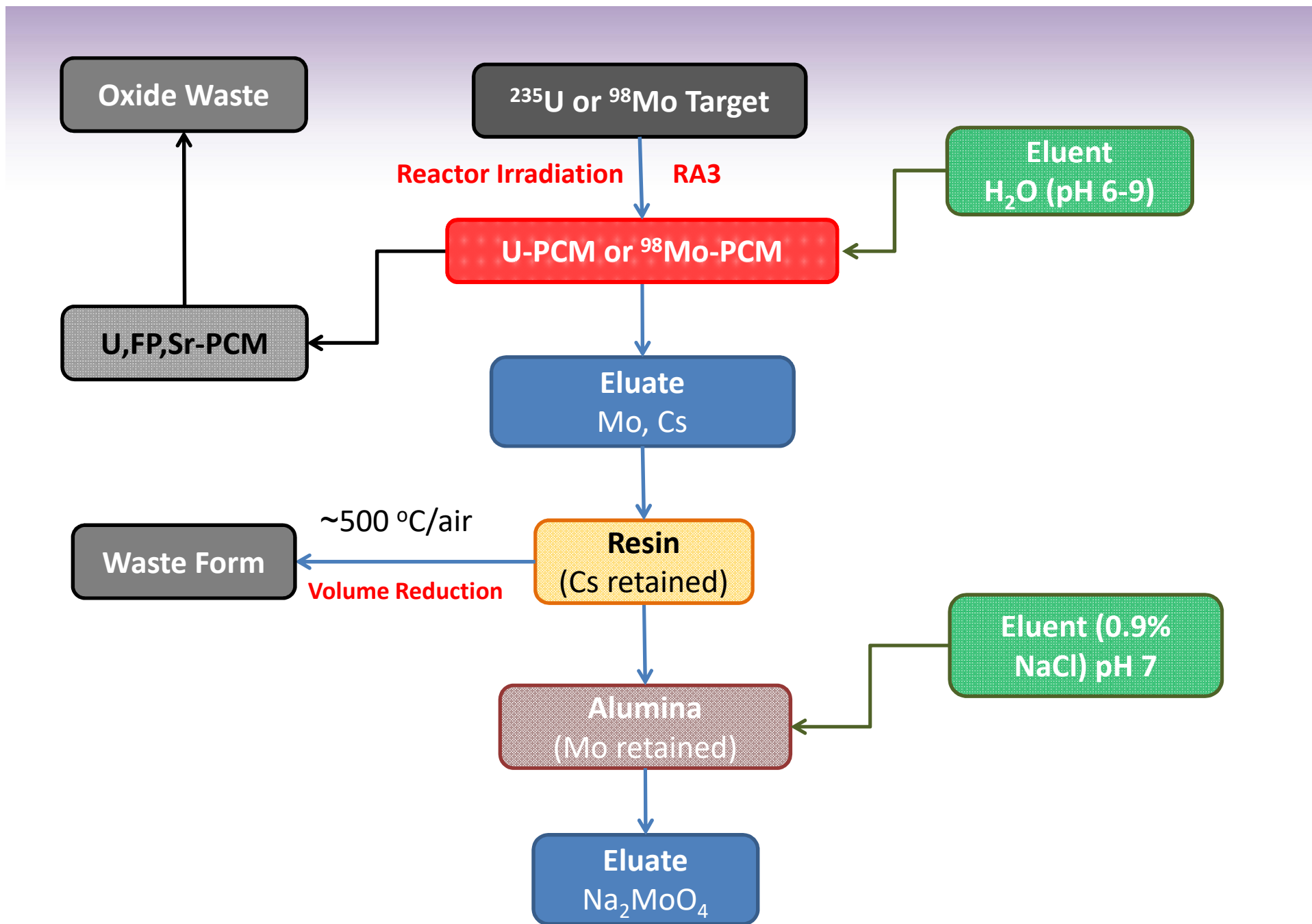
37 barns (^{99}Mo) 6.1 %

Microporous Carbon Felt Targets (Kynol®)

