

# Radiation Induced Corrosion of Nuclear Fuel and Materials

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## 1. Introduction

In some cases, a corrosion system may be exposed to radiation field. Most usually, it occurs as a part of atmospheric corrosion, when materials are, besides other factors, exposed also to visible and ultraviolet radiation. Technical significance of corrosion caused by such types of radiation is rather small. On the other hand, metallic materials may be exposed to high energy ionizing radiation (IR), emitted e.g. during operation of nuclear reactors, or during storage/processing of irradiated nuclear fuel. Contrary to non-ionizing radiation, IR significantly affects properties of corrosion system and reactions which proceed inside the system. Therefore, three main areas of research of radiation induced corrosion exist:

- corrosion of both fresh and irradiated nuclear fuel;
- corrosion of barrier materials (cladding of fuel elements, containers for irradiated fuel);
- corrosion of metal parts of nuclear and irradiation devices.

In the case of corrosion processes induced by IR (radiation oxidation), radiation-induced redox reactions are essential. Water plays very important role in all parts of nuclear fuel cycle - it is used as coolant and/or moderator in nuclear reactors; it is also used as coolant and/or shielding material in various radiation sources; ingress of deoxygenated granitic water into deep repository with spent nuclear fuel is an expected event. The direct effects of IR on corrosion of solid materials are usually negligible; in anoxic/deoxygenated aqueous environment, the majority of radiation damage and corrosion processes occur due to reactions of materials with products of water radiolysis. Therefore, strong influence of IR on corrosion processes may be expected in aqueous environment especially at higher temperatures. Radiation may change physico-chemical condition in corrosion systems, as well as its composition. Actions of primary intermediates of water radiolysis may complete change reactions proceeding in corrosion system (e.g. inside the container with irradiated nuclear fuel) - especially, they may increase electrochemical potential (Eh) and decrease pH of environment. Such changes may result in change of corrosion rate when compared to non-irradiated system. Also, due to irradiation, solid corrosion products of irradiated material may be formed.

This chapter is focused on review of radiation corrosion of uranium oxides and various materials used for nuclear waste packaging, shielding, or engineered barriers against migration of radionuclides from irradiated nuclear fuel matrix.

## 2. Radiolysis of water

As was mentioned above, radiolysis of water plays crucial role in corrosive processes occurring at the interface of liquid/solid environment in the presence of IR. Because of its optimum properties and availability, water is the most wide spread coolant used in nuclear reactors (Pikaev et al., 1988; Woods & Pikaev, 1994). It acts as a corrosive agent in the field of IR (namely at the presence of oxygen). Therefore, the development of nuclear powers depends also on the knowledge of the radiation chemistry of water. Also owing to this reason, water was among the first systems whose radiation chemistry was studied (Wishart & Nocera, 1998). But although our knowledge of the radiation chemistry of water at the steady state (when the concentrations of radiolytic products seems to be time-independent in the course of irradiation) at ambient temperature is rather complete, there are still not so many papers (Sehested & Christensen, 1987) on water radiolysis at the initial state of the process or at higher - up to supercritical - temperatures and pressures. Moreover, except for nuclear technology, the radiation-chemical transformations in liquid water are important also for radiobiological and medicine research and for "pure" radiation chemistry (Stepanov & Byakov, 2005). It is so because the water is, *inter alia*, a convenient object for investigating the key regularities of the interaction of IR with condensed matter (Erskov & Gordeev, 2008). Therefore, the basic features and mechanisms of the water radiolysis are contained in every monograph or general article devoted to radiation chemistry (Allen, 1961; Draganic & Draganic, 1971; Pikaev, 1986; Buxton, 1987; Spinks & Woods, 1990; Woods & Pikaev, 1994; Wishart & Rao, 2010).

### 2.1 Radiolysis of pure water

A general concept of radiolysis is conventionally divided into three main steps: the physical stage, physico-chemical stage and the chemical stage.

In the physical stage, the energy of ionizing particles, e.g. gamma photon or a charged particles, such as an electron, proton or an  $\alpha$ -particle is transferred to water molecule which is ionized or excited to upper electronic states (usually denoted by a star). The products of these fast processes (less than  $10^{-14}$  s) in the water are:  $\text{H}_2\text{O}^+$ ,  $e^-$ ,  $\text{H}_2\text{O}^*$ ,  $\text{H}_2\text{O}^{**}$  and  $(\text{H}_2\text{O})^*$ . In the next physico-chemical stage ( $10^{-14}$  -  $10^{-12}$  s) the products undergo intra track ion-molecule reactions followed by further reactions such as fast dissociations, ionizations and recombination. Following products may be detected at this stage: H (0.62), OH (5.6), O,  $\text{H}_2$  (0.15),  $e_{\text{aq}}^-$  (4.78),  $\text{H}^+_{\text{aq}}$  (4.78),  $\text{H}_3\text{O}^+$ ,  $\text{H}_2\text{O}^-$ ,  $\text{H}_2\text{O}^*$ . The yields at this stage are defined as the initial radiation chemical yields ( $G_i^0$ ) and they are shown here, in some cases, in the brackets according to literature (Buxton, 1987) in the  $10^{-2} \text{eV}^{-1}$  units (the radiation chemical yields - G-values - may be expressed as the number of species created/destroyed per 100 eV of absorbed energy or less often in SI units  $\text{mol J}^{-1}$  which is equivalent to  $9.65 \times 10^6$  molecules  $\times 10^{-2} \text{eV}^{-1}$ ). The initial yields were found (Watanabe & Saito, 2001) to be decreasing as the initial energy of monoenergetic electrons becomes low (in the energy region lower than 1 keV). For the third stage (chemical stage), it is typical that the resulting above mentioned

transient species as well as new products of further ionizations are distributed along the track. The length of the track determines the number of primary events; e.g., for 100 eV electron, only about 10 primary events occur in water (Watanabe & Saito, 2001) along its 4 nm long track and for the 1 keV electron the highest density of chemical species is given for a radius of 20 nm. This leads to the formation of clusters of ions and radicals which are called spurs and blobs. The reactions proceeding within the spur structures in the time range from  $10^{-12}$  to  $10^{-7}$  s including their rate constants are given (Buxton, 1987; Motl, 2004) in Table 1. The two last reactions from the Table 1 take place just only in the case of high LET (linear energy transfer) radiation, e.g.  $\alpha$ -particles or heavy accelerated ions. It is evident from the Table 1 that at the end of chemical stage there are the OH,  $H_2O_2$  and eventually  $HO_2$  species present in the spur (in addition to the above mentioned species). Overall, following are the species remaining when all the spur reactions are complete (Buxton, 1987):  $e^-_{aq}$ , H, OH,  $HO_2$ ,  $H_2O_2$  and  $H_3O^+$ . The radiation chemical yield of the product created in chemical stage is so-called primary yield usually denoted as  $G_i$  or  $g(i)$ . The primary yields depend, besides the presence of oxygen in water (Watanabe & Saito, 2001), strongly on the LET of applied radiation as is shown in Table 2 for the most important species from the point of view of material corrosion.

