ISTITUTO NAZIONALE DI FISICA NUCLEARE

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NUCLEAR CHEMISTRY, RADIOCHEMISTRY, RADIATION CHEMISTRY, HEALTH PHYSICS AND SUSTAINABLE NUCLEAR ENERGY PRODUCTION

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Abstract

Nuclear Chemistry, Radiochemistry, Radiation Chemistry and Heath Physics play a fundamental role in sustainable nuclear energy production. Their applications are crucial in each stage of the nuclear power cycle. There will be stressed some particular chemical steps concerning the extraction and production of fuel pellets, claddings and assemblies, water radiolysis, plant decommissioning and their reprocessing or disposal cycle. The objectives of this work are: the presentation and the discussion about strength and weakness of the nuclear and radiochemical methods to be used in the sustainable production of nuclear energy and the stressing of the great need of education and training of young scientists in the field of. nuclear and radiochemical (N&R) techniques, in order to ensure a sustainable supply of qualified personnel, whose number have declined steadily and dramatically in the last 20 years. A review on main problematic regarding the different fuel cycles is presented, distinguishing between the traditional open fuel cycle (UOT) adopted in many Countries and the more advanced close cycle, with reprocessing of the nuclear rad-waste, taking into account the partitioning (P) and transmutation (P&T) of U and Pu radionuclides, fission products (FPs), minor actinoids (MAs) and activation products.

1   INTRODUCTION

Jáchymov (from "Saint Joachim's Valley") is a small Spa village in north-west Bohemia, belonging to the Karlovy Vary region, close to the border to Germany. A silver mine and smelter for coin production, that is still operating today, attracted there the pioneering father of mineralogy, Georgius Agricola (the Latinized name of Georg Pawer or Bauer, 1494–1555), author of the famous *De Re Metallica*, because a series of new unknown ores were extracted in large amounts. Amongst them, there was a mineral that was named pitchblende, whose use was devoted for some centuries to the preparations of dusts and colored phosphorescent glasses. In 1789 the German chemist M.H. Klaproth recognized and isolated a new element in pitchblende, that he baptized uranium. One more century was necessary to discover that the mineral extracted in a site of the Jáchymov mine (already called *Agricola pit*) and its components had radioactive properties (Henry Becquerel 1896 and Marie Sklodowska Curie 1898). Since those events Radiochemistry and Nuclear Chemistry started to play a fundamental role in the life sciences and a few decades later, together with Health Physics, on sustainable energy production.

Their applications are crucial in each stage of the nuclear power cycle and regards in summary:

1.1   identification of uranium and thorium minerals by modern survey techniques by aircrafts and helicopters, equipped with suitable radiometric instrumentation;

1.2   assessment of the environmental and human health status before the installation of a new nuclear power plant (NPP). This requires the development of environmental and human models that are based on experimental data: measurements of trace elements and environmental radionuclides (RNs) in soil, water, air and bio-monitors, and human samples as well (e.g. blood and hair), of the population living near the selected site of mine and NPP;

1.3   operations related to the nuclear fuel production: uranium (and thorium mining and extraction from ores, isotopic enrichment (is necessary) and production of solid fuel pellets and rods from uranium hexafluoride vapor, HF_6;

1.4   assessment of the potential environmental contamination and human exposure (workers and general population) as determined by a regular monitoring of the eventual leakage of radionuclides (RNs) during the operation of the NPP;

1.5   alternative applications of nuclear energy for production of either RNs, nuclear hydrogen or for desalinization of water;

1.6   management, storage and disposal of radioactive waste (rad-waste) from exhaust fuel, either ad interim storage or by "Partitioning and Transmutation" (P&T). This requires the radiochemical separation and the concentration of the fissile and fertile recyclable RNs of U and Pu separating them from Minor Actinoids (MAs, according to IUPAC the terms *actinides* and *lanthanides is obsolete*), Fission and Corrosion Products (FPs and CPs);

1.7   dismantlement and decommissioning of the NPP. This demands a huge amount of radioprotection and health physics measurements, and the control of the radioactivity of the environment, re-assessing the environmental and human health status.

2   OBJECTIVES OF PRESENT PAPER
The objectives of present paper are as a summary:

2.1   to present and discuss items such as:

- a fast review of fuel cycle from mine to rad-waste, involving Nuclear Chemistry, Radiochemistry and Radiation Chemistry techniques.
- nuclear analytical techniques (NATs): Instrumental- and Radiochemical Separation Neutron Activation Analysis (INAA and RSNAA respectively) and others [1,2], applied to monitor environmental and biological matrices and to characterize the nuclear fuel;
- radioanalytical techniques: use of High Specific Activity Radiotracers produced by cyclotron or nuclear reactor in no-carrier added (NCA) form [2], applied to the development and calibration of the radioanalytical and radiochemical processing procedures;
- radiation protection techniques: alpha, beta and gamma spectrometries, applied to control the environmental contamination and to the health physics protection of general population and workers.

2.2   to stress the great need of education and training of young scientists in the field of. nuclear and radiochemical techniques, in order to ensure sustainable supply of qualified nuclear chemists and health physicists, whose number has declined steadily and dramatically in the last twenty years as a consequence of several anti-nuclear moratoria all over the world and in Italy in particular. We propose that health physics, nuclear chemistry and related courses re-enter into the university programs in full.

3 THE ROLE OF RADIOCHEMISTRY, NUCLEAR CHEMISTRY AND HEALTH PHYSICS, IN NUCLEAR POWER GENERATION

Since the discovery of radioactivity of natural salts of uranium by H. Becquerel (1896) and the discovery of radium and polonium by M. Curie (1898), in the following few decades, scientists like, the Curie's, F.E. Dorn, K. Fajans, F. Soddy, G. von Hévesy, E. Rutherford and many others [3,4,5,6,7,8], understood clearly that the applications of this new natural phenomenon would offer plenty benefits to mankind and human well-being [8,9].

With the discovery of neutron activation in Roma by E. Fermi (1934) and Co., the cyclotron by E. Lawrence in Berkeley (1932), the induced fission of natural U in Berlin by O. Hahn and Co. (1939) and natural fission by G.N. Flerov and K.A. Petrzhak in Russia (1940), plenty artificial radionuclides by either fission or activation in nuclear reactor and activation in cyclotron or proton linac, become available in addition to natural ones. Moreover, induced fission promised suddenly to became a powerful and inexhaustible source of energy (both thermal and electrical) for industry, transportation and basic necessities of human life. In this scenario the novel disciplines namely Radiochemistry, Nuclear Chemistry, Radiation Chemistry (in short N&R) and Health Physics [10] started to develop quickly, up to the more update applications like: Radiopharmaceutical Chemistry (*i.e.* for both radiodiagnostics and metabolic radiotherapy) [11,12], *curing* of materials, protection of human heritage handicrafts and sterilization of different kinds of food, medical and surgical specimen as well [13], and last but not least the direct dissociation of water in gaseous H_2 (*i.e.* hydricity) and O_2, either pyrochemically in presence of a catalyst at temperatures much higher than 1 000 °C in very high temperature nuclear reactor (VHTGR) or by thermochemical cycles at a bit lower temperatures (HTGR). The heat generated by NPPs can also solve the problem of lacking of potable water, by desalting the inexhaustible sea and ocean sources [9,10,14,15,16].

3.1 The Nuclear Fuel Cycle from mining to rad-waste

In the next sections we deal mainly with the plenty applications of N&R in the various steps of fuel cycle for energy production, based on fission of either fissile (or fertile) materials, from ore mining, plant operation, decommissioning and rad-waste disposal.

3.1.1 Site evaluation for new nuclear power plants

The first step to be faced is the site evaluation for nuclear installations in terms of nuclear safety is to protect the public and the environment from the radiological consequences of radioactive releases due to accidents. Three basic requirements that govern siting of nuclear power plant (NPP) installation are: (i) effects of external events (natural and man-induced) on the installation; (ii) effects of the installation on site environment and population; (iii) factors affecting implementation of emergency measures

in public domain, and evaluation of risks to individuals and the population.

Site characteristics and characteristics of natural environment in the site region which may affect safety of the nuclear installation are investigated and assessed for a projected time period encompassing the lifetime of the installation. In particular, safety guides on this matter are published by the International Atomic Energy Agency (IAEA) [17] and the International Nuclear Incident Scale (INIS) scale of 7 kinds of accident was established: 0 no safety significance, 1 anomaly, 2 incident, 3 serious accident (Vandellos NPP, Spain 1989), 4 accident without significant out-site risk (Windscale Reprocessing Plant 1973), 5 accident with off-site risk (Three Mile Island NPP, USA 1979), 6 serious accident (Kyshtym Reprocessing Plant, USSR 1957), 7 major accident (Chernobyl NPP, Russia 1986). The IAEA guides include the following requirements: (i) site characteristics that may affect the safety of the nuclear installation shall be investigated and assessed, characteristics of the natural environment in the region that may be affected by potential radiological impacts in operational states and accident conditions shall be investigated. All these characteristics shall be observed and monitored throughout the lifetime of the installation; (ii) the possible non-radiological impact of the installation due to chemical or thermal releases, and the potential for explosion and the dispersion of chemical products shall be taken into account in the site evaluation process; (iii) the direct and indirect pathways by which radioactive material released from the nuclear installation could potentially reach and affect people and the environment shall be identified and evaluated; in such an evaluation specific regional and site characteristics shall be taken into account, with special attention paid to the function of the biosphere in the accumulation and transport of radionuclides; (iv) a description of the surface hydrological characteristics of the region shall be developed, including descriptions of the main characteristics of water bodies, both natural and artificial, the major structures for water control, the locations of water intake structures and information on water use in the region. In this context, the site evaluation includes a description of the geology and structural geology in regional, local, and site scales. In addition, radiological safety of the public and the environment is an important further consideration for siting of nuclear installations. The environmental radioactivity and hazardous substances for the proposed site must be characterized from historic or present activities, with respect to both natural and anthropogenic sources. Atmospheric, terrestrial, aquatic, and groundwater radioactivity levels, and ambient radionuclide activity levels in ingested water and food used in the human pathways modeling must be also assessed. This imposes the assessment of the ambient background radioactivity of the atmosphere, hydrosphere, lithosphere and biota in the site region prior to commissioning as a baseline in future investigations so as to be able to determine the effects of the installation. Moreover, areas that have received substantial contamination from previous nuclear or non-nuclear industrial activities require baseline characterization of radionuclide (RN) and hazardous substance levels within biota of interest. In this context, nuclear analytical techniques (NATs) such as neutron activation analysis (NAA),

widely used for environmental studies and well recognized as very sensitive, multielemental and accurate analytical technique, can play a fundamental role for the assessment of trace metals in environmental matrices such as rock, soil, water, air, bio-monitors (e.g. lichens). Furthermore, radiochemical measurements by high resolution computer-based HPGe *gamma* spectrometry are indispensable to get data on ambient radioactivity. Studies on uranium, radium, polonium, and lead in drinking water, foods, and the environment are gaining more interest. Polonium and lead are especially challenging elements that need more consideration in the future.

An aspect which is not adequately considered when new NPPs are installed and that we strongly recommend concerns the health status of the population living near the site in which nuclear plants would be installed. In parallel to the definition of baseline data on trace metals and ambient radioactivity in environmental matrices, campaigns would be carried out to assess the background levels of trace and radioactive elements human biological matrices as indicators of exposure such as biological fluids (blood, urine) and tissues (e.g. hair, nails, autoptic tissues) from selected groups of population. These data will be important in assessing the risk to humans arising from the activity of a nuclear power plant. Again, in this context, nuclear and radioanalytical techniques can have an important role [18,19,20].

3.1.2 The natural nuclear fuels

The two chemical elements present in nature - in a "inexhaustible" amount are uranium, the even Z elements U (Z = 92) and in 3-4 fold amount the even Z thorium, Th (Z = 94) [21]. The first is constituted by 3 radioisotopes: the even-even ^{238}U ($T_{1/2}$ = 4,468 Ga, *i.e.* fertile with thermal neutrons, fissile with fast neutrons), at secular equilibrium with the even-even ^{234}U ($T_{1/2}$ = 0,2455 Ma), and the even-odd ^{235}U (fissile) which is present unfortunately in a small percentage of 0,72% in natural U 21. Thus, only the even-odd ^{235}U ($T_{1/2}$ = 7,038 Ma) is fissile with low energy neutrons in thermal nuclear reactor (*i.e.* conventionally, having a most probable energy of the Maxwellian distribution of 0,025 eV, corresponding to a velocity of 2,200 km.s^{-1}, through the equation: $<E> = k \, T = \frac{1}{2} \, m \cdot v^2$). The even-even ^{238}U constitutes the 99,2745% of the total natural U, while the ^{234}U represents only the 0,0055 % (*i.e.* if it is at secular equilibrium with previous one). The thorium element is not fissile, but fertile and it is constituted by a single very long-lived RN, the ^{232}Th ($T_{1/2}$ = 14,05 Ga), that at the moment is not used on a large scale for energy production, because necessitates for the start-up of the breeding cycle to produce energy in a thermal breeder reactor of a mixed fuel (*i.e.* U/Th or Pu/Th).

Besides, it can be shown by theory and practical applications that ^{235}U can be used without any enrichment process in heavy water (D_2O) moderated and cooled thermal reactor (HWR), and about 56 NPPs (CANDU type) [22,23,24] presently operating all over the world, are based on this concept. Conversely, the majority of the 440 NPPs presently operating - and 40 under construction - is fed with U slightly enriched at 3-4% in ^{235}U and

moderated and cooled by light water (LWR), while a few others are fast-breeder reactors (FBR) using Pu radionuclides or MOX (Mixed Oxide fuel) as fuel. The most important Pu radionuclide, the even-odd ^{239}Pu ($T_{1/2}$ = 24,11 ka), is obtained by fast breeding of ^{238}U through the chain ^{238}U(n,γ)^{239}U → ^{239}Np → ^{239}Pu (where → indicates a beta minus decay). Other Pu even-odd RNs (A = 241 and 243) produced by multiple neutron capture in thermal NPP are fissile too. It must be stressed that even in thermal NPP, about 20% of the energy is produced by Pu RNs bred from ^{238}U by multiple neutron captures, whose build-up increases with burn-up of the fuel and reactor flux density [23,24,25,26,27,28].

The ^{238}U natural series (4 n + 2) The chain decay is **blocked** after the purification of natural U or DU by the long half-life of ^{234}U			^{238}U 4.468 10^9 a alpha ↓ ^{234}Th
(n,γ) ← 96 barn ↓ ⤹ ^{235}U ⤸	^{234}U 2.455 10^5 a alpha ↓	⇐ ^{234m}Pa beta, (IT) 1.17 min (gamma 1001 keV) ⇐ ^{234g}Pa beta 6.70 h	m ⤸ 24.10 d beta The short-lived ^{234g}Pa is
(n,fiss) 586 barn ↓↓ FPs	7.038 10^4 a alpha ↓	^{230}Th 7.54 10^4 a alpha ↓	partially burned in a NPP, due to the significantly
		(n,fiss) 500 (m) + 5000 (g) barn ↓↓ FPs	high fission cross-sections.

FIG. 1: In the (4 n + 2) natural decay chain at secular equilibrium in a closed geological system, all RNs have the same activity (apart the branching decay value), but after the purification of either ^{238}U or ^{238}DU, only 4 RNs reach relatively quickly the equilibrium, because the long-lived ^{234}U blocks the chain and the following daughters are absent. All neutron capture and fission cross-sections reported in this paper (TAB. 1) are related to a thermal reactor with Maxwellian neutron spectrum and are sometimes substantially different (*i.e.* higher or lower) from those that are present in a real fuel of a NPP [27].

