Primus.inter.pares

SAFE
Centre for Accelerator Based
Research and Energy Physics

IFE Institutt for energiteknikk

The Interaction Between Nuclear Chemistry and Hydrometallurgy

A Strategy for the Future

By
Tor Bjørnstad and Dag Øistein Eriksen

April 2013

A short history of radiochemistry

- 1898: Marie and Pierre Curie discovered Po and Ra by chemical separations of dissolved uranium ore
- 1923: de Hevesy uses ^{212}Pb as a tracer to follow the absorption in the roots, stems and leaves of the broad bean
- 1929: Ellen Gleditsch appointed professor in inorganic chemistry. Established radiochemistry in Norway in 1916.
- 1938: Hahn proves fission of uranium as Ba is separated from irradiated uranium solution
- 1940: First transurane produced: Np by McMillan and Abelson
- Nuclear power requires separation of fission products

Nuclear chemistry has contributed to the development of hydrometallurgy

The need for safe, remote handling of the laborious separations required in the nuclear sector boosted innovation in:

- Solvent extraction:
  - Continuous, counter current process enabled large quantities to be processed
  - Contactors like mixer-settlers were developed
- Ion exchange to perform difficult purifications

Hydrometallurgy and nuclear chemistry

Nuclear (radio-)chemistry offers special methods useful in hydrometallurgy:

- Use of radioactive tracers, i.e. radioactive isotopes of the elements studied
  - Particularly important in liquid-liquid extraction
- Neutron activation can be used on all phases: solid, aqueous-, organic phases (and gas)
- AKUFVE-method very efficient in measuring extraction kinetics
- Many "hydrometallurgical" elements have suitable isotopes for use as tracers
  - In addition, e.g. Eu(III) can be used as tracer for Am(III), and Nd^{3+} has equal ionic radius as Am^{3+}

Some strategic metals

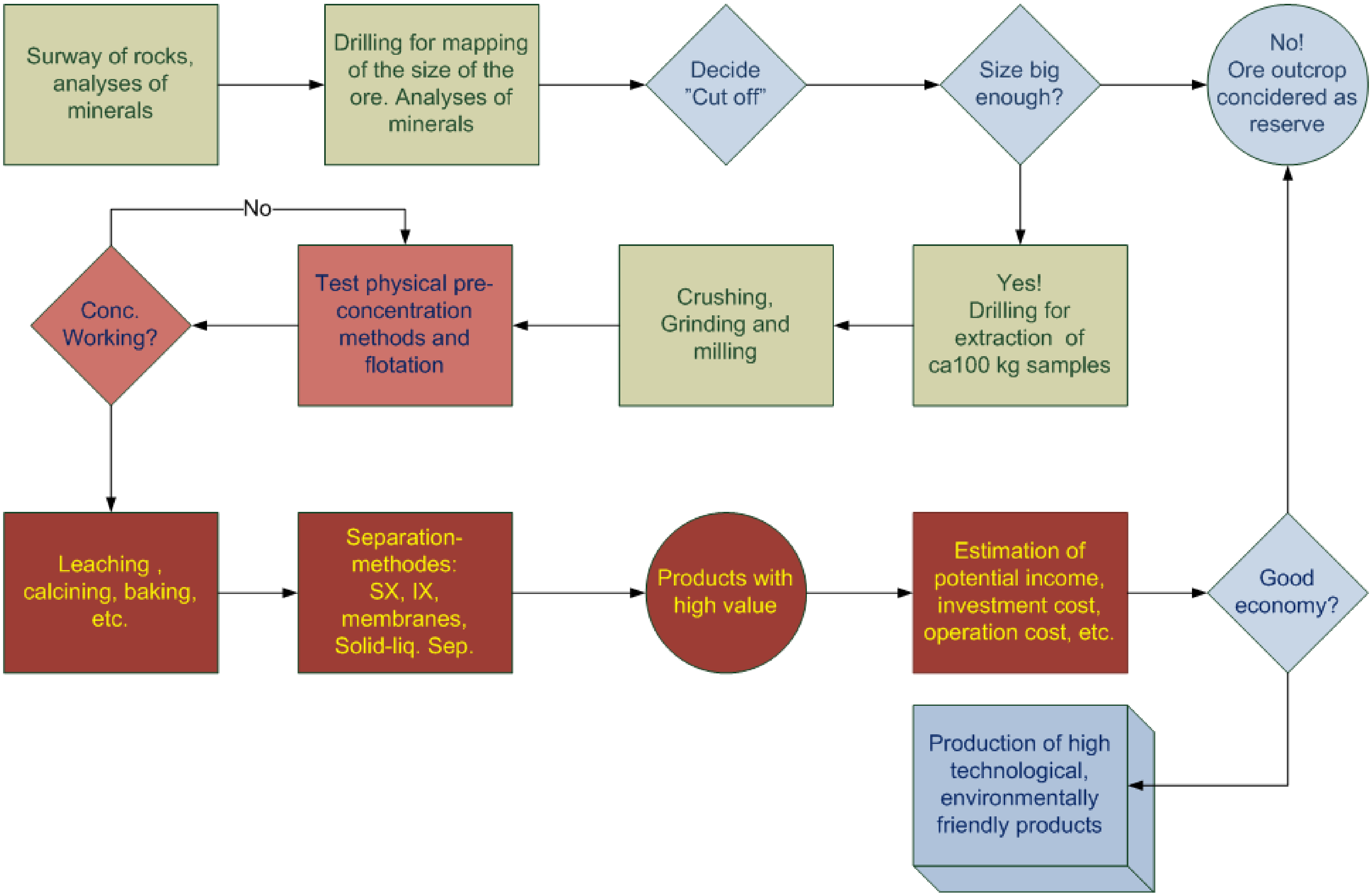
- Lithium for batteries
  - Scarcity of Li may be a reality. One solution may be to increase yield from today's 50 %
- Gallium, indium, and germanium for electronics and solar cells
- Zirkonium and hafnium for nuclear power
- Niobium and tantalum for high temperature-alloys
- Titanium for leight, but strong metals
  - Is often alloyed with Si, Sc o.a.
- Rare earth elements (REE)