Reactions	$k \times 10^{-10}$ [L mol <sup>-1</sup> s <sup>-1</sup> ]
$e^-_{aq} + e^-_{aq} + 2H_2O \rightarrow H_2 + 2OH^-$	0.54
$e^-_{aq} + OH \rightarrow OH^-$	3.0
$e^-_{aq} + H_3O^+ \rightarrow H + H_2O$	2.3
$H + H \rightarrow H_2$	1.3
$OH + OH \rightarrow H_2O_2$	0.53
$OH + H \rightarrow H_2O$	3.2
$H_3O^+ + OH^- \rightarrow 2H_2O$	14.3
$OH + H_2O_2 \rightarrow HO_2 + H_2O$	0.0045
$O + OH \rightarrow HO_2$	-

Table 1. Spur reactions in water

LET [eV nm <sup>-1</sup> ]	G [10 <sup>-2</sup> eV <sup>-1</sup> ]					
	$e^-_{aq}$	OH	H	$HO_2$	$H_2$	$H_2O_2$
0.23	2.63	2.72	0.55	0.008	0.45	0.68
12.3	1.48	1.78	0.62	-	0.68	0.84
61	0.72	0.91	0.42	0.05	0.96	1.00
108	0.42	0.54	0.27	0.07	1.11	1.08

Table 2. Dependence of the primary yields of some radiolysis products on LET (Buxton, 1987)

The comparison of the values from the Table 2 with those presented earlier for the initial yields gives evidence that the  $G_i^0$  values are quite different from the  $G_i$  values. It is worth mentioning that the experimentally measured yields at a stationary state ( $G(i)$ ) are also different both from the  $G_i^0$  and  $G_i$  values. Besides both the mechanism of reactions and radiation chemical yields, water radiolysis is characterized also by material balance equations. For the primary products, following equation applies (Buxton, 1987):

$$G_{-H_2O} = 2G_{H_2} + G_H + G_{e-(aq)} - G_{H_2O_2} = 2G_{H_2O_2} + G_{OH} + 2G_{HO_2} \quad (1)$$

(for a low LET radiation without the  $G_{HO_2}$  or  $2G_{HO_2}$  terms). Next, at the time greater than  $10^{-7}$  s the radiolysis products begin to diffuse randomly and either react together or escape into the bulk solution. The reactions at this time period proceed outside the spurs. They lead, *inter alia*, to the creation of oxygen *via* decomposition of perhydroxyl (hydroperoxide) radicals  $HO_2$  as well as to the reverse conversion both of hydrogen and hydrogen peroxide back to the molecules of water and H or OH radicals or various secondary radicals according to the oxidizing or reducing conditions in water. In such a way, the final stable products of water radiolysis are hydrogen, hydrogen peroxide and eventually oxygen. However, the decomposition of pure water is minimal, including in pressurized-water reactors (PWRs) (Wishart & Rao, 2010), owing to the back reactions which re-form water from the above mentioned stable products (Spinks & Woods, 1990). The charged particles created in radiolytic process are hydrated in the water or solvated in other solvents.

It was found (Wishart & Rao, 2010) that the H bond network of water needs approximately 1.6 ps to accept a new created "dry" electrons  $e^-$  and transform them to the "wet"  $e_{-aq}^-$  electrons. Water molecules create a hydration shell around the electron forming, in such a way, cavities surviving some tens of fs ( $10^{-15}$  s). The standard reduction potentials of hydrated electron range from -2.77 V (Wishart & Nocera, 1998) to -2.9 V (Buxton, 1987). Its half-life reaches about of  $2.1 \times 10^{-4}$  s in neutral water. Hence, it is powerful reducing agent acting in one-electron transfer processes. The electrons are assumed to be transported in water medium until their energies fall below 7.4 eV (the threshold for electronic excitation in liquid water (Watanabe & Saito, 2001)). Using the ultrafast liquid-jet photoelectron spectroscopy measurements, it was possible to postulate (Siefertmann et al., 2010) the existence of hydrated electron at the water surface with the lifetimes longer than 100 ps. Its characteristic may be different from the electron hydrated in the bulk solution.

The OH radical, besides the molecular hydrogen peroxide, as the most important oxidizing species (the standard redox potential  $E^0(OH/OH^-)$  is 2.32 V at pH = 7), is assumed to be closely related to the corrosion of the materials in nuclear reactors as well as the containers containing the spent nuclear fuel. Other oxidants such as hydroperoxide  $HO_2$  and molecular oxygen are produced in very low quantities with low LET radiations. The OH radical often reacts *via* a simple electron transfer ( $R + OH \rightarrow R \cdot + OH^-$ ). In a strongly alkaline solution, OH is rapidly deprotonized with  $OH^-$  ions producing a new  $O^-$  radical with the half-life of 5 ns (Wishart & Nocera, 1998):



The molecular hydrogen can transform the oxidizing OH radical to the reducing H radical which can be transformed up to  $e_{-aq}^-$  under severe (high pH and pressure of 10 MPa) conditions:



As the Monte Carlo simulations showed (Watanabe & Saito, 2001), more reactions of OH radicals occur for 1 and 10 keV electrons than for 1 MeV electrons. The recombination of two OH radicals leads fast to creation of hydrogen peroxide (Table 1). That is, why the decay of OH radicals occurs on the same time scale as formation of H<sub>2</sub>O<sub>2</sub> molecules. But as it was shown by La Verne (La Verne, 2000), not all of the OH radicals lead to production of hydrogen peroxide.

The H atoms are connected with the hydrated electrons which may be assumed to be conjugate base of H radicals. Hence, the H atoms create very fast ( $k=2.3 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ ) (Wishart & Nocera, 1998) from  $e_{\text{aq}}^-$  in acidic solutions:  $e_{\text{aq}}^- + \text{H}^+_{\text{aq}} \rightarrow \text{H}$ . The reverse conversion of H radicals back to the  $e_{\text{aq}}^-$  is possible in highly alkaline solution but this reaction is about three orders slower than the mentioned last one. The standard reduction potential of H atoms equals -2.1 V (that is a similar value as for the  $e_{\text{aq}}^-$  - see above).

The perhydroxyl radical (or hydroperoxide) HO<sub>2</sub> is a secondary radical formed in oxygenated solutions from primary radicals such as:



As it can be seen from the last reaction, the HO<sub>2</sub> forms in acidic solutions from the deprotonized O<sub>2</sub><sup>-</sup> with pK of HO<sub>2</sub> equal to 4.7 (Buxton, 1987). The standard reduction potentials are -0.05 V for HO<sub>2</sub> (acidic solutions) and -0.33 V for a stronger reducing agent O<sub>2</sub><sup>-</sup>. On the other hand, the HO<sub>2</sub> radical is a stronger oxidant than is the O<sub>2</sub><sup>-</sup>.

From the text above it is clear that the features of water radiolysis depend on conditions of the radiolysis. First of all, the primary yields of  $e_{\text{aq}}^-$ , H, OH, H<sub>2</sub>O<sub>2</sub> (not H<sub>2</sub>) decrease (Buxton, 1987) with increasing pH but only up to pH = 3. In the range from pH = 3 up to pH = 13, the G<sub>i</sub> values seem to be unchanged. But, especially in the alkali region "the effect of pH on the primary yields is still an open question" (Ferradini & Jay-Gerin, 2000). The increasing pH value leads (Pikaev, 1986) also to the decreasing in stationary concentrations of molecular hydrogen and hydrogen peroxide. Another important factor affecting both stationary concentration of molecular products and the G<sub>i</sub> values is the LET. It is well known (Ferradini & Jay-Gerin, 2000) that the first mentioned quantity increases with increasing LET. In the same manner change the primary yields of molecular products and HO<sub>2</sub> radical but, on the other hand, the G-values of primary radicals decline in this direction. The effect of pH and LET on the G<sub>i</sub><sup>0</sup> quantity was found to be similar as in the case of the primary G<sub>i</sub> yield. The dose rate may affect the G values or the stationary concentrations in the same manner as the LET does.

