Radiation Physics and Chemistry 124 (2016) 235–240

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Radiation chemistry for modern nuclear energy development

Andrzej G. Chmielewski *, Monika M. Szołucha

Institute of Nuclear Chemistry and Technology, 16 Dorodna Street, Warsaw 03-195, Poland

HIGHLIGHTS

- Radiation effects on materials are crucial in nuclear reactor operation procedures.
- The radiolysis of extractants and solvents are fundamental in the development of fuel reprocessing.
- Water radiation chemistry are important issues in many aspects of NPP operation.
- Radiation effects on materials, enhanced corrosion are crucial in nuclear reactor operation procedures.

ARTICLE INFO

Article history:
Received 1 October 2015
Received in revised form
18 December 2015
Accepted 4 January 2016
Available online 4 January 2016

Keywords:
Radiation chemistry
Radiolysis
Radiation effects
Nuclear energy

ABSTRACT

Radiation chemistry plays a significant role in modern nuclear energy development. Pioneering research in nuclear science, for example the development of generation IV nuclear reactors, cannot be pursued without chemical solutions. Present issues related to light water reactors concern radiolysis of water in the primary circuit; long-term storage of spent nuclear fuel; radiation effects on cables and wire insulation, and on ion exchangers used for water purification; as well as the procedures of radioactive waste reprocessing and storage. Radiation effects on materials and enhanced corrosion are crucial in current (II/III/III+) and future (IV) generation reactors, and in waste management, deep geological disposal and spent fuel reprocessing. The new generation of reactors (III+ and IV) impose new challenges for radiation chemists due to their new conditions of operation and the usage of new types of coolant. In the case of the supercritical water-cooled reactor (SCWR), water chemistry control may be the key factor in preventing corrosion of reactor structural materials. This paper mainly focuses on radiation effects on long-term performance and safety in the development of nuclear power plants.

1. Introduction

Generation II reactors have been in operation for many years. These are light water-cooled reactors of the BWR (Boiling Water Reactor) and PWR (Pressurised Water Reactor) type, and CANDU (Canadian Deuterium Uranium) heavy water-cooled reactors. Some reactors with graphite moderators were and are in operation as well. Generation III and III+ reactors develop the technology from phase II, with improvements related to reactor safety and economy.

Current policy regarding the fuel cycle is aiming towards a closed cycle, although some experts are questioning the economy of the process. However, fuel reprocessing is a future issue concerning the optimal utilization of fission elements, and radioactive waste volume reduction is a fundamental feature of generation IV implementation and future nuclear energy development. The generation IV fast reactors will also have further improvements in fuel economy and better techniques for radioactive waste handling.

Radiation chemistry plays a significant role in the field of nuclear safety, especially regarding water radiolysis in the primary circuit and spent fuel storage pools, radiation effects on the insulation of cables and wires, and in ion exchangers used for water purification. The other processes that fall under this field of science are radioactive waste reprocessing and storage. In the PUREX (Plutonium Uranium Reduction Extraction) process the radiolysis of extractants and solvents has been studied. In this technology an aqueous nitric acid phase is in contact with an organic phase. Consequently, the intense radiation field i.e. α – particles, β – particles, γ – rays generates large amounts of degradation products affecting the production of the PUREX solvent, with effects on its redox and physicochemical properties, as well as its extraction affinities and kinetics.

The accidents in Chernobyl (1986), and especially Fukushima (2011), have led to the opinion that this field has to be revisited. In many countries including Poland, where nuclear programmes are

* Corresponding author.
E-mail address: A.Chmielewski@ichtj.waw.pl (A.G. Chmielewski).

http://dx.doi.org/10.1016/j.radphyschem.2016.01.002
0969-806X/

in the development phase (Chmielewski, 2013), new research programs on the subject are being carried out. Additionally, new fuel reprocessing technologies are being developed and geological high waste/spent fuel storage is an increasingly important issue for future nuclear power applications.

Generation IV reactors are in different phases of research and development. Some solutions have been demonstrated at reasonable scale. These reactors use alternative coolants and most of the related problems are in the field of materials science. However there are still some issues related to the ageing of insulation in new types of radiation fields and we may expect other problems that are interesting from the point of view of radiation chemistry. This area has not been explored in depth, at this moment development is in the hands of nuclear physicists and energy experts. Even the chemistry of the fuel preparation for this new generation is still in the early stages of development (Chmielewski et al., 2012). An overview of the work on going in the field and some forecasts regarding future research and development are presented in this paper.

2. Radiation chemistry in nuclear energy

2.1. Light water reactors and spent fuel storage pools

It is well known that coolant water in nuclear reactors receives high absorbed doses under a mixed radiation field of gamma rays and fast neutrons at high temperature and pressure. Radiation controls the chemical condition of the coolant and precise prediction of radiolysis effects is essential to avoid detrimental radiation-induced corrosion processes such as stress corrosion cracking (SCC). A chemistry program is fundamental for the safe operation of a nuclear power plant. Few data are available in the literature on the role of the water radiolysis on the corrosion of stainless steel core components under PWR operating conditions (300 °C, 155 bar). The effect of water radiolysis on the electrochemical potential of stainless steel has been observed. Irradiation of the interfaces with protons induces a change in the potential. Moreover, the higher the flux, the higher the electrochemical potential shift due to irradiation. The ageing effect has been observed at the irradiated stainless steel/water interfaces. The electrochemical response to irradiation decreases and even disappears with time spent at 300 °C/90 bar and/or after several irradiations (Muzeau et al., 2011). 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, including the effects of radiolytic phenomena on corrosion (Takagi et al., 2010). Boiling Water Reactors (BWR) use high purity water as the neutron moderator and the primary coolant, producing steam. As a result of water radiolysis, gas stripping in the core, and recirculation, reactor recirculation water contains from 100 to 300 ppb of hydrogen peroxide. This concentration of hydrogen peroxide under normal water chemistry operation increases the susceptibility of austenitic stainless steel to intergranular stress corrosion cracking (IGSCC). Each section of the various modelled regions of the reactor flow is treated as one-dimensional, representing mass flux and dose rates as radial averages. The concentration of hydrogen peroxide, H_2O_2, is an important parameter in BWR reactor water. This molecule is too unstable to get its concentration in situ by sampling methods. Measurements of this parameter have only been made in the laboratory by applying radiolysis models (Lister and Uchida, 2015). Reducing the peroxide level to 1–10 ppb results in a decrease in the electrochemical potential to less than 230 mV, which can effectively eliminate IGSCC in austenitic stainless steels. Experimental work has shown that the oxidant concentration can be effectively reduced by adding hydrogen, eliminating IGSCC. The addition of hydrogen suppresses radiolytic production of oxidising species, such as O_2, H_2O_2 and a number of other transient species in the region of the reactor core where boiling does not occur. Such modifications of the reactor water have created an environment not previously experienced by Zircaloy fuel and structure components. The presence of zirconium dioxide (ZrO_2) greatly increases H_2 yields in water radiolysis, an inevitable process in nuclear power plants (Skotnicki and Bobrowski, 2015). Studies (Shimada et al., 2006) have shown that hydrogen uptake and pickup fractions of the water rod and spacer materials were similar to those of water rods and spacer materials under normal water chemistry (NWC) conditions. The addition of alcohol into the primary coolant of pressurized water reactors (PWRs) has been proposed as an alternative to hydrogen addition. At low doses, the addition of 1.0 ppm methanol considerably suppresses radiolysis of the coolant. At high doses, the addition of at least 10 ppm methanol is necessary to lower the concentrations of radiolytic oxidising products. In the presence of fast neutron radiation, methanol acts to decompose the radiolytic oxidising products (Sunayro and Domae, 2008).

Prolonging the lifetime of old and new nuclear reactors is a challenge for materials engineering and related industries. This subject concerns all areas of materials science, especially with respect to construction metals, concrete and, most importantly, polymeric materials which easily undergo degradation in radiation fields. The formation of volatile alkyl iodides other than methyl iodide during a serious nuclear reactor accident may have radiological significance. The hypothesis that radioactive alkyl iodides, other than methyl iodide, could form from paint solvents under the conditions of a serious nuclear accident in light water reactors (under boiling water reactor (BWR) and pressurised water reactor (PWR) conditions) has been tested using stable elemental iodine, a gamma irradiator and gas chromatography equipment. It was found that methyl and isopropyl iodides were formed from the texanol ester, which is used in many modern water-based paints. Also, methyl, ethyl, propyl and butyl iodides were formed from a hydrocarbon solvent (white spirit) commonly used in paint products in the past. Detailed studies of the paints present inside the reactor buildings of nuclear power plants would enable an estimation of the influence of different paint solvents on the volatile (organic) iodine source term during severe accidents such as Fukushima Daiichi in 2011 (Tietze et al., 2013). Organic iodides are difficult to remove using filtration systems (Klein-Heßling et al., 2014). A variety of physicochemical processes can change the state of the volatiles, with partitioning taking place between the gaseous, aerosol, aqueous and condensed phases (Konings et al., 2015). Research regarding the radiolysis of iodine species in concentrated solutions is sparse but it is possible that such droplets would, under irradiation, re-release volatile iodine (Dickinson et al., 2014). In spent fuel pools at the Fukushima Daiichi nuclear power plant, hydrazine was added to salt-containing water in order to reduce dissolved oxygen. Hydrazine is known to reduce dissolved oxygen in high temperature pure water, but its deoxygenation behaviour in salt-containing water at ambient temperature in the presence of radiation is unknown. Deoxygenation using hydrazine in salt-containing water was therefore investigated using a ^{60}Co gamma-ray source and artificial seawater at room temperature. Water samples containing a small amount of hydrazine were irradiated at dose rates of 100–10,000 Gy/h. The concentration of dissolved oxygen in the water samples was measured before and after irradiation. Notably, a decrease in the dissolved oxygen was only observed after irradiation, and the dissolved oxygen concentration decreased with increasing dose rate and irradiation time. The rate of decrease in the amount of dissolved oxygen using hydrazine was slow in the presence of