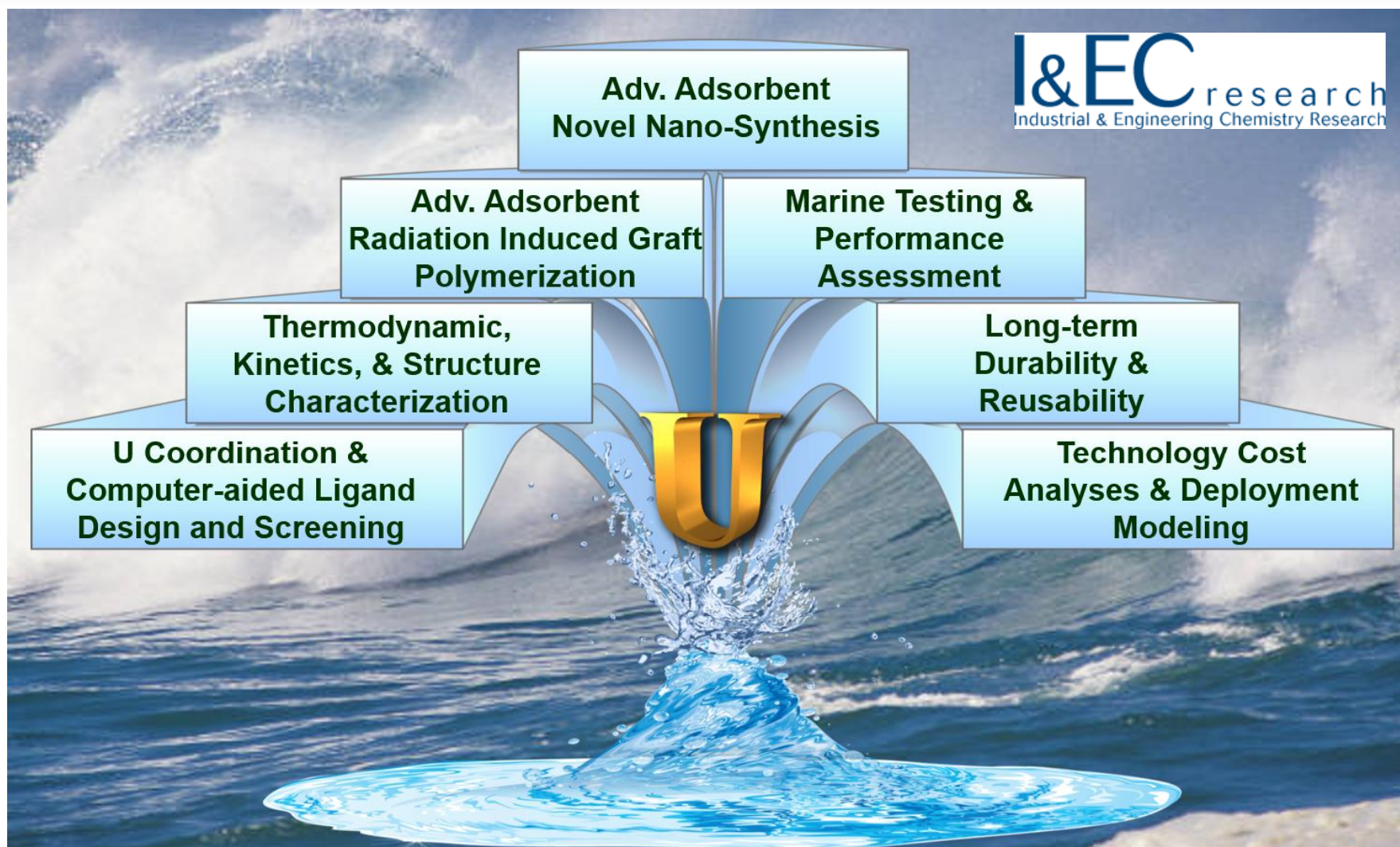


Load uranium as UO_2^{2+} at $4 < \text{pH} < 11$.

Strip MoO_4^- using water pH 6-8.



Recovery of Uranium from Seawater



<https://pubs.acs.org/doi/10.1021/acs.iecr.6b01293>

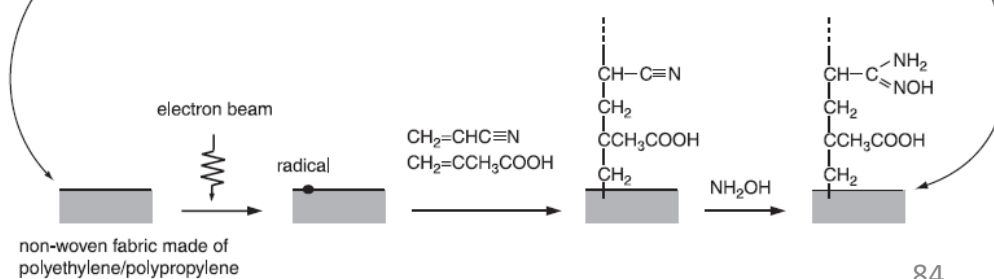
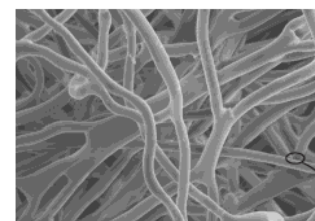
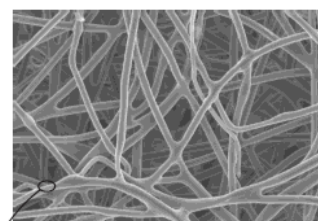
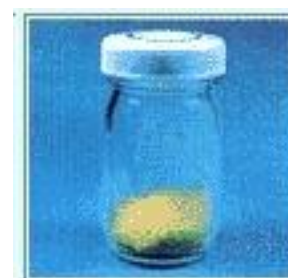
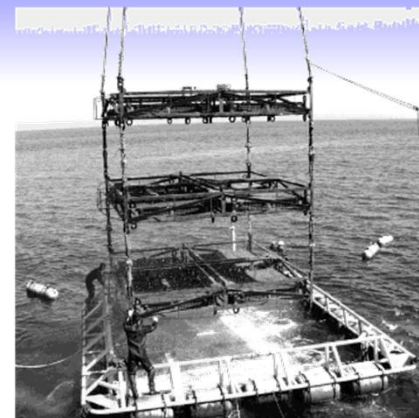
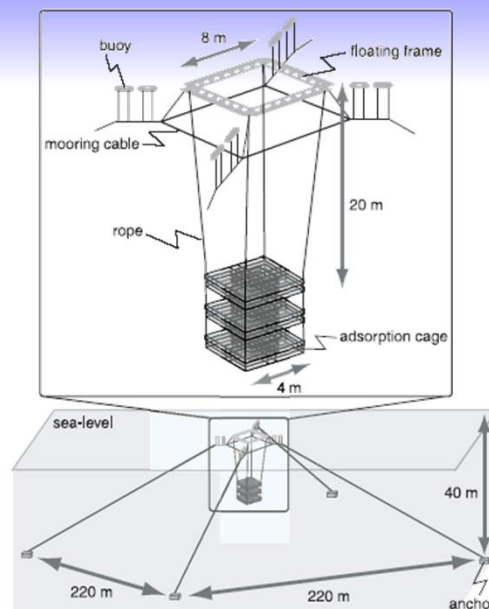
Seko et al. *Nucl. Technol.* **2003**, *144*, 274

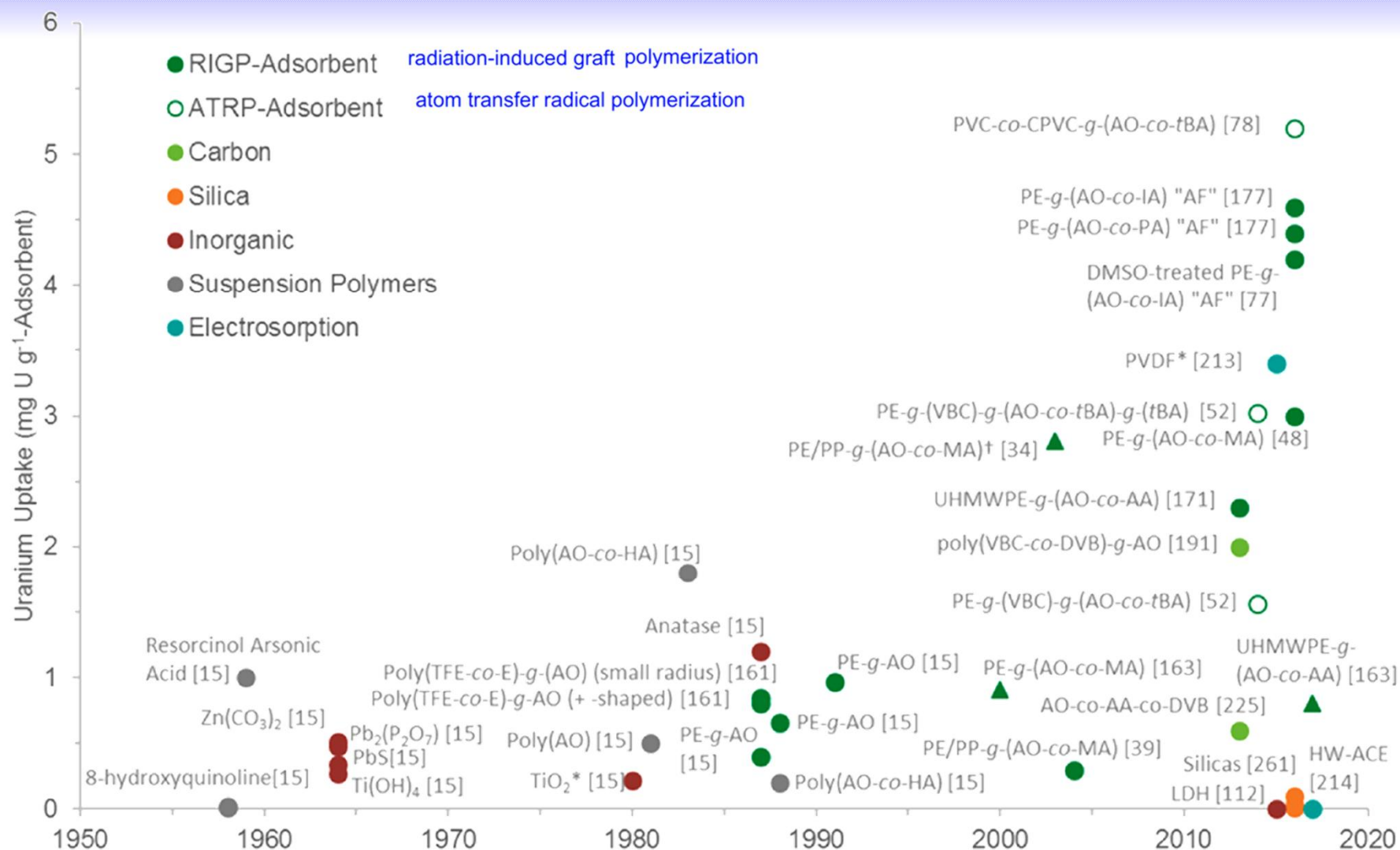


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