Although the main characteristic data on water radiolysis are independent on the temperature up to about 100°C, their changes at higher temperatures are conspicuous and important e.g. for the gas evolution from water heat-transfer agent. Unfortunately, there is

still only few and often conflicting data on the water radiolysis at the higher temperatures and pressures. Many new reactions with high activation energies are suggested (Sehested & Christensen, 1987) at the temperatures 200-300°C (e.g.  $O_2^- + O_2^- \leftrightarrow O_4^{2-}$ ;  $O_4^{2-} + H^+ \rightarrow HO_2^- + O_2$ ;  $O_3^- + O^- \rightarrow O_4^{2-} \rightarrow 2O_2^-$ ). As a rule, the yield of water radiolysis ( $G(-H_2O)$ ) and the yields of primary radical products ( $G_i$ ) increase and the yields of molecular products decrease with increasing temperatures, though some experimental data (e.g. the yield of hydrated electrons (Sehested & Christensen, 1987)) may be contradictory. These all changes lead to an increase in the stationary concentration of hydrogen in an open system (the hydrogen gas can escape from the system) (Pikaev, 1986). They are connected (Pikaev et al., 1988) with a broadening of spurs and creation of more diffusive distribution of primary products at higher temperatures. At higher temperatures, the probability of recombination processes of primary products in spurs is lower than at ambient temperatures. The radiolysis of water is extremely affected by the temperature especially in the supercritical state ( $T > 374^\circ\text{C}$ ;  $P > 22.1 \text{ MPa}$ ). The study of such systems is motivated by the development of the 4<sup>th</sup> generation of nuclear reactors using supercritical water as the coolant. The density of supercritical water is much lower than that under the ambient conditions and, therefore, the hydration shell is composed from only a small count of molecules of water. That is, besides other things, the reason why different radiation chemical yields (and their ratios), the reaction rate constants and many spectral properties of transient species were observed (Wishart & Rao, 2010) under supercritical conditions in comparison with the normal conditions. Besides, the Arrhenius law does not apply for many radical reactions in the supercritical state. It was experimentally proved that, under these conditions, the radiation yields  $G(e_{-aq}^-)$ ,  $G(OH)$  and the sum ( $G(e_{-aq}^-) + G(OH) + G(H)$ ) dramatically increase with increasing temperature in the supercritical range. Therefore, all simulations of a radiolytic processes should consider this anomaly.

A deeper insight into the radiolytic processes in liquid water provides pulse radiolysis, leading to the detailed knowledge of the ultrafast primary events within the spurs. After the nanosecond pulse radiolysis, the picosecond pulse accelerated electron beams were used (Belloni et al., 2005) from the year 1968. Nowadays, the time resolved ultra-short pulses in the femtosecond ( $1 \text{ fs}=10^{-15} \text{ s}$ ) and, in near future, attosecond ( $1 \text{ as}=10^{-18} \text{ s}$ ) regime may be used (Haarlamert & Zacharias, 2009). Using the excellent equipments working in the above mentioned regime it was for example shown (Crowell et al., 2005) that in the time interval below 5 ps after ultrafast laser photo-ionization there are many complicated events between electronic relaxations and vibrational energy redistribution. But it is worth mentioning that the IR can not be adequately replaced by laser irradiation owing to different mechanisms of energy deposition in the condensed phase. It was also found (Buxton, 1972) that the spur structures in irradiated water are practically complete at the time of 120 ns. By the same time, the primary radiation yield of hydrated electrons  $G_{e-aq}$  was found to be  $2.8 \times 10^{-2} \text{ eV}^{-1}$  whereas at the time of 7.5 ns it reaches the value of 3.6 and the initial radiation yields  $G_{e-aq}^0$  measured by the femtosecond technique was found to be of  $4.6 \pm 0.3 \times 10^{-2} \text{ eV}^{-1}$  (Yang et al., 2011). Using the same fast pulse water radiolysis, it was discovered that about 10% of hydrated electrons react in spurs with the  $H_3O^+$  and OH species within 10 ps. Similarly, the lifetime of the basic initial particle  $H_2O^+$  was assumed to be less than 100 fs and the hydration time of the "dry" electron may be much lower than it was determined earlier (see above), i.e. of 250-500fs (Domae et al., 1996). The results obtained in the pulse radiolysis experiments including application of the concept of equivalent velocity spectroscopy (Yang

et al., 2009), are often used for the simulation of the radiolytic reactions. Up to now, there were developed several kinds of various models such as widely known diffusion model, Freeman's model or Hamill's model. None of them describes the radiolytic process exactly. The quality of every one can be considered according to the agreement of the  $G_i^0$  values calculated from the model with them following from the measurements or according the reaction of model on the changes in the LET values or on the presence of various solutes. From this point of view, the diffusion model seems to be most convenient. The model is assumed for all chemical species in the track to have the Gaussian distribution. For the better description, namely when the diffusion is slow or for the short times (sub-picosecond) or for a large number of particles, the improved extended spur diffusion models are formulated (Stepanov & Byakov, 2005; Domae et al., 1996). Mostly, they consider 32 or 34 basic elemental reactions (Stepanov & Byakov, 2005; Erskov & Gordeev, 2008; Watanabe & Saito, 2001; Domae et al., 1996) leading to the decomposition of water. The Laplace transform method is applicable in many cases. Using these methods, it was for example found that no evidence has been obtained to support the dry charge recombination (Buxton, 1972).

The pulse radiolysis of water and the simulation of radiation processes play an important role in the storage of nuclear waste or a spent nuclear fuel (Wishart & Rao, 2010). Generally, the radiolysis of water increases the rate of  $UO_2$  dissolution (Christensen & Sunder, 2000) because the redox conditions may be changed due to radiolytic products and the stability of the waste form and container may be affected by them. The main role in these processes possess the oxidants (i.e.  $H_2O_2$  and the alkaline form of  $HO_2$  radical -  $O_2^-$  radical). Their concentrations in oxygenated solutions increase with increasing total dose. The saturated concentration of  $H_2O_2$  is assumed to be about of  $10^{-3}$  mol  $dm^{-3}$  (Sunder & Christensen, 1993). The suggested models of the corrosion processes are in agreement with measured rates in the case of gamma radiolysis and in unirradiated solutions containing oxygen or hydrogen peroxide. There are some difficulties with  $\alpha$ -radiolysis or, generally, with a high-LET radiation. Therefore, further studies are required to fully understand the effects of high-LET radiation on corrosion of used nuclear fuel.

In connection with the storage of nuclear waste or spent fuel, a special attention is devoted to the radiolysis of water in micro- and nano-porous confining materials such as concrete and clays, zeolites, silica gels, etc. which trap important quantities of interstitial water. Many characteristics of water radiolysis may be changed in micro- or nano-confined water in comparison with the bulk process: real dose absorbed by water, kinetics, radiation chemical yields of various radiolytic products. These changes may be due to the high viscosity of water inside the pores, the formation of OH radicals *via* transfer of holes from the solid material to the water ( $h^+ + H_2O \rightarrow H^+ + OH$ ) or creation of hydrated electron *via* transfer of electron from the ionized solid to the water ( $e^- + H_2O \rightarrow e_{aq}^-$ ) and, last but not least, the energy transfer from a solid phase to the chemisorbed or physisorbed molecules of water. As a consequence of these (and many others) processes, high radiation yields are found for one or two mater layers which are decreasing with increasing size of pores. Therefore, the decrease in reaction rates of  $e_{aq}^-$  or OH with organics in the course of pulse radiolysis in zeolites was found (Liu et al., 1997).

Just as a matter of interest, it may be mentioned that according some authors (Sawasaki et al., 2003) the gamma radiolysis of water could serve in the future as a manner for the

hydrogen gas production. They suggest to combine two methods: first-the conversion of gamma radiation emitted by radioactive waste to electrons and photons with energies from tens to thousands eV, using the high Z-materials (Ta, Pd and Pb) and secondly the removal of molecular hydrogen from the system, using hydrogen occluders (Pd, Ta). But, the efficiency of this method seems to be still very low. May be that a higher efficiency may be achieved when some solid promoters participating in the H-radical production will be used (Wishard & Rao, 2010).

