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RADIATION CHEMISTRY OF POLYMERIC COMPONENTS
OF RADIOACTIVE WASTE

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Abstract

The presentation covers fragments of research on the role of radiation chemistry in radioactive waste management. Radioactive waste often contains polymeric materials contaminated with actinides, which exhibit α activity for thousands of years. Rules of safety of transportation and environmental security of permanent storage demand the understanding of radiation chemistry of typical waste matrices. Due to a slow decay and a short range of penetration of α emitters, the experiments with actinides are not easy. Therefore, accelerated experiments have been performed

using 10 MeV electrons of high intensity. That way chemical effects proceeding over thousands of years could be reduced to minutes in the laboratory. Simulation of the effect of α -radiolysis on polymers by low LET radiation is justified, because low LET radiation produces multi-ionization spurs resulting in the same chemistry as high LET radiation.

Keywords: α -radiolysis, dehydrogenation, electron beam radiolysis, multi-ionization spurs, radiolysis of polymers, single-ionization spurs

The present paper describes a specific part of problems discussed in general in [1, 2]. A recent survey of the history of radiation chemistry with the outlook at its future, offered by Zimbrick [3], stresses the necessity of engaging radiation chemistry while dealing with the most difficult radioactive waste, such as waste at Hanford Site in Washington State. However, that paper, published after we began our research, does not mention the problems of radiolysis of polymeric constituents of the waste. Radioactive nuclides, which contaminate materials of mixed composition, including polymers, can be stored hundreds of meters below the surface, in various deposits such as salts, volcanics and granitics. For wastes containing long-lived radionuclides, such as the transuranic elements, particularly Pu, the α emission induces chemical changes in waste materials, which often contain polymers. Knowledge of the products of radiolysis of waste constituents is therefore desirable while considering safety of transportation to the final storage site, and for the very long-term effects occurring during permanent storage. For instance, advanced stages of degradation of polymers should be considered while elaborating the scenarios of water penetration into the repository.

Due to a slow decay of α emitters, and a short range of alpha penetration, experiments, which use the radionuclides themselves are difficult. Therefore, accelerated experiments have been performed. They use 10 MeV electrons of high intensity, usually monoenergetical after bending and scanning [4]. Such experiments, lasting only minutes in the laboratory, simulate the effects occurring during thousands of years. When delivering a dose higher than 20 kGy, the split dose techniques are applied, thus avoiding excessive heating of the polymer [5]. Because of the low specific heat of polymers compared to water and aqueous solutions, the increments of 20 kGy are practically the highest allowed.

The question arises how justified is the simulation of the effect of α -radiolysis on polymers by low LET radiation. The answer lies in the basic radiation chemistry of polymers, executed by irradiations having different linear energy transfer (LET) values. With low LET radiations, most of the energy (80%) is deposited as single ionizations, well separated, with no possibility to overlap. The rest of the energy is deposited in multi-ionization spurs. With higher LET radiation, which is the case of alpha emitting actinides, the situation is reversed, i.e. most of the energy is deposited in multi-ionization spurs and a smaller part (20%) in single ionization spurs. These facts have been found almost a century ago in studies of radiolysis of aqueous solutions. Similar proportions of single- and multi-ionization spurs occur in irradiations of solids, including polymers [6, 7].

Hydrogenated nitrile-butadiene rubber (HNBR) was chosen as a model polymer for study. Hydrogenation in material A was 99.5 %, and in material C, 94.5 % of the initial double bonds. The HNBR is a high technology rubber, which can be found in mixed, alpha emitter contaminated radioactive waste, originated as, e.g. gaskets in chemical apparatus, tubing, or gloves. Rubbers lend themselves as excellent objects of study of radiation chemistry for the purpose of waste management, because they represent the highest hydrogen generation hazard. As the polymers, which contain mainly carbon and hydrogen, and no oxygen, they are the most prone to generate hydrogen as the main volatile product of radiolysis. Polymers, which contain oxygen, produce less hydrogen, because some of the hydrogen atoms formed in the secondary radiolytic reactions appear eventually as water.

Another reason for the choice of elastomers is a relative simplicity of the matrix from the point of view of interpretation of results. Rubbers do not contain crystalline phase, as almost all other polymers do. Therefore, in searching for mechanisms, they can be treated as fully amorphous

bodies, almost like glasses. Another important reason for their selection was that HNBR is one of the few polymers, in which the participation of multi-ionization spurs at low LET irradiation can be observed. The study of radiation chemistry of that material [8] showed, that the polymer crosslinks at a radiation yield of 2.6 acts per 100 eV. The single ionization spurs cause X type of crosslinking when a free radical site formed in one chain, reacts with another macromolecule, which hadn't been affected by radiation. However, for each 100 of crosslinks, there are 6-9 acts of chain-scission, supposed to be resulting from multi-ionization spurs. That value is lower than expected based on the participation of multi-ionization spurs as primary acts. This apparent lower yield of multi-ionization spurs is explained by partial conversion of products of these spurs into another type of crosslinks of trifunctional Y type. Loose ends of a broken chain, formed in a high energy multi-ionization spur, react with unaffected neighboring macromolecules. The crosslinking results also indicate the existence of multi-ionization spurs in polymers irradiated with low LET radiation, which until now seemed to be reserved for aqueous solutions and was observed only in a few solids [6].

