Nuclear-Powered Task-Force One

Mauro L. Bonardi[a,b,e], Flavia Groppi[a], Simone Manenti[a], Enrico Rizzio[d], Enrico Sabbioni[a,b,c]
[a]Università di Milano and Istituto Nazionale di Fisica Nucleare LASA, Radiochemistry Laboratory Segrate (MI)
[b]Board of the Interdivisional Group of Radiochemistry and Radiation Chemistry applied to Environment, Health and Industry of SCI http://wwwGIR.mi.infn.it
[c]Centro di Scienze dell'Invecchiamento (CeSI) Fondazione Università "G. d'Annunzio" Chieti
[d]Eni SpA, Division Exploration & Production San Donato Milanese (MI)
[e]International Committee of the American Nuclear Society www.ANS.org

GEN IV NUCLEAR REACTORS NUCLEAR H_2 AND RADWASTE

Nuclear and radiochemistry, radiation chemistry and health physics play a fundamental role in nuclear energy production. Production of hydricity and rad-waste transmutation by high T reactors is discussed. We need education in N&R, in order to supply qualified personnel, whose number have declined in the last 20 years.

There are two main kinds of *Fuel Cycles* that are well established, due to diverse political and strategic approaches [1, 2]: 1) the *once-through open 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,* near to the nuclear power plant (NPP) for some years and then sent to the repository, in order to be reutilized in *Gen IV* NPPs; 2) the *re-cycle of U and Pu* RNs, or *closed fuel cycle*, in which the exhaust fuel rods are *reprocessed*, converted to MOX and reused in thermal or fast NPP. A modern scheme of reprocess and fuel fabrication by recycling is shown in Fig. 1. Of course the non-energetic applications of the energy of the nucleus are of paramount relevance too [2-7].

Generation III+ and Generation IV reactors (*Gen IV*)

The European Pressurized light water Reactor, EPR of 1.6 GWe capacity (AREVA-Siemens, Fig. 2) and the Advanced and Passive light water reactor AP1000 of 1.140 GWe (Westinghouse-Toshiba), belonging to the *Gen III+* are already licensed by NRC, USA and are being built in an increasing number [8, 9]. These two designs would be the main choice for the next 20 years, together with the canadian type D_2O moderated and cooled *natural* U, NPPs (CANDU). Conversely the current reactors in operation around the world are generally considered 2nd- or 3rd-generation systems (*Gen II* and *Gen III*). Regarding the *Gen IV* reactors, these are a set of nuclear reactor designs currently being researched. Most of these designs are generally not expect-

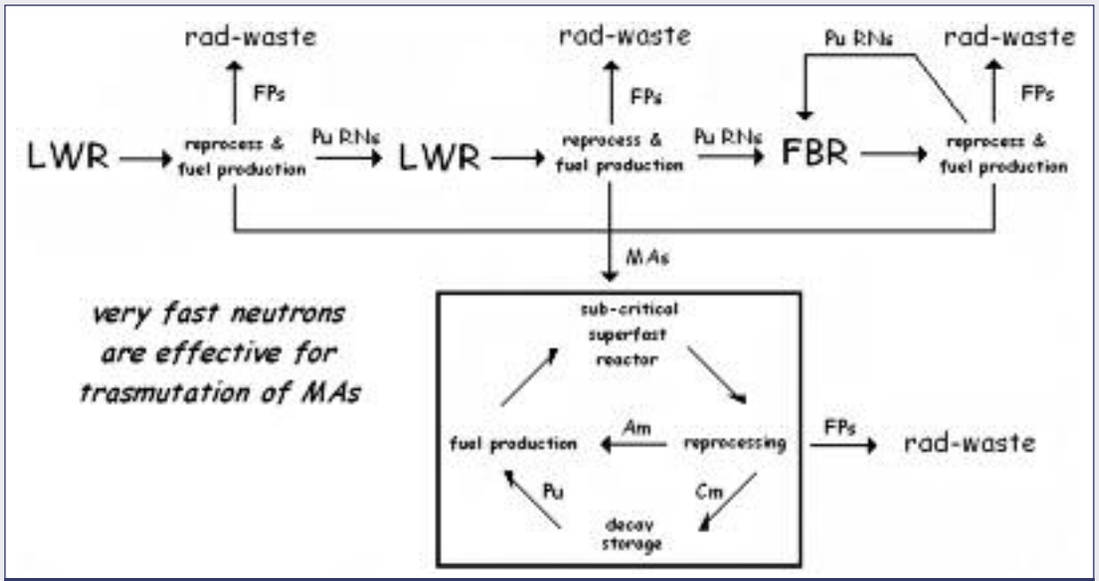

Fig. 1 - A fuel recycle of a light water reactor, LWR (in two phases) in which the minor actinoids, MAs are treated separately from U and Pu radionuclides RNs. More phases can be added if the spent fuel does not contain high neutron absorbing RNs (poisons), whose concentration increases with burn-out