In conclusion, it may be said that even though many aspects of the water radiolysis are very well known further systematic studies (both experimental and theoretic) are needed to fully understand both the early elemental processes of the radiolysis and the reactions under extreme conditions.

## 2.2 Radiolysis of aqueous solutions relevant to nuclear waste programs

The corrosion resistance of various parts of containers with spent nuclear fuel depends mainly on the geological subsoil and chemical composition of surrounding groundwater. (Nishimura, 2009). Both mentioned factors are different in various localities. Several concepts of repository for geological disposal such as rock salt, clay/argillaceous rock and crystalline (granitic) rock were compared according to different parameters (FMET, 2008) with result that the disposal site built in granitic structure appears to be most suitable for minimizing the entry of radionuclides into the biosphere. Therefore, nuclear fuel waste programmes by many countries, not only European, are planned for disposal vault in granitic rock (Sunder & Christensen, 1993). Because these sites are located some hundreds of meters underground, the concentration of oxygen dissolved in water is very low due to its consumption in various chemical and biochemical processes (Pitter, 1999).

The most likely pathway for releasing of corrosion products and radionuclides appears to be transport of groundwater namely its ingress into repository or to the inner container with latent material defect, although the dissolution rate of fuel, predominantly  $\text{UO}_2$  in anoxic reduction environment is very low (Parks & Pohl, 1988). The redox conditions may be substantially changed due to radiolysis of water by IR associated with the fuel which produces not only reductive but also several oxidative species with high reactivity (Spinks & Woods, 1990). The last mentioned radiolytic products substantially increase the corrosion rate of all relevant materials and parts of container.

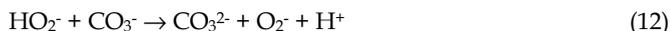
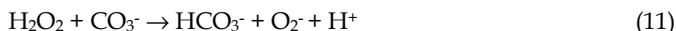
It is generally known that contrary to pure water the irradiation of diluted aqueous solutions of inorganic compounds present predominantly in dissociated forms leads to various chemical and physicochemical processes such as redox reaction, gas evolution, changes in pH value, formation of precipitate etc. All these processes appear to be a result of mutual interaction of dissolved compounds with products of water radiolysis, while the effect of direct interaction of radiation with dissolved compound is virtually negligible. On the contrary, with concentrated solutions (higher than  $1 \text{ mol dm}^{-3}$ ) the direct deposition of radiation energy to the solute cannot be neglected. Energy deposition in this case occurs in proportional to the electron fraction of each components i. e. solvent ( $\text{H}_2\text{O}$ ) and corresponding solute (Katsumura, 2001). In both cases the radiolysis and concentration of radiolytic products are affected by many another factors such as nature of radiation, dose

rate, composition of solution undergoing radiolysis, pH value and presence of different gases especially oxygen dissolved in solution.

Various inorganic ions present in granitic groundwater (Ollila, 1992) such as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and cations  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Si}^{4+}$  act as scavengers of intermediates of water radiolysis further affecting the properties and behavior of the whole system. With regards to corrosion resistivity of containers and its components, among aforementioned species are very important (hydro)carbonate ions  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  which are quite strong scavengers for OH radical (Buxton et al., 1988):



Therefore, aqueous solutions of  $\text{Na}_2\text{CO}_3$  saturated with inert gases such as Ar, He,  $\text{N}_2$  are used for simulation of underground granitic water (Sunder and Christensen, 1993). After achieving the steady state during sufficient long period gamma radiolysis, the concentration of radiolytic products is relatively low. However created carbonate radicals appear to be strong oxidative agents, analogously to OH radicals. The mechanism of alkaline solution containing carbonate during irradiation with low LET includes further following elemental reactions:



Saturation with  $\text{N}_2\text{O}$  leads to the increase of steady-state concentration of  $\text{H}_2\text{O}_2$ , and ionradical  $\text{O}_2^-$  whereas concentration of oxidizing OH radical does not change:





Rather different conditions are in oxygenated solutions possessing a high concentration of  $\text{H}_2\text{O}_2$  and oxidizing species  $\text{O}_2^-$ . Presence of oxygen promotes the formation of  $\text{O}_2^-$  due to reaction:



On the contrary, the concentration of oxidizing OH radicals is relatively low due to their removal by reaction (22). Moreover the OH radicals may be intensively scavenged by addition of formate ions or t-butanol. The former case appears to be less suitable because the amount of  $\text{O}_2^-$  radical formed by reaction (25). Its amount is increased (Sunder et al., 1992) due to reactions:



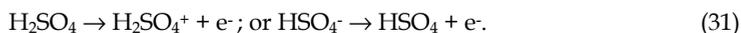
As compared with carbonate or hydrocarbonate ions the reactivity of sulfate or hydrosulfate anions is rather different (Jiang et al., 1992). It is supposed that reaction of OH radicals with sulfate anion



leading to the sulfate radicals is very slow or does not occur at all. Therefore  $\text{HSO}_4^-$  and undissociated  $\text{H}_2\text{SO}_4$  react with OH radicals forming sulfate radical:



Moreover, in concentrated sulfuric acid solution, the fast formation process of sulfate radicals takes place in the first step probably by the electron abstraction:



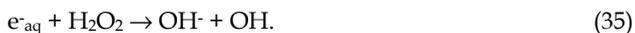
The decay processes include minimally five elemental reactions leading to molecular oxygen and peroxydisulfate  $\text{S}_2\text{O}_8^{2-}$ :



It follows from the study (Anbar and Thomas, 1964) that OH radicals react with  $\text{Cl}^-$  ions in the presence of  $\text{H}^+$  to produce  $\text{Cl}_2^-$ :



Therefore reaction (33) is strongly affected by pH and the formation of transient  $\text{Cl}_2^-$  and its yield also depends on the pH and concentration of chloride ions. Hydroxyl ions may be formed e.g. by reaction



Moreover it is supposed (Sunder and Christensen, 1993) that the formation of HOCl $\cdot$  takes place



and that under suitable concentration of Cl $^-$  ions the significant percentage of the OH radicals would exist as HOCl $\cdot$ .

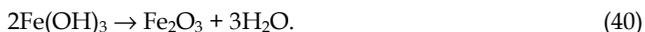
The presence of Fe $^{2+}$  ions in groundwater may be caused mainly by its ingress into container or by leaching of packaging material, most commonly carbon steel. Due to anaerobic conditions the only oxidizing species are products of water radiolysis, predominantly OH and O $_2$  radicals which can oxidize ferrous ions e. g.



Another species such as H $_2$ O $_2$  and product of its radiation decomposition-HO $_2$  radicals are also strong oxidizing agents (Ferradini and Jay-Gerin, 2000; Daub et al., 2010). Moreover both Fe $^{2+}$  ions and formed ferric ions may be hydrolyzed



and deposited hydroxide may be converted to oxide:



Sulfate radicals can also react with species present in granitic groundwater. In more detail e.g. the kinetics of their reactions with Cl $^-$  or HCO $_3^-$  ions was studied (Huie and Clifton, 1990) as well as with Fe $^{2+}$  ions (McElroy and Waygood, 1990), leading also to the oxidation Fe $^{2+} \rightarrow Fe^{3+}$  and to the decay of SO $_4^- \rightarrow SO_4^{2-}$ .

Special group represent aqueous solutions of actinide ions and fission fragments during the reprocessing of spent nuclear fuels. They undergo different valence changes due to irradiation by numerous radionuclides. The understanding of elemental reactions taking place is very important especially for separation of individual elements. Therefore this problematic has been the subject of various studies (Pikaev et al., 1988; Vladimirova, 1990).