In case of partitioning and recycling of exhaust fuel elements rods, pins or assemblies), U (A = 238, 235 and small amounts of 232 and 236) and Pu (A = 239, 240, 241, 242, 243 and small amounts of 238) radionuclides are recovered in the oxidation state IV as MO_2 and used to produce a mixture of the two in a form of MOX, to be recycled in thermal or fast reactors. The amount of MOX mixed with enriched ^{235}U does not exceed

the 30% - and exceptionally the 50% - of the total fuel mass and the Pu in MOX does not exceed 5% in ^{233}Pu up to 7% in total Pu RNs.

TAB. 1: Thermal radiative capture and fission cross-sections and half-lives, for a selected number of U, Pu RNs and MAs [28].

| RNuclide	$\sigma_{(n,\gamma)}$ (barn)	σ_{fiss} (barn)	$T_{1/2}$
^{233}U	47	530	0,1592 Ma
^{235}U	95	586	70,38 Ma
^{238}U	2,7	3•10^{-6}	4,468 Ga
^{237}Np	170	0,020	2,144 Ma
^{239}Pu	270	752	24,11 k a
^{241}Pu	370	1 010	14,35 a
^{241}Am	60 + 640	3,15	432,2 a
^{242m}Am	1 700	5 900	141 a
^{243}Am	75 + 5	0,079	7,370 ka
^{242}Cm	20	5	162,94 d
^{243}Cm	130	620	29,1 a
^{244}Cm	15	1.1	18,10 a
^{245}Cm	350	2 100	8,500 ka
^{246}Cm	1,2	0,16	4,730 ka
^{247}Cm	60	82	15,6 Ma
^{248}Cm	2,6	0,36	0,340 Ma

Looking either at FIG. 1 (or other similar cases in which there is a competition between neutron capture, induced fission and alpha or beta decay), it is possible to evaluate the percent ratio $\psi_{(fiss)}{}^{\%}$ between the direct fission of a particular radionuclide (RN) in a NPP and the overall consumption of the same RN due to decay and total absorption (*radiative neutron capture + neutron induced fission, excluding only elastic scattering and prompt gamma emission*), through the simple Eq. (1), that in the case of ^{234m}Pa leads to ~ 0.51% for a flux density $\phi = 10^{15}$ cm^{-2}.s^{-1}, making its fission absolutely negligible in spite of the significant cross-section of 500 barn:

$$\Psi_{(fiss)}{}^{\%} = 100 \cdot \phi \cdot \sigma_{(fiss)} / [\lambda + \phi \cdot (\sigma_{(n,\gamma)} + \sigma_{(fiss)})] = 100 \cdot \phi \cdot \sigma_{(fiss)} / \Lambda \qquad (1)$$

Of course, this behaviour depends on the very short half-life of the odd-odd ^{234m}Pa and in any case the further decay chain is blocked by the very long-lived ^{234}U. The same equation can be used for calculating the $\psi_{(n,\gamma)}{}^{\%}$, as it is shown in FIG. 2.

Another example applies to the chain ^{231}Pa($T_{1/2}$ = 32,76 ka) (n,γ) 200 barn to ^{232}Pa($T_{1/2}$ = 1,31 d) → ^{232}U($T_{1/2}$ = 68,9 a) ➜ ^{228}Th($T_{1/2}$ = 1.913 a) ➜ ^{224}Ra ➜ ^{220}Rn ➜ down to ^{208}Pb (stable, where → indicates a beta decay and ➜ an alpha decay), the fission of the odd-odd ^{232}Pa ($\sigma_{(n,\gamma)}$ = 460 barn, $\sigma_{(fiss)}$ = 1 500 barn) in a NPP of the same flux density ϕ, competes with the beta decay to ^{232}U and radiative neutron capture to ^{233}Pa($T_{1/2}$ = 27,0 d) → ^{233}U($T_{1/2}$ = 0,1592 Ma), with $\psi_{(fiss)}{}^{\%}$ ~ 18,6% of the total. In the case of ^{236}Pu($T_{1/2}$ = 2,858 a) to ^{237}Pu($T_{1/2}$ = 45,2 d) → ^{237}Np($T_{1/2}$ = 2,144 Ma) (n,γ) 170 barn to ^{238}Np($T_{1/2}$ = 2,117 d) → ^{238}Pu($T_{1/2}$ = 87,74 a), the fission of the odd-odd ^{238}Np (σ_{fiss} = 2 600 barn) is of confrontable with beta decay to ^{238}Pu, with $\psi_{fiss}{}^{\%}$ ~ 40,7%.
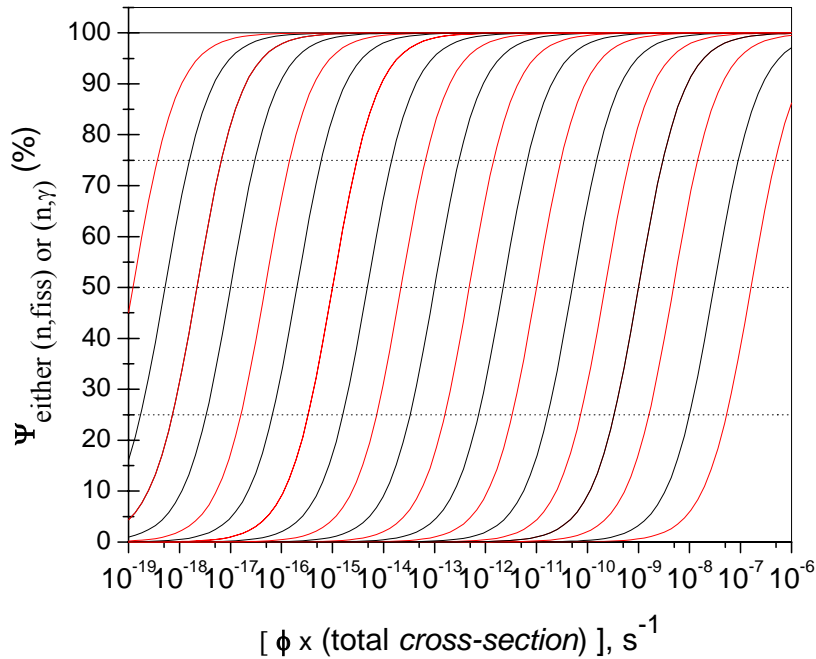
FIG 2: Behaviour of the parameter $\psi(\phi_{(fiss),(n,\gamma)}{}^{\%}$ defined in Eq. (1), as a function of the total cross-section (radiative neutron capture + neutron induced fission) = 500 barn and of the half-life of a radionuclide. The decay half-life varies from some a few ms (right side) to some hundred years (left side).

3.2   The xenon transient

Some isobars from fission chains contain RNs with very high neutron capture cross-sections. This is the case of A = 135 and its existence affects the reactor kinetics in case of

shut-down. The genetic relation in the A = 135 chain is, by reporting the independent yield of the main isotopes (TAB. 2).

During the normal operation with a constant flux density $\phi = 10^{15}$ cm^{-2}.s^{-1}, the very large $\sigma_{(n,\gamma)}$ converts ^{135}Xe to ^{136}Xe, taking its amount small, with $\psi_{(n,\gamma)}^{\%} \sim 99.2$ %. After an abrupt reduction of ϕ to a lower value (e.g. 10^{11} cm^{-2}.s^{-1}), with the $\psi_{(n,\gamma)}^{\%} \sim 1.2$ % and the ^{135}Xe production is faster by decay of its precursor ^{135}I, leading to a transient equilibrium. Therefore, after a shut-down of a NPP, it is necessary to wait some time to restart until the amount of ^{135}Xe has been reduced by decay (xenon poisoning). The reactor can be during the xenon transient be difficult to control to reach again a steady state [23,24,27].

TAB 2: Genetic relation of isobar A = 135, leading to the xenon transient
in case of NPP shut-down. Beta decay →, fission ⬇⬇, neutron capture ⬇.

Independent fission yield	**3.5** (%)		**2.5** (%)		**0.6** (%)				
	⬇⬇ ^{135}Te	→ 18.6 s	⬇⬇ **^{135}I**	→ 6.61 h	⬇⬇ **^{135}Xe** ⬇ **(n,γ)** 2.65 10^6 b ⬇ ^{136}Xe stable (n,γ) 0.26 barn ⬇ ^{137}Xe	→ 9.10 h → 3.83 m	^{135}Cs ^{137}Cs	→ 2 Ma → 30.17 a	^{135}Ba **stable** ^{137}Ba **stable**

3.3 Thorium Reactors

A brief digression must be made about the thorium based NPPs. The ^{232}Th itself is not a fissile radionuclide, but a fertile one. Thus the start-up of this kind of fuel necessitates of either a mixture of enriched ^{235}U and thorium (U/Th reactor), a mixture of Pu and thorium (Pu/Th reactor), or an external strong source of neutrons, like a Spallation Neutron Source (SNS), in order to reach a concentration of fissile ^{233}U (T$_{1/2}$ = 0,1592 Ma) in the fuel suitable to obtain the criticality and an auto-sustainable nuclear reaction. In fact the ^{232}Th can be bred in thermal nuclear reactor in which the following beta chain is induced for starting up the process, Eq. (2):

$$^{232}Th(n,\gamma)^{233}Th \rightarrow {}^{233}Pa \rightarrow {}^{233}U \text{ (fissile)} \qquad (2)$$
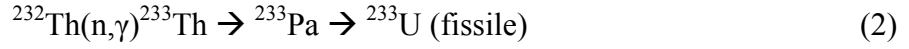
in slight competition with the reaction induced by the fast component of the neutron spectrum: $^{232}Th(n,2n)$ 0.012 barn to $^{231}Th \rightarrow {}^{231}Pa \rightarrow$.

Mixed U and Th fuel elements have been already produced and used by a sol-gel process, in which a colloidal solution of U/Pu complexes is added to an inert solvent, able to de-hydratate and freeze the complexes. Then the solvent is heated and decomposed leaving a "kernel" of pellets. The kernel is washed, air dried and eventually reduced by H_2 to form UO_2. The kernel of the pellet is then sintered at high temperature. A similar method can be used to prepare An (*i.e.* An means the family of actinoids, or 5f elements, while according to IUPAC, the term *actinides* or *attinidi* is obsolete since a long time), and to cover them of a protective layer of either pyrolitic graphite PyC, SiO_2 or SiC.
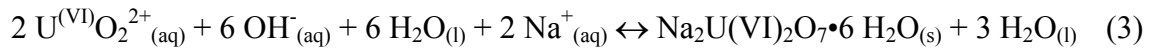
It is remarkable that between the thermally fissile RNs, the ^{233}U has the highest fission efficiency, $\Theta = 1 / \alpha = \sigma_{(fiss)} / \sigma_{(n,\gamma)}$, compared to ^{235}U and ^{239}Pu. Looking again at Eq. 1, after the purification of ^{232}Th from ore mining, the following decay chain holds in a "closed" system: ^{232}Th ($T_{1/2} = 1,405 \ 10^{10}$ a) $\rightarrow {}^{228}Ra$ ($T_{1/2} = 5,75$ a) $\rightarrow {}^{228}Ac$ ($T_{1/2} = 6,13$ h) $\rightarrow {}^{228}Th$ ($T_{1/2} = 1,913$ a), thus after 5,75 a, the 50% of the secular equilibrium with ^{232}Th should be reached (*i.e.* or 75% after 2 x 5,75 a and 99.2 % after 7 x 5,75 a decay half-lives), but in an operating Th reactor with $\phi = 10^{15}$ cm^{-2}.s^{-1}, a $\psi_{(fiss)}{}^{\%}$ ~ 4.8% of ^{228}Ra (*i.e.* $\sigma_{(n,\gamma)}$ = 36 barn, $\sigma_{(n,fiss)}$ = 2 barn) is fissioned instead of decaying to ^{228}Th and this behaviour is due mainly to the relatively long half-life of ^{228}Ra itself, in spite of the very low fission cross-section.

One of the main advantages of Th reactors is that this element is present in the earth crust in concentration 3-4 folds those of U, *i.e.* mainly in a mineral monazite, a very insoluble phosphate of Th^{4+} and different percentages of Ln (*i.e.* Ln means the family of *lanthanois*, or 4f elements, while according to IUPAC the terms *lanthanides* and *lantanidi* are obsolete), that are normally in the oxidation state III, but sometimes IV (Ce) and II (Eu). Conversely, Th is almost absent in water due to the very poor solubility of most of its compounds (*i.e.* except chlorides and nitrates). This last property facilitates strongly the fuel separation and the fuel recycling, with a significant smaller amount of rad-waste. Finally, the ^{232}Th decays on the relatively long-lived ^{228}Ra ($T_{1/2} = 5,75$ a) and its daughters (*e.g.* ^{228}Th, $T_{1/2} = 1,913$ a), whose build-up requires several years after ^{232}Th extraction and purification (see above). At last, the Th recycle does contain ^{233}U slightly contaminated by the fissile and fertile ^{232}U ($T_{1/2} = 68,9$ a), which contributes by radiative neutron capture to the production of other ^{233}U. Very old ^{233}U specimen does contain small amounts of the fertile and fissile ^{229}Th ($T_{1/2} = 7\ 880$ a), which is also a γ emitter at 194 and 211 keV [21].
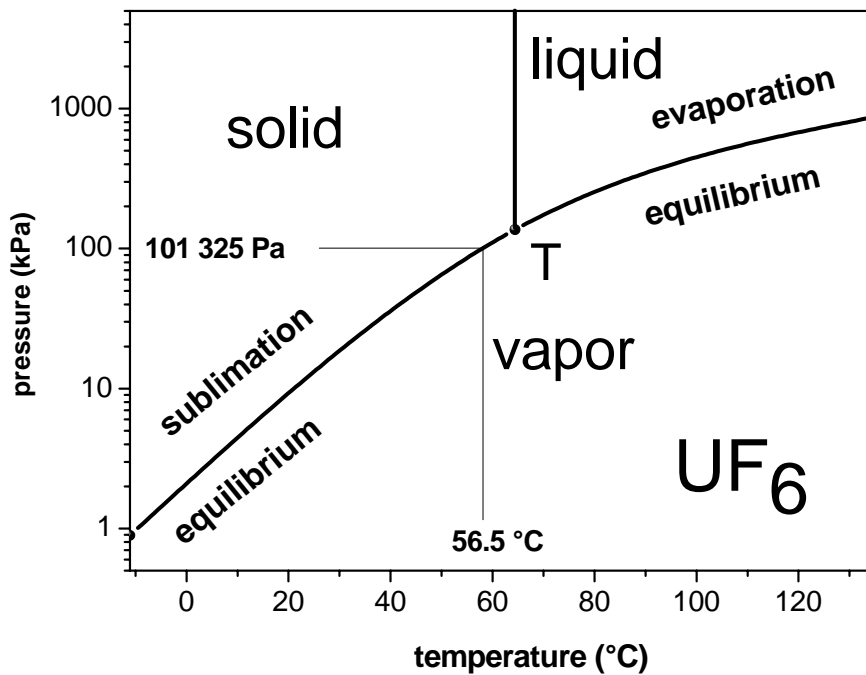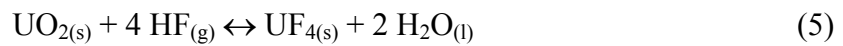
3.4 Uranium (and thorium) mining

Uranium is present in substantial amounts both in the earth crust (2,7 ppm) and in the salty water of seas and oceans (3 ppb or 3 tonnes.km^{-3}), *i.e.* 68 fold more concentrated that gold, with a concentration in the crust similar to Sn 2,3 ppm, Ta 2,5 ppm, W 1,25 ppm, but a bit less concentrated than Pb 14 ppm and more than I, 0,45 ppm) [21,29]. The reason for this behaviour is that U is easily oxidable to the relatively stable oxidation state VI, in which it forms a very soluble cation UO_2^{2+}, namely uranyl cation or dioxo-uranium(2+), which explains its concentration in particular veins and minerals due to the underground water leaching of the original ore for billion of years and its transportation as hydroxido- and carbonato-complexes like: UO_2^{2+}, $[UO_2(OH)]^+$, $[(UO_2)_2(OH)_2]^{2+}$, $[UO_2(OH)_2]^{2-}$, $[UO_2(OH)_2]_{(s)}$, $[UO_2(CO_3)_2]_{(s)}$, $[UO_2(CO_3)_2]^{2-}$ and $[UO_2(CO_3)_3]^{4-}$ set in order of stability by increasing pH value of underground water [27]. Nowadays are known about 250 different minerals containing U in low percentage, but at the moment its extraction is carried out from the more concentrated ones, like pitchblende (UO_3, U_2O_5 or U_3O_8), uraninite (UO_2), carnotite, autunite, uranophane, torbernite, coffinite or minerals having a U content not lower than 0,1% of U metal.

In short, the two main methods of extraction are *open-pit mining*, also known as open-cast mining and open-cut mining, which refers to a method of extracting rock or minerals from the earth by their removal from an open pit or borrow and heap leaching which is an industrial mining process to extract precious metals and copper compounds from ore. by injecting underground dilute sulfuric acid to extract the soluble UO_2^{2+} cation. The final product is called yellowcake ($[Na_2U^{(VI)}_2O_7 \cdot 6\ H_2O]_{(s)}$ or UO_2) and as explained in the next section requires significant further processing to produce fuel-grade feed. After extraction, the U ore (normally containing the mixed oxide U_3O_8, even if other oxides are known (U_4O_9, U_3O_7, U_3O_8 and $UO_3 \cdot 2\ H_2O$) is crushed and milled into a fine powder and than dissolved in sulphuric acid (sometimes mixed with nitric acid), leaving back all insoluble sulphates (*i.e.* after addition of some Ba^{2+} as an *isomorphous carrier* for Ra^{2+}), like those of $^{226}Ra^{2+}$, $^{210}Pb^{2+}$, $^{210}Po^{2+}$, $^{214}Bi^{3+}$ and $^{232}Th^{4+}$). The further non-soluble residue made of silicates is discharged too. Of course the elimination by *filtration with non-isotopic carrier* of the insoluble $^{226}RaSO_4$ and most of its radioactive daughters, is fundamental to eliminate the major activity of U minerals, making the discharge of the process a **TENORM**. After this purification, the only RNs, which in a short time reach the equilibrium with ^{238}U are the beta emitters ^{234}Th and $^{234(m+g)}Pa$ (*i.e.* easily identifiable by the characteristic *gamma* emission at 1 001 keV of ^{234m}Pa, see FIG. 1), making the concentrated U as soluble uranyl sulphate $U^{(VI)}O_2SO_4$. By addition of NaOH the insoluble sodium diuranato(6+) $[Na_2U^{(VI)}_2O_7 \cdot 6\ H_2O]_{(s)}$ (*i.e.* the *yellow cake*) is obtained, Eq. (3), a very low radiotoxic material easy to handle by rubber gloves. Let's remember that all chemical reaction are basically equilibrium reaction ($\leftrightarrow$) and rarely are completely shifted toward the products:

$$2\ U^{(VI)}O_2{}^{2+}{}_{(aq)} + 6\ OH^-{}_{(aq)} + 6\ H_2O_{(l)} + 2\ Na^+{}_{(aq)} \leftrightarrow Na_2U(VI)_2O_7 \bullet 6\ H_2O_{(s)} + 3\ H_2O_{(l)} \quad (3)$$

The diuranate is reduced to U(IV) by H_2 (or by the thermally unstable NH_3 as an H_2 source) and calcinated to $U^{(IV)}O_2$, then it is converted by anhydrous HF to $U^{(IV)}F_4$ using N_2 as carrier gas and then re-oxidized to $U^{(VI)}F_6$ (i.e. a solid that sublimes at 330 K, at 100 kPa, see FIG. 3) by addition of F_2 gas (Eqs. 4,5,6):

$$[Na_2U^{(VI)}{}_2O_7 \bullet 6\ H_2O]_{(s)} + H_{2\ (g)} \leftrightarrow 2\ UO_{2(s)} + 9\ H_2O_{(l)} + 2\ Na^+{}_{(aq)} \quad (4)$$

$$UO_{2(s)} + 4\ HF_{(g)} \leftrightarrow UF_{4(s)} + 2\ H_2O_{(l)} \quad (5)$$

$$UF_{4(s)} + F_{2(g)} \leftrightarrow UF_{6(s)} \quad (6)$$

FIG. 3: Phase diagram of UF_6. T represents the triple point at 64,8 °C and 137 kPa, while at atmospheric pressure (101,325 kPa) the sublimation point is 56,5 °C.

3.5 Uranium enrichment

At this stage - if enrichment in [235]U is required for some kind of NPP – UF_6 vapours - or in minor extent U metal vapours - are subjected to various possible enrichment processes, that are reported in historical order of relevance; in all cases the final concentration of depleted uranium tails (DU) is of the order of 98-99% [e.g. 30]:

3.5.1 mass separation (with suitable magnets, called calutrons or California Cyclotrons in early times). More sophisticated mass separation methods have been abandoned due to the very high cost.

3.5.2. membrane diffusion: based on the different velocities of heavy and light UF6 vapours passing through a porose membrane, by following the Graham law.

3.5.3 nozzle or aerodynamic separation: based on the separation of heavy and light UF_6 that is injected at high velocity in a shaped nozzle, with a separation septum at the exit.

3.5.4 chemical isotope separation: based on enhanced kinetic isotopic effect, to separate low and high mass U isotopes developed in Japan. There is also the French CHEMEX process in which enrichment takes place during repeated exchanges between an aqueous phase with U(III) and an organic phase with U(IV). Solutions were prepared using natural U and not UF_6. Four elements constituted the mixture: a solvent, Hg metal, HCl and uranium salts.

3.5.5 ultracentrifugation: in either aluminium or maraging alloy (martensitic ageing SS, *i.e.* G. Zippe type ultrasound ultracentrifuge), that is the most important method at present, due to the high separation efficiency that increases as the root of peripheral speed of the centrifuge, that reaches ultrasound speeds. A part of a battery of ultra-centrifuges of an enrichment plant is shown in FIG. 4.
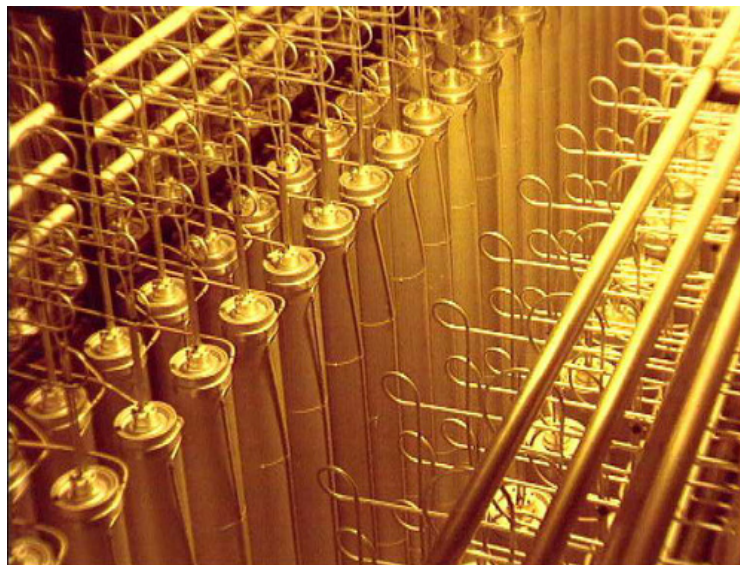
FIG. 4: A series of Zippe type ultrasonic ultracentrifuges for UF_6 enrichment. Many thousand of them are necessary to obtain either reactor grade LEU or HEU.
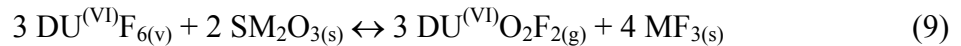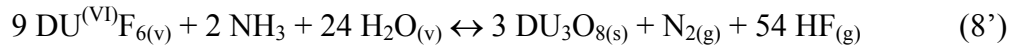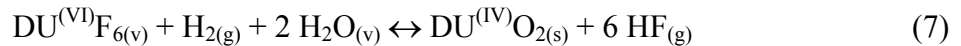
3.5.6 laser separation: on both uranium compounds (**MVLIS**, molecular vapour laser isotope separation) or uranium metal (**AVLIS**, atomic vapour LIS). These last techniques, already demonstrated, will be probably the future of U enrichment industry.
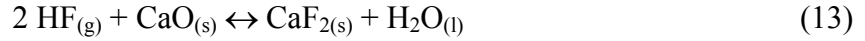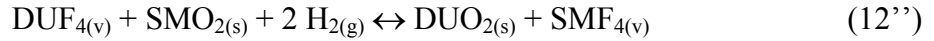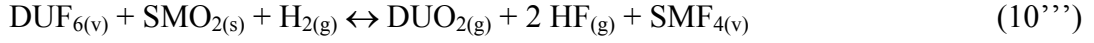
3.5.7 cyclotron ion resonance separation: based on the isotope separation of a plasma injected in an Ion Cyclotron Resonance (**ICR**) source.

In all cases the depleted uranium (DU in the form of DUF_6), that contains ^{238}U in percentages close to 98-99% *is a valuable and safe by-product* to be used in the future in fast breeder reactors of *Gen IV*, multiplying the total production yield of the order of 100, thus making the nuclear energy an inexhaustible resource for thousand of years.

3.6   Uranium hexafluoride deconversion

The DUF_6 tails can be later deconverted (DU de-conversion Process, **DUP**) to the more safe DUF_4 by a patented fluorine extraction process named DUP/FEP, based on the reaction at high temperature with granular oxides of semimetals (SM) with high affinity for fluorine, like: B(III), Ge(IV), As(III), Si(IV), Sb(III) and anhydrous HF (AHF), while DU is then recycled either as very stable DUO_2 or DU_3O_8, slightly contaminated by fluorides of ^{99g}Tc and the transuranic (**TRU**) elements Np, Pu, Am and Cm, see TAB. 1) [31]. The thermally unstable anhydrous NH_3 is used to generate the H_2 as a reducing agent, see Eqs. (7) to (12). The B, Ge, As, Si fluorides are gaseous, and are a very suitable and valuable material for electronic industry of semiconductors and solar cell production. Finally the HF wastes can be converted to a safe fluoride, Eq. (13):

$$DU^{(VI)}F_{6(v)} + H_{2(g)} + 2\ H_2O_{(v)} \leftrightarrow DU^{(IV)}O_{2(s)} + 6\ HF_{(g)} \qquad (7)$$

$$2\ NH_{3(g)} \leftrightarrow 3\ H_{2(g)} + N_{2(g)} \qquad (8)$$

$$9\ DU^{(VI)}F_{6(v)} + 2\ NH_3 + 24\ H_2O_{(v)} \leftrightarrow 3\ DU_3O_{8(s)} + N_{2(g)} + 54\ HF_{(g)} \qquad (8')$$

$$3\ DU^{(VI)}F_{6(v)} + 2\ SM_2O_{3(s)} \leftrightarrow 3\ DU^{(VI)}O_2F_{2(g)} + 4\ MF_{3(s)} \qquad (9)$$

$$2\ DU^{(VI)}O_2F_{2(s)} + 4\ SMO_{2(s)} + H_{2(g)} \leftrightarrow 2\ DU^{(IV)}O_{2(g)} + 3\ HF_{(g)} + 4\ MF_{4(g)} \qquad (10)$$

$$3\ DUF_{6(v)} + 2\ M_2O_{3(s)} + 3\ H_{2(g)} \leftrightarrow 3\ DUO_{2(g)} + 6\ HF_{(g)} + 4\ MF_{3(g)} \qquad (10')$$

$$3\ DUF_{6(v)} + 2\ M_2O_{3(s)} + 2\ NH_{3(g)} \leftrightarrow 3\ DUO_{2(g)} + N_{2(g)} + 6\ HF_{(g)} + 4\ MF_{3(g)} \qquad (10'')$$

$$DUF_{6(v)} + SMO_{2(s)} + H_{2(g)} \leftrightarrow DUO_{2(g)} + 2\ HF_{(g)} + SMF_{4(v)} \tag{10'''}$$

$$DUF_{6(v)} + MO_{2(s)} + 2\ NH_{3(g)} \leftrightarrow DUO_{2(g)} + N_{2(g)} + 2\ H_{2(g)} + 2\ HF_{(g)} + MF_{4(v)} \tag{11}$$

$$DUF_{6(v)} \leftrightarrow DUF_{4(v)} + F_{2(g)} \tag{12}$$

$$DUF_{6(v)} + SMO_{2(s)} + F_{2(g)} + 2\ H_{2(g)} \leftrightarrow DUO_{2(g)} + 4\ HF_{(g)} + SMF_{4(g)} \tag{12'}$$

$$DUF_{4(v)} + SMO_{2(s)} + 2\ H_{2(g)} \leftrightarrow DUO_{2(s)} + SMF_{4(v)} \tag{12''}$$

$$2\ HF_{(g)} + CaO_{(s)} \leftrightarrow CaF_{2(s)} + H_2O_{(l)} \tag{13}$$
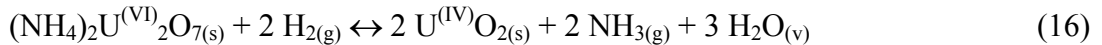
3.7 Production of fuel pellets, elements, and assemblies

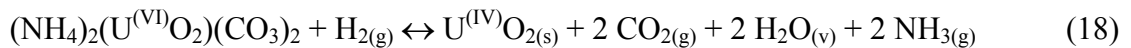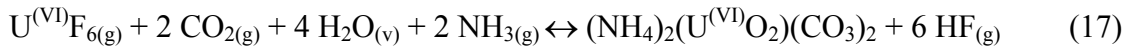The raw material UF_6 is transformed to an aqueous solution of uranyl fluoride, $U^{(VI)}O_2F_2$ by hydrolysis with water, according to the traditional Eq. (14):

$$UF_{6(g)} + H_2O_{(l)} \leftrightarrow UO_2F_{2(aq)} + 4\ HF_{(aq)} \tag{14}$$

The next step is the precipitation of poorly soluble diammonium uranate $(NH_4)_2U_2O_7$, with aqueous ammonia, followed by drying and decomposition with reduction to UO_2 by H_2 at 820 °C, according to Eqs. (15) and (16):

$$2\ U^{(VI)}O_2F_{2(aq)} + 6\ NH_{3(aq)} + 3\ H_2O_{(l)} \leftrightarrow (NH_4)_2U^{(VI)}_2O_{7(s)} + 4\ NH_4F_{(aq)} \tag{15}$$

$$(NH_4)_2U^{(VI)}_2O_{7(s)} + 2\ H_{2(g)} \leftrightarrow 2\ U^{(IV)}O_{2(s)} + 2\ NH_{3(g)} + 3\ H_2O_{(v)} \tag{16}$$