ed 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) to be completed by 2021. Research into these reactor types was officially started by the *Generation IV International Forum* (GIF) based on eight technological goals. The primary goals are to improve nuclear safety, improve proliferation resistance, to minimize rad-waste and natural resource utilization, and to decrease the cost to build and run such NPPs. 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 *Gen IV* reactors can be classified in two main types, some based on the *UOT* process other on *Partitioning and Transmutation* (P&T) of fuel. They are: A) Thermal reactors: Very-High-Temperature Reactor (VHTR); SuperCritical-Water-cooled Reactor (SCWR); Molten Salt Reactor (MSR); B) Fast reactors: Gas-cooled Fast Reactor (GFR); Sodium-cooled Fast Reactor (SFR); Lead-cooled Fast Reactor (LFR).

Nuclear waste transmutation

From the nuclear reactions reported in Eqs. 1-8 (beta decay →, alpha decay →) many long-lived fission products (FPs) and minor actinoids (MAs: Pa, Np, Am, Cm) can be transmuted into either shorter-lived or stable ones, by use of either dedicated nuclear reactor transmuters (NRTs) or by a more complex approach that is being studied, based on very energetic (0.6 to 2 GeV) linac or cyclotron accelerated proton beam irradiation of rad-waste after partitioning (P, see Fig. 1), that are filled in a *subcritical 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% of the total): 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-circulating liquid Hg, liquid Pb or liquid Lead-Bismuth Eutectic (LBE). Any electricity stop due to any kind of accident, suddenly makes the NRT sub-critical, avoiding dangerous power divergence. The very fast neutrons, could be either thermalized or used for (n,xn) 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. 3):

1) ^{81g}Kr ($T_{1/2}$ = 0.23 Ma) (n,γ) ^{82}Kr (stable)
2) ^{99g}Tc ($T_{1/2}$ = 0.21 Ma) (n,γ) ^{100}Tc ($T_{1/2}$ = 15.8 s) → ^{100}Ru + ^{100}Mo (stables)
3) ^{107}Pd ($T_{1/2}$ = 6.5 Ma) (n,γ) ^{108}Pd (stable)

Fig. 2 - Schematics of EPR, with turbine building and water cooling. No big hyperboloid cooling towers and scrubbers are necessary for the operation, but just a vast source of cooling water