### 3. Radiolytically induced corrosion

Radiolytic corrosion of nuclear fuel and/or parts of nuclear devices presents significant and long term studied problem. To emulate corrosive processes in various cooling loops (used in nuclear reactors or irradiation devices), cooling pools (for storage of irradiated fuel) and deep repositories, the studies are performed in both pure water and aqueous solutions relevant to the anticipated conditions. Moreover, since significant amount of heat is often generated during interaction of IR with matter, the radiation-corrosion experiments are often performed at elevated temperatures; this makes such studies even more experimentally difficult. Rate of both non-radiolytic and radiolytic corrosion may be expressed as an increase of the corrosion products layer on corroded material per time unit.

Corrosion processes (and effects of radiation) are often evaluated via changes in corrosion potentials; hydrogen evolution due to corrosion may be also followed. Characterization of corrosion products may help in making quantitative assumptions regarding mechanisms of corrosion processes.

### 3.1 Nuclear fuel

Irradiated nuclear fuel is accumulated worldwide in many countries using nuclear power. Although the opinion that reprocessing of nuclear fuel is more convenient from both economical and environmental point of view dominates nowadays, concept of nuclear fuel disposal in corrosive resistant containers is being still carefully considered. Proper disposal method should ensure the release of the least possible amount of radionuclides back to geo- and biosphere. Currently, deep repositories are prepared for future use. Until that time, irradiated fuel is stored in transport/storage containers, placed in separate repositories, often directly in the areas of nuclear power plants.

Safety of storages and repositories for radioactive waste may be proven only by experimental studying and modelling of all processes that may lead to release of radionuclides to the environment. For more than 30 years, those processes are studied in many countries operating nuclear power plants. Thorough safety analyses, including studies of all anticipated processes and incidents that may occur during time of high radioactivity of irradiated fuel proved, that by disposal of irradiated nuclear fuel in dry corrosion resistant containers surrounded by compacted bentonite in the granite structure hundreds of meters below surface, it is possible to prevent releasing of radionuclides into geo- and biosphere above limits allowed by state authorities. It is presumed that the most probable carrier of corrosion products to biosphere would be deoxygenated groundwater, because its ingress into disposal site must be expected. Another factor, which cannot be totally neglected, is human random mistake, resulting in disposal of container with hidden defect. This may lead to damage of container in shorter time than is its projected lifetime (e.g. 1000 years in Czech reference project of deep repository). Consequently, groundwater may ingress to a container with irradiated nuclear fuel during still high activity of gamma and beta emitters. As was discussed in previous sections, the mechanism of corrosion of materials of containers and fuel elements cladding may change due to irradiation. Moreover, significant change of conditions inside the container may occur, as well as faster degradation of materials and faster oxidation of fuel matrix, presenting one of the most significant barriers against release of radionuclides. It was shown (Bruno et al., 1999), that radionuclides are firmly bonded in fuel matrix in the case, that oxidation state of  $\text{UO}_2$  matrix does not exceed upper limit of stability, corresponding to stoichiometry  $\text{U}_3\text{O}_7$ .

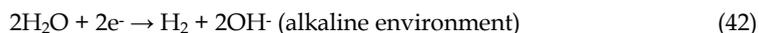
Probability of such scenario is rather low and depends on level of quality control during radioactive waste disposal. According to data published on this topic (Andersson, 1999), we may expect that probability of defective container occurrence, which evades noticing of personnel is lower than  $1 \times 10^{-3}$ , i.e. 1 container of 1000. However, those containers may present the greatest risk for safety of whole disposal site. Study of influence of radiation on inner environment of container with spent nuclear fuel is relevant also for storage of spent nuclear fuel containing residual water after reloading of fuel from pools near reactor into transport/storage containers.

Direct research of environment inside storage container was performed by authors from USA (Domski, 2003) and Canada (Shoesmith et al., 2003). The first of both works is related to preparation of deep repository in Yucca Mountain, USA. This repository is placed in non-saturated zone, i.e. in oxidative environment. On the contrary, some other repositories (e.g. in Europe) are planned in granitic structures hundreds of meters below surface. Generally, corrosion may be described by following oxidative reaction

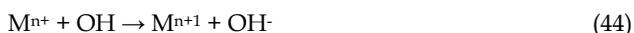


where  $n$  is number of exchanged electrons. In closed environment of disposal container after water ingress may formed ions further hydrolyze for example by reactions (38) and (39), with simultaneous formation of hydrogen ions. Thus, hydrogen ions may accumulate inside the container, which leads to significant decrease of pH. Solubility of compounds forming protective films on surface of metals may increase due to low pH, which may lead to further accelerating of degradation of materials inside the storage container, including faster dissolution of spent nuclear fuel (Burns et al., 1983; Smart et al., 2008). In the work of (Pan et al., 2002) authors observed value of  $pH = 2$  due to hydrolysis of inner metal parts of container.

Rate of processes occurring inside the container is also significantly affected by corrosion products precipitated on surface of metallic materials. Character of those products depends on material of container and also on composition of groundwater and on other components of disposal site (e.g. bentonite). Under anoxic reductive conditions, water accepts electrons released during anodic dissolution of metals and following reactions occur:



The rate of those reactions is very low and therefore, the rate of metal corrosion in anoxic environment is also very low. However, as was described in section 2.1, OH radicals are formed during water radiolysis. Such strong oxidants may significantly contribute to corrosion of metals (or metal ions) by their transfer to higher oxidation states:



Due to the fact, that groundwater will be presumably free of oxygen in the environment of geological disposal site, the only oxidizing species after groundwater ingress into geological disposal site will be reactive intermediates of water radiolysis. Reactive intermediates may increase rate of corrosion due to intensification of cathode depolarization process (Kaesche, 1985; Lillard et al., 2000). Concentration of compounds acting as strong cathodic reactants will increase due to radiation. However, hydrated electrons may reduce dissolved metal ions to lower valences or into metallic form (Buxton et al., 1988) according to equation



and thus decrease the corrosion rate.

Lots of works were published, dealing with experimental study, evaluation or modeling of radiolytic processes related to corrosion of uranium or nuclear fuel in water. A model, based on radiation energy deposition in the pore water and other constituents of natural uranium ore, was developed for radiation energy deposition and its consequences for water radiolysis (Liu & Neretnieks, 1996). Monte Carlo method was used for calculation of randomly generated radiation within grains of uranium minerals in the ore. The radiation energy was then allowed to deposit into the various constituents in the ore. The model was used for prediction of IR with different LET (alpha, beta, and gamma decay). The results showed that in the real system, due to dissipation of energy in solids, only a small fraction of total radiation energy may be available for radiolysis (and possible participating in corrosion processes). Generally, the efficiency of radiolysis (the actual oxidant production rate over the maximum possible oxidant production rate) is about 1%. (Shoesmith et al., 2003) used a mixed-potential model to predict fuel corrosion within a failed nuclear waste container under anticipated repository conditions. The model accounts for the effects of high LET radiation (alpha radiolysis), the formation of corrosion product deposits on both the fuel surface and the surface of the carbon steel container liner, and the homogeneous redox reactions between radiolysis products and soluble fuel and steel corrosion products. The model was used to predict the corrosion potential - usually defined as steady state corrosion potential in volts versus standard (e.g. saturated calomel) electrode - and corrosion rate of the fuel and the extent of fuel conversion over an exposure period of  $10^6$  years.

