



Hydration effect on ion exchange resin irradiated by swift heavy ions and gamma rays



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HIGHLIGHTS

- In ion exchange resins submitted to ionizing radiation, hydrogen production evolves as function of water content and form.
- A linear energy transfer effect on radiolytic hydrogen production is revealed in cationic and anionic exchange resins.
- Radiolytic degradation mechanisms of cationic and anionic exchange resins are proposed

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ABSTRACT

Gamma radiolysis of ion exchange resins (IER) is widely studied since the sixties, as a function of different parameters (resin type, dose, atmosphere, water content ...). However, to our knowledge, there are very few data concerning hydrogen emission from anionic and cationic resins irradiated at high Linear Energy Transfers (LET). In the present work, we focus on the influence of hydration on hydrogen emission, in anionic and cationic resins irradiated under inert atmosphere using Swift Heavy Ions (SHI) and gamma irradiations. The radiation chemical yield of molecular hydrogen is nonlinear with water content for both resins. The molecular hydrogen production depends first on the water form in IER (free or linked) and second on the solubility of degradation products. Three steps have been observed: at lower water content where $G(H_2)$ is stable, at 50%, $G(H_2)$ increases due to reactions between water radiolytic species and the resin functional groups and at high water content, $G(H_2)$ decreases probably due to its accumulation in water and its consumption by hydroxyl radicals in the supernatant.

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1. Introduction

Ion exchange resins (IERS) with polystyrene divinylbenzene matrix are widely used in nuclear industry for purification processes making them important constituents of long lived and intermediate level waste packages; due to their contamination in actinide mostly in plutonium [1,2]. Therefore, IER are subjected to auto-irradiation and the absorbed doses could reach several MGy during the repository or the storage periods, depending on the radioelement. Therefore within the context of nuclear waste

recovery, the radiolytic degradation of IERS has to be investigated and, more particularly, the influence of water on this degradation needs to be understood, since IER are moist materials and water can influence the radiolytic degradation. In this work, we focused on swift heavy ions irradiation and the effect of water during irradiation on commercial macroporous resins used for nuclear reprocessing which are cationic resins (IRN 77) and anionic resins (IRN 78).

The most common resins used in nuclear industry are polystyrene divinylbenzene resins functionalized either with sulfonic or quaternary ammonium groups, for cationic and anionic resins, respectively, subject of this study. As reported in the literature, gamma irradiation up to 1 MGy induces significantly damages on these IERS which lead to outgassing, molecular defects in the polymer chains and degradation products. So, for safe disposal, the integrity and the safety of waste packages should be proven. Therefore, investigating the effects of ionizing radiation on ion

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exchange resins functionalized with sulfonic or quaternary ammonium groups appears mandatory. Most of the studies performed on the moist resins (45–60% of water content), nuclear grade, have been made in the decade of 1960–1980. On the basis of literature data, radiolytic damage of ionic exchange resins can be assigned to two processes: first, the direct effect of ionizing radiations on IERs which leads to hydrogen emission along with the decomposition of functional groups [3–19]. The second process is associated to the reaction between water radiolysis products and degradation products from the resins. Highly reactive water species are formed (HO^\bullet , H_2O_2 , e^-_{aq} ...) and react with the resins leading to an additional degradation with hydrogen release. These processes are influenced by different factors as the resin type (anionic or cationic), degree of crosslinking, absorbed dose, atmosphere and the phenomena at the interface *i.e.* dissociation of water at the surface, steric effects, or energy transfers [20].

Using different techniques, authors show that gamma irradiation of resins with sulfonated groups leads to the formation of gas products (H_2 , CO_2 , SO_2 ...) depending on the atmosphere and the water content of the resins and aqueous products, mainly H_2SO_4 , in wet resins with the loss of total exchange capacity [3,9,10,14,21]. In the case of resins with quaternary ammonium functional groups, the darkness and the amine smell are observed as well as the loss of exchange capacity, the gas formation and the degradation of the polystyrene divinylbenzene matrix [3,8,13,22].

Main of the gas and radiolytic product formed in dry resins by irradiation is due to decomposition of functional groups. In the case of cationic resins functionalized by sulfonate, in dry environment, SO_2 gas is observed with hydrogen and CO_2 [3,19]. According to Pillay review, in dry environment (atmosphere is not described) the H^+ form resins are the less stable [19]. The main process described in literature is a radiolytic scission of the functional groups [3]. In presence of water (up to 50% of water content), $\text{SO}_{2\text{g}}$ is not observed due to its high solubility in water. To understand the effect of the water, most of the data available in literature describe the loss of exchange capacity for nuclear grade resins in different ionic forms (Na^+ , H^+ , Li^+ ...). The loss of exchange capacity is correlated to the release of sulfate, the increase of pH in leaching water and the decrosslinking of the resin [9,14,18,23]. According to Ichikawa et al., the decrease of the crosslinking rate, the loss of exchange capacity and the formation of SO_4^{2-} and H^+ are due to the formation of reducing species from the radiolysis of cationic resin in H^+ form and water [14]. In their work, Ichikawa et al., attributed the decomposition of the resin to the hydrogen atom from water radiolysis or by the resin itself [14]. But, Clay et al. suggested, for a resins in Na^+ form, that hydroxyl radicals are involved in the cleavage of SO_3Na^+ . In fact, by using scavengers, methanol and ethanol (hydroxyl scavenger), the authors showed a decrease of sulfate ions production and no significant change using perchloric acid (electron atom scavenger). They deduced that hydroxyl radicals are responsible for indirect radiolytic capacity loss and determined that G-value of SO_4^{2-} by direct radiolysis is about 0.28 molecules/100 eV [12].

In this paper, the radiolytic decomposition of polystyrene divinylbenzene functionalized by quaternary ammonium in OH^- forms is also investigated. In the same way, stability of the resins at different humidity content is determined by exchange capacity measurements, radiolytic product release in the aqueous phase and some data concerned gas measurements. In 1963, Hall et al., showed in their studies that irradiation of slurries anionic resins in OH^- form lead to the formation of aqueous species such as trimethylamine (TAM_{aq}), dimethylamine (DMA_{aq}), methylamine (MMA_{aq}) and ammonium ($\text{NH}_4^+_{\text{aq}}$). In this work, the authors described the formation of each specie by direct decomposition of the radiolytic product of functional groups in presence of oxygen

and water [7]. In 1966, Ahmed et al., using a series of scavenger on anionic resins in sulfate forms and chloride forms demonstrated that the deamination process occurs by direct and indirect radiolysis [8]. In fact in this work it appears that deamination for slurries resins in chlorine forms is due to the hydrated electron formed by water radiolysis [8]. Recently, gas investigation on anionic resins in different ionic forms was investigated [22,24]. Baidak et al., investigated the effect of water in hydrogen formation for anionic resins in hydroxyl, chloride and nitrate forms [24]. They demonstrated that the increase of the radiolytic yield of hydrogen with water is mainly due to the solvated electron [24]. Besides hydrogen formation, Traboulsi et al. investigated the gas and aqueous radiolytic products of anionic resins in OH^- form in presence of air and argon with and without liquid water [22]. In this work, the authors demonstrated that radiolytic degradation of wet anionic resins (around 50% of water content) leads to the formation of trimethylamine in gaseous form and hydrogen. In presence of liquid water, aqueous TMA was detected and associated to the formation of methylamine and ammonium ions in aqueous forms. An increase of hydrogen gas was observed and according to the authors, is mainly due to the degradation of the ammonium functional groups and the radiolysis products.

Literature is well furnished about the gamma radiolysis of cationic and anionic resins with polystyrene backbone. But in this work, we are interested in the effect of heavy ions in different humidity range. In fact, heavy ions allow us to simulate the effect of alpha particles on organic compound.

As we known, there are few experiments concerning alpha irradiation of IERs. Marsh and Pillay have compiled several studies performed on anionic and cationic IERs with in situ alpha particles [25]. However, in Marsh and Pillay review, no information is given on the molecular hydrogen yield or on the effect of water content in the behavior of the IERs under irradiation. But it is well known that water radiolysis depends of the linear energy transfer (LET). In fact, at low LET, the literature reported a value of $0.41 \cdot 10^{-7} \text{ mol/J}$ of hydrogen yield to $1.63 \cdot 10^{-7} \text{ mol/J}$ at high LET. Only a recent study by Baidak et al. deals with the effect of water content during irradiation by alpha particles of anionic resins [24]. Unlike gamma irradiations, few detailed studies exist on the effect of alpha particles on either dry or hydrated IERs.

In this study, new insights are provided on the evolution of the molecular hydrogen radiolytic yield as a function of the water content in cationic and anionic resins, H^+ and OH^- forms respectively. The main objectives are to understand how the different water forms present in resin affect the general radiolytic mechanism and how this mechanism is modified by the high density of excitation induced by high LET irradiations. In this study, instead of irradiating the IERs with alpha particles, they are irradiated with ^{36}Ar (95 MeV/A) ions, giving a LET very close to the one induced by actinides alpha particles at the Bragg peak. With the purpose of simulating actinide-emitted α particles, what we consider is the He ion LET at the Bragg peak. The use of the He LET at Bragg peak is justified by the following point: due to their weaker penetration range (38 μm for cationic IER and 35 μm for anionic resins), the LET of particles of 5 MeV significantly varies along the He ion path from $0.86 \text{ MeV mg}^{-1} \text{ cm}^2$ at the entrance to $2.2 \text{ MeV mg}^{-1} \text{ cm}^2$ at the Bragg peak for cationic resins and $0.93 \text{ MeV mg}^{-1} \text{ cm}^2$ to $2.4 \text{ MeV mg}^{-1} \text{ cm}^2$ for anionic resins. Using Ar beams with an almost constant LET value, close to the LET value at the Bragg peak for He ion, enables a confident simulation of the effect of actinide-emitted α particles with accelerated ion beams [26].

This was achieved through the quantification of molecular hydrogen, amines and sulfates in a sulfonic cationic and quaternary ammonium anionic DVB-crosslinked polystyrene IERs, with different water contents, irradiated under inert atmosphere.

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