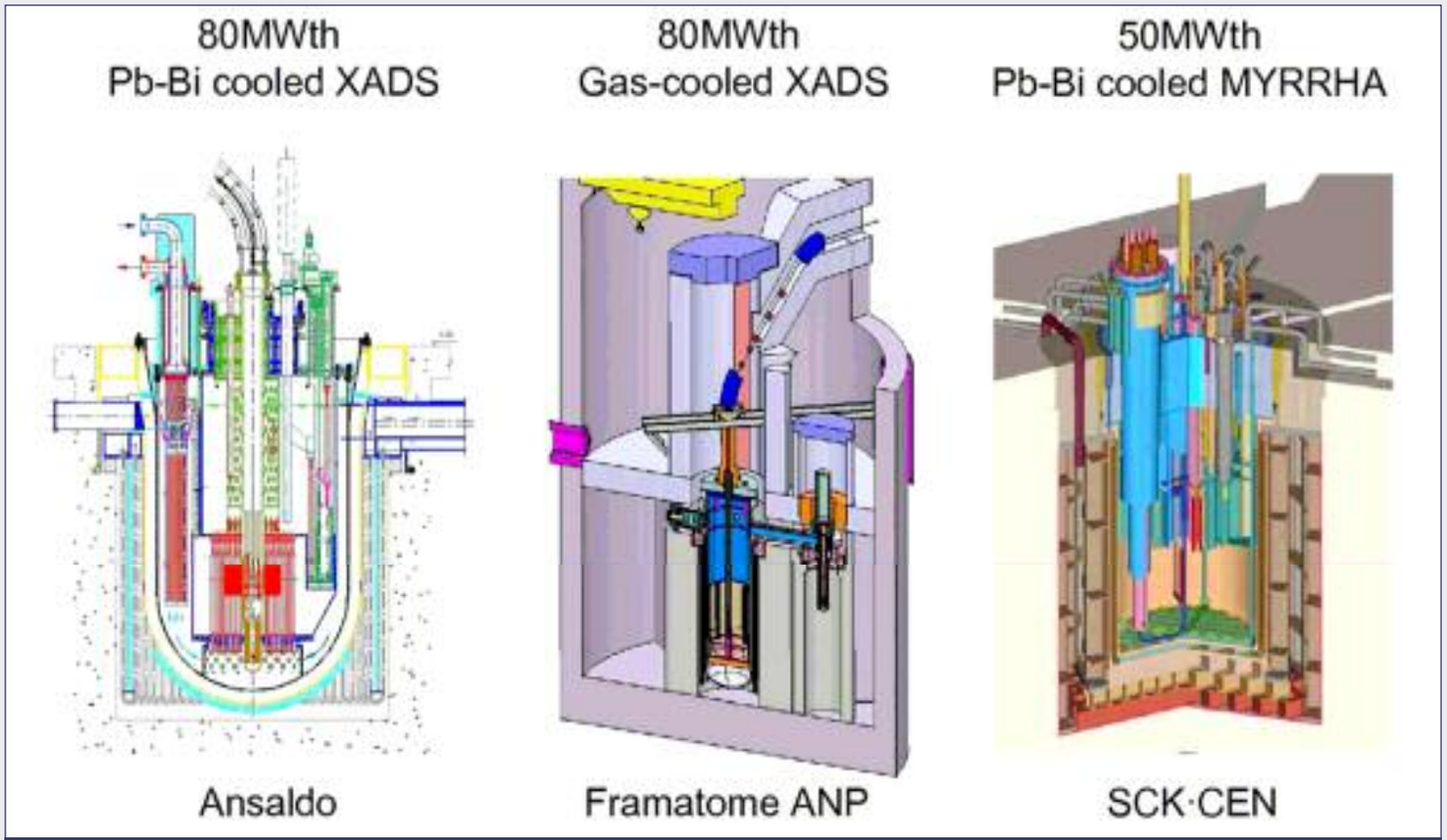

Fig. 3 - Three simplified designs of sub-critical reactors for ADT, under study in Europe (Ansaldo Nucleare, Genova, Italy; Framatome ANP, France; SCK-CEN, Belgium). These reactors must be interfaced with an high energy proton accelerator of very high intensity beam current to reach the criticality

4) ^{129}I ($T_{1/2}$ = 15.7 10^7 Ma) (n,γ) ^{130}I ($T_{1/2}$ = 12.36 h) → ^{130}Xe (stable)
5) ^{231}Pa ($T_{1/2}$ = 32.76 ka) (n,γ) ^{232}Pa ($T_{1/2}$ = 1.31 d) → ^{232}U ($T_{1/2}$ = 68.9 a) →
6) ^{237}Np ($T_{1/2}$ = 2.144 Ma) (n,γ) ^{238}Np ($T_{1/2}$ = 2.117 d) → ^{238}Pu ($T_{1/2}$ = 87.74 a) →
7) ^{241}Am ($T_{1/2}$ = 432.2 a) (n,γ) $^{242(m+g)}Am$ ($T_{1/2}$ = 141 a, 16 h) → ^{242}Cm ($T_{1/2}$ = 162.9 d) → ^{238}Pu →
8) ^{243}Am ($T_{1/2}$ = 7.370 ka) (n,γ) $^{244(A+B)}Am$ ($T_{1/2}$ = 26 min, 10.1 h) →^{238}Cm ($T_{1/2}$ = 18.10 a) → ^{240}Pu