Fuel matrix in contact with water constitutes a dynamic redox system due to the time dependent radiolytic generation of oxidants and reductants at the fuel interface. (Bruno et al., 1999) performed experimental determination and chemical modelling of radiolytic processes at the irradiated fuel/water interface to better understand the main processes and mechanisms that control the impact of radiolytically generated reactants on the stability of  $UO_2$  matrix and release of radionuclides. Since the actual fuel rods fragments were used in the experiments, the corrosion system was exposed to a mixture of alpha, beta and gamma radiation. Mass balance calculations indicate that consumption of radiolytically produced oxidants by the fuel corresponds to the formation of and oxidized  $UO_{2+x}$  surface layer in distilled water and the formation and release of soluble U(VI) carbonate complexes in bicarbonate media. It was concluded, that uranium release in early contact times is controlled by oxidative dissolution of the fuel matrix. This process also controls the release of Sr, Np and Pu. The measured concentrations of actinides appeared to be limited by the solubility of Ac(IV) hydroxide phases. The release of Tc and Mo appeared to be controlled by oxidative dissolution of their metallic phases, Mo showing higher oxygen affinity than Tc in accordance with their thermodynamic properties. The behavior of Nd and Y gives no evidence of congruent release with the fuel matrix. The concentration of Cs in contacting solutions follows similar trends as Sr and U. Long time experiments indicate that some elements reach saturation with respect to secondary phases. Uranium concentrations seem to be in equilibrium with U(VI) oxohydroxide, excluding when contacting medium contained high concentration of bicarbonate ( $10^{-2}$  mol  $dm^{-3}$ ). Np and Pu seem to be solubility limited by the formation of their Ac(IV) hydroxide phases and Tc by the formation of TC(IV) hydroxide phase. Sr is not close to saturation with respect to any secondary phase.

Various authors studied the influence of gamma radiolysis on corrosion of  $\text{UO}_2$ , compared to influence of oxygen or hydrogen peroxide in aqueous environment (Shoesmith et al., 1985; 1989; Sunder et al., 1987). It was found that the values of corrosion potential, at which the stationary state is established, obtained in the presence of gamma radiation, are higher than those reached in solutions containing oxygen or hydrogen peroxide. This shows how significant the contribution of products of water radiolysis to corrosion processes actually is. It was shown that rate of both fuel ( $\text{UO}_2$ ) and packaging materials dissolution increases with dose rate (Christensen & Sunder, 2000). Corrosion potential of water -  $\text{UO}_2$  system increases with dose rate, too. The important parameter is the presence of dissolved oxygen in corrosion system - the corrosion potential increases (among others) faster and to higher values in the presence of dissolved oxygen, when compared to solutions purged with Ar or  $\text{N}_2\text{O}$ . As was discussed in section 2.1, in aqueous solutions containing dissolved oxygen, the radical ion  $\text{O}_2^-$  is formed during radiolysis according to equation (6), which is an effective oxidant of  $\text{UO}_2$ . Thickness of layer of corrosion products on the corroding material surface is directly proportional to the corrosion potential up to the value  $\sim 0$  mV and it does not depend on corrosion rate, nor character of predominating products of products of radiolysis (Christensen & Sunder, 2000). At higher values of corrosion potential, the thickness of surface layer increases due to irradiation, even after reaching the steady state. Oxidation of  $\text{UO}_2$  proceeds in the presence of oxidative products of gamma radiolysis in two steps:

1. Formation of thin layer with stoichiometry nearing  $\text{UO}_{2.33}$ .
2. Oxidative dissolution of this surface layer, accompanied by formation of soluble forms U(VI) and secondary phases (probably hydrated schoepite) on the surface of electrode. Finally, the steady state of corrosion potential at the value determined by absorbed dose is reached.

Alpha activity of irradiated fuel decreases slower than gamma and beta activities. Therefore, high probability exists that radiation-corrosive processes will proceed for a long time due to alpha radiolysis. Studies of many authors (e.g. Sunder et al., 1997) shown, that rate of corrosion of nuclear fuel and packaging materials due to alpha radiolysis is significantly lower compared to gamma radiolysis. The reason for this is probably the fact that low LET radiation (gamma and beta) leads to higher primary radical yields and lower primary molecular yields than high LET radiation. Therefore, the corrosion effect of alpha radiolysis is caused mainly by hydrogen peroxide, whose oxidative capabilities were observed to be much lower than effects of radicals OH and  $\text{O}_2^-$ . Thus, in many studies, the complicated alpha irradiation is substituted by adding hydrogen peroxide to aqueous solution, because similar behavior of corroding material may be expected (e.g. Daub et al., 2010).

Simulation of the fact that corroding system may be composed of iron (packaging material) and  $\text{UO}_2$  (fuel) was by authors (Loida et al., 1995) solved by adding powder iron. In this case, the corrosion rate was measured by gas evolution. Authors came to conclusion, that gamma radiolysis contributes to gas evolution much more than alpha radiolysis. They also concluded, that rate of fuel dissolution is in the same order as rate of production of radiolytic gases. Many performed experiments show that corrosion of both packaging materials and fuel is governed by intensity of radiation, degree of burning and degree of

non-stoichiometry of corroding material. According to some authors involved in modelling radiolytic processes, it is important to determine dose rates in water layer which is in contact with corroding material, but in practice, such value can be obtained only with great difficulties.

### 3.2 Packaging and barrier materials

Corrosion of fuel and packaging materials is strongly related. Processes leading to degradation of both material types are often studied together (see some remarks on the corrosion of packaging material in the previous section). Opinions of different authors vary, whether the corrosion, even though undoubtedly increased by the presence of radiation field, may actually threaten the stability of packaging/barrier material or not.

#### 3.2.1 Iron and steel

The majority of published works focused on study of radiolytic corrosion of water/iron or steel system use gamma radiation for increased simplicity of experimental setup and high penetration of gamma rays. Usually, doses up to few MGy with dose rates up to tens of kGy have been used. In many experimental studies, pure water as well as synthetic groundwater relevant to anticipated conditions in repository was used. Characterization of corrosion process is often performed via evaluation of changes in corrosion potential, tendency to cracks developing and/or determination of amount and character of corrosion products under various conditions. Generally, the obtained data indicate, that there is rather small effect of radiation on corrosion of stainless steel, especially under deaerated conditions (see fig.1 for example of experimental setup). On the contrary, carbon steel and iron corrode always much faster in radiation field when compared to non-irradiated materials. Similarly to non-radiolytic corrosion, the corrosion induced by radiation strongly depends on temperature of corroding system, as is discussed further in the text.

The effect of gamma radiation on the corrosion of carbon steel and stainless steel contacting high-temperature water has been studied since seventies and it was shown that while irradiation does not seem to have a marked effect on the corrosion of stainless steel, it accelerates the corrosion of carbon steel about 3–4 times (Ershov et al., 1977). It was observed, that the concentration of  $H_2O_2$  in irradiated water contacting carbon steel changes according to the fluctuation law with a period of 20–25 h and remains at the same level as for carbon steel. Later, it was concluded that when pure water saturated with air was irradiated at normal temperature by high doses of gamma rays (1–10 MGy) in sealed stainless steel containers, hydrogen and oxygen were formed (Burns et al., 1983). The amounts were less than one tenth of the maximum possible for continuous aqueous radiolysis but the increase in oxygen appearing as gas was less than that equivalent to the hydrogen formed from the water present, indicating that metallic corrosion had occurred. In the absence of radiation no change in gas composition was observed. When the air in solution and in the gas space was replaced by argon or by hydrogen, radiolysis and corrosion were virtually suppressed. When the container was made of mild steel or strips of mild steel were initially introduced into a sealed stainless steel container containing air and water, oxygen was consumed on irradiation, and hydrogen was formed, together with a

