

## Radiation chemistry of radioactive waste to be stored in the salt mine repository

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**Abstract** Different aspects of radiation chemistry connected with long storage of radioactive waste are discussed. More details are given on the dehydrogenation of organic, and in particular polymeric waste, contaminated with transuranium nuclides. Determinations of radiation yields of hydrogen from typical waste were made, indicating limits of safe activities tolerable. No danger of chain reactions of hydrogen release was detected.

**Key words** dehydrogenation • ionization spurs • radioactive waste • radiolysis of polymers • repository chemistry

### Introduction

Radiation chemistry is fundamentally involved in the management of radioactive waste on every time scale, from the zero point of waste generation, throughout its preliminary storage and processing, transportation and final rest in geological repositories.

During decades of investigations, time and again the observations were made in the Department of Radiation Chemistry and Technology of the Institute of Nuclear Chemistry and Technology (INCT), that radiochemists do not fully accept the facts of chemical reactions generated by ionizing radiation. Therefore, the purpose of report of investigations will mean a proposal to consider by radiochemists, especially those dealing with radioactive waste management. Relations between radiochemistry and radiation chemistry are still insufficiently close and unsatisfactory [15]. As a rule, radiochemists do not have the access to the tools and methods of modern radiation chemistry, i.e. powerful sources, especially to accelerators of electrons. Hopefully, the problem of radiation-induced chemical effects connected with handling of radioactive materials, especially in the case of long time waste storage, can be solved with the help of radiation chemistry. This Department deals with problems connected with chemical aspects of waste management, in particular to the long time storage. The key are both experimental projects described in the present paper and computer assisted simulation of expected chemical effects to be published later on.

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## Radioactive waste depository: radiation chemistry connection

The present paper deals with fragments of collaboration between the INCT in Warsaw, Poland, and the Los Alamos National Laboratory, Carlsbad Operations, New Mexico, USA. Several years ago, the Department of Energy in the USA decided to promote the idea of permanent storage of low activity, but long-lived transuranic (TRU), mainly plutonium waste in a waste isolation pilot plant (WIPP), located in a methane free salt mine at Carlsbad, dedicated entirely to that purpose [1]. The decision made headlines in media, because it met a full success and created new jobs for the New Mexico population. Underground corridors, at a level of 700 m deep below surface, can accept all TRU waste of concentration of fissile nuclides too low to attain reasonable economics from their recovery. The salt mine storage was an alternative to the waste incineration, involving effective filters for flue gases, with the subsequent storage of ashes of much reduced volume.

The origin of the waste are materials, mainly organic, contaminated during plutonium production, reprocessing of nuclear weapons, production of MOX fuel, basic research in chemistry and biology etc.

## Methodics of investigation

The problem is that the activity of  $\alpha$ -emitters, although low, can cause radiolysis of organic material present in the waste. The main and most dangerous gaseous product of radiolysis, is hydrogen. Our task consisted in the determination of hydrogen yields for polymers and other organic material present in the waste. All experimental approaches were possible only with the assistance of tools of radiation chemistry, which are not in disposition of Los Alamos National Laboratory. The key hardware in the realization of the project were electron accelerators in this Department able to simulate any dose, dose rate and LET value of ionizing radiation. The last mentioned property of electrically generated ionizing radiation is especially important in the project, as the main radioactive contaminant in the waste under consideration are plutonium isotopes, which emit high LET alpha particles [11, 13]. The simulation of higher LETs is achieved by increasing the dose rate from straight beam of electrons, deposited in small volume of the condensed phase material. Under such conditions, spurs overlap, creating conditions in which single ionization spurs behave like multi-ionization spurs [6, 7, 9].

## Determination of radiolytic hydrogen

All analytical methods applied in the project have a specific mode of application being realized on line with the electron beam (EB). An example is the gas chromatography method combined with electron beam irradiation. That combination of irradiation and hydrogen determination helps us to determine the most

dangerous product of waste radiolysis, i.e. molecular hydrogen from contaminated polymers.