Nuclear Hydrogen, NuH_2 or hydricity

The world chemical industry does produce ~50-60 Mton of hydrogen annually, basically by *steam reforming* of light hydrocarbons and high temperature conversion of coal though the Fischer-Tropsch gasification, followed by *water gas shift* reaction to CO_2 (Dussan's reaction). Most of H_2 is used for production of NH_3 and then nitrates as explosives, polymers 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 syn-gasoline as well. The mixture of H_2 and CO (city gas, syngas) is used since a long time for heating and lighting houses and cities and for production of *methanol*, that is - together with H_2 itself - a suitable feed for fuel cells for supplying motorvehicles, buses, motorcycles, aircraft, PCs and many public and home utilities [10-12]. Several methods have been proposed for preparation of even larger amounts of hydricity (*i.e.* Nuclear Hydrogen or NuH_2) by heating water in a gas-cooled high temperature nuclear reactor, HTGR, without any use of fossil fuels, that lead to the co-production of CO_x, NO_x, SO_x and HMs, or even worse any use of electrolysis of water, which is thermodynamically very unfavorable. Amongst them, the most promising is the sulfur-iodine cycle (S-I cycle), which is a series of *thermochemical* processes based on Bunsen's reaction and used to produce H_2. The three reactions 9-11 that produce H_2 are as follows:

9) $I_{2(v)} + SO_{2(g)} + 2H_2O_{(v)} \rightleftarrows 2HI_{(v)} + H_2SO_{4(l)}$
(Bunsen's reaction, at 120 °C; $\Delta H_R^{\varnothing}$(298.15 K) = -41.08 kJ<0; $\Delta G_R^{\varnothing}$(298.15 K) = +51.47 kJ>0).

The HI is then separated as a vapour by distillation. Note that concentrated H_2SO_4 may react with HI, giving I_2, SO_2 and H_2O (backward reaction, ΔG>0), but removing the desired product will shift equilibrium to the right.

10) $2H_2SO_{4(v)} \rightleftarrows 2SO_{2(g)} + 2H_2O_{(v)} + O_{2(g)}$
(at 830-850 °C in vapour phase; $\Delta H_R^{\varnothing}$(298.15 K) = +629.7 kJ>0; $\Delta G_R^{\varnothing}$(298.15 K) = +486.1 kJ>0).

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 of Eq. 11 now produce H_2 and recycle the I_2:

11) $2HI_{(v)} \leftrightarrows I_{2(v)} + H_{2(g)}$
(at 400-450 °C in gaseous phase; $\Delta H_R^{\varnothing}(298.15\ K) = +9.48\ kJ>0$; $\Delta G_R^{\varnothing}(298.15\ K) = +15.93\ kJ>0$).

12) $[\delta(\Delta G(T)/T)/\delta T]_P = -\Delta H(T)/T^2$ (isobare Gibbs-Helmoltz Eq.), $\Delta H(T) = [\delta(\Delta C_P(T))/\delta T]_P$.

By using Eq. 12, it is possible calculating and optimizing the ΔG(T) and T from the knowledge of the behavior of tabulated $C_P(T)$ of different components, *i.e.* ΔH(T), by using for example the 5 parameters *Shomate's Eq.*: $C_P^{\varnothing} = \alpha + \beta T + \gamma T^2 + \delta T^3 + \varepsilon/T^2$ [13]. Iodine and any accompanying H_2O or SO_2 are separated by condensation, and the H_2 product remains as a gas. Then H_2 can be either compressed, adsorbed as metal hydride or into nanotubes, or liquefied by isoenthalpic Joule-Thompson free expansion, after pre-cooling with liquid nitrogen at 78 K (-195 °C) and than stored at 20 K (-253 °C). The S and I compounds are recovered and reused, hence the consideration of the process as a catalytic cycle (Fig. 4). All reactions are *endoergonic* at room temperature. This S-I process is a chemical heat engine; heat enters the cycle in high temperature *endothermic* chemical reactions 10 and 11, and heat exits the cycle in the low temperature *exothermic* reaction 9. 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 H_2 produced. In conclusion the net reaction is the decomposition of water and oxygen is a valuable by-product of the process.

Apart the S-I cycle developed by General Atomics and Argonne-NL in USA, there are several hybrid termochemical-electrochemical cycles to be cited for completeness, combined between a medium-high temperature termochemical and an electrolytical step at low temperature. There are several variant of the *Fe-Ca-Br adiabatic* cycle (UT-3) at 1,033 K of ANL, USA and Japan, the process *hybrid-sulfur* (HyS) combined with electrolysis of Westinghouse-USA and Savannah-River-NL, USA, the *reverse Deacon cycle (Mg-Cl)* with electrolysis and the process *Cu-Cl at low temperature* (Cu-Cl) of ANL, USA and AECL, CA combined with electrolysis too (Eqs. 13-16 [14, 15]); all these methods do not utilize fossil fuels and do not have undesired combustion products, apart water vapors, and the net reaction is $2H_2O \leftrightarrow 2H_2 + O_2$:

13) $2Cu_{(s)} + 2HCl_{(g)} \leftrightarrows 2CuCl_{(l)} + H_{2(g)}$ (at 430-475 °C)
14) $2Cu_2OCl_{2(s)} \leftrightarrows 4CuCl_{(s)} + O_{2(g)}$ (at 500-530 °C)
15) $2CuCl_{2(s)} + H_2O_{(v)} \leftrightarrows Cu_2OCl_{2(s)} + 2HCl_{(g)}$ (at 400 °C)
16) $2CuCl_{(s)} \leftrightarrows CuCl_{2(aq)} + Cu_{(s)}$ (ambient-temperature electrolysis).