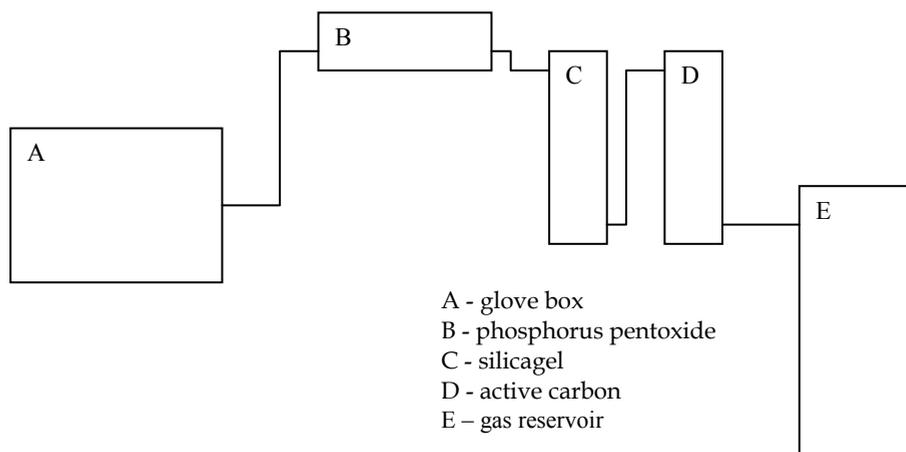


Fig. 1. Experimental setup for working in deaerated conditions. Upper - photo of glove box for working under inert atmosphere with corrosion vials. Lower - example of nitrogen purification prior admitting the gas into glove box

suspended brown oxide, probably  $\text{Fe}_3\text{O}_4$ . In the absence of radiation oxygen was consumed and hydrogen was formed, too but both at a lower rate than in the presence of radiation. In this case, unlike the case of stainless steel, the formation of hydrogen was not prevented by replacing the air present with argon. The rate of product formation from either system in the presence of air was found to be proportional to dose-rate, in the applied range 2 - 20  $\text{kGy h}^{-1}$  and mass changes of the solids, when measurable, corresponded to the oxygen deficit in the gas phase if the oxide was taken to be  $\text{Fe}_3\text{O}_4$  (Burns et al., 1983).

The corrosion behavior of several iron-base as well as titanium-base alloys was studied in synthetic groundwater at temperatures from 150°C to 250°C and under gamma radiation with dose rates up to 20  $\text{kGy h}^{-1}$ . The study was performed with regards to repository in basalt (Nelson et al., 1984). Similarly to observations of previously discussed papers, iron-base alloys exhibited a general corrosion rate enhancement factor of 2 to 3 higher when exposed to 250°C synthetic groundwater in the presence of  $^{60}\text{Co}$  gamma radiation of about 3  $\text{kGy h}^{-1}$  than when the radiation was absent. The four different iron-base alloys tested corroded at similar rates. The cast steel containing chromium and molybdenum generally exhibited the greatest resistance to corrosion. Nevertheless, it was concluded that iron-base alloys show rather low corrosion rates under conditions that are much more severe than those anticipated in deep repositories constructed in basalt. Irradiation corrosion studies of titanium in 250°C synthetic groundwater show very low corrosion rates and no tendency to environmentally enhanced cracking. Ahn & Soo (1995) also studied the long term corrosion processes at elevated temperatures. Corrosion properties of carbon steel were evaluated in concentrated synthetic groundwater at 80-150°C, with regards to the use of the steel as a container material in the Yucca Mountain repository project. Corrosion rates were obtained at 150°C under conditions of no irradiation and a gamma irradiation field of 13  $\text{kGy h}^{-1}$ . Long term experiments with aerated solutions were performed for 4 months. The long-term uniform corrosion rates were 10-40  $\text{m year}^{-1}$  under irradiation conditions. Irradiation effects on uniform corrosion were not discernible. Pitting corrosion was also observed but the pitting factor was small. Microstructural effects on corrosion were not significant. During corrosion, hydrogen was generated. Under irradiation conditions, the hydrogen generation was greater and there was an indication that large amounts of hydrogen were absorbed in the steel during the radiation corrosion. Indication of stress corrosion cracking was observed as well as strong evidence for hydrogen embrittlement. Similarly to Nelson et al. (1984), authors concluded that general corrosion rates of the steel appear to be low enough to maintain integrity of containers for an extended period.

Few studies on the mechanisms of corrosion processes on stainless steels in groundwater were performed. Under gamma irradiation, the corrosion potential shifts in the positive direction were observed (Glass et al., 1986). These potential shifts were associated with the radiation-induced production of hydrogen peroxide. Another study of gamma radiation - induced corrosion in deaerated water/carbon steel systems was performed by Neufuss et al. (2006). It was concluded, that kinetics of releasing corrosion products into the water and their sorption on the surface of steel tablets is affected by various factors (redox potential, absorbed dose, temperature, irradiation duration). Concentration of corrosion products in the solution and solid phase was evaluated and corrosion processes were studied in deaerated pure water and synthetic granitic water. Based on results obtained from

performed experiments, several general conclusions regarding influence of IR on corrosion of carbon steel/water system were made:

- Under the given conditions, irradiation strongly affects the corrosion kinetics. This effect is clearly observable not only in the corrosion system with dissolved oxygen, but also in the deoxygenated systems.
- Type and distribution of corrosion products depends on some experimental parameters (i.e., temperature, presence of oxygen). Concentration of corrosion products increases with dose of radiation.
- Presence of impurities in granitic water affects corrosion to a small extent.
- Differences in corrosion products concentration were observed between samples saturated with nitrogen and helium – nitrogen is less suitable for radiation experiments under anoxic conditions.

Thorough long term experiments taking several months, aimed to investigate the effect of gamma radiation on the corrosion of carbon steel in repository environments, were carried out (Smart et al., 2008). Corrosion experiments were performed at two temperatures (30°C and 50°C), two dose rates (11 Gy h<sup>-1</sup> and 300 Gy h<sup>-1</sup>), and in two different artificial groundwaters. In full agreement with previously discussed results, radiation was found to enhance the corrosion rate at both dose rates but the greatest enhancement occurred at the higher dose rate. The corrosion products were predominantly magnetite, with some indications of unidentified higher oxidation state corrosion products being formed at the higher dose rates.

In the work of Daub et al. (2011), the effect of gamma-radiation on the kinetics of carbon steel corrosion has been investigated by characterizing the oxide films formed on steel coupons at 150 °C in aqueous solutions and at two pH values. Though variations in system temperature and pH may affect rates of oxide film growth and dissolution, they do not play a significant role in determining the chemical composition of the oxide film. Gamma irradiation had a major impact on the corrosion process by increasing corrosion potential in the system and therefore determining which oxide phase forms on the steel surface. Specifically at mildly basic pH, the presence of IR leads to the formation of a more passive film composed of a mixture of Fe<sub>3</sub>O<sub>4</sub> and γ-Fe<sub>2</sub>O<sub>3</sub>. These results suggest that water radiolysis does not necessarily increase, but rather limits, carbon steel corrosion under the conditions studied. In the similar study (Cuba et al., 2011), the influence of gamma irradiation on the formation of Fe-ions was investigated at different temperatures up to 90°C, with respect to the expected ingress of groundwater into the disposal site with spent nuclear fuel containers. Specifically, the kinetics of Fe<sup>2+</sup> and Fe<sup>3+</sup> formation in the presence of IR was studied. It was confirmed, that in the absence of oxygen, or after consumption of oxygen by corrosion in a closed system, corrosion in the presence of γ-radiation proceeds mainly via reaction with the intermediate products of water radiolysis (mainly H<sub>2</sub>O<sub>2</sub>, and radicals OH, HO<sub>2</sub>). The radiation increases amount of corrosion products; it affects their composition predominantly via radiation oxidation of ferrous to ferric ions. Characterization of crystalline solid corrosion products revealed that under given conditions, the composition of solid crystalline corrosion products does not depend on temperature, but rather on the presence of other compounds in water. On the other hand, the amount of corrosion products in an irradiated system depends on the temperature and on the dose; other compounds

