

# Chemistry for the nuclear energy of the future

Andrzej G. Chmielewski

**Abstract.** Chemistry – radiochemistry, radiation chemistry and nuclear chemical engineering play a very important role in the nuclear power development. Even at present, the offered technology is well developed, but still several improvements are needed and proposed. These developments concern all stages of the technology; front end, reactor operation (coolant chemistry and installation components decontamination, noble gas release control), back end of fuel cycle, etc. Chemistry for a partitioning and a transmutation is a new challenge for the chemists and chemical engineers. The IVth generation of nuclear reactors cannot be developed without chemical solutions for fuel fabrication, radiation-coolants interaction phenomena understanding and spent fuel/waste treatment technologies elaboration. Radiochemical analytical methods are fundamental for radioecological monitoring of radioisotopes of natural and anthropological origin. This paper addresses just a few subjects and is not a detailed overview of the field, however it illustrates a role of chemistry for a safe and economical nuclear power development.

**Key words:** radiochemistry • nuclear chemistry • nuclear chemical engineering • nuclear energy • coolant chemistry • fuel cycle • radioactive waste • radioecology

## Introduction

The first radiochemical separation scheme was developed by Maria Skłodowska-Curie and Pierre Curie more than hundred years ago (Hurwic [14]). Radiation chemistry through radium medical applications and observation of radiation effects (e.g. paper degradation) started at those years as well. Then the biggest development of the science was related to military and peaceful applications of fissile and radioactive elements in nuclear power, industry and medicine. This year we play attribute to the achievements of Madame Curie but also to all chemists who developed through the century basic understanding for radiochemistry of elements and their compounds and also radiation chemistry explaining the mechanisms of induced reactions. These studies made foundation for practical, important for the human being applications. So the science deserved to call the year 2011 the YEAR OF CHEMISTRY. In the last decade the paper on the subject has been published as a review paper by Narbutt [40]. There have been many new developments since that time, the Polish Government decided to establish a Polish Nuclear Energy Program which assumes the construction of first blocks by the year 2020. The Institute of Nuclear Chemistry and Technology (INCT, known in Poland as IChTJ) have elaborated own programme considering a role of their expertise in radiochemistry, radiation chemistry,

A. G. Chmielewski  
Institute of Nuclear Chemistry and Technology,  
16 Dorodna Str., 03-195 Warsaw, Poland,  
Tel.: +4822 504 1368, Fax: +4822 504 1277,  
E-mail: a.chmielewski@ichtj.waw.pl  
and Faculty of Chemical and Process Engineering,  
Warsaw University of Technology,  
1 Waryńskiego Str., 00-645 Warsaw, Poland

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radiobiology and radiometric methods to support this programme. The construction of the Center of Radiochemistry and Nuclear Chemistry for Nuclear Power and Nuclear Medicine has started this year.

### Radio- and radiation chemistry in nuclear power development

This year being so important anniversary of the science development breakthrough, is also the year of a terrible disaster in Japan devastated by earthquake and tsunami. The Fukushima nuclear power plant (NPP) was seriously damaged but survived this apocalypses, however the sequence of the accident has illustrated importance of radiation- and radiochemistry on the safe operation and shut down of nuclear reactor and decontamination of formed wastes. This is other lesson learned that chemistry is one of the key factors for a further nuclear energy development, a motto of the conference organized by the CEA Center Marcoule in Montpellier, April 2011 (Montpellier [37]). The recently established Institute for Separation Chemistry, Marcoule is one of the leading R&D institutions carrying out research in the field of radio- and nuclear chemistry.

### Radiochemistry

Development of nuclear power was a challenge for the physics, engineering and chemistry as well. Early works of the Curies were a good start for the uranium extraction process development and yellow cake production, the fact that only 0.7% natural uranium is the fissile uranium isotope  $^{235}\text{U}$  was a driving force for isotope separation methods development. Search for a good moderator leads to deuterium and elaboration of technologies for enrichment of heavy water. But first of all, the theory of isotope effects was studied experimentally and developed theoretically. Isotope separation cascade is a master piece of the science, which founded its applications in the modern chemical engineering. Radiochemistry in this frame has developed ion exchange, extraction, precipitation and other separation methods. The main fields of nuclear industry where chemistry plays a very important role are uranium extraction and enrichment, production of oxide fuels, chemistry of coolant, fuel reprocessing and radioactive waste separation and immobilization. Other areas are decontamination processes and barrier materials synthesis for waste disposal facilities. The radioactive substances deposition and migration monitoring requires development of precise analytical methods as well.