Finally, in the gas-cooled very high temperature reactor of *Gen IV* VHTGR, it would be possible to dissociate water by direct *pyrolysis* at temperatures higher than 1,000 °C up to 1,600 °C, either directly or on a metal catalyst (Fe, Co, V) or a refractory metal oxide.

Unfortunately, inside this optimistic scenario might be an unexpected drawback to be remembered: there are some researchers claiming that the physiological losses of hydrogen of about 10% (during production, storage and transportation), could increase the H_2 concentration in the troposphere and be hazardous for the *ozone hole* in the stratosphere [16].

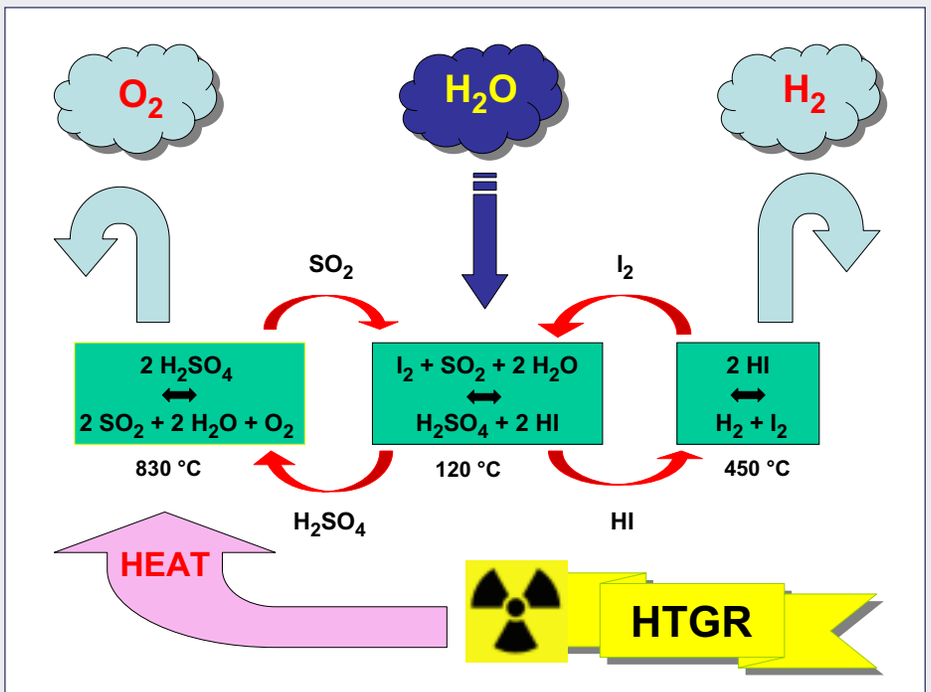

Fig. 4 - Production of hydrogen (and oxygen) by thermochemical decomposition of water in high temperature nuclear reactor, by using the S-I cycle

Education and training

Due to the great number of operations concerning manipulation of radioactive materials radiochemical and health physics surveillance of an NPP is a relevant part of the reactor operations. The NPP 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 ionizing radiation. Nuclear and radioanalytical techniques (NATs) 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 radioactivities by *gamma* spectrometry using a high resolution solid state detector (HPGe) is the most frequently used technique in a NPP to monitor continuously the

radioactivity concentration in the reactor coolant, as well as in the process effluents. Other activities involving the use of NATs involve radiotoxicology surveillance programs which include Whole Body Counter measurements for employees, presenting a high level of contamination risk and environmental radioprotection surveillance programs. These programs 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 Sixties of XX century, Italy abandoned its excellent leadership in the field of NPPs design and starting up, thus only 4 NPPs for energy production were built and operated. In 1987 a popular referendum voted against the collaboration of Italian Government with foreign countries about peaceful nuclear activities, 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. In order to stress the great need in Italy of *education and training* of new young scientists in the field of N&R techniques and Health Physics, to ensure sustainable supply of qualified nuclear chemists and health physicists, whose the number have declined steadily in the last 20 years, we propose that health physics, nuclear chemistry and related courses enter strongly in the university programs in full [17].