## Technical details of hydrogen determination

Although the determination of hydrogen in the gas over the irradiated polymer is possible by the mass spectrometric method, gas chromatography has been chosen as the most appropriate method. A gas chromatograph Shimadzu-14 B has been installed in an air conditioned and thermostated room. A 1 m long column was packed with molecular sieves 5 A, the detector was a thermoconductivity (TCD) element by Shimadzu. The chromatograph was attached by interface ADAM (range 1 V or 0.15 V), with sampling frequency of 10 Hz, to a PC computer where the data were acquired by program CHROMNEW and processed by program CHROMAP, both developed at the INCT. The carrier gas was argon (99.99%), the calibration gas – hydrogen 99.99%. Operations were done with 10, 25 and 500  $\mu$ L syringes. The system was working at 22°C, on a column kept at 70°C and a detector at 100°C. The flow rate of the carrier gas was 10 mL/min. According to criteria of chromatographic peak symmetry and separation coefficients, the method is suitable to quantitative determination of H<sub>2</sub> in gas mixtures like air. The minimum detectable amount of H<sub>2</sub>, which generates a signal in the detector twice as high as the noise amplitude was estimated as  $\sim 0.005 \mu$ L, which corresponds under normal conditions to  $\sim 2 \times 10^{-10}$  mole or  $\sim 4 \times 10^{-10}$  g of H<sub>2</sub>. Using the method of “head space” for the determination of hydrogen in solid samples of density close to 1, irradiated to a dose of 10 kGy in cells of the gas phase to the solid phase volume ratio of ca. 3 and gas phase sampling by 20  $\mu$ L, the limit of hydrogen detection would allow to determine the radiation yield corresponding to the dose of 0.0003  $\mu$ mol/J i.e. ca. 0.003 G.

The application of the developed technique to the particular polymer was always preceded by a study of kinetics of the release of hydrogen, as well as of its distribution between the sample and the gas phase. The behavior of different polymers, even of comparable surface area of the sample, is different in this respect.

The use of straight beam of electrons has created some problems of dosimetry [8]. The increased inhomogeneity (in comparison to scanned beam) of the radiation field is neutralized by the special alanine-powder dosimetry, with diffuse reflection spectrophotometry (DRS) measuring method. The method is based on the fact that the free radical derived from alanine shows an optical absorption spectrum [4, 14]. The use of straight electron beam is similar to its use in the first versions of our pulse radiolysis system [6].

Application of higher (kilogray) doses proved to be more convenient by the conventional technological irradiation on the conveyor by the bent beam of electrons. The septa were covered with a thick hood made of lead in this case. Experiment with an empty vial did not show the presence of hydrogen, what has demonstrated no significant irradiation of septa made of rubber. This technique was applied for high doses only; application of this mode for low doses of radiation

yields erratic doses, because of the structure of the scanned beam. That limitation has been recognized already before the construction of the machine and cannot be avoided due to the pulsing regime of the accelerator action and scanning frequency of 5 Hz.

Several types of commercial polymers and biopolymers have been investigated. Irradiation by the EB produced by the most reliable, versatile, oldest linear accelerator LAE 13/9 in this Department was applied. All samples were of geometry and size securing the homogeneity DUR (dose uniform ratio) = 1.2 of dose distribution. The split dose technique has been applied to avoid the warming of samples higher than by 35 kelvins [5]. Goals of investigations were well defined: the simulation of radiolytic effects in all kind of polymers, i.e. of elastomers (e.g. gaskets) contaminated with  $\alpha$ -emitters, investigated from the point of view of storage of radioactive waste. Dose applied were also adjusted to realize the primary task. Important were the lowest doses, which represented the fate of waste at the initial stage, from the preparation to the transportation to the WIPP. Higher doses were also applied to exclude unforeseen phenomena. The radiation yield at higher doses, when the additives are destroyed, was accepted as the maximum radiation yield.

### Yields and mechanisms of hydrogen release

Detachment of gaseous hydrogen from polymers at ambient temperature is unknown in the conventional polymer chemistry. In the latter, gaseous hydrogen can appear only over polymers heated to high temperatures, well above the melting or decomposition temperature. Free  $H_2$  formation is incorporated in that case in the thermal degradation process.

In the radiolytic decomposition of organic compounds, including polymers, at room temperatures and also under cryogenic conditions, hydrogen is the main constituent of the gas phase above irradiated substance. Hydrogen dominates over the concentration of low molecular weight debris of the degraded polymer, mainly formed in multi-ionization spurs [12].

Release of hydrogen from organic matter by the action of ionizing radiation has been noticed and investigated early in the LANL, in connection with the immobilization of radioactive waste ( $\alpha$ -emitters) in asphalt. Later, the investigations were extended to organic compounds contaminated with the waste [2, 3]. These papers show how complicated is the investigation of effects caused by alpha emitters and how efficient is our approach of simulation of these effects by electron radiation permitting to make wider investigation, incorporating long list of very different materials and very different doses, i.e. equivalent to very different concentrations of radionuclides.

This phenomenon occurs only in the case of neat polymers, but those dissolved, e.g. in water, exceptionally only do release hydrogen in the result of radiolysis. The radioactive waste can contain material looking like solid, but indeed being a gel of high water content. Aqua-gels used in medical practice can be contaminated. In the case of polymer solutions or

aqueous gels, the solvent is absorbing most of the ionizing energy and its reactive products are entering the reaction with macromolecules. For instance, gelatin in aqueous solution shows during irradiation many different products of reaction with water radiolysis intermediates. Also the cross-linking of gelatin into collagen-like supramolecular entities occurs, but without release of gaseous hydrogen. However,  $H_2$  appears with the yield of 0.45/100 eV in radiolysis of aqueous solution of polymers as the product of multi-ionization spurs in water. Products of multi-ionization spurs are not involved in reactions with dissolved polymer and are not destroyed by radical products of  $H_2O$ .

We have systematically investigated the formation of hydrogen, referring to different types of polymers occurring in the waste, including biopolymers. The analytical method to be applied for hydrogen determination is obviously gas chromatography already applied successfully to the determination of radiation yield of multi-ionization spurs in alanine, from the radiation yield of carbon dioxide [7]. However, the link between irradiation and the gas chromatography (GC) operation, developed for that purpose cannot be applied for the case of hydrogen. The integration of irradiation and the GC determination, for the case of solid polymers involved a special approach to the specific technique of EB irradiation of cells closed with septa and consideration of different solubility of hydrogen in a variety of polymers, resulted in new procedures. Three milliliter glass vials, closed by septa, are filled only in one third with the sample and only this part is irradiated with a straight beam of electrons from the linear electron accelerator LAE 13/9 ([6] and references therein) leaving the rubber septa intact. This technique allows application of small doses of radiation energy, by triggering single pulses. The arrangement of the cell in the beam is precisely controlled; the positioning is secured by a laser beam.

Basic aspects of radiation chemistry of polymers became involved when the  $H_2$  radiation yields were confronted with the composition of commercial polymers and with the effects of polymer irradiation. As concerns the composition: the spectrum of additives present in commercial polymers is very wide; otherwise the processing of polymers for their application in industry and household would have been impossible. Technically pure polymers, i.e. obtained directly from the polymerization line, are used in basic research only, after basic purification from catalysts and unwanted isomers. For the completeness of research, hydrogen determination in irradiated polypropylene has been investigated. That kind of polymer yields important results concerning its radiation chemistry, in spite of the fact that it can be processed, e.g. into films, only after addition of stabilizers. The definitive conclusions for the purpose of effects in waste, could have been reached only after investigation of radiation chemistry of real life polymers, i.e. commercial compositions.

Consideration of  $G_{H_2}$  radiation yields as a part of complete radiation chemistry of polymers, had permitted to draw important conclusions. The majority of commercial polymers show a typical curve of hydrogen yield

vs. the dose, with a visibly lower yield at the beginning of the curve. After that initial step, the growth of hydrogen production is linear with dose. Production of hydrogen from a neat polymer, polypropylene, is linear from the beginning. Evidently, the mechanism of radiolysis of commercial polymer at the beginning of irradiation is different. Leaving the full discussion to the detailed publications, we can explain the phenomenon by the consumption of additives present in polymers, by intermediate species of radiolysis. The degree of cross-linking vs. the dose is usually parallel to the hydrogen-detachment curve, i.e. at the beginning the cross-linking cannot occur. The additive which is present next to the chain is winning here the competition for the positive hole ( $h^+$ ). The loser is the energetically favorable site where two chains of the polymer are sufficiently close to each other. At subsequent higher doses, the meeting sites of two chains, the irradiated and unirradiated chain are only places where the transfer of  $h^+$  comes to rest, to release hydrogen and form the cross-linking bond. Comparison of hydrogen yields vs. dose is a vital part of the future work, because cross-linking of polymers shows also the effect of diminished yield at starting doses of irradiation.

If a polymer-additive has aromatic groups, and that is usually the case, or the polymer is an aliphatic-aromatic mixture or co-polymer, the energy transfer to aromatic moieties results in dissipation of absorbed energy in single ionization spurs. The ionizing energy is changing into emission of visible light, and/or changing into molecular vibrations manifested as chemically ineffective heat. The main source of hydrogen in the zone of low dose irradiated, protected polymers are multi-ionization spurs which occur also in random sites of the polymer, but cannot be transferred. The result is an immediately broken chain of the polymer and sometimes additional formation of low molecular weight debris of the polymer from sites around the scission site.

The initial (on the dose vs. effect diagram), low degradation zone of radiolysis is welcomed, if radiolysis of polymers is considered from the point of view of safety of transportation of contaminated waste.

The behavior of biopolymers (cellulose, wool etc.) present in the waste is, in general, different. The radiation yield of hydrogen is lower, and the starting part of the curve does not show the pre-step like in C-H polymers with additives. As an example, radiolytic hydrogen generation curve of two kinds of keratin were found. The radiation chemistry of biopolymers as a part of our hydrogen research was not developed as thoroughly as of C-H polymers, due to much lower yields of hydrogen. Hydrogen released from C, H, O, N, S polymers does not appear as the dangerous  $H_2$ , but as water, ammonia, or other compounds which can have unpleasant smell but do not present the danger of fire or explosion.

## Discussion

Our investigations of radiation yields of hydrogen release from irradiated polymers have shown important regularities. In general, the detachment of  $H_2$  is an

irreversible reaction, a substantial element of definite degradation, positive from the point of view of desintegration of waste. Another fact, also advantageous from the point of view of repository chemistry, is the presence of additives in commercial polymers present in the waste. All known additives, according to our investigations, do cause diminished production of hydrogen.

Every organic compound degrades under ionizing radiation, releasing hydrogen. The phenomenon of decomposition of this kind is not known in conventional organic chemistry, including polymers. Radiation induced dehydrogenation can have their variants, e.g. in chlorine containing compounds (e.g. poly[vinyl chloride], PVC) the hydrogen is released rather as hydrogen chloride HCl. It does not present the danger of explosion or fire, but is highly corrosive and speeds up the decay of drums pressed into salt deposits.

Polymers containing nitrogen, from amines to proteins, release hydrogen as ammonia, because the radiation induced deamination reaction is energetically most probable. It is again non-interesting from the point of view of transportation safety. Pure hydrogen yields from such materials are low, e.g. from natural wool it is only 0.26/100 eV.

Radiation yield of hydrogen can be modified in wide limits, especially at starting doses of radiation. At that stage, the results of radiolysis are influenced by additives always present in real life polymers. From the point of view of the safety at WIPP site and at the transportation of the waste to it, one must answer the question if and how the radiation yield of hydrogen could reach dangerous values. All the experiments on the radiation yield of hydrogen are directed to answer this important question, that is whether a chemical chain reaction is possible, i.e. if a G value of  $H_2$  higher than three effects per 100 eV is possible. That could generate concern about safety; however, nothing like this has been observed for the decades of history of radiation chemistry of hydrogen generating systems, mainly polymers.