Important metals for environmentally friendly technology:

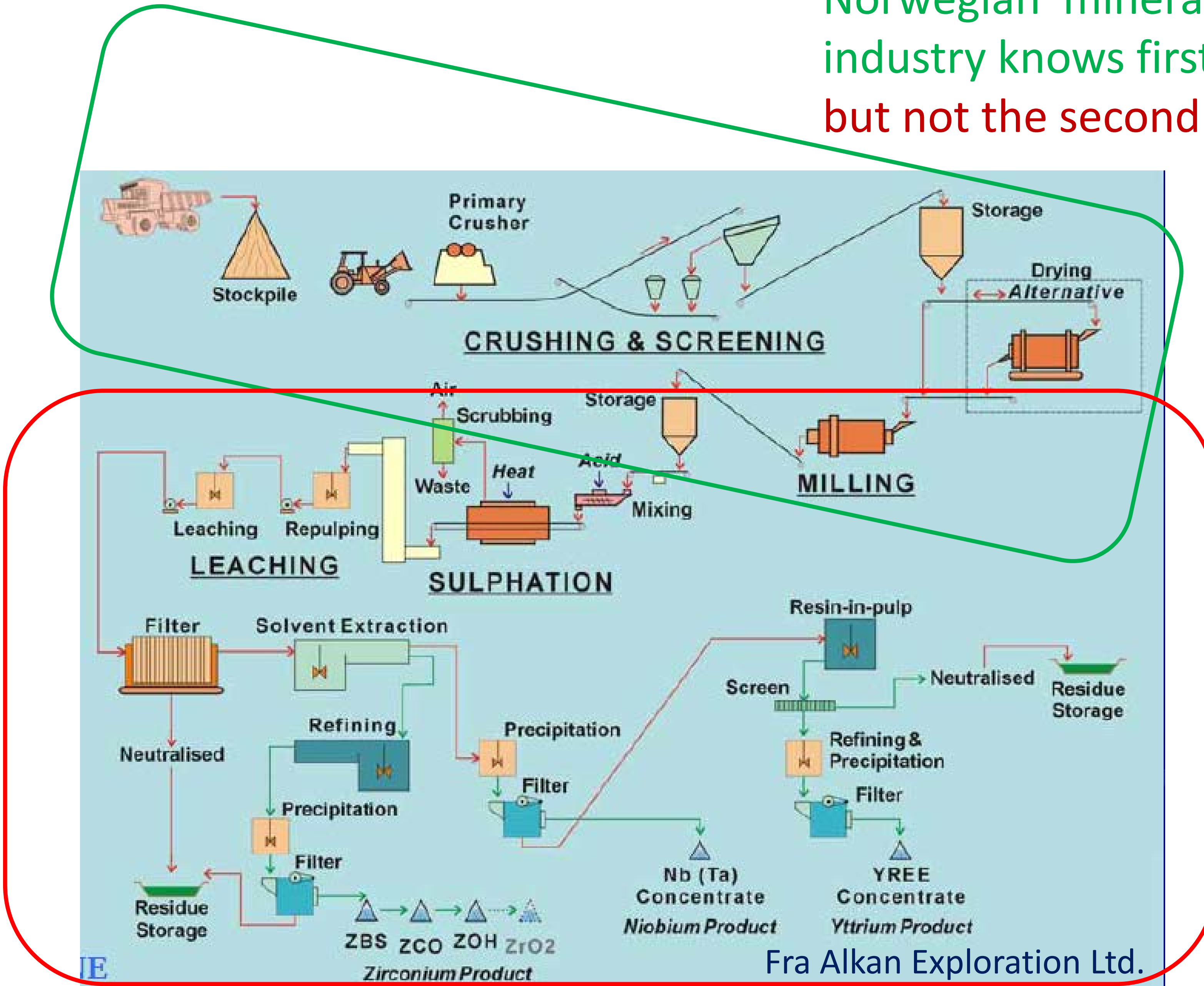
Rare earths metals are crucial:

- Neodymium, Nd, is used in FeNdB-magnets
  - These need dysprosium, Dy, to be used in hybrid cars due to temperature resistance
  - Also praseodymium, Pr, og lantanum, La, are necessary in certain magnet types
- Yttrium is used as substrate for catalysts and lasers, in addition to LEDs (as Y_2O_3)
- Europium is used as colorant in LED etc.
- Terbium, Tb, is used in LEDs, magnets, displays
- Most REEs are important in modern technology
  - This means that several REEs are cost carriers

Steps in the development of a mineral project



Norwegian mineral industry knows first part, but not the second



Hydrometallurgy – Separation chemistry

Leaching:

- Alkaline
- Acid based
- Other: chlorination, baking, calcining, …

Phase separations:

- solid phase – liquid,
- liquid – gas,
- solid –gas,
- liquid – liquid,
- distillation, …

Separation chemistry:

- Precipitation, crystallisation
- Ion-exchange, IX
- Solvent Extraction (Liquid Liquid Extraction, LLX)
- Membranes
- Mixing of methodes: impreg.resin, SLM, …

Nuclear- and radiochemistry has strong interactions with hydrometallurgy

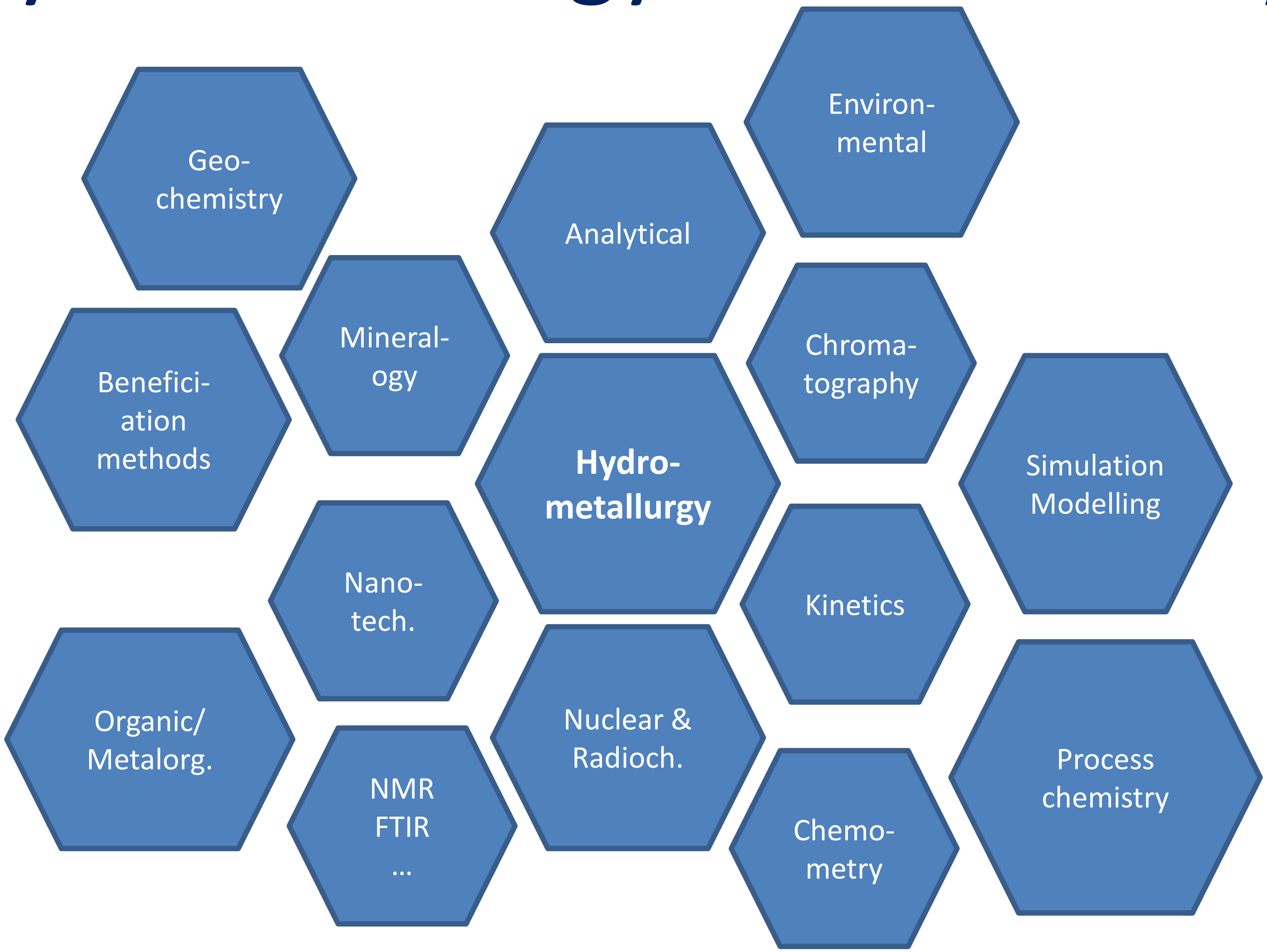
- The world needs access to rare metals and compounds
- Norway has:
  - Huge mineral resources
  - High competence and increasing innovation in enterprices
  - High cost structure
  - Industry in need of competent emploies
- Nuclear chemistry at SAFE offers:
  - Production of tracers at OCL and IFE