The effects of alpha particle irradiations have been detected applying determinations typically used for measuring radon in the air. They consist of counting the etched traces of α particles (5.5 MeV) in polymers. The phenomenon of Rn atom decaying at the surface of a polymer is exactly the same as the one of an α -emitter decaying in waste. The polymer used in Rn determination is polycarbonate (allyl-diglycol-carbonate, CR-39), a material of different chemistry than rubbers, but identical as far as the physics of deposition of ionizing energy is concerned. Polycarbonate is the best material for visualization of the absorption of α particles, due to the ease of etching (warm 6M NaOH) of the footprints initiated by the multi-ionization spurs in this polymer. The

diversity of polymers showing similar effects indicates that tracing of α emitters is not limited to polyesters, but it is a general phenomenon of alpha interaction with polymers.

Single α -decay of one atom causes the deposition of energy in an astonishingly large volume of a polymer. The polymer is later etched with a concentrated, heated NaOH, which enlarges the footprints initiated by ionizations. In spite of the easily measured size of cavities, only orders of magnitude computations are justified and they yield the conclusion, that one destroyed mere in the polymer chain is surrounded by 1000 unaffected mers. The mechanism of the amplification of the primary ionization effects by the action of highly concentrated OH^- at an elevated temperature is not clear, but the low concentration of the centers of reaction in the footprint of an α particle interaction indicates no overlap inside of a spur. The primary effect of radiation absorption is finished in attoseconds. The fragmentation of the polymer and the formation of gaseous products, mainly hydrogen as H_2 , proceeds in the next femtoseconds. The only processes involved are: very rapid transfer of energy (electron excitations and holes), no-delay chain scission, and slightly slower but also very rapid diffusion of H atoms to form H_2 . Very rapid also are processes of crosslinking of loose ends of broken chains, which generate additional amounts of hydrogen by accompanying reactions.

The elastomer chosen as a model for investigations of radiolysis is a commercial product and contains additives, without which the production of gaskets, gloves, and the like, would not be possible. Therefore, the first doses of radiation up to 30 kGy showed lower yields of crosslinking. The diagrams 1 and 2 in paper [8] show that the starting yield of crosslinks is disturbed, by the protecting action of the additives. Due to the transfer of active sites along the chain to the location of the additive, the latter is destroyed or inactivated. Therefore, the curve of hydrogen production, overlayed on the crosslinking curve, also shows a lower yield. Any act of crosslinking, whether X

or Y type, is accompanied by the release of H atom, later combining to H₂. Other sources of hydrogen originate at both types of spurs.

Hydrogen was formed as a result of the irradiation with the straight beam of electrons, which produces a narrow beam geometry. It is similar to the beam applied in pulse radiolysis, as a no-way-out necessity [9], and in our case it was used for the determination of the radiation yield of hydrogen from polymers, irradiated in special vessels, which were compatible with GC determinations. Special techniques of dosimetry, more difficult than those applied for broad beam irradiations, were therefore needed [4]. The radiation yields of hydrogen in the HNBR were 0.94 per 100 eV for fully hydrogenated material, and 0.79 for partly unsaturated material (details to be published).

The assumption of identity of chemical products of the multi-ionization spurs obtained with low LET radiation and the spurs obtained with higher LET radiation applies only to the discussed case of alphas of about 5 MeV. It cannot be applied to the cases of much higher LET values, as in heavy ion irradiations, e.g. N⁷⁺. Spurs from heavy ion irradiations result from flash heating rather than from ionizing radiation. Accordingly, they are called thermal spikes as local increase of temperature may reach 1000K.

The spurs in the case of LET values, not exceeding those for alphas emitted by isotopes, show only a slight increase of temperature. The thermal effect is easily calculated from the deposited energy in a known volume of a medium, of known heat capacity, corrected for the change of enthalpy of the system [5]. The temperature increase is low enough to be neglected from the point of view of its influence on the course of chemical reactions induced by ionizing radiation. The thermal effects in this case also have no connection to the etching process in alpha-footprint imaging.

The above discussion shows that the answer to the question asked at the beginning of the study: “Can low LET radiation simulate the effects of higher LET irradiations and be used for predicting the action of α -particles on polymers?”, is positive. Although the high chemical yield of observable changes in a polyester suggests a chemical chain reaction, it has nothing to do with chain ionizations. Only the primary ionizations and their consequences alone produce hydrogen, the most hazardous product in radioactive waste management. Thus, the radiation chemistry of polymers contributes to the safe management of radioactive waste.

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