### *Uranium and thorium extraction from ores and diluted resources*

According to the IAEA-NEA 'Red Book', the reserves of uranium resources in known deposits will last for the next 80 years at the present consumption rate. The uranium contained in phosphates and other low-grade ores will prolong this period up to 200 years and even sea water can be a resource for this fissile  $^{235}\text{U}$  and fissionable  $^{238}\text{U}$  production, the new chemical processes are being developed to meet the new challenges

(Chmielewski [4]). An improved process for the separation of uranium from the leached pulp of low-grade uranium ore is reported using the resin in-pulp method (Mirjalili and Roshani [34]).

Uranium present in ion exchange eluates is purified by liquid-liquid extraction processes. Tri-n-butyl phosphate (TBP) and dibutyl butylphosphonate (DBBP) were used as extractants from nitrate eluates. A tertiary amine was used in the case of sulfuric acid eluates. Optimum conditions for high recovery and low reagent costs were established, and the adaptability of the processes to existing leach plants was analysed. The suitability of the ammonium diuranate product as a source of ceramic-grade  $\text{UO}_2$  was considered in early years of research (Simard *et al.* [50]).

In two-phase emulsion separations, it is customary to employ large settling volumes (for mixer-settling apparatus) or large centrifugal forces (for centrifugal contactors). Improvement can sometimes be achieved by using an extractant with magnetic properties in the presence of a variable field. In the work reported, two different extractants (D2EHPA and TBP) were employed in magnetic field experiments. These compounds are both stable and resistant to acid (15%  $\text{H}_2\text{SO}_4$ ) and basic (NaOH, pH = 10) media. The test results for extraction of  $\text{Cu}^{2+}$  (with D2EHPA) and  $\text{UO}_2^{2+}$  (with TBP) from aqueous media were positive. The emulsion separation for these two systems in the presence of a magnetic field was 160 times faster than in the gravitational field alone (Palyska and Chmielewski [45]).

### *Uranium and heavy water enrichment*

The next step after uranium concentration ("yellow cake") is the purification of the concentrate and its conversion into a  $\text{UF}_6$  chemically suitable form for enrichment of the  $^{235}\text{U}$  isotope content in the feed. Isotope enrichment proceeds in the gas phase via uranium hexafluoride, the only uranium compound which boils at low temperatures and is stable in the vapor phase. Two processes are employed for the production of  $\text{UF}_6$ , namely the wet and dry processes. In both processes  $\text{UO}_2$  and  $\text{UF}_4$  are formed as intermediates. In the wet process  $\text{UO}_2$  is produced from the uranium concentrate by way of uranyl nitrate, whereas in the dry process the uranium concentrate is directly reduced to  $\text{UO}_2$ . The methods of purification used are also different: in the wet process the purification proceeds at the uranyl nitrate stage, by solvent extraction, whereas in the dry process the end product uranium hexafluoride is purified by distillation.

Commercial uranium enrichment currently employs one of two technologies: gaseous diffusion or gas centrifuge. Both use  $\text{UF}_6$  as the chemical form of uranium for processing.

Due to the fact that separation factors are much higher for the second process it is gaining the biggest part of uranium enrichment market.

Heavy water used as a moderator is produces applying distillation or chemical exchange processes. The process is well developed and implemented in some countries including Romania, which runs two heavy water reactors and is manufacturing their own fuel from natural uranium (Prisecaru *et al.* [47]).

Deuterium- $^2\text{H}$  and oxygen- $^{18}\text{O}$  isotope enrichment in water by membrane distillation were studied in a 4-stage cascade. Two configurations of membrane distillation (MD) employing PTFE-flat-sheet membranes were investigated, including direct contact MD and air gap MD. The first, direct contact MD is more efficient. It is characterized by high distillate flow rate. The temperature polarization coefficients were higher for direct contact MD. H/D and  $^{16}\text{O}/^{18}\text{O}$  separation factors were determined in the 4-stage cascade (Chmielewski *et al.* [7]). Due to the fact that separation coefficient is rather low the multistage cascades have to be designed on the basis of cascade theory (Chmielewski *et al.* [6]).

#### *Fuel precursors manufacturing*

Even a manufacturing of uranium oxide fuels is well developed process, synthesis of mixed uranium-thorium fuels is a process under development. A new method of synthesis of uranium and thorium dioxides by original variant of sol-gel method – complex sol-gel process (CSGP), has been elaborated. The main modification step is the formation of nitrate-ascorbate sols from components alkalized by aqueous ammonia. Those sols were gelled into: 1) irregularly agglomerates by evaporation of water; 2) medium sized microspheres (diameter  $< 150\ \mu\text{m}$ ) by INCT variant of sol-gel processes by water extraction from drops of emulsion sols in 2-ethylhexanol-1 by this solvent. Uranium dioxide was obtained by a reduction of gels with hydrogen at temperatures  $> 700^\circ\text{C}$ , while thorium dioxide by a simple calcination in the air atmosphere (Deptuła *et al.* [10]).