  - Long experience in separation science like solvent extraction
  - Knowledge of thorium and uranium chemistry
  - International network and collaborations

SAFE offers already key items

- Lecturing – courses:
  - KJM5940 - Solvent Extraction and Ion Exchange, i.e. separation science
  - KJM5901 - Radiochemical methods, i.e. how to apply and produce tracers, etc.

- Master theses:
  - SISAK-related solvent extraction of e.g. Os, Rh, ..
  - Th-extraction from rødberg ore (Henrik Noren)
  - Simulation of counter current solvent extraction (to be started)

Hydrometallurgy and chemistry



Education:

Virtual institute of separation science, collaboration with NTNU, UiB, UMB(?)

Covering:

- Leaching of minerals and waste
- Solvent extraction and Ion exchange
- Solid-liquid separation
- Crystallisation and precipitation
- Simulation of processes
- Chemometry
- Fluid dynamics
- Environmental issues: Recycling, emissions,..

Laboratory test work

- R&D at lab scale
  - High quality research
- Experimental validation of models and simulators
- Creation of data bases for use in science and industry

The jewel of knowledge

External income possibility:

Provide technical and chemical expertise at all levels of R&D and at all scales

International collaborations:

- Chalmers Technical University, SE
- European Institute of Hydrometallurgy (CEA), FR
- Lappeenranta University of Technology, SF
- Technische Universität Aachen, DE
- …