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. The reprocessing and transmutation of exhaust material should be carried out or nuclear H_2 production, a series of different radiotoxicity wastes, must be managed and incapsulated by radiochemical methods, to avoid spill over in the environment. The technology of production of nuclear hydricity will cover a wide range of essential knowledges about utilities and transportation in particular, and it will save a precious resource for chemical industry, that is presently wasted for termoelectrical energy production. The radiodioanalytical controls on the environment to detect possible escapes of radioactivity must be carried out with gamma spectrometry, but it must follow a selective radiochemical processing of the samples in order to determine *alpha* and *beta* emitters by liquid scintillation counting (LSC) and other techniques in order to distinguish them from natural background [17].

References

[1] R.G. Cochran, N. Tsoulfanidis, The Nuclear Fuel Cycle: Analysis and Management, American Nuclear Society, La Grange Park, IL, USA, 2nd Ed., 1999.

[2] M. Bonardi, *et al.*, at www.lnf.infn.it/user.html, Preprints INFN/TC-01/21, 20 Dic 2001.

[3] M.L. Bonardi, D.S. Moore, *Chem. Int., The News Magazine of IUPAC*, 2007, **29(6)**, 10 and 2008, **30(1)** 8.

[4] A. Vértes, S. Nagy, Z. Klencsár (Eds.), Handbook on Nuclear Chemistry, Vol. 5, Kluwer Academic, Amsterdam, 2003.

[5] A.E. Waltar, Radiation and Modern Life, Fulfilling Marie Curie's Dream, Prometheus Book, NY, 2004.

[6] M.L. Bonardi, *Rad. Phys. Chem.,* 2005, **72**, 737.

[7] G. Choppin, J.O. Liljenzin, J. Rydberg, Radiochemistry and Nuclear Chemistry, Butterworth-Heinemann, Oxford, 3rd Ed., 2002.

[8] R.C. Twilley, EPR development - An evolutionary design process, Nuclear News of the ANS, ed ANS, La Grange Park, Il, USA, Apr. 2004, 26.

[9] H.J. Bruschi, The Westinghouse AP1000 - Final Design Approved, Nuclear News of the ANS, ed ANS, La Grange Park, Il, USA. Nov. 2004, 30.

[10] 2001 ANS Winter Meeting, Hydrogen Systems and Nuclear Development, distributed on CD-ROM by Inst. Integ. Energy Systems, University of Victoria, Canada, www.iesvic.uvic.ca

[11] D.L. Simbeck, E. Chang, Hydrogen Supply: Cost Estimate for Hydrogen Pathways - Scoping Analysis, Report NREL/SR-540-32525, US DOE, Golden, CO, 2002.

[12] OECD Nuclear Energy Agency, Nuclear Production of Hydrogen: Second Information Exchange Meeting, Argonne, IL, www.nea.fr/

[13] http://webbook.nist.gov/chemistry/

[14] M. Dokiya, Y. Kotera, *Int. J. Hydrogen Energy,* 1967, **1**, 117.

[15] G.F. Naterer *et. al., Int. J. Hydrogen Energy*, 2009, **34**, 2901.

[16] T.K. Tromp *et. al., Science*, 2003, **300**, 1740.

[17] M.L. Bonardi *et. al.,* Nuclear chemistry, radiochemistry, radiation chemistry, health physics and sustainable nuclear energy production, 1st Europ. Energy Conf., I-ECC. Barcelona, Spain, Apr. 2010, preprints *INFN/TC-10/02,* 18 giugno 2010.

RIASSUNTO

Reattori nucleari della Gen IV. Idrogeno nucleare e trasmutazione delle scorie

La radiochimica, la chimica nucleare, la chimica delle radiazioni e la fisica sanitaria giocano un ruolo fondamentale nel ciclo dell'energia nucleare, dalla miniera allo stoccaggio di eventuali scorie. Viene trattata la produzione di idricità e la trasmutazione delle scorie nucleari a lunga emivita o altamente radiotossiche, mediante impiego di reattori della Gen IV. Risulta necessaria la preparazione di ricercatori per affrontare tali tecnologie in vista della ripresa dei programmi nucleari nel nostro Paese.