Alternatively, the $U^{(IV)}O_2$ can be obtained starting from di-ammonium and uranyl carbonate (**AUC**), according to Eqs. (17) and (18), where Eq. (17) is carried out in a fluidized bed with a mixture of H_2, H_2O and N_2:

$$U^{(VI)}F_{6(g)} + 2\ CO_{2(g)} + 4\ H_2O_{(v)} + 2\ NH_{3(g)} \leftrightarrow (NH_4)_2(U^{(VI)}O_2)(CO_3)_2 + 6\ HF_{(g)} \tag{17}$$

$$(NH_4)_2(U^{(VI)}O_2)(CO_3)_2 + H_{2(g)} \leftrightarrow U^{(IV)}O_{2(s)} + 2\ CO_{2(g)} + 2\ H_2O_{(v)} + 2\ NH_{3(g)} \tag{18}$$

Now the UO_2 powder is pressed in green pellets, later sintered at 1 700 °C in H_2 atmosphere in order to reach a density of about 10,40 Mg.m^{-3} (5% of porosity) [27]. The cylindrical UO_{2+x} pellets - of about 1 cm in diameter and 1 cm in height - are now filled in a Zircaloy tube and electron beam welded on both caps under a 200 bar He atmosphere, after previous evacuation to avoid the presence of any atmospheric gas and moisture. A

spring is put on the top, inside the Zircaloy tube to prevent fuel expansion with temperature and formation of gaseous FPs, and adding a few pellets of DUO_2 on both pin sides as neutron reflectors, to minimize neutron leakage. In FIG. 5 is shown the crystalline structure of $U^{(IV)}O_2$. Finally in FIG. 6 are shown the TRISO and QUADRISO spherical fuels used in Pebble Bed Reactors (PBR) developed in Germany, South Africa and Japan.
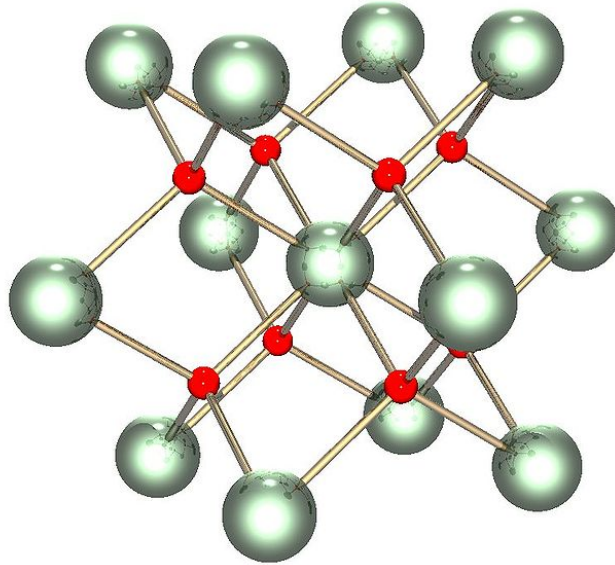
FIG 5: crystalline structure of $U^{(IV)}O_2$ (the U atoms are the big spheres, not to scale).

Apart UO_2 or UO_x , the fuel materials have been studied like uranium metal, U carbide UC, nitride UN, silicides USi_2 or U_3Si_2, carbo-oxide UCO and others. Metallic U in particular is produced by conversion of UF_6 to UF_4, followed by metallotermic reduction with Ca or Mg metals at high temperature, Eq. (19).

$$U^{(IV)}F_{4(s)} + M_{(s)} \leftrightarrow U^{(0)}_{(s)} + MF_{2(v)} \qquad (19)$$
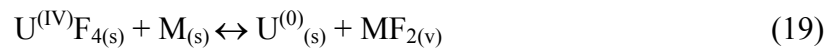
3.8   The cladding materials

The more common material for construction of fuel pins (or rods) and assemblies of them is **Zircaloy**, a *group of alloys* of ultrapure Zr metal, containing small percentages of other metals (*e.g.* Zrg-1 contains 2,5% Sn; Zrg-2 contains 1,4 % Sn, 0,1 % Cr, 0,135% Fe, 0,055% Ni and in particular < 0,01% Hf; Zrg-4 contains 1,45% Sn, 0,21% Fe, 0,1% Cr, and < 0,01% Hf, Zr705 with 5% Nb, or reactor-grade Zr-5Nb with similar composition but Hf-free, or 3Zi (97% Zr, 1% Al, 1% Sn and 1% Mo). These alloys, must not contain high neutron cross-section impurities; amongst them, the hafnium, Hf is particularly difficult to separate from Zr due to the very similar chemical properties of the two elements that

belong to Group 4 of Periodic Table and are normally found together in the same ores [32,33].

In the case of recycling of exhaust fuel, the Zr alloys have the further vantage to be almost insoluble in nitric acid, HNO_3 (containing the Lewis acid AlF_3 at < 0.05 M concentration) that is used to dissolve the UO_2, PuO_2 or MOX pellets.
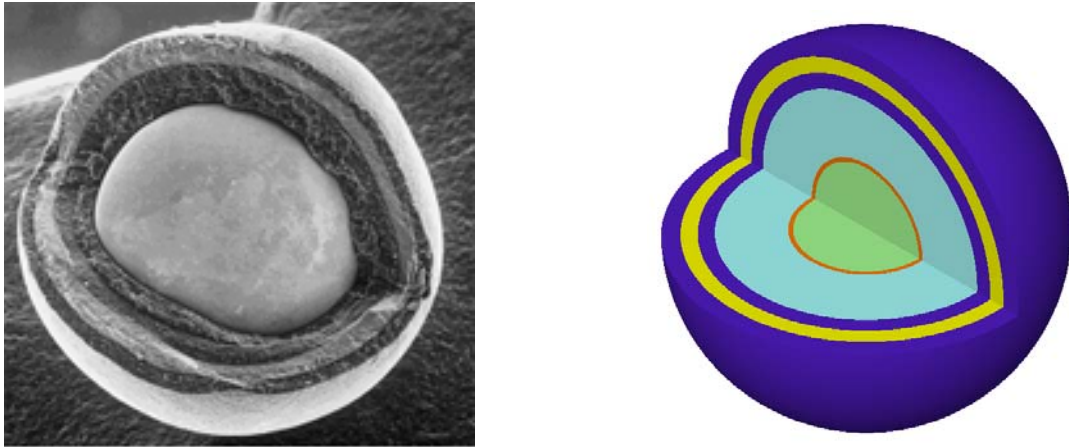
FIG 6: TRISO (left) and QUADRISO (right) particles. In QUADRISO, the *kernel* is protected by an external layer of SiO_2, SiC or PyC and further layers of *burnable poisons*.

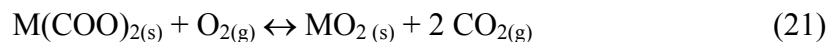A relevant limitation of Zr is that at temperatures higher than 400 °C, it starts to adsorb H_2, with and increase of brightness and formation of hydrides like ZrH_2. For high temperatures and for liquid metal cooled reactors are preferred *SS claddings* (*e.g.* 10% Cr, 8% Ni). Other cladding materials which can be used are Al and Mg alloys.

Regarding the MOX preparation, the mixture of U and Pu must be more homogeneous as possible, thus after dissolution in nitric acid the two tetravalent metals are precipitated as oxalates and then calcinated to MOX, Eqs. (20) and (21).

$$M(COO)_{2(s)} \leftrightarrow MO_{2(s)} + 2\, CO_{(g)} \tag{20}$$

$$M(COO)_{2(s)} + O_{2(g)} \leftrightarrow MO_{2\,(s)} + 2\, CO_{2(g)} \tag{21}$$
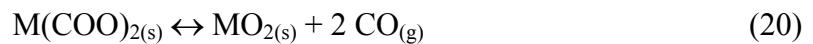
3.9 Chemistry of water-cooled reactors and Radiation Chemistry

The conditions of water (light or deuterium enriched) in a NPP (LWR or HWR) are characterized by high temperature (> 350 °C), a pressure lower than 16 MPa and presence of intense fields of X, gamma and neutron radiation, all leading to potential corrosion problems. The decomposition of water by radiolysis leads to the formation of corrosive

radicals and dangerous decomposition products like H_2 and O_2, that must be recombined catalytically to avoid possible explosions. In particular the corrosion of SS led to the formation of a deposit normally called *crud* (Chalk River Unidentified Deposit). In FIG. 7 is shown in some details the behaviour of water submitted to radiolysis by ionizing radiations. After the excitation of water and formation of *solvated electrons* $e^-_{(aq)}$ a series of reactions led to very active and often ultra-short lived-specie like the thermodynamically unstable hydrogen peroxide H_2O_2 and the hydrogen $H^\bullet$, hydroxyl $OH^\bullet$, hydroperoxyl $HO_2^\bullet$, peroxide $O_2^{\bullet-}$ radicals and hydroxide (OH^-) and superoxide ($H_2O_2^{\bullet-}$) anions as well, which contribute substantially to corrosion and formation of a dangerous mixture of H_2 and O_2 gases. Of course, being impossible the existence of free protons in water (and any other material) with the symbol $H^+_{(aq)}$, must be intended the solvated covalent cation $H_3O^+ \bullet 3\ H_2O_{(aq)}$.

There are several methods to reduce the radiolysis and formation of crud, like the charge of pH to slightly basic values by ^7LiOH (*i.e.* because ^6Li is a strong neutron absorber), NH_3, hydrazine or H_2, according to the Eqs. (22 to 24).

$$N_{2(g)} + 6\ H^\bullet_{(aq)} \leftrightarrow 2\ NH_{3\ (aq)} \tag{22}$$

$$N_2H_{4(aq)} + 2\ H^\bullet_{(aq)} \leftrightarrow 2\ NH_{3\ (aq)} \tag{23}$$

$$NH_{3(aq)} + H_2O_{(l)} \leftrightarrow NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \tag{24}$$
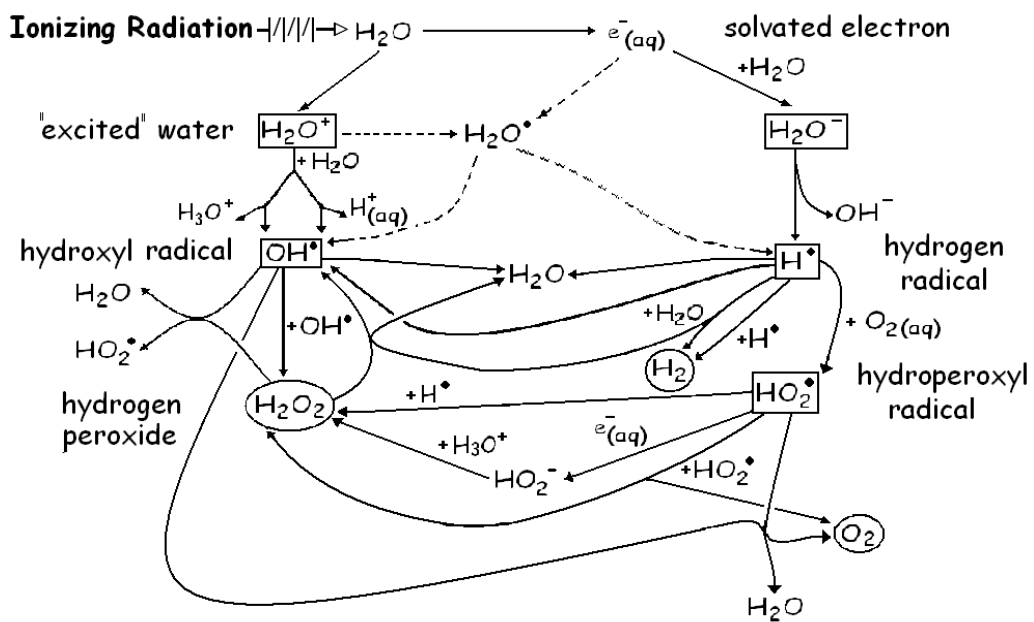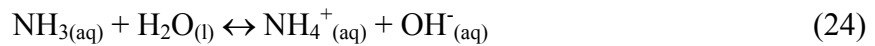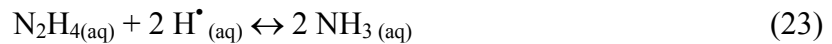

FIG 7: The scheme of radiolysis of water by Ionizing Radiations.

Crud itself can be removed by mechanical cleaning during maintenance shut down, or by addition to the coolant of either oxidizing agents like alkaline permanganate or complexants like EDTA, DTPA, oxalic and citric acids.

3.9 Some examples of radiochemical separations of radionuclides from spent fuel

The nuclear fuel cycle, especially the management and disposal of nuclear waste, is perhaps the most extensive field in which radiochemistry finds a major place. There are approximately three hundred major radioactive and stable nuclides which can be found in a spent fuel, some of them are reported in TAB. 1). Spent nuclear fuel from the reactors must be disposed, the main approaches to managing radioactive waste to date being segregation and storage for short-lived wastes, near-surface disposal for low and some intermediate level wastes, and deep and secure burial for the long-lived high-level rad-waste. The radiochemical characterization and the separation of radionuclides from the used fuel are the basis for any further operation concerning its disposal. Here the work of the radiochemist is irreplaceable. As examples of the types of radiochemical separations involving solvent extraction, precipitation and ion exchange chromatography [34] of radionuclides from spent fuel we mention here those of ^{129}**I,** ^{90}**Sr,** ^{63}**Ni** and ^{55}**Fe**.

Radio-iodine is separated from the other radioactive species by extraction into carbon tetrachloride. Before this extraction is made, a complete interchange must be affected between the added iodine isotopic carrier and the tracer iodine present in the sample. The *isotopic carrier* iodide (I^-) is added to the radioactive solution and oxidized to periodate [tetraoxido-iodato(1-), $[^{129}I]IO_4^-$] in alkaline solution by NaOCl. The $[^{129}I]IO_4^-$ is reduced to $[^{129}I]I_2$ by hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) and extracted into CCl_4. The *carrier added* (CA) $[^{129}I]I_2$ is than back-extracted (stripped) by reduction to $[^{129}I]I^-$ with $NaHSO_3$. The iodide is then precipitated as $[^{129}I]AgI$ for chemical yield measurement and radioactivity counting. The classical radiochemical separation of radio-Sr from other fission and corrosion products involves precipitations of $SrCO_3$ from $Sr(NO_3)_2$. The gross activity of purified $[^{89}Sr]Sr$ is first measured. The $[^{90}Y]Y$ is then allowed to grow ($^{90}Sr \rightarrow$ ^{90}Y) into the $[^{90}Sr]Sr$ sample, and at a later time, the $[^{90}Y]Y$ activity is separated and measured. The ^{90}Sr activity is calculated from the $[^{90}Y]Y$ activity, and the $[^{89}Sr]Sr$ activity is calculated from the difference between the total $[^{89}Sr]Sr$ and $[^{90}Sr]Sr$ activities measured and the calculated $[^{90}Sr]Sr$ activity. More recently a substantial improvement of the separation was obtained by using mini-columns containing chelating agents and NCA $[^{85}Sr]Sr$ as an internal *gamma emitting spike* [35]. The procedure to separate the $[^{63}Ni]Ni$ from fission and corrosion products is based on anion ion-exchange resins and organic extractions. The $[^{63}Ni]Ni$ is purified in chloroform as nickel-dimethylglyoximate and back-extracted with diluted HCl and then complexed with ammonium thiocyanate and precipitated with pyridine. Nickel precipitate is then dissolved in a cocktail for counting with a liquid scintillation counter (**LSC**). The procedure to determine the $[^{55}Fe]Fe$ content

in the presence of [^{59}Fe]Fe in water or solid wastes is based on the following steps: the two iron RNs are separated from fission and corrosion products by ion exchange and organic extraction. The organic phase is then transferred into a counting vial containing toluene based scintillation cocktail. The sample is counted with a liquid scintillation detector (LSC).

3.10 Kinds of fuel Cycles

It is now relevant to remember that due to different political and strategic approaches there are at least two different fuel cycles that are well established:

3.10.1   *the once-through cycle (UOT)*, in which the enriched or natural U is used in the form of pellets filled in the Zircaloy tubular cladding only one time before storage in cooling water pools close to the NPP for some years (ad interim cooling and storage) and then sent to the repository for a suitable period of time, in order to be reutilized in *Gen IV* NPPs (the Yukka Mountain Repository, Nevada, is now ready for operation, but it will have in any case only a 75 year license from NRC, in prevision of a possible reprocessing of useful U and Pu RNs). At the moment some countries like USA, adopted this concept leaving a large amount of fissile or fertile material unused, but well protected by possible proliferation and terrorist attacks. It must be say that USA is looking forward to restart the reprocessing plants, which have been closed in the '80s. Several European Countries adopted the fuel recycling approach.

3.10.2   *The re-cycle of U and Pu RNs, or closed fuel cycle*, in which the exhaust assemblies of fuel rods or pins are reprocessed, converted to **MOX** and reused in thermal NPP (about 95% of U can be recovered with this cycle). This approach is adopted by countries like England (BNLF, Sellafield plant, UK) and France (COGEMA-AREVA, La Hague plant, France), in which the U and Pu radionuclides are radiochemically separated by minor actinoids, MAs (i.e. RNs of Np, Am, Cm and small amounts of Bk and Cf) and fission products, FPs. The final fate of these MAs and FPs is normally the *vitrification*, *encapsulation* in suitable cans made of copper and SS and storage in final repository. Amongst the FPs, it is relevant to remember the very long-lived ^{99g}Tc ($T_{1/2}$ = 0,21 Ma) and ^{129}I ($T_{1/2}$ = 15,7 Ma), even if both have a very low radiotoxicity, but are produced in large amount. In a NPP of power P (in MWe), for an operation time τ (in days) the amount m (in mg) of ^{99g}Tc is given by the semiempirical expression: m = 20 P τ (*i.e.* ~ 7 kg.a^{-1} at steady state for 1 GWe NPP).

The specifications for purified U and Pu to be recycled are very strict. At $t_{cooling}$ of about 1 a, the FPs activity must be reduces by a factor of 10^7 and the U content in Pu by a factor of ~ 2 10^4, in respect to the purest U and Pu of nuclear grade (for *UOT cycle*). The large number of chemical elements involved (FPs, An, activation and corrosion products)

make the separation a very difficult task. Additional complications arise from radiation decomposition and criticality risk and from the necessity to conduct all processes remotely in heavily shielded enclosures, under extensive Heath Physics measures. Advantages are taken from the relative stability of the oxidation state VI of U and most FPs, and the redox instability of Pu(III, IV and VI) [36,37,38,39,34]. In the earliest process, only Pu was isolated by precipitation in the reduced states as PuF_3 or PuF_4 together with all insoluble FP fluorides. This was followed by a second stage dissolving the precipitate by oxidation of Pu to Pu(VI), and new fluoride precipitation of the other elements leaving relatively pure Pu in the supernatant. In a final step Pu was against reduced and precipitated as PuF_3. This principle is adopted for Pu(III) and Pu(IV) phosphates, but not of U(VI) which does not have any insoluble phosphate. Since Bi(III) was used as a iso-dimorphous carrier for the precipitate, it is referred to as the bismuth phosphate process and this principle is already retained in present technology. No other element has the same set of redox and radiochemical properties as Pu, too some elements behave as Pu(III) (*e.g.* the Ln), some like Pu(IV), *e.g.* Zr and some like plutonyl cation $Pu^{(VI)}O_2^{2+}$, *e.g.* U(VI). Numerous redox agents had been tested, *e.g.* $K_2Cr_2O_7$ (to PuO_2^{2+}), NO_2 to Pu(IV), iron(III) sulfamate, hydrazine and U(IV) to Pu(III).

This precipitation technique was replaced in the late 1940's by solvent extraction, in which the fuel were dissolved in HNO_3 and contacted with an organic solvent, which selectively extracted the desired elements. The first solvent adopted was methyl-isobutyl-ketone (MIBK or Hexone); this solvent forms coordination compounds with coordinatively unsaturated compounds like the actinoid nitrates, *e.g.* $Pu(NO_3)_4S_2$, where **S** represents the adduct molecule.
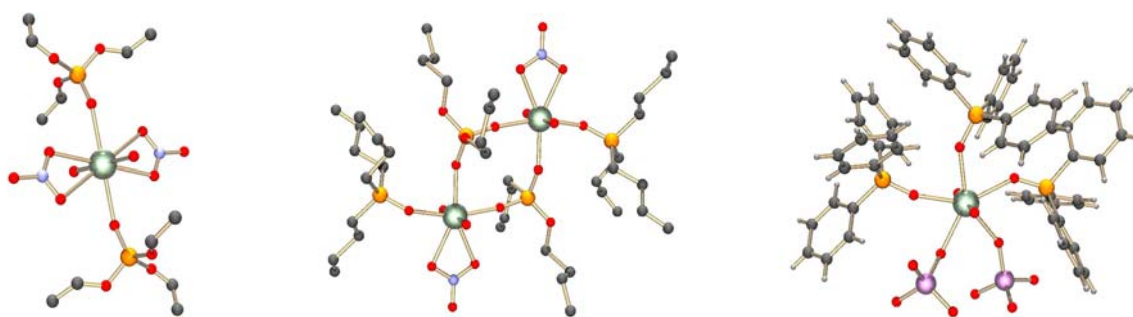
FIG 8: (Left) structure of $[(U^{(VI)}O_2)(NO_3)_2]•TEP_2$; centre) structure of $[(U^{(VI)}O_2)(NO_3)_2]•DBP_2•TBP_2$; right) structure of $[(U^{(VI)}O_2)(NO_3)_2]•TBPO_3$ in this case the anions are in the first coordination sphere of the metal. Notation: **TEP** triethyl-phosphate, **DBP** dibutyl-phosphate, **TBP** trybutyl-phosphate, **TBPO** trybutyl-phosphane-oxide (the U atoms is the big sphere, in order of decreasing size are P, N, C, O and H).

In spite of the many possibilities shown in FIG. 8, at present, tributyl-phosphate (**TBP**), is the extractant in all reprocessing plants; it alone also acts as a complex former and is normally used as a 30% solution in kerosene. It forms the basis for the PUREX process (Pu U Redox EXtraction). Other chelating agents, like thenoyl-trifluoroacetone, HTTA forming very selective complexes for Pu^{4+} and UO_2^{2+} and di-2-ethyl-hexyl-phosphoric acid, **HDEDP**, very selective for the separation of lanthanoids, as Ln^{3+} had been used.

Both tertiary amines (R_3N) like trioctyl-amine TOA and tryoctyl-amine-oxide (R_3NO) like try-normal-octyl-amine-oxide TNOA and tertiary phosphanes (R_3P) and their oxides (R_3PO), like trioctyl-phosphane TOP and trioctyl-phosphane-oxide TPOA, had been tested for some steps in reprocessing [39]. The amines forms organic soluble complexes with negatively charged metal complexes (used in U purification). The use of the **PUREX** cycle of a secondary extracting reagent improves strongly the decontamination factor, **DF** (i.e. concentration ratio between the elemental ion before and after the extraction).

A modern reprocess and fuel fabrication cycle is shown in FIG. 9.
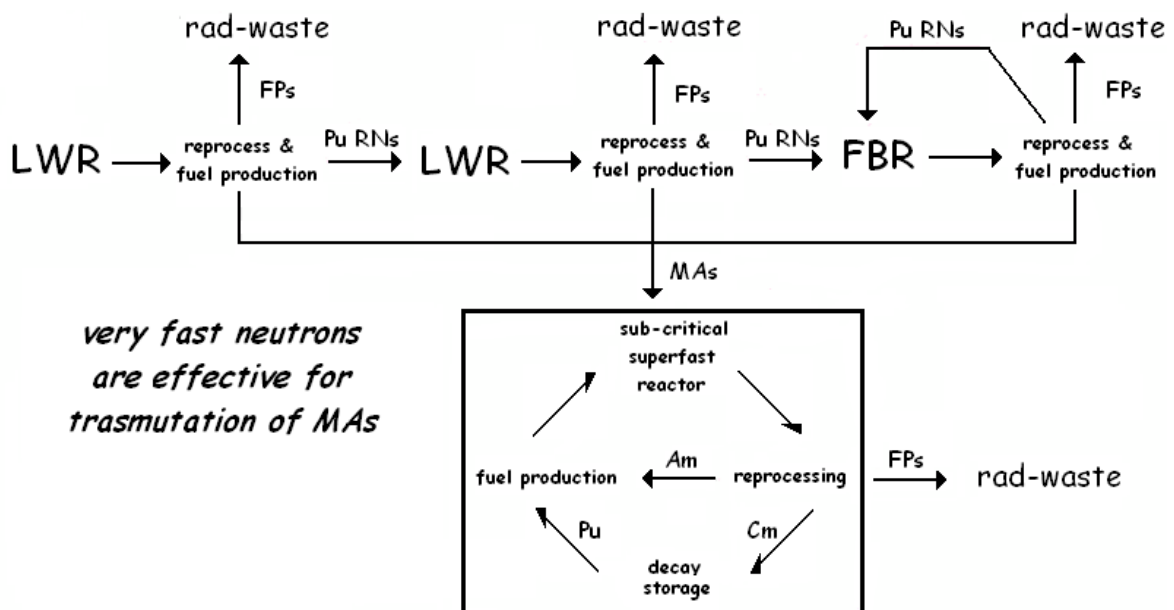
FIG. 9: a fuel recycle of a light water reactor, LWR (in two phases) in which the minor actinoids (MAs) are treated separately from U and Pu RNs. More phases can be added if the spent fuel does not contain high neutron absorbing RNs, whose concentration increases with burnout.

As alternatives to the aqueous "wet" chemistry, several separation processes of "dry" chemistry have also been studied, but none has been used on industrial scale. Examples are: halide volatilization, molten salt extraction and molten salt transport, molten metal purification, molten salt electrorefining and pyrometallurgical chemistry.

3.11 Generation III+ reactors

The European Pressurized light water Reactor **EPR** of 1,6 GWe (AREVA-Siemens) (FIGS. 10a and 10b) [40] and the Advanced and Passive light water reactor **AP1000** of 1 GWe (Westinghouse-Toshiba) [41] belonging to the *Gen III+*, are licensed by **NRC**, USA and are being built in some increasing number (Finland, France, Sweden, USA and possibly Italy too). The EPR in particular, as at least double (redundant) passive safety equipment for all expected failures and in case of very improbable core melting due to a accident of level 7, like a **LOCA** (loose of coolant accident) has a vast containment of concrete in the basement of the building in order to collect the melted material (corium). Due to its building close to vast water sources (sea, ocean or large river), it does not need of very big evaporating tower, but just a stack for the water vapours. The electrical power yield would reach the 41%, instead of the 33% of a conventional NPP.

FIG 10a: Schematics of the nuclear island of **EPR** (European Pressurized water Reactor of AREVA-Siemens). This reactor of 1,6 GWe belongs to *Gen III+*, and is inherently passive. The dimensions can be appreciated by comparison with the truck on the right side.

Due to the great success of the first prototype of EPR (Olkuiloto-3 unit, OL3, Finland), other EPRs are being built (Flamanville, Normandia, France), or are going to be commissioned (Finland, Sweden, USA). It is to note that in France, the about 100 sites that are licensed to build a new NPP made a great effort to gain the opportunity, with a large support of local population.

FIG 10b: Schematics of **EPR**, with turbine building and water cooling.
No big cooling towers are necessary for the operation.

3.13 Generation IV reactors (Gen IV)

These are a set of theoretical nuclear reactor designs currently being researched. Most of these designs are generally not expected to be available for commercial construction before 2030, with the exception of a version of the Very High Temperature Reactor (VHTR) called the Next Generation Nuclear Plant (**NGNP**). The NGNP is to be completed by 2021.

Current reactors in operation around the world are generally considered second- or third-generation systems (*Gen II* and *Gen III*), with the first-generation systems having been retired some time ago. Research into these reactor types was officially started by the *Generation IV International Forum* (**GIF**) based on eight technology goals [42].
The primary goals being to improve nuclear safety, improve proliferation resistance, minimize waste and natural resource utilization, and to decrease the cost to build and run such plants [43].

An Integrated Nuclear Energy Model is central to standardized and credible economic evaluation of *Gen IV* nuclear energy systems. The innovative nuclear systems

considered within *Gen IV* require new tools for their economic assessment, since their characteristics differ significantly from those of current *Gen II* and *III* NPPs. The current economic models were not designed to compare alternative nuclear technologies or systems, but rather to compare nuclear energy with fossil alternatives. They can be classified in two main types, some based on the *UOT* process other on *P&T* of fuel:

3.13.1   Thermal reactors

Very-High-Temperature Reactor (VHTR): The very high temperature reactor concept utilizes a graphite-moderated core with a UOT fuel cycle. This reactor design envisions an outlet temperature of 1 000 °C. The reactor core can be either a prismatic-block or a pebble bed reactor design. The high temperatures enable applications such as process heat or hydrogen production via the thermochemical iodine-sulphur process (see previous section). It would also be passively safe.

Supercritical-water-cooled reactor (SCWR): The supercritical water reactor (SCWR) is a concept that uses supercritical water as the working fluid. The SCWRs are basically light water reactors (LWR) operating at higher pressure and temperatures with a UOT cycle. As most commonly envisioned, it would operate on a direct cycle, much like a Boiling Water Reactor (BWR), but since it uses supercritical water as the working fluid, would have only one phase present, like the Pressurized Water Reactor (PWR). It could operate at much higher temperatures than both current PWRs and BWRs. The SCWRs are promising advanced nuclear systems, because of their high thermal efficiency (i.e. about 45% vs. about 33% efficiency for current LWRs) and considerable plant simplification. The SCWR concept is being investigated by 32 organizations in 13 countries to generate low-cost electricity.

Molten Salt Reactor (MSR): A molten salt reactor is a type of nuclear reactor where the coolant is a molten salt. There have been many designs put forward for this type of reactor and a few prototypes built. The early concepts and many current ones had the nuclear fuel dissolved in the molten fluoride salt as uranium tetra-fluoride (UF_4), the fluid would reach criticality by flowing into a graphite core which would also serve as the moderator.

3.13.2   Fast reactors

Gas-Cooled Fast Reactor (GFR): The gas-cooled fast reactor (GFR) system features a fast-neutron spectrum and closed fuel cycle for efficient conversion of fertile ^{238}U and management of An. The reactor is He-cooled, with an outlet temperature of 850 °C and using a direct Brayton cycle gas turbine for high thermal efficiency. Several fuel forms are being considered for their potential to operate at very high temperatures and to ensure an excellent retention of fission products: composite ceramic fuel, advanced fuel particles, or ceramic clad elements of An compounds. Core configurations are being considered based on pin- or plate-based fuel assemblies or prismatic blocks.

Sodium-Cooled Fast Reactor (SFR): The SFR is a project that builds on two closely related existing projects, the liquid metal fast breeder reactor and the Integral Fast Reactor. The goals are to increase the efficiency of U usage by breeding Pu and eliminating the need for transuranic RNs ever to leave the site. The reactor design uses an un-moderated core running on fast neutrons, designed to allow any transuranic RNs to be consumed (and in some cases used as fuel). In addition the SFR fuel expands when the reactor overheats, and the chain reaction automatically slows down. In this manner, it is passively safe. Integral Fast Reactor (**IFR**): is a design for a nuclear reactor with a specialized nuclear fuel cycle. The IFR (originally Advanced Liquid-Metal Reactor) of *Gen IV* is a design for a fast breeder use almost all of the energy in U or Th, thus decreasing fuel requirements by two orders of magnitude. It practically removes concern about fuel supply or energy used in mining – thus we already have fuel enough for many centuries. Breeder reactors can "burn" some components (An: reactor-grade Pu and MAs) of rad-waste, thus turning the world's biggest headache with respect to nuclear into an asset. The IFR (a nuclear reactor using fast neutrons and no neutron moderator) distinguish by a nuclear fuel cycle using reprocessing via electrorefining at the reactor site itself.

This reactor is cooled by liquid sodium and fuelled by a metallic alloy of uranium and plutonium. The fuel is contained in steel cladding with liquid sodium filling in the space between the fuel and the cladding. A prototype of the reactor was built, but the project was cancelled before it could be copied elsewhere. The SFR reactor concept is cooled by liquid sodium and fuelled by a metallic alloy of U and Pu. The fuel is contained in SS cladding with liquid Na filling in the space between the clad elements which make up the fuel assembly. One of the design challenges of an SFR are the risks of handling Na, which reacts explosively if it comes into contact with water. However, the use of liquid metal instead of water as coolant allows the system to work at atmospheric pressure, reducing the risk of leakage.

Lead-Cooled Fast Reactor (LFR): The LFR features are a fast-neutron-spectrum lead or lead/bismuth eutectic (LBE) liquid-metal-cooled reactor, with a closed fuel cycle. Options include a range of plant ratings, including a "battery" of 50 to 150 MWe of electricity that features a very long refuelling interval, a modular system rated at 300 to 400 MWe, and a large monolithic plant option at 1,2 GWe. The term battery refers to the long-life, factory-fabricated core, not to any provision for electrochemical energy conversion. The fuel is metal or nitride-based containing fertile ^{238}U and transuranics. The LFR is cooled by natural convection with a reactor outlet coolant temperature of 550 °C, possibly ranging up to 800 °C with advanced materials. The higher temperature enables the production of *hydrogen* by thermochemical processes.

More details and schematics of *Gen IV* reactors, with heat exchangers, cooling systems and pressurising circuits, can be found at *Gen IV* official web sire [42].

3.14 Radioanalytical and Nuclear Analytical techniques (NATs)

Radioanalytical chemistry is an important cross-cutting field throughout radiochemistry, and the development of analytical methods, both radiochemical and instrumental, will always be very important in the cycle of the nuclear energy production. In wet radiochemical methods, the introduction of extraction chromatographic resins has been the biggest improvement during the last ten years. They have simplified considerably some separation procedures, for example that of Am. In the development of instrumental analytical methods, **ICP-MS** is becoming a standard tool in radiochemistry in the determination of very long-lived RNs. A lot of analytical development has been directed to the chemical speciation of radionuclides in various matrices, environmental and geological samples, as well as nuclear waste. All too often radiochemical studies have concentrated on bulk determination of radionuclide quantities. Chemical species that are present in the system have been often ignored. They are, however, the most important considering their transport processes in any system. Chemical speciation of radionuclides is certainly not an easy task, since their concentrations are most often too low for direct speciation, and only indirect speciation methods are applicable such as selective extractions. *Selectivities* and *detection limits* of the direct instrumental speciation methods have increased greatly, and this development will certainly continue. Laser-induced fluorescence, X-ray absorption and mass-spectrometric methods, to mention only a few, increase their role in the speciation of radionuclides. The introduction of modern chemical methods and equipment is very important, but also problematic since the instrumentation is often very expensive.

Neutron Activation Analysis (**NAA**) is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements in samples from almost every conceivable field of scientific or technical interest. For many elements and applications, NAA offers sensitivities that are superior to those attainable by other methods, on the order of parts per billion or better. In addition, because of its accuracy and reliability, NAA is generally recognized as the "referee method" of choice when new procedures are being developed or when other methods yield results that do not agree. Worldwide application of NAA is so widespread it is estimated that approximately 10^5 samples undergo analysis each year [1,18,19,20]. With the use of automated sample handling, gamma measurement with solid-state detectors, and computerized data processing it is generally possible to simultaneously measure more than thirty elements, in most sample types without chemical processing. The application of purely instrumental procedures is commonly called instrumental neutron activation analysis (**INAA**) and is one of NAA's most important advantages over other analytical techniques. If chemical separations are done to samples after irradiation to remove interferences or to concentrate the radioisotope of interest, the technique is called radiochemical separation neutron activation analysis (**RSNAA**). The latter technique is performed infrequently due to its high labour cost.

The procedure generally used to calculate concentration (generally in the range ppm-ppb of element) in the unknown sample is to irradiate the unknown sample and a comparator standard containing a known amount of the element of interest together in the reactor. If the unknown sample and the comparator standard are both measured on the same detector, then one needs to correct the difference in decay between the two. One usually decay corrects the measured counts (or activity) for both samples back to the end of irradiation using the half-life of the measured isotope.

TAB. 3: Estimated detection limits for INAA using off-line high-resolution HPGe gamma spectrometry. Assuming irradiation in a reactor neutron flux density $\phi = 10^{13}$ cm^{-2}.s^{-1}.

Detection Limit (pg)	Elements
1	Dy, Eu
1 -10	In, Lu, Mn
10 -100	Au, Ho, Ir, Re, Sm, W
$100 - 10^3$	Ag, Ar, As, Br, Cl, Co, Cs, Cu, Er, Ga, Hf, I, La, Sb, Sc, Se, Ta, Tb, Th, Tm, U, V, Yb
$10^3 - 10^4$	Al, Ba, Cd, Ce, Cr, Hg, Kr, Gd, Ge, Mo, Na, Nd, Ni, Os, Pd, Rb, Rh, Ru, Sr, Te, Zn, Zr
$10^4 - 10^5$	Bi, Ca, K, Mg, P, Pt, Si, Sn, Ti, Tl, Xe, Y
$10^5 - 10^6$	F, Fe, Nb, Ne
10^7	Pb, S

The Eqs. (25) and (26) are used to calculate the mass of an element in the unknown sample relative to the comparator standard is:

$$\frac{A_{sam}}{A_{std}} = \frac{m_{sam}}{m_{std}} \frac{(e^{-\lambda \cdot T_d})_{sam}}{(e^{-\lambda \cdot T_d})_{std}} \qquad (25)$$

where A = activity of sample (sam) and standard (std), m = mass of the element, λ = decay constant for the isotope, and T_d = decay time. When performing short irradiations, the irradiation, decay and counting times are normally fixed the same for all samples and standards such that the time-dependent factors cancel. Thus the above equation simplifies into Eq .(26). where C is the concentration of the element and W is the weights of the sample and the standard.

$$C_{sam} = C_{std} \frac{W_{std}}{W_{sam}} \frac{A_{sam}}{A_{std}} \qquad (26)$$

3.14 Nuclear Hydrogen, or Hydricity

At present the world chemical industry does produce ~ 50-60 Mtonnes of hydrogen annually, basically by steam reforming of methane and light hydrocarbons and high temperature combustion of coal too, with very well known and experienced methodologies. Most of H_2 is used for production of NH_3 and then nitrates as explosives and ammonium salts as fertilizers. Besides, a large part of H_2 is used for catalyzed hydrogenation of heavy unsaturated hydrocarbons for production of lubricants and gasoline as well.

Several methods have been proposed for preparation of hydricity by heating in a gas-cooled high temperature nuclear reactor, HTGR (*i.e.* Nuclear Hydrogen or NuH2), by improving the present methods based on steam reforming of light hydrocarbons or, even worse, the direct use of electrolysis of water, which is thermodynamically very unfavourable [14,15,16]. Amongst them, the most promising is the sulphur-iodine cycle (S-I cycle) is a series of thermochemical processes used to produce hydrogen, Eqs. (27 to 29) and FIG. 11. The three reactions that produce hydrogen are as follows:

$$I_{2(v)} + SO_{2(g)} + 2\ H_2O_{(v)} \leftrightarrow 2\ HI_{(g)} + H_2SO_{4(l)} \text{ (at about 120°C, Bunsen's reaction)} \quad (27)$$
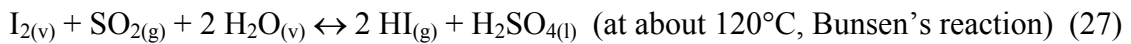
The HI is then separated as a vapor by distillation. Note that concentrated H_2SO_4 may react with HI, giving I_2, SO_2 and H_2O (backward reaction), but removing the desired product will shift equilibrium to the right. This reaction is sometimes referred to as Bunsen's reaction (27).

$$2\ H_2SO_{4(v)} \leftrightarrow 2\ SO_{2(g)} + 2\ H_2O_{(v)} + O_{2(g)} \text{ (at 830°C in vapor phase)} \qquad (28)$$
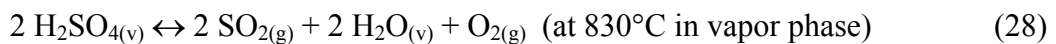
The H_2O, SO_2 and residual H_2SO_4 must be separated from the O_2 (that is a valuable by-product) by condensation. The decomposition reaction Eq. 12 now produce H_2 and recycle the I_2:

$$2\ HI_{(g)} \leftrightarrow I_{2(g)} + H_{2(g)} \text{ (at 450°C in gaseous phase)} \qquad (29)$$
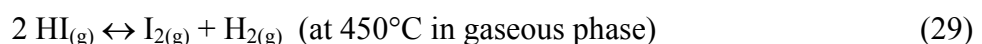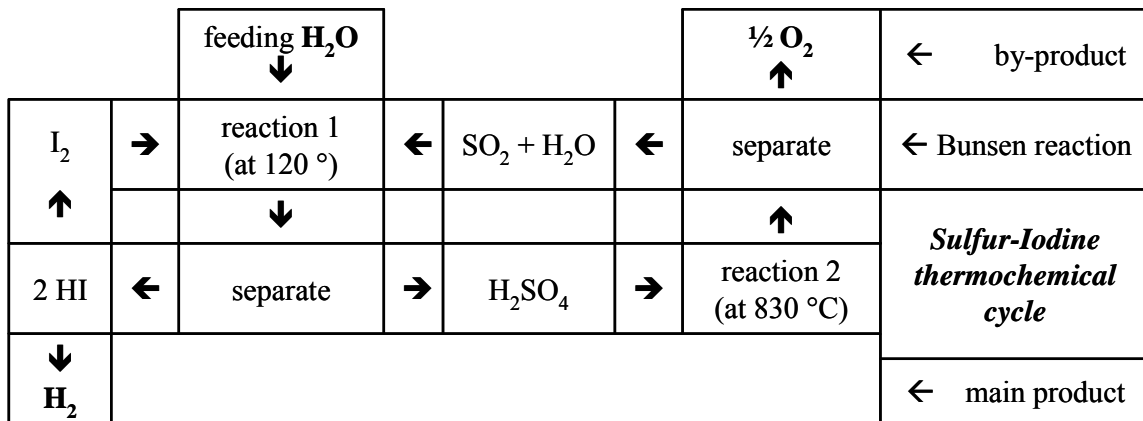
Iodine and any accompanying water or SO_2 are separated by condensation, and the hydrogen product remains as a gas, H_2. The sulphur and iodine compounds are recovered and reused, hence the consideration of the process as a cycle. This S-I process is a

chemical heat engine; heat enters the cycle in high temperature endothermic chemical reactions (28) and (29), and heat exits the cycle in the low temperature exothermic reaction (27).

The difference between the heat entering the cycle and the heat leaving the cycle exits the cycle in the form of the heat of combustion of the hydrogen produced. In conclusion the net reaction is the decomposition of water: $2\,H_2O \leftrightarrow 2\,H_2 + O_2$.

In the gas-cooled very high temperature reactor of *Gen IV* VHTR [42], it would be possible to dissociate water by direct pyrolysis at temperatures higher than 1 000 °C up to 1 600 °C on a metal catalyzer (Fe, Co, V) or a refractory metal oxide.

		feeding H_2O ⬇				½ O_2 ⬆	← by-product
I_2	→	reaction 1 (at 120 °)	←	$SO_2 + H_2O$	←	separate	← Bunsen reaction
⬆		⬇				⬆	*Sulfur-Iodine thermochemical cycle*
2 HI	←	separate	→	H_2SO_4	→	reaction 2 (at 830 °C)	
⬇ H_2							← main product

FIG. 11: Production of hydrogen (and oxygen) by thermochemical decomposition of water in high temperature nuclear reactor.

3.15 Radionuclide by-production for Medical and Industrial applications

Fission and activation of exhaust nuclear fuel and structural components of a NPP are a fertile source of RNs, which have plenty uses in research, health, life sciences, environmental studies, irradiation and sterilization of foodstuff [13], safety issues, space exploration [9]. Most of them, like the well known ^{131}I ($T_{1/2}$ = 8,02 d) for thyroid gland cancer treatment and ^{99}Mo ($T_{1/2}$ = 66,0 h) → ^{99m}Tc ($T_{1/2}$ = 6,0 h) for labeling plenty biological molecules, have an half-life that is too short to be extracted from the very hot exhaust fuel rods and are produced by activation in dedicated Research and Isotope Production reactors. But several others, like the beta emitter ^{90}Sr ($T_{1/2}$ = 28,64 a) → ^{90}Y ($T_{1/2}$ = 64,1 h) and the gamma emitter ^{137}Cs ($T_{1/2}$ = 30,17 a) → ^{133m}Ba ($T_{1/2}$ = 2,55 min, E_γ = 660 keV), have half-lives suitable to be separated during fuel recycling processes. The ^{137}Cs is used as a γ source (660 keV) for γ radiography and irradiation and sterilization of

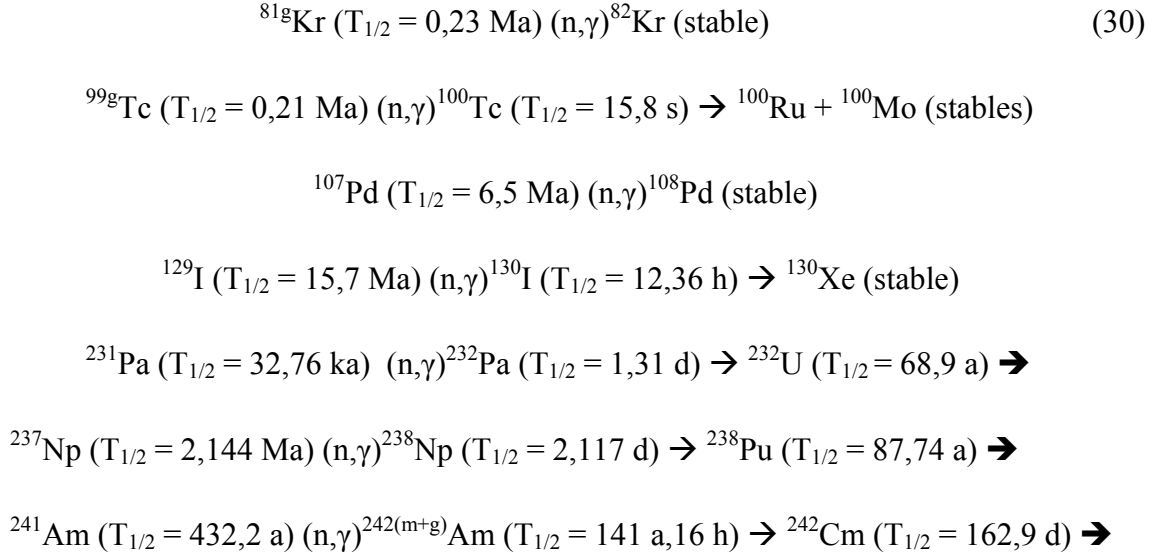food and human heritage specimen (*e.g.* ancient books, wood handicrafts, old paintings). The generator ^{90}Sr → ^{90}Y ($T_{1/2}$ = 64,1 h) finds very effective applications in metabolic radiotherapy of bulky cancers due to the high energy of its beta emission, *i.e.* 2,3 MeV. It is labelled to macrocyclic chelants (*e.g.* DOTA), linked to an oligopeptides (*e.g.* octreotide), monoclonal antibodies (Mab) or fragments of proteins (Fab') [10,11,12]. The activation product ^{238}Pu ($T_{1/2}$ = 87,74 a) finds several applications to supply radionuclide thermoelectric generators (RTG, RITEG) or nuclear batteries for landing of aircrafts in the airports and for hostile environment devices (*e.g.* oceanic navigation lights), space exploration (power supply for on board instrumentation) [9]. The ^{242m}Am ($T_{1/2}$ = 141 a) was considered as a supply of neutron and fission energy for space propulsion (*e.g.* Mars exploration). The fast neutron emitter ^{252}Cf ($T_{1/2}$ = 2,645 a) is used efficiently for destroying arterial plaques (*i.e.* coronary restenosis) after angioplasty surgery onto patients. The activation products ^{60}Co ($T_{1/2}$ = 5,72 a) and ^{192g}Ir ($T_{1/2}$ = 73,83 d), are used since a long time for γ radiotherapy and brachytherapy onto humans, and for γ radiography of mechanical specimen as well. In conclusion there are at least 300 FPs (stable and radioactive) and several of them could be used in the so-called non-energetic applications of the energy of the nucleus. Amongst the stable elements there are the *precious metals* like ^{105,106,1108,110}Pd, ^{103}Rh, Ru and some *rare lanthanoids*, Ln). Finally, by use of cyclotron beams is it possible to produce γ emitting radiotracers of some An, e.g. via the reactions ^{235}U(p,n)^{235}Np ($T_{1/2}$ = 396,1 d, E_γ = 26 and 84 keV) and ^{235}U(α,2n)^{237}Pu ($T_{1/2}$ = 45,2 d, E_γ = 60 keV), to be used as spikes for setting up the processing and recycle of these elements and for environmental and metallo-toxicological studies as well [9].

3.16 Partitioning and Transmutation recycle (P&T)

Regarding P&T, let's remember that a further classification of nuclear reactors as breeders, converters and burners (or transmuter) is related to the conversion factor C (i.e. number of fissile atoms of ^{239}Pu and ^{241}Pu produced on the number of atoms of ^{235}U fissioned): C = η − 1 − S (where the *fission factor*: η = ν / (1 + α), with α = $\sigma_{(n,\gamma)}$ / $\sigma_{(fiss)}$, ν is the average number of neutrons emitted per each fission of ^{235}U (*neutron yield*) and S is the number of neutrons lost in processes other than fission and neutron capture to produce fissile atoms in the fuel. Thus, in order to obtain a chain reaction, the fission factor η must be > 1. For C ~ 0,8 − 1,0 the reactor is a conventional converter, for C > 1 is a breeder and for C < 0,7 is classified as a transmuter (like a normal LWR !). Thus if C < 0,6 − 0,7, the NPP can be use to transmute either U and Pu RNS, MOX, FPs and MAs, that are inserted either in the reactor core or outside, reaching a transmutation up to 99,9%. This process is already demonstrated, but it was calculated that it would be necessary to operate one dedicated critical nuclear reactor transmuter (NTR) for "burning" the very long-lived and highly radiotoxic rad-waste of 3 NPPs. In order to make some examples, we can look at the very long-lived FPs ^{81g}Kr, ^{99g}Tc, ^{107}Pd and ^{129}I and the MAs ^{231}Pa, ^{237}Np and ^{241,243}Am,

already cited in the previous sections. Unfortunately, with the exclusion of ^{99g}Tc, ^{107}Pd and ^{129}I, the cross-sections of neutron capture on these RNs are normally low (i.e. of the order of 0,01 to 1 barn), making hardly advisable the use of very high flux density NTRs, Eqs. 30 shows some example of effective transmutation reactions:

$$^{81g}\text{Kr } (T_{1/2} = 0,23 \text{ Ma}) (n,\gamma)^{82}\text{Kr (stable)} \qquad (30)$$

$$^{99g}\text{Tc } (T_{1/2} = 0,21 \text{ Ma}) (n,\gamma)^{100}\text{Tc } (T_{1/2} = 15,8 \text{ s}) \rightarrow {}^{100}\text{Ru} + {}^{100}\text{Mo (stables)}$$

$$^{107}\text{Pd } (T_{1/2} = 6,5 \text{ Ma}) (n,\gamma)^{108}\text{Pd (stable)}$$

$$^{129}\text{I } (T_{1/2} = 15,7 \text{ Ma}) (n,\gamma)^{130}\text{I } (T_{1/2} = 12,36 \text{ h}) \rightarrow {}^{130}\text{Xe (stable)}$$

$$^{231}\text{Pa } (T_{1/2} = 32,76 \text{ ka}) \ (n,\gamma)^{232}\text{Pa } (T_{1/2} = 1,31 \text{ d}) \rightarrow {}^{232}\text{U } (T_{1/2} = 68,9 \text{ a}) \rightarrow$$

$$^{237}\text{Np } (T_{1/2} = 2,144 \text{ Ma}) (n,\gamma)^{238}\text{Np } (T_{1/2} = 2,117 \text{ d}) \rightarrow {}^{238}\text{Pu } (T_{1/2} = 87,74 \text{ a}) \rightarrow$$

$$^{241}\text{Am } (T_{1/2} = 432,2 \text{ a}) (n,\gamma)^{242(m+g)}\text{Am } (T_{1/2} = 141 \text{ a},16 \text{ h}) \rightarrow {}^{242}\text{Cm } (T_{1/2} = 162,9 \text{ d}) \rightarrow$$

It is clear from the reactions (30) that many RNs can be *transmuted* into either shorter-lived or stable ones. Of course, if the short-lived RN obtained does decay again on a very long-lived one Eq. (31), the initial problem dos not repeat anymore, because – as explained in FIG. 1 – whenever a very long-lived RN is charged by decay of a shorter-lived one, the activity $A_B = N_B \bullet \lambda_B$ of the latter does increase very slowly, often in a negligible way (*i.e.* while indeed the number of atoms of the long-lived one does increase more quickly, accordingly to the non-equilibrium limit law: $N_B \rightarrow N_A \bullet \lambda_A/\lambda_B = N_A \bullet t_B/t_A$).

$$^{243}\text{Am } (T_{1/2} = 7,370 \text{ ka}) (n,\gamma)^{244(A+B)}\text{Am } (T_{1/2} = 26 \text{ min}, 10,1 \text{ h}) \rightarrow$$

$$^{238}\text{Cm } (T_{1/2} = 18,10 \text{ a}) \rightarrow {}^{240}\text{Pu } (T_{1/2} = 6,563 \text{ ka}) \rightarrow {}^{236}\text{U } (T_{1/2} = 23,42 \text{ Ma}) \qquad (31)$$
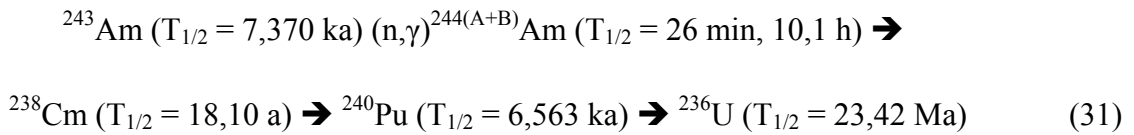
3.16.1 Transmutation by ADS

In the last decades, a more complex approach is being studied, based on very energetic (0.6 to 2 GeV) proton beams irradiation of rad-waste after partitioning (**P**, see FIG. 9), that are inserted is a sub-critical reactor, in between or externally to the fuel rods.

The power necessary to reach the criticality is given by the power transported by the beam (~ 3 %): with 1 GeV proton beam of 10 mA current, a thermal power of 10 MW$_{th}$ is injected into the reactor coolant, that is normally made of re-cyrculating liquid Hg, liquid Pb or liquid Pb-Bi eutectic (LBE).

Any electricity stop due to any kind of accident, suddenly makes the NRT sub-

critical, avoiding dangerous power divergence. A 1 GeV proton beam does produce about 15-20 fast neutrons per each proton and the neutron multiplicity can reach a value of 30-40 with proton energies up to 2 GeV.
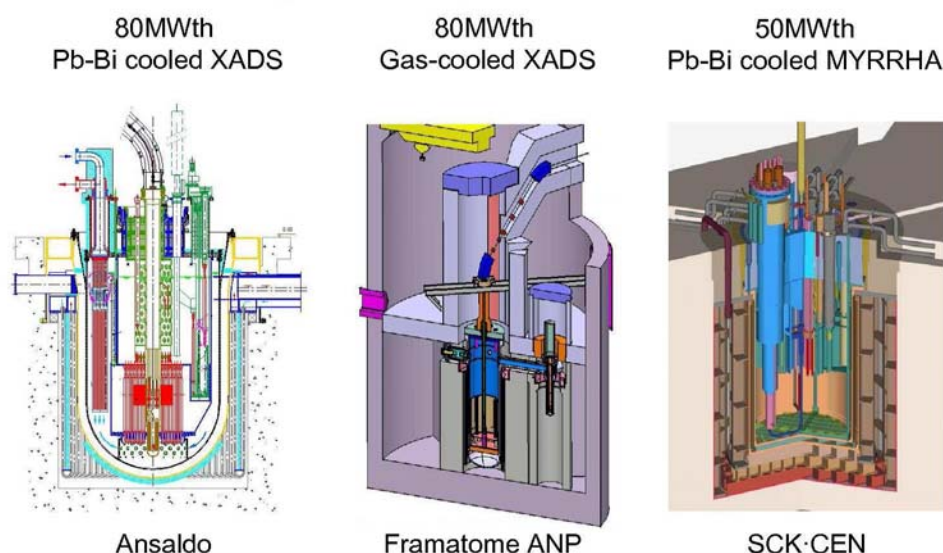
FIG. 12: Three simplified designs of sub-critical reactors for ADT, under study in Europe (Ansaldo Nucleare, Genova, Italy; Framatome ANP, France and SCK-CEN, Belgium).
These reactors must be interfaced with an high energy proton accelerator
of very high intensity beam current to reach the criticality.

In practice, the liquid circulating metal or alloy operates as a Spallation Neutron Source (SNS), producing a high number of spallation neutrons, which are used for transmutation. The very fast neutrons, could be either thermalized or used for **(n,xn)**, (n,p) and (n,α) nuclear reactions.

These systems are called ADS, *i.e.* Accelerator Driven Systems for transmutation (also ADT), and are intrinsically safe due to the sub-criticality of NPP used (FIG. 12).

3.17 Radioactive Waste treatment and disposal

We think that the problem of the nuclear waste disposal is not fully solved. To establish new or improve the existing technologies used for safe, permanent disposal of wastes associated with nuclear power production and to ensure that nuclear waste will have no significant health impact on humans or environment at any time, research programmes in this area are needed. Research topics related to the management and disposal of nuclear waste will most probably continue to remain in the forefront of radiochemical research in the coming years. In this context, nuclear and radioanalytical

techniques are key analytical tools. Examples of studies in which they have been applied concern that of the migration and retention of radionuclides in the geosphere for the safety analysis of the final disposal [44,45,46]. The radiochemical characterization of the used fuel is the starting point for studies that includes: waste-chemical speciation leaching studies, radionuclide sorption and migration, diffusion, synergistic effects, geological investigations, use of natural analogues [47,48,49,50]. In this context, migration studies are of crucial importance. The only credible way by which radionuclides could be transported from a nuclear fuel wastes disposal vault to the biosphere is by groundwater flowing through a network of fractures in the surrounding rocks.

A large amount of laboratory and field work is being carried out internationally to study the extent of radionuclide migration, that includes the determination of sorption, distribution, coefficients for fission products and actinides from a wide range of groundwater compositions on unaltered or altered rock, on unconsolidated mineral infillings from water-bearing fractures, and on the clay buffer and backfill materials. The spike of groundwater or simulated groundwater with one or more radionuclides and the contact with the geological material is an indispensable experimental approach. Another important research field related to the application of radiochemistry to the problem of nuclear waste is the development of inorganic ion exchangers for the selective removal of radionuclides from nuclear waste effluents. Thus, the study of the geochemistry and hydrology of the host rock, the understanding of the behaviour of waste forms under disposal conditions and the assessment of the rate if radionuclide migration through the geosphere are strongly dependent on the figure of the nuclear and radiochemist. Now it also appears that there will be a new rise in the nuclear power industry to fulfil the lack of energy. This, if it will happen, will certainly give a positive impact on radiochemistry.

The Liquid Radioactive Waste systems are used to collect, process, and store liquids from: pumps in potentially contaminated areas as the containment, auxiliary or reactor buildings, and turbine building (if a BWR); systems which collect radioactive leakage; normal discharge from the reactor cooling systems (*e.g.* during a start-up) or other systems which may be connected to the reactor cooling system (*e.g.* pressurizer relief tank) or located in potentially radioactive contamination areas. Typically, the liquids are collected in large storage tanks. The liquids are then processed using ion exchangers [34] to remove radioactive and chemical contaminants. Water which meets suitable chemical criteria (*e.g.* chlorides, fluorides) can be reused. If not, it can be reprocessed. Chemical and radioactivity levels in the tanks and process streams are monitored by sampling. In some plants reverse osmosis units may be used.

The Gaseous Radioactive Waste systems are used to collect, process, and store gases from Reactor Cooling System Pressurizer Relief Tank (PWR) - usually nitrogen if pressure is higher than desired, Chemical and Volume Control System Volume Control Tank (PWR) - usually hydrogen and potentially fission products, Containment/Drywell (BWR) - usually nitrogen, Air Ejector exhaust (in a BWR) - usually nitrogen with some hydrogen.

The gases are typically routed to storage tanks. When appropriate, compressors may be used to regulate the pressure in the tanks. Sometimes the gaseous system may connected to the vent header of the tanks in the liquid rad-waste systems to regulate pressure to reduce the likelihood of a vacuum being drawn in large tanks.

The Solid Radioactive Waste systems are used to collect, process, and store solids from: pump sludges or accumulation, spent (exhausted) ion exchange resins [34] (as used in waste and reactor water chemical cleanup systems), anti-contamination clothing that is no longer usable or can be laundered (many plants clean and reuse this clothing until no longer re-useable, rags or other materials used in cleaning .These materials are normally stored onsite and periodically shipped to authorized low level waste storage facilities. Special containers are used for shipment of spent resins. Super-compaction is used.

Not all the radioactive products of nuclear fission (U, Pu, MAs and FPs) and activation are contained in the fuel elements. The main sources of these products are roughly divided in 4 categories (below) and can be in solid, liquid or aqueous phase:

1.   radioactivity induced in the coolant and impurities present in it or intentionally added to avoid or decrease corrosion problems.

2.   impurities present in the coolant due to corrosion of activated structural materials

3.   leakage of FP and actinoids from damaged fuel rods.

4.   fission produced on the surface of the core

3.17 Nuclear chemistry, radiochemistry and health physics contribution at LASA

Many measurements and evaluations are needed at each stage starting since the planning of the installation of a facility. In particular it is necessary the analysis of the assessment of the environmental and the evaluation of the human health status before the installation of the NPP in order to determine reference basal values. This requires the development of environmental and human models that are based on experimental data derived from the measurements of trace elements; the measurements of natural or artificial radionuclides in soil, water, air and bio-monitors; the measurement of trace elements and natural radiotracers in human samples (*i.e.* blood and hair) of the population in general and specifically of people living near the selected site of the installation. During the normal operation the assessment of the potential environmental contamination and the human exposure of workers and general population as a consequence of the normal operation of NPP requires regular and routinely monitoring of the eventual leak of radionuclides during the operation of the nuclear plant and the monitoring of the environmental contamination.

At the end of the life of the facility a huge amount of radioprotection measurements for the control of the radioactivity of the environment are needed as to test the status as to re-assess the environmental and human health status as the starting condition.

The techniques that can be successfully implied for the measurements are related

again to nuclear field and can be summarized as:

a)   nuclear techniques: Instrumental- and Radiochemical Separation Neutron Activation Analysis (INAA and RSNAA, respectively), applied to monitor environmental and biological matrices and to characterize the nuclear fuel;

b)   radioanalytical techniques: use of High Specific Activity Radiotracers produced by cyclotron or nuclear reactor in No Carrier Added - NCA form, applied to the development and calibration of the analytical procedures; to make metallo-biochemistry and environmental toxicological studies;

c)   radiation protection techniques: beta and gamma spectrometry, applied to control the environmental contamination and to the health physics protection of general population and workers.

The INAA is a powerful multielemental technique that bombarding stable isotopes and with the successive gamma spectrometry of the activated samples reaches a high sensibility for many elements, high accuracy and precision and minimum effect of the matrix. It is excellent for environmental and biological matrices. In our laboratory we use the Research Nuclear reactor TRIGA MARC II – 250 kW (General Atomic – USA) of the Pavia University, that in the central thimble facility "Lazy Susan" can reach a neutron flux of 10^{13} cm^{-2}.s^{-1}. In Fig. 13 is reported, as an example, the results obtained analyzing the human blood [19].

With the same technique we monitor the trace element (TE) content in the atmospheric particulate in order to control and evaluate the degree of the air pollution and furnish additional information for assessing the air quality of our environment. Many TE of anthropogenic origin may be considered dangerous to the human health and their presence in the air constitute a potential risk for the population, not only at level of threshold concentrations, but also in terms of prolonged exposure to low levels. However, the knowledge of the concentrations in the total suspended air particulate, which represents an important parameter, is nevertheless not sufficient for a more close evaluation of the possible impact onto the public health. The monitoring must be comprehensive of the concentrations in the fine particulate fractions involved in the respiratory system at alveolar and bronchial levels. By means of inertial multistage impactors, the air particulate can be collected in fractions, to distinguish among the deposition in the alveolar (particles from 0 to 1.1 mm nominal diameter), bronchial (from 1,1 to 4.6 μm) and tracheo-pharynx (from 4,6 to < 9 μm) areas of our respiratory system (FIG. 14-b). After the sampling campaign consisting in the aspiration of dust upon filters by aspiration FIG. 14-a), the INAA followed by high resolution gamma spectrometry measurements and the Electrothermal Atomic Absorption Spectrophotometry (ET-AAS) can be employed to evaluate the concentration in ng•m-3 of many elements, of toxicological interest.
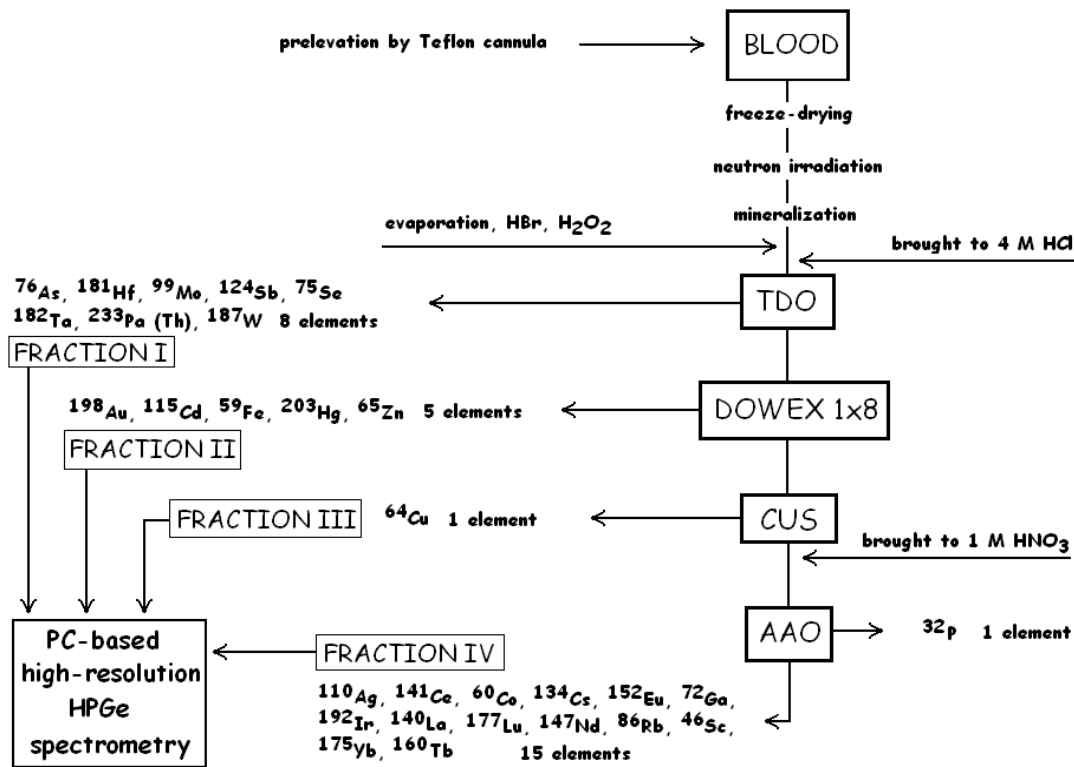
FIG. 13: Analysis of the human blood by INAA and the determination at the same time of
30 different elements [19]. Inorganic Ion Exchangers: TDO tin dioxide,
CUS copper sulphide, AAO acidic aluminium oxide;
the DOWEX 1X8 is an anionic organic exchanger.
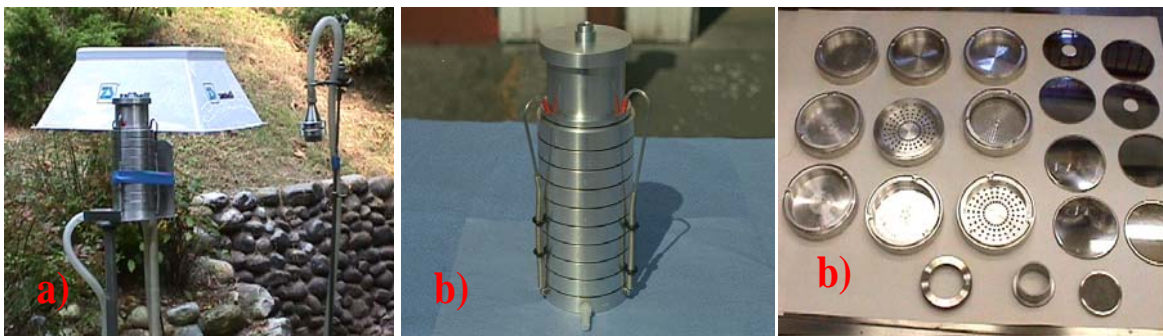
FIG. 14: a) sampling system used to monitor the trace element (TE) content in the
atmospheric particulate; b) inertial multistage impactor.

The concentration of the TE in the corresponding total air particulate allows us to compare the state of the air quality among the different locations investigated. The knowledge of the TE distribution trends in the different size particle fractions furnishes information about their mobility and their paths followed in the different human respiratory areas [51,52].

3.19 Very High Specific Activity RadioNuclides - HSARN

The High Specific Activity Radiotracers produced by cyclotron or by nuclear reactor in No Carrier Added (NCA) form is a long tradition at LASA – Milano. In Table 4 are reported the RNs produced in the last 30 years, together with nuclear reaction adopted, optimum energy range (MeV), theoretical carrier free (CF) Specific Activity AS(CF) (coherent SI unit $GBq.\mu g^{-1}$) and experimental Isotope Dilution Factor at the End of Radiochemical Processing IDF° (dimensionless) [53,54,55,56,57,58,59].

Such radiotracers are a powerful tool to label a wide variety of chemical elements and compounds present in the biosphere in ultra-trace amounts. Medium and high Z radionuclides, can be produced by irradiation in light-ions accelerator and sometimes nuclear reactor.

If the nuclear reaction product has atomic number different from irradiated target, it is possible separating the radioactive nuclide from irradiated target, without addition of isotopic carrier. These kinds of radionuclides are named *no-carrier added*, NCA, and their specific activity is very high and can reach values close to the theoretical *carrier-free* one (CF). The true specific activity must be determined by use of very sensitive radioanalytical techniques. If a low isotopic dilution factor is obtained, these radiotracers are used to label inorganic species and complexes of elements, which are presently introduced into the echo-systems by human activities. The "accurate" knowledge of the behaviour of thin-target excitation functions for nuclear reaction leading to cyclotron production of relevant RNs, allows increasing both radionuclidic purity and specific activity of RN itself, obviously by use of very selective radiochemical separations, without the addition of *isotopic carrier*.

The radioprotection measurements need suitable equipped laboratory. At LASA we have a Physics Measurements Laboratory where are installed eight HPGe gamma spectrometers filled with a LN_2 automatic system, two alpha spectrometers with a Si surface barrier detector and two different liquid scintillation counting systems - Beckman LD5000 system and the high-resolution a-liquid scintillation with a/b pulse shape analysis (PSA) discrimination - TRIATHLER "multilabel tester".

Moreover there is a Hot Radiochemical Laboratory – ISO Class II – UICEN 7815 equipped with radiochemistry hoods and glove boxes in order to can manage large activities, under the supervision of Qualified Expert for the protection against ionizing radiation.

TAB. 4: Cyclotron and nuclear reactor radiotracers, produced for environmental and metallo-toxicological studies in suitable oxidation states or as organo-metallic compounds. In general, after a suitable radiochemical separation, the specific activity of cyclotron RNs that are produced in *no-carrier added* form (NCA) is much larger than the nuclear reactor ones, which are in *carrier-added* form (CA) [54,55].

Cyclotron RadioNuclide		Reactor RNuclide
^{7}Be(II)	^{24}Na(I)	^{51}Cr(III,VI)
^{44}Ti(IV)	^{48}V(III,IV,V)	^{56}Mn(II,IV,VII)
^{51}Cr(III,VI)	^{57}Ni(II)	^{64}Cu(II)
^{58}Co(II)	^{64}Cu(II)	^{75}Se(IV,VI)
^{65}Zn(II)	^{66,67}Ga(III)	^{76}As(III,V)
^{69}Ge(IV)	^{74}As(III,V,org)	^{99}Mo(VI)
^{101}Rh(III)	^{103}Pd(II)	^{109}Cd(II)
^{106}Ag(I)	^{107,109}Cd(II)	^{125}Sb(III,V)
^{119m,121g}Te(VI)	^{123}I(I-,V)	^{127}Te(VI)
^{186g}Re(VI)	^{177g}Lu(III)	^{131}I(I-,V)
^{191}Pt(II,IV)	^{197}Hg(0,II)	^{137}Cs(I)
^{199}Au(III)	^{201,202}Tl(I,III,org)	^{140}La(III)
^{201,203}Pb(II)	^{205,206}Bi(III)	^{144}Ce(IV)

3.20 Education and Training

Due to the great number of operations concerning manipulation of radioactive materials radiochemical surveillance of an NPP is a relevant part of reactor operations. The plant operator is required to continuously monitor fuel performance, correctly account for release of radioactivity through gas and liquid effluents from the plant, and minimize the exposure of personnel to radiation. Nuclear and radioanalytical techniques play a major role during this phase in which a great number of analytical determinations and radiometric measurements must be carried out. The measurement of activities by gamma-ray spectrometry using a high resolution solid state detector is the most frequently used technique in a nuclear power plant to monitor continuously the radioactivity concentration in the reactor coolant as well as in the process effluents. Other activities involving the use of nuclear and radioanalytical techniques involve radiotoxicology surveillance

programmes which include Whole Body Counter measurements for employees, presenting a high level of contamination risk and environmental radioprotection surveillance programmes. These programmes must be carried out not only on samples collected inside the area of the nuclear plant but also on samples of water, air, soil surrounding the site of the operating nuclear reactor to ensure that no radioactivity is released to the environment.

Unfortunately, after the '60s of XX century, Italy decreased its excellent leadership in the field of NPPs design and starting up, thus only 4 NPPs for energy production were built and operated (i.e. the biggest one was a BWR of 860 MWe located in Caorso, near Piacenza on the Po river), until the Chernobyl accident of April 1986. In 1987, a popular referendum voted against the collaboration of Italian Government with foreign countries, but it was interpreted by all political parties as a clear attitude of the majority of the population to stop any activity in the field of nuclear energy. To stress the great need in Italy of education and training of new young scientists in the field of health physics, nuclear and radiochemical techniques in order to ensure sustainable supply of qualified nuclear chemists and health physicists, whose the number have declined steadily and dramatically in the last twenty years. We propose that health physics, nuclear chemistry and related courses enter strongly in the university programs in full.

4   Conclusions

Radiochemistry, Nuclear Chemistry and Radiation Chemistry (N&R) together with Health Physics and Radiation Protection, play a relevant role in all phases of the nuclear fuel cycle in different kinds of NPPs and other utilities and equipment, using the powerful energy of the atomic nucleus (*e.g.* FIG. 15).

The first step is the mining of U (and Th) ores and concentration followed normally by isotopic enrichment in order to produce the fuel pellets, that are normally made of either UO_2 or MO_x After the first operations the UO_2 pellets contains variable amounts of Minor Actinoids and Fission Products. Moreover the coolant that could be H_2O, D_2O or liquid metal, does contain radioactive species coming from activation of water itself, corrosion of activated structural materials or coming from failures of fuel pins. The water radiochemistry is a central item in the operation of a NPP. Gaseous radioactive nuclides are also produced during NPP operation and are mainly constituted by tritium, radiohalogens and radioactive noble gases. Should the reprocessing of exhaust material be carried out, a series of different radiotoxic wastes, must be managed and encapsulated by radiochemical methods, to avoid spill over in the environment.

At last, the radioanalytical controls on the environment to detect possible escapes of radioactivity, must be carried out with *gamma* spectrometry, but must follow a selective radiochemical processing of the samples in order to determine *alpha* and *beta* emitters and to distinguish them from natural background.

FIG. 15: Task Force One. Several hundreds nuclear ships, submarines and ice-breakers operated around the world, without significant radiological accidents, for several decades.

5   ACKNOWLEDGEMENTS

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