E.g.: Solvent Extraction - SX

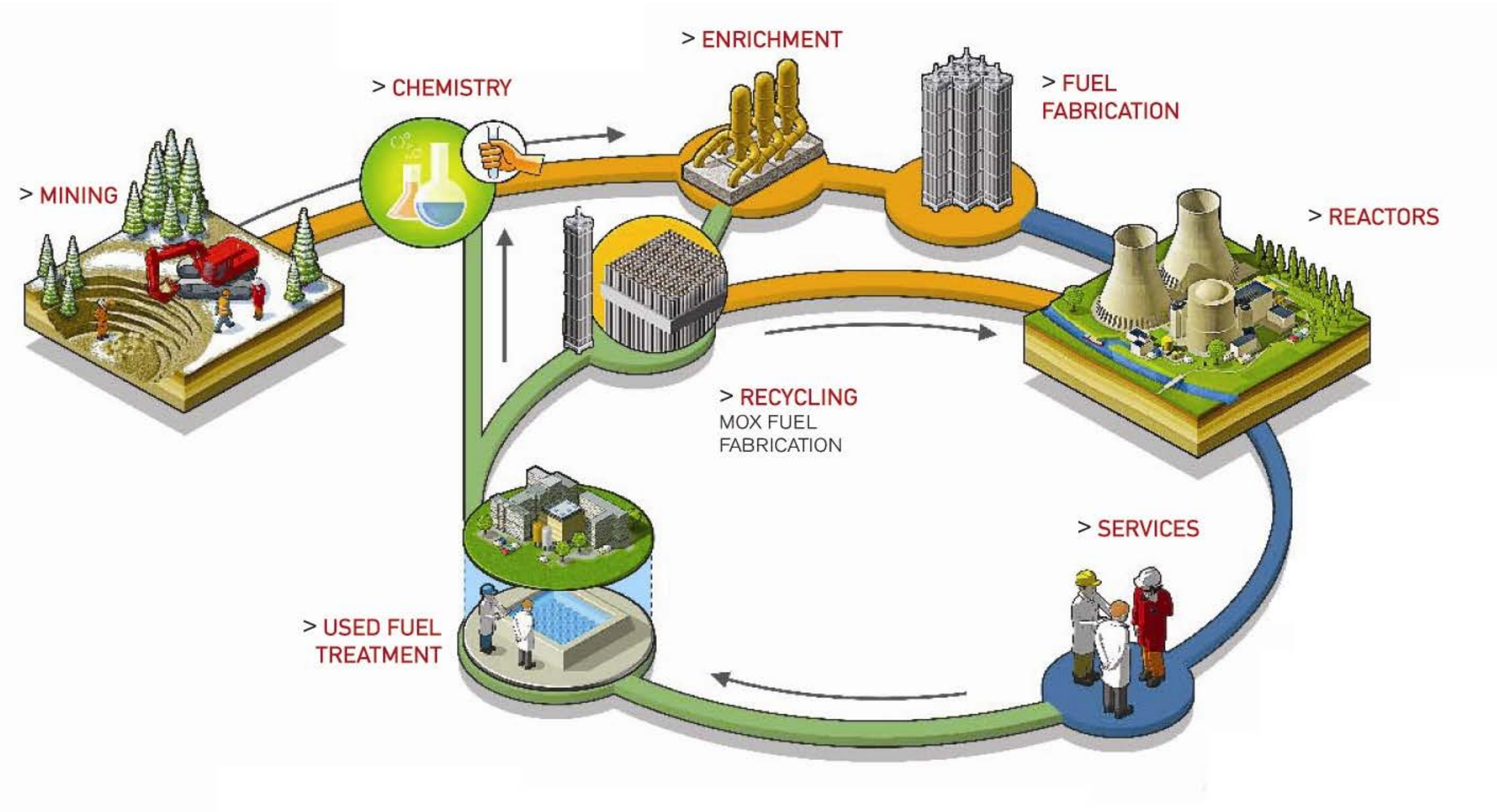
Basic SX

- Acidic, basic and solvating extractants
- D-, %E-, K-values
- Solvents and solvabilities
- Complexes
- Lewis' acid-base concept (HSAB)
- Salting out effects
- Solubility curves
- Kinetics – extraction and strip

Phase separation

- Gravitational
  - Electrostatic
- Centrifuges, e.g. SISAK, AKUFVE
- One continuous phase – Electrodynamic contactor
- Crud-formation
- Modifiers
- Interfacial tension and formation of micells
- Liquid membranes
- Impregnated resins