#### *Coolant chemistry and reactor elements corrosion*

A chemistry programme is essential for the safe operation of a nuclear power plant. It ensures the integrity, reliability and availability of the main plant structures, systems and components important to safety, in accordance with the assumptions and intent of the design. A chemistry programme minimizes the harmful effects of chemical impurities and corrosion on plant structures, systems and components. It supports the minimization of buildup of radioactive material and occupational radiation exposure as well as limiting of the release of chemicals and radioactive material to the environment (IAEA [17]).

Monitoring of fuel clad integrity, the first and the most important barrier against radioactivity release into the environment, is the most important line of process radiation monitoring at nuclear power installations (NPIs). Radiochemical methods based on measuring the activity of diagnostic (reference) radionuclides of fission and activation products in primary coolant samples are practically the only means to gain information on the fuel state under real operation conditions. Therefore, this kind of radiation monitoring in nuclear power engineering is traditionally termed radiochemical monitoring (RCM) of fuel failure (Orlenkov and Moskvina [44]).

The radiation situation in the maintenance area of NPIs is largely determined by loose deposits of activated corrosion products (ACPs) in primary circuits. The  $^{60}\text{Co}$  radionuclide produce the largest dose burden for the

personnel because of long half-life and hard  $\gamma$ -radiation. To improve the radiation situation at NPIs, it was suggested to add into primary coolants salts of metals capable to replace  $^{60}\text{Co}$  in corrosion deposits. On the empirical level, salts of zinc depleted of  $^{64}\text{Zn}$  and aluminum salts were chosen as such additives to coolants. Apparent drawback of the zinc salts depleted of  $^{64}\text{Zn}$  is their relatively high cost; furthermore, such depletion does not fully eliminate production of  $^{65}\text{Zn}$  radionuclides in the coolant. Nevertheless, up to now, zinc salts as additives to NPI coolants were preferred. Additions of salts of aluminum, which does not form long-lived radionuclides and does not require preliminary isotope enrichment, are apparently preferable. The formation of polymeric hydrolysis products in mixed solutions of  $\text{Fe(III)} + \text{Al(III)} + \text{Co(II)}$  nitrates were studied under the conditions simulating the hydrolysis of corrosion products in primary coolants on adding aluminum salts. A study by gel chromatography in combination with radioisotope and elemental analyses showed that the  $\text{Co(II)}$  ions incorporated in polymeric hydrolysis products in the step of their formation were practically fully replaced by aluminum ions in the course of the polymer aging. Because such polymers are precursors of loose corrosion product deposits formed in primary circuits of NPIs and incorporating the most radiation-hazardous radionuclide  $^{60}\text{Co}$ , addition of aluminum salts to primary coolants improves the radiation situation in the maintenance area of NPIs and, therefore, can be appropriate solution (T. V. Epimakhov *et al.* [12]).

Chemical decontamination of the primary circuit equipment of a nuclear reactor is the most efficient way to improve the radiation situation and to reduce the personnel radiation exposure. The main decontamination stages are injection of the appropriate chemical reagents into the circuit, dissolution of loose corrosion deposits containing corrosion-produced radionuclides and fission products, in-circuit circulation of the decontaminating solution at the predetermined temperature, and its replacement in the circuit by high purity water (Aleshin *et al.* [1]). Among procedures developed for decontamination of primary circuits of NPIs, the most widely used in the world are liquid, circulation procedures for chemical treatment of their internal surfaces (Moskvina *et al.* [39]). Radionuclides affecting the radiation situation in the maintenance area of a nuclear reactor, irrespective of their origin in the primary circuits activated corrosion products (ACPs), fission products (FPs), are removed from the equipment surfaces and converted to the soluble state together with corrosion product (CP) deposits as a result of the action of solutions of specially chosen reagents. The solutions should efficiently dissolve CPs, firmly retain chemical elements and radionuclides present in them in the dissolved state, and, at the same time, exert a minimal corrosive effect on structural materials (SMs) of the circuits. The possibilities of improving the efficiency of “low-concentration” processes for chemical decontamination of primary circuits of water-cooled NPIs are examined. Laboratory experiments demonstrated the advantages of chemical dissolution of radioactive deposits of the circuits, combined with sorption treatment of the decontaminating solutions. The influence of equilibrium pH of solutions on the

volumetric distribution coefficients of Fe(II), Fe(III), Co(II), and Cr(III) ions between decontaminating solutions based on complexing acids and strongly basic anion exchanger was studied. The main characteristics of processes involving sorption on the anion exchanger in the EDTA form from solutions containing ethylenediamine tetra acetic, oxalic, and citric acids and on the anion exchanger in the HEDP form from solutions containing 1-hydroxyethane-1,1-diphosphonic acid, hydrazine, and ammonia were compared and reported (Moskvin *et al.* [38]).