present in water affected the total amount of corrosion products only marginally. In the solid phase formed during contact with deionized water, the predominant crystalline corrosion products were magnetite and lepidocrocite, which is in agreement with (Smart et al., 2008) and partially (Daub et al., 2011). Other published studies discussed here dealing with water-steel system and providing data on various corrosion parameters (e.g. corrosion rate, corrosion potential, hydrogen evolution, etc.) in radiation field generally concluded, that under aerated or deaerated conditions in temperature range 30-250°C, the corrosion is affected by ionizing radiation at dose rates 0.01 kGy. h<sup>-1</sup> (Smailos, 2002), 0.011-0.3 kGy.h<sup>-1</sup> (Smart et al., 2008), 3 kGy.h<sup>-1</sup> (Nelson et al., 1984), 13 kGy.h<sup>-1</sup> (Ahn and Soo, 1995), which is consistent with observations made by Cuba et al. (2011) at dose rate 0.22 kGy h<sup>-1</sup> and temperatures 50 and 70°C. Similarly, the slow rates of corrosion processes in irradiated deaerated water at room temperature were also observed by others (Burns et al, 1983; Lapuerta et al., 2005).

### 3.2.2 Other materials

Similarly to corrosion studies of iron and steel, some other materials are also studied for possible use in container manufacture or as matrices for immobilization of irradiated fuel. Studies including gamma radiation predominate, not only due to relative experimental simplicity, but also because among the various types of radiation relevant for nuclear waste disposal, only gamma radiation can penetrate the container wall and affect the corrosion of its outer wall (Michaelis et al., 1998). Besides from already discussed work (Nelson et al., 1984), other authors also studied radiation corrosion or corrosion resistance of various metallic materials considered for construction of engineering barriers. Interesting study of corrosion of Ti and its alloy TiO.ZPd in pH 4.6 aqueous solutions simulating the salt brine environment was performed, because those materials are considered as promising for the manufacture of high level nuclear waste containers which could act as an engineered barrier in a rock salt repository (Michaelis et al., 1998). Despite their extremely high resistance to general corrosion in salt brines, localized corrosion might be critical. Instead of gamma irradiation, authors used in-situ UV-laser illumination with high power density at high local resolution. It was shown that after formation of stable corrosion (amorphous and crystalline oxidic) layers, virtually no further corrosion was observed under given conditions, which confirms older conclusions of (Nelson et al., 1984), i.e. that Ti-based alloys are promising container materials.

For the long-term disposal (immobilization of various radioactive wastes, including actinides, host matrices with a very high resistance to corrosion are needed. Promising matrix material is thorium phosphate-diphosphate (TPD). Irradiation effects of radiation on TPD were studied (Pichot et al., 2001). At low doses (~ kGy), the gamma radiation induced damage (formation of free radicals) could be healed by annealing at higher temperature. At high doses (~ MGy) gamma radiation induced the presence of paramagnetic defects. Effect of accelerated heavy charged particles, used for simulating  $\alpha$ -decay effects included modification of the chemical stoichiometry at the surface of the samples, though it was interpreted as a pure ballistic differential sputtering effect involving elastic collisions. The important conclusion was made - due to irradiation, crystalline structure of TPD did not change under given conditions (Pichot et al., 2001).

### 3.3 Nuclear machinery

During operation of nuclear devices, corrosion threat is especially serious. Corrosion may lead to a) decrease of functional properties of materials, and/or to b) significantly increased difficulties in operational control and maintenance due to its contamination by radioactive corrosion products. To fully explore possible consequences of radiolytic corrosion in nuclear/irradiation devices, irradiation with heavy particles must be employed aside from gamma radiation. For example, spallation neutron sources generate a mixed radiation environment when a beam of high energy particles (e.g. protons or deuterons) hits a heavy metal target. Radiolysis results when these primary and secondary (spallation) particles lose energy by Coulomb interaction with the electrons in the hydrogen and oxygen atoms of water (Lillard, 2003). In either case, the corrosion threatens reliability and safeguard of operation of nuclear device.

Corrosion of spallation neutron sources was studied (Lillard et al., 2000). In those sources, high energy neutrons are produced, via interaction of accelerated protons with convenient target material. Cooling loop, which keeps low temperature of target material is usually constructed from stainless steel and filled with deionized water, serving also as moderator of neutrons. However, radiolysis of coolant water may result in increase in corrosion of construction materials. Referred work is interesting also from experimental point of view: authors irradiated water and let it react with corrosion probes, which were placed outside of radiation field and shielded. By this, authors aimed at eliminating of direct radiation influence on selected corrosive materials – stainless steel and alloys of aluminium, tungsten, nickel and copper. The effects of water system fabrication materials, hydrogen water chemistry, and pre-cleaning of the water system on radiation corrosion rate have been demonstrated to be dramatic. Study of corrosion rates in real time resulted in observation, that under given conditions, the most significant corrosion occurs at materials containing copper and aside from radiation, the corrosion rate is affected mainly by amount of impurities present in irradiated water. Other findings indicate that proton irradiation and the resulting water radiolysis products do not influence passive film formation and reduction (Lillard, 2003).

The effect of IR on carbon steel corrosion as an important materials issue in nuclear reactors was investigated (Daub et al., 2010) at pH 10.6. The effect of gamma-radiation on corrosion kinetics was compared with that of chemically added  $H_2O_2$ , which is considered to be the key radiolytically produced oxidant at room temperature (see section 2.1 for details on its formation). It was confirmed that  $H_2O_2$  is really the key radiolysis product controlling carbon steel corrosion. The discussed study illustrates that the corrosion rate of carbon steel in a gamma-radiation environment at alkaline pH and room temperature can be predicted from the dependence of corrosion potential and polarization resistance on  $H_2O_2$  concentration, if the concentration of radiolytically produced  $H_2O_2$  can be determined.

## 4. Conclusions

It was demonstrated, that corrosion processes in aqueous environment may be strongly affected by the presence of radiation field. IR contributes to corrosion mainly via production

of highly reactive intermediates of water radiolysis. Similarly to chemical corrosion, the effects of radiation induced corrosion are also enhanced when the corroding system operates at elevated temperatures and they depend on pH value of a liquid irradiated system. The effects of radiation corrosion are also strongly dependent on dose, dose rate and LET of applied radiation. Due to high (long term) level of corrosion caused by radiation, it is important aspect to consider in all steps of nuclear fuel cycle, especially in storage / disposal of irradiated nuclear fuel. Radiation corrosion may also present important technological problem in operation of nuclear reactors and various irradiation devices.

## 5. Acknowledgements

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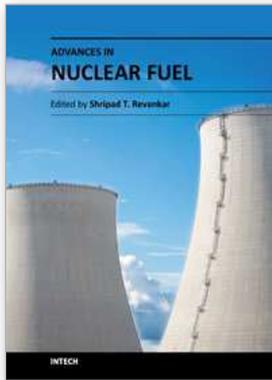
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Worldwide there are more than 430 nuclear power plants operating and more plants are being constructed or planned for construction. For nuclear power to be sustainable the nuclear fuel must be sustainable and there should be adequate nuclear fuel waste management program. Continuous technological advances will lead towards sustainable nuclear fuel through closed fuel cycles and advance fuel development. This focuses on challenges and issues that need to be addressed for better performance and safety of nuclear fuel in nuclear plants. These focused areas are on development of high conductivity new fuels, radiation induced corrosion, fuel behavior during abnormal events in reactor, and decontamination of radioactive material.

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