Nuclear Fuel Cycle - Uranium



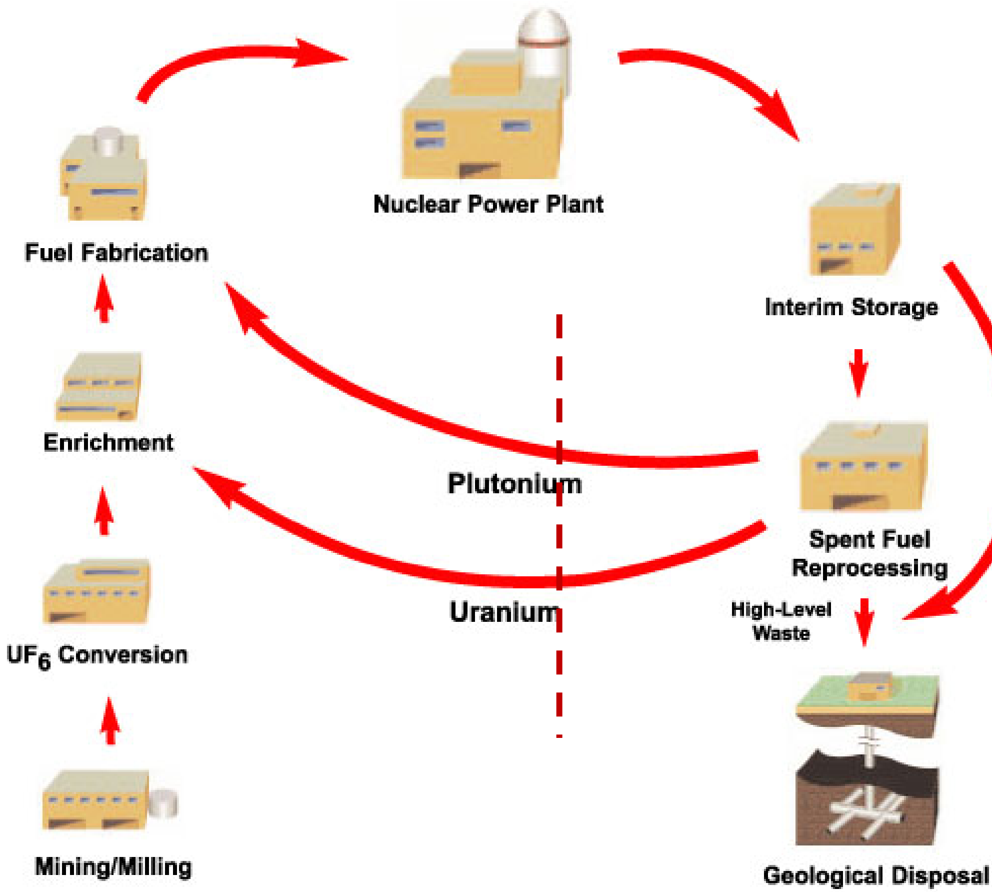
The uranium fuel cycle

- Spent fuel is cooled,
- then dissolved in nitric acid
- U, Pu + actinides are separated from fission products, by solvent extraction processes
- U & Pu recycled if possible
- Fission products and other radioactive species separated and deposited, e.g. ^{90}Sr and ^{137}Cs

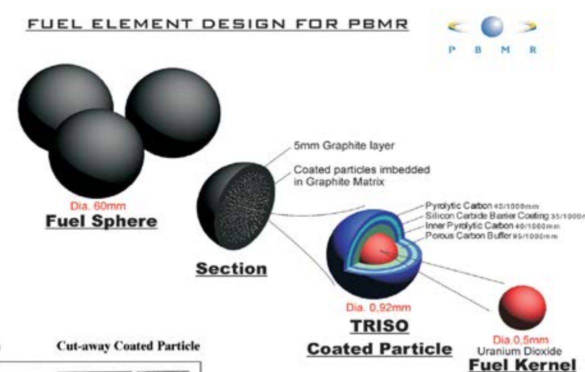
"Closed circle"

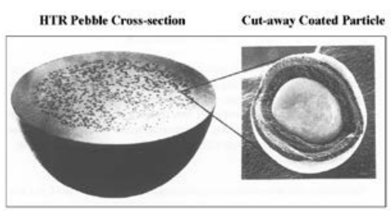
The fuel cycle - Thorium

Heavily depending on the uranium fuel cycle as enriched ^{235}U or ^{239}Pu is needed