Production of hydrogen in organic waste, in polymers in particular, although very important, represents only a fragment of the total radiolysis, always complex. Dehydrogenation is closely related to formation of double bonds, sometimes in a cumulated form, which are responsible for specific characteristics of the material, change of color including. Our method of optical investigation, diffuse reflected light spectrophotometry (DRS) [10] allows to estimate the quality and quantity of other than hydrogen products of radiolysis, enabling formulation of the total balance of products. Unsaturated sites occurring in the consequence of dehydrogenation are related to chain oxidation reactions, which can run to the point of exhaustion of oxygen in a closed system. These reactions do not present any danger, but are responsible for the decay of the organic, in particular polymeric material in the waste.

Practically all parts of radiation chemistry are involved in the problems of management of radioactive waste. Especially radiation chemistry of polymers must be considered. Polymers that are most likely to produce hydrogen (polyethylene, polypropylene, rubber-like

elastomers) contaminated with  $\alpha$ -emitters have to be investigated for  $G_{H_2}$ . One can decide after the investigation if the transportation, during which accumulation of hydrogen occurs, is safe.

Diagrams of radiation yield of hydrogen show a particular role of additives to polymers appearing in the waste. For the purpose of waste management, the highest possible yields are to be considered. Here are examples: polyethylene of different sources in the USA was investigated: the G value in 7 different products, as  $G_{H_2}$  was in the range from 3.96 to 4.68. That is the highest observed level of hydrogen which should be taken in estimates of safety of the transportation of drums to WIPP. There are no indications of chain decomposition of that polyolefin. The next group of similar yields of hydrogen are polypropylene products. Their virgin form, without additives, as obtained from polymerization line, shows hydrogen with the yield almost exactly like in the case of polyethylene, i.e. 3.9. That kind of polypropylene cannot appear in such a form in the waste. In a typical composition with additives, which contain aromatic compounds, radiation yield is already down to 2.46. Mixtures with increasing amounts of aromatics, e.g. with polystyrene, lower the hydrogen yield rapidly (to 1.96 with 10% of polystyrene, respectively to 1.55 at 25%, 1.08 at 50% and to 0.61 at 75%). Polystyrene, which can occur in different varieties in the waste is most resistant to ionizing radiation (typically, the yield of hydrogen is 0.03).

Polyethylene occurring as the so called Parafilm, widely used in chemical laboratories and present in the waste, yields hydrogen with  $G_{H_2} = 3.24$ .

Rubbers, widely found in the waste, are producing hydrogen with lower yields than polyolefins. The high technology rubber, hydrogenated nitrile butadiene rubber has been carefully investigated, as common component of the contaminated waste. The typical yields were  $1.17 \div 1.33$ , which do not present danger of explosion. This yield is worth mentioning because almost fully hydrogenated rubber was suspected as the source of radiation generated hydrogen. Nothing like this was observed, probably due to specific cross-linking reactions by entangling which reduce by half the yield of hydrogen produced in the case of olefins. The low danger of increased hydrogen production resembles early fears, 50 years ago, in nuclear reactor technology, when polyethylene insulations of electric cables were suspected of generating explosive mixtures. At that time, the radiation induced cross-linking was not known and total decomposition of polyethylene rather was expected.

## Conclusions

The most important conclusions were the yields of molecular hydrogen, much lower than assumed, generated by most hydrogen bearing polymers. No chemical chain reaction was found, which could increase hydrogen yield above  $G_{H_2} = 5$  per 100 eV of absorbed energy.

Our investigations have answered the query how much alpha activity can be loaded into every drum, producing still safe amounts of hydrogen, which is able to escape by vents. The main danger is a possibility of

explosion during the transportation to the WIPP centre from many distant places in the USA.

Proper use of this experimental approach to the questions of danger connected with radiolytic products of waste management and storage can mean substantial savings. For instance, the drum containing waste can be considered of too high activity of plutonium and before storage it has to be repacked at the expense of tens of thousand of USD. Our investigations have shown the upper limits of permissible activity, producing hydrogen from most dangerous plastics. These data show that the activity inside the drums can be left much higher than the earlier accepted value, thus avoiding repackage and cutting high additional costs.

All reported investigations have been performed under rigorous conditions of Quality Assurance (QA), as demanded by proper basic research and/or commercial radiation processing, controlled by the ASTM/ISO standards and traced to NIST samples.

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