After unloading from the reactor and before delivery to a final storage or reprocessing plant, spent fuel is stored in storage basins (SBs) for no less than 3 years to ensure the decay of short-lived radionuclides and decrease in the residual energy release to values acceptable for safe transportation. The water activity in SBs is mainly due to fission products washed out from fuel cladding flaws. If after storage for 15 days the volume activity of water with respect to  $^{137}\text{Cs}$  exceeds  $3.7 \times 10^5$  Bq/l, the fuel elements are considered untight and should be stored in special sealed containers. The walls and bottom of SBs for spent fuel assemblies (SFAs) are made of stainless steel and do not undergo significant corrosion. Nevertheless, water in the basins can be contaminated with radioactive corrosion products (up to 1.5 mg/kg), mainly owing to their washout from SFAs placed in them. The water activity with respect to activated corrosion products can reach  $10^4$ – $10^5$  Bq/l. Ion-exchange resins modified with hexacyanoferrates were suggested as a material for charging filters for the treatment of water from spent nuclear fuel (SNF) storage basins. Modification of ion-exchange resins in the filter increases the degree of removal of  $^{137}\text{Cs}$  radionuclide by a factor of more than 10, with high performance with respect to strontium radionuclide preserved (V. N. Epimakhov *et al.* [13]).

### Fuel reprocessing

The development of nuclear power engineering is oriented on closed nuclear fuel cycle, which requires, in particular, the development of new, environmentally safe, economically feasible, and low-waste technologies for reprocessing of SNF both from operating reactors and from fast reactors of the third and fourth generations, operating on mixed oxide uranium-plutonium fuel. Therefore, the development and optimization of processes alternative to the Purex process used today for SNF reprocessing is a topical problem of radiochemistry (Kulyako *et al.* [23]). The development of new procedures for SNF dissolution and subsequent efficient recovery of U and Pu from the resulting solutions in the form of compounds that can be readily converted to impurity-free dioxides is a promising way to improve the technologies for SNF reprocessing and MOX fuel production. Addition of aqueous ammonia and hydroxylamine hydrochloride to a nitric acid solution containing U(VI) and Pu(VI) causes at pH  $\sim 7$  precipitation of a mixture of U(VI) hydroxylamine and Pu(III) hydroxide. The precipitate separated from the mother liquor and dried at 60°C upon further calcination in air at 300°C transforms into a solid solution of  $\text{PuO}_2$  in  $\text{UO}_2$  as a result of thermal decomposition

of the precipitate with the reduction of U(VI) to U(IV) by the ligand coordinated to the uranyl ion (II' in *et al.* [18]). Even the liquid-liquid extraction process applications have a long history in a nuclear technology, still the new methods of process modeling are being developed i.e. colloidal approach (Testard *et al.* [56]).

### Radioactive waste treatment

The modern concept of safe management of high-level liquid radioactive wastes (HLRW) provides for the necessity in fractional separation of highly active components of these wastes including  $^{235}\text{U}$  and  $^{239}\text{Pu}$ , minor actinides ( $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ ,  $^{237}\text{Np}$ ), and fission products ( $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ ) followed by their immobilization or transmutation into short-lived or stable isotopes prior to disposal (Maryutina *et al.* [28]).

Selective removal of radionuclides from the bottoms residue of evaporation equipment used in NPPs has an enormous advantage over the conventional methods currently being used to condition liquid radwastes (cementing, bituminization). The advantage is primarily due to the decrease in the volume of the conditioned wastes put into solid radwaste repositories. Selective purification was first used at the Lovisa nuclear power plant, but the quality of this operation was too low to consider the purified bottoms residue as being non-radioactive. The removal of radionuclides of corrosion origin, primarily cobalt, remained unsolved. The only currently used technology for completely cleaning bottoms residue is ion-selective purification used at the Russian Kola nuclear power plant. However, it has limitations associated with ozonization, which is used to oxidize the organic component. Hydrothermal oxidation makes it possible to use pre-removal of cesium using ferrocyanide sorbents, since further oxidation destroys the ferrocyanide colloids formed during sorption in an alkaline medium during peptization. In the process, the cesium passes into a truly soluble form, which makes it possible to increase the effectiveness of the additional purification on the same ferrocyanide sorbents. Such a process is impossible without hydrothermal oxidation. The use of a two-step scheme for removing cesium from the bottoms residue makes it possible to increase many-fold the service life of the ferrocyanide sorbents as well as the safety of the process (Avramenko *et al.* [2]).

The nuclear industry produces large volumes of radioactive solution waste, which requires treatment prior to final disposal or storage. A highly efficient treatment concept is the removal of harmful radionuclides from the bulk waste solution. Application of such a technique will result in considerable reductions in the volumes of waste that require solidification prior to final disposal, as well as in radioactive discharges from storage containers into the environment. Number of methods are used to treat aqueous radioactive wastes, including chemical precipitation, evaporation and ion exchange, as well as less developed solvent extraction, biotechnological processes and membrane methods. The method for efficient removal of trace radionuclides from effluents, which contain large amounts of inactive metal ions ( $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ), must be highly selective for the radioactive component. This requirement can be met with the use of inorganic ion exchangers (Nar-

butt *et al.* [41], Satyanarayana *et al.* [48], Möller [36]). Although membrane processes are still considered as novel technologies in this field, many applications in nuclear centers exist (Chmielewski *et al.* [5]).

#### *Radiomonitoring, radioecology and emergency preparedness*

In this point the Fukushima accident should be mentioned again. The information regarding environment pollution were in the very beginning inconsistent and misleading the public opinion. They had an impact on the actions undertaken as well. Radiochemical analysis at NPIs is aimed to solve problems of process and radiation monitoring (Moskvin *et al.* [38]). The rapid radiochemical procedures leading to precise and unequivocal results are required for timely response (Larivière *et al.* [24]). Nowadays it is also need for reliable, faster methods of determination of low activity long-lived radionuclides, especially alpha- and beta-emitters. Determination of long-lived radioisotopes is of increasing importance for radioactive waste control, management of radioactive waste for final storage, as well as for identification of nuclear contamination or nuclear fallout in the environment. Current radioanalytical methods for detection of such radionuclides are usually difficult and time consuming, they require a great effort for sample separation and long-time measurements. Inductively coupled plasma mass spectrometry (ICP-MS) can be a complementary method to radiometric ones. ICP-MS methods of radionuclide determination have started to be developed since the last 15 years. In the INCT works on ICP-MS methods for U, Pu,  $^{90}\text{Sr}$ ,  $^{241}\text{Am}$  are being carried out. The procedures are developed mainly for application to environmental analysis and preparation of test materials for proficiency tests on radionuclide determination which the INCT is a provider (Polkowska-Motrenko and Fuks [46]).

#### **Radiation chemistry**

Radiation chemistry plays a very important role in nuclear engineering, covering all aspects of water radiolysis in boiling water reactor (BWR) and pressurized water reactor (PWR) units, effects of radiolytic phenomena on corrosion, etc. (Takagi *et al.* [55]). On the other hand, the knowledge of radiolytic processes governed by physics and chemistry plays a very important role in the development of fuel reprocessing technologies, waste reprocessing and spent fuel and conditioned waste storage.

#### *Coolant radiolysis*

Radiolysis in reactor water is important for the operation of power reactors. The products of radiolysis are strongly oxidizing and can cause problems with corrosion of reactor materials. In BWR oxidizing radiolysis products have caused intergranular stress corrosion cracking (IGSCC) of stainless steel. In PWR stress corrosion cracking of the Inconel material of steam generator tubes has often been related to large concentrations of hydrogen. In order to mitigate or at least

decrease these problems it is important to acquire a better knowledge of radiolysis at the operational temperatures of BWR and PWR (Christensen [8]). In order to predict the chemical conditions of the water coolant it is important to have a reliable radiolysis model for computer calculations. In addition to high-temperature data for rate constants and  $G$ -values, as discussed above, it is also necessary to have a reliable reaction mechanism (Światła-Wójcik and Buxton [54]).

Hydrogen evolution and explosion in the Fukushima NPP accident drawn back attention to the water coolant radiolysis and water decomposition catalyzed by hot metal cladding. Radiolysis of the coolant proceeds at a higher rate in a boiling water reactor as compared to a water-moderated, water-cooled reactor. The radiolytic gases (hydrogen and oxygen) exiting the reactor together with steam can form a potentially explosive mixture. The knowledge of the basic laws of the radiolytic processes may allow optimization of the process to prevent explosion (Zabelin and Shmelev [57]).

#### *Radiation degradation of system materials*

Prolongation of life time of old and new nuclear reactors is a challenge for material engineering and involved industries. This subject concerns all material sciences areas construction metals, concrete and first of all polymeric materials which easily undergo degradation in radiation field.

#### *Radiation degradation of extractants and ion-exchange resins*

Radiolysis of solvents in liquid-liquid extraction fuel reprocessing stage is one of the main factors regarding the process operation (Berthon and Charbonnel [3]). The partitioning of the long-lived  $\alpha$ -emitters and the high-yield fission products from dissolved nuclear fuel is a key component of processes envisioned for the safe recycling of nuclear fuel and the disposition of high-level waste. These future processes will likely be based on aqueous solvent-extraction technologies for light-water reactor fuel and consist of four main components for the separation of uranium, fission products, and group trivalent actinides and lanthanides and separation of trivalent actinides from lanthanides. Since the solvent systems will be in contact with highly radioactive solutions, they must be robust toward radiolytic degradation in an irradiated, mixed organic and aqueous acidic environment. Therefore, an understanding of their radiation chemistry is important to the design of a practical system. The review on the radiation chemistry of irradiated aqueous nitric acid and the tributyl phosphate ligand used for uranium extraction in the first step of the series of four extractions and the radiation chemistry of the ligands proposed for use in the second extraction of cesium and strontium fission products is presented by Mincher *et al.* in the series of the papers [30–32]. This includes not only the crown ethers and calixarenes but also cobalt dicarbollide and polyethylene glycol. The separation of trivalent actinides from the lanthanides is possibly the most formidable challenge associated with the new fuel cycle. Research is underway on three continents to solve this problem (Mincher *et al.* [29]).

The ligand and solvent formulation adopted will need to be robust in a high radiation environment. This series of reviews is concluded with a summary of the important radiation chemical reactions related to the fuel cycle, and recommendations for stable ligand design (Mincher *et al.* [33]).

### *Geological storage of waste*

The possible water penetration and dissolution of the stored radioactive waste casks depends on the phenomena induced by radiation on solid-liquid interfaces. Geometrical dose distribution, radiolysis of aqueous phase and diffusion of radiolysis products consideration is of great importance for the storage safety assessment (Jonsson [19]).

### **Radio- and radiation chemistry in Poland**

The only R&D Institute in Poland which covers most of the fields of nuclear chemistry, radiochemistry, nuclear chemical engineering and radiation chemistry is the INCT. The Institute runs the PhD studies in the field. Some works of the Institute were presented earlier in the thematic chapters.

Concerning the radiochemistry, it is important to mention that a very strong radiopharmaceuticals development and manufacturing center exists in the Institute for Atomic Energy POLATOM (Otwock/Świerk, Poland).

Other activities regarding radio- and radiation chemistry are ongoing at some universities.

Regarding the radiochemistry, the most academic centers are working in the radioecology field. Department of Radiochemistry and Colloid Chemistry, Faculty of Chemistry, Maria Curie-Skłodowska University, Lublin after Chernobyl accident focused its activities on defining a radiological state of environment – determination of the contamination level of soil, river and lake sediments, as well as ground level air with the anthropogenic isotopes such as:  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$  and plutonium. The occurrence of plutonium isotopes in ground level, air and indoor radon as well as radon in bottled mineral waters was studied. Later, a study of radionuclide transport in soil profiles was undertaken and vertical migration rate of alpha emitting  $^{239,240}\text{Pu}$ , beta emitting  $^{241}\text{Pu}$  and  $^{90}\text{Sr}$ , as well as gamma radiating  $^{137}\text{Cs}$  was determined in various types of soil. Continuing study in the subject of the radionuclide behavior in the environment a fractionation method was used to explain the bioavailability of plutonium from soil. Fast method of plutonium determination in environmental samples (using liquid extraction method and liquid scintillation spectrometry) was established (Komosa and Piekarz [22]). Simultaneously, the development of new and fast radioanalytical methods for the determination of environmentally important radionuclides is still a subject of the study. Among others, the procedures for the determination of plutonium isotopes (including direct determination of beta emitter  $^{241}\text{Pu}$ ),  $^{90}\text{Sr}/^{90}\text{Y}$  and polonium were elaborated and used for the determination of these radionuclides in environmental samples (Komosa and Piekarz [21]), both for flora and some fauna species (Komosa *et al.* [20]). General

research interest of the Analytics and Environmental Radiochemistry Chair at Faculty of Chemistry, University of Gdańsk, is focused on analytical chemistry and radiochemistry. In particular, the research is related to: chemical and radiochemical trace analysis; speciation of metals and radionuclides in the natural environment; determination of natural ( $^{210}\text{Po}$ ,  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ ,  $^{234}\text{U}$ ,  $^{238}\text{U}$ ) and artificial ( $^{55}\text{Fe}$ ,  $^{63}\text{Ni}$ ,  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$ ,  $^{241}\text{Pu}$ ,  $^{241}\text{Am}$ ) radionuclides as well as trace elements in environmental samples (Skwarzec [51]); distribution and bioaccumulation of radionuclides and trace elements in land and marine organisms; biogeochemistry of polonium, uranium and plutonium in the southern Baltic ecosystem (Strumińska-Parulska and Skwarzec [53]); polonium, uranium and plutonium radionuclides run-off from the European Rivers drainage areas (Skwarzec *et al.* [52]); application of activity disequilibrium between  $^{210}\text{Po}/^{210}\text{Pb}$ ,  $^{234}\text{U}/^{238}\text{U}$ ,  $^{238}\text{Pu}/^{239+240}\text{Pu}$  and  $^{241}\text{Pu}/^{239+240}\text{Pu}$  as well as isotopic ratio  $^{240}\text{Pu}/^{239}\text{Pu}$  for research on polonium, uranium and plutonium sources in the natural environment; impact of the Chernobyl accident on radioactive pollution; radiological risk of radionuclides intake with air, water and food consumption as well as cigarette smoking by consumers. The group working in the Department of Chemistry of the University of Warsaw has been engaged for years in the study of isotope effects on various physicochemical properties of chemical substances (Makowska *et al.* [27]). Regarding stable isotopes physicochemistry, this Department research is focused mainly on deuterium isotope effects on liquid-liquid phase equilibria in recent years. The objects of interest are polymer solutions and binary mixtures of ionic liquid with water, alcohols and hydrocarbons. These investigations are important not only from the scientific, academic point of view. Ionic liquids being in virtue melted salts in ambient temperature are considered as the excellent replacement for volatile organic solvents used in synthesis, electrochemistry and separation processes. The impressive potential applications in different fields of the chemical technology stimulates a broad study of thermophysical properties of pure ionic liquids and their solutions, among others, liquid-liquid equilibria including more sophisticated approaches like isotope methods. With a detailed knowledge of the impact of different factors on the properties of ionic liquids, the use of ionic liquids as “designer greener solvents” for specific applications can be envisioned. Some of them are considered as the extractants at the fuel reprocessing technologies and their radiolytic behavior is studied in other laboratories, including INCT.

There are three research groups active in the field of radiation chemistry in Poland. One exists at the INCT and uses as a main experimental method nanosecond pulse radiolysis with UV/VIS detection based on the electron linear accelerator 10 MeV. The second is located at the Institute of Applied Radiation Chemistry (IARC), Technical University of Łódź equipped in PR1 – pulse radiolysis system using electron beam pulses of duration variable from 2.5 ns to 4.5  $\mu\text{s}$ , dose per pulse from 2 Gy to 1 kGy, wavelength spectroscopic range 250–2000 nm at room temperature, recorded data time range from 500 ns to 2 s FS (full scale) with 1 ns resolution time. IARC is working on some aspects of radiochemistry as well (Długosz *et al.* [11]). The third one exists in the

Chemistry Department of the University of Podlasie, Siedlce.

## Chemistry for the future nuclear power

Radiochemistry, nuclear chemistry and nuclear chemical engineering further developments

Present light-water reactor fuel for LWRs – UO<sub>2</sub> fuel, Zircaloy cladding, He bond – has been in continuous use for 50 years. Recently, economics-driven extension of fuel burn-up has resulted in stresses on both the cladding and the fuels. The limitations of LWR fuels are outlet coolant temperatures not high enough for use in H<sub>2</sub> production, destruction of plutonium to eliminate proliferation concerns, and burning of the minor actinides to reduce the waste radiotoxicity. Oxide-based fuel rod designs, the hydride fuel with liquid-metal thermal bonding of the fuel-cladding gap, are being studied. Generation IV reactor concepts, the very high temperature reactor and sodium fast reactor, and the accompanying reprocessing technologies, aqueous-based UREX+1a and pyrometallurgical, is a new challenge from the chemistry point of view (Olander [43]). Several other processes using various types of solvents have been studied and tested in many countries. To significantly reduce long term radio-toxicity of high activity liquid waste is necessary to achieve very high efficiency in separation processes. The examples are COEX, supercritical CO<sub>2</sub>, UREX, DIAMEX, TRUOX, SESAME. Non-aqueous processes beside the mentioned pyroprocesses include fluoride volatility, FLUOREX (Silverio and Lamas [49]).

Partitioning and transmutation (P&T) is radioactive waste management option complementary to deep geological repositories. The P&T consists of a partitioning process and a transmutation cycle. In the partitioning process the most of transuranics (TRU: Np, Pu, Am, Cm) and in some cases long-lived fission products (LLFP: <sup>99</sup>Tc, <sup>129</sup>I and <sup>135</sup>Cs) and heat generating fission products (<sup>90</sup>Sr and <sup>137</sup>Cs), are partitioned by chemical separation in addition to uranium. In the transmutation cycle, the transuranium actinides are transmuted in either a thermal or a fast spectrum irradiation (NEA [42]). The EU AcSEPT programme in which INCT is active plays a very important role to achieve the progress in the chemical separations field.

Thorium-uranium fuel cycle has recently aroused growing interest because it provides a way of more economic nuclear energy production with lower radioactivity waste. <sup>232</sup>Th is a fertile material. During neutron irradiation, <sup>232</sup>Th forms <sup>233</sup>Pa – the precursor of the fissile nuclide <sup>233</sup>U. The Th-U fuel cycle is also attractive for molten salt reactors (generation IV type) (LeBlanc [25]). To explore possibilities of thorium and thorium-uranium fuel future use in molten salt reactors, it is necessary to develop methods of determination of <sup>233</sup>Pa and <sup>233</sup>U as well as uranium isotope ratio in irradiated fuel. The need for improvement of nuclear data and models concerning thorium fuel cycle is also emphasized in the literature (IAEA [15], IAEA [16]). INCT works on the analysis of irradiated ThO<sub>2</sub> have been carried out. It has been elaborated a procedure

for the separation of <sup>233</sup>Pa, U and Th from neutron irradiated ThO<sub>2</sub> using extraction chromatography and determination of uranium isotope ratio by the ICP-MS method. There is still progress expected in development of sorption methods for preconcentration and separation, in particular, for radiochemical purposes, e.g. is based on the development of novel selective sorbents prepared using advanced materials and alternative synthesis procedures. Of particular interest are solid-phase extractants prepared by impregnation of solid supports with various ligands like carbon nanotubes and ionic liquids (Mokhodoeva *et al.* [35]). Finally, chemists and chemical engineering specialists will provide substrates for the energy of the far future. Medium sized spherical particles of Li<sub>2</sub>TiO<sub>3</sub> (with diameters below 100 μm) can be prepared from peroxy lithium titanate solution (stabilized with citric acid) by a modified INCT variant of the sol-gel process. The process consists of the following main steps: (I) formation of aqueous phase emulsion in 2-ethylhexanol-1; (II) gelation of emulsion drops by extraction of water with partially dehydrated EH; (III) filtration and washing with carbon tetrachloride or acetone; (IV) non-destructive thermal treatment. The medium size particles can be used for increasing pebble bed density by infiltration them into bed larger spheres (1 mm diameter). The tritium release from the sol-gel process preparation of Li<sub>2</sub>TiO<sub>3</sub> microspheres was found very close to that observed for other traditional material however, the new process is more efficient than other processes because of the morphology of the sintered specimens (Deptuła *et al.* [9]).

## Radiation chemistry for the next generation

The new generation of reactors, generation III+ and IV presents new challenges for radiation chemists. The new conditions of operation and new type coolant applications are some of them. One of the next generation (Gen IV) solution is a supercritical water cooled reactor (SCWR). The proper water chemistry control may represent the key factor to prevent corrosion of structural materials in the reactor. Computer simulation of the phenomena of water decomposition in such conditions require a knowledge of the temperature dependent *G*-values (Lin *et al.* [26]).

## Conclusions

This paper prepared on the occasion of important anniversary celebration and UNESCO attribute to the role of chemistry in the sustainable social and civilization development of the humanity, do not address all issues related to the chemistry and chemical engineering contribution to the nuclear energy power development. Mostly, it is referring to the INCT and author's works. However, its content illustrate well the role of chemistry in the present safe and effective operation of all stages of nuclear power related technology. Hopefully, it will initiate series of the review papers related to the subject to be published in this journal.

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**Prof. Andrzej G. Chmielewski, Ph.D., D.Sc.** is Director of the INCT and Professor at the Warsaw University of Technology. He was employed at the University of Tennessee, Knoxville, USA in the years 1976–1977 and at the IAEA, Vienna, Austria 2003–2005. He was lecturer at the University of Sao Paulo, Brasil; Hefai, China and Pavia, Italy and UN expert to more than 30 countries worldwide. He published over 150 scientific papers and books and possesses more than 60 patents. Under his supervision 11 Ph.D. and over 50 M.Sc. theses were carried out. He is Chairman of the Council for Nuclear Matters and a member of Engineering Academy in Poland.