For Th/Pu- and Th/U-fuels no recycling is considered



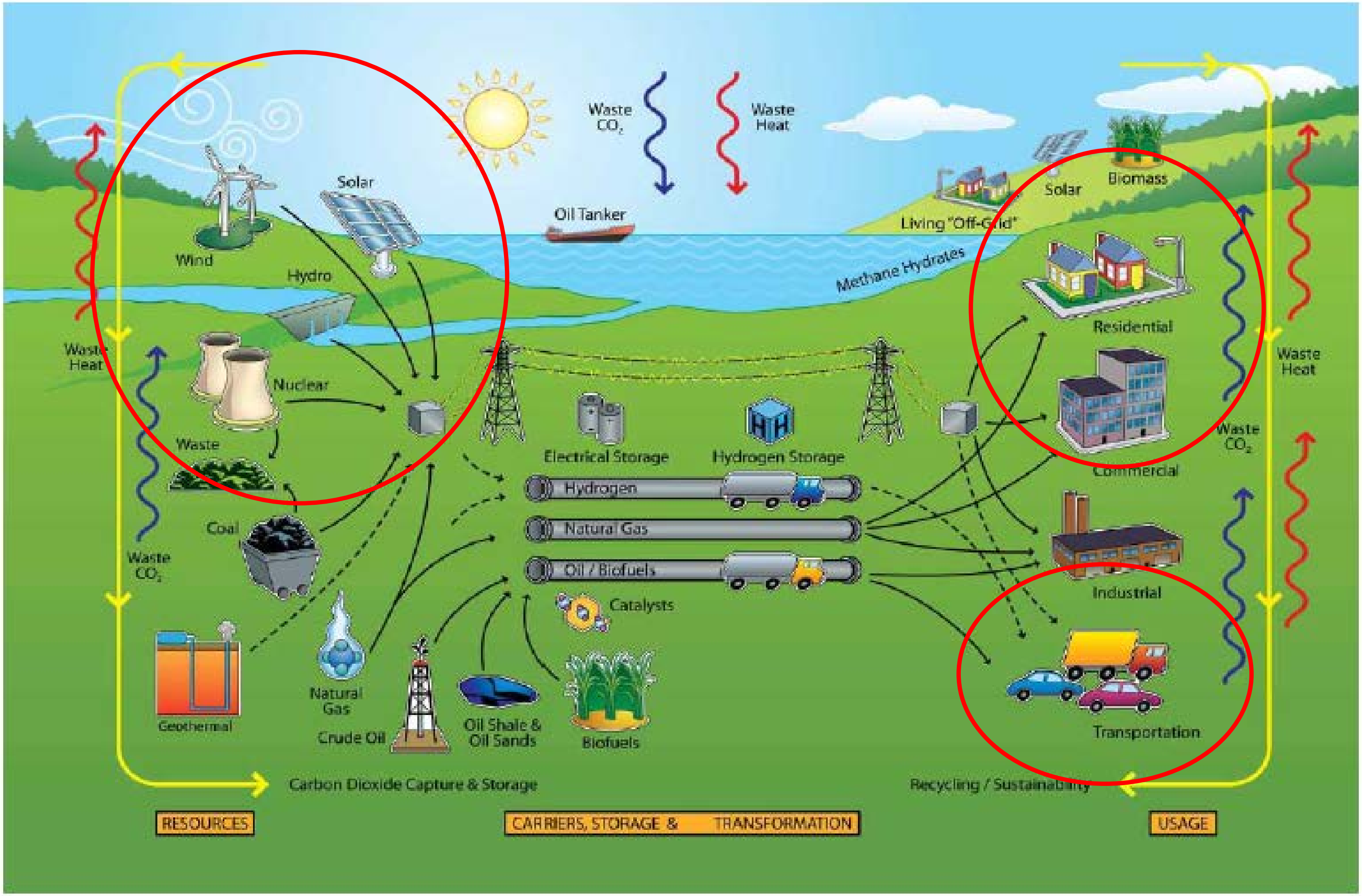


The periodic table of elements

Group → / ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Energy forms and -use



MRS Bulletin 33, (April 2008)

Why the market for niche technology will increase: