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Gamma radiation effect on gas production in anion exchange resins

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ABSTRACT

Radiation-induced decomposition of Amberlite IRA400 anion exchange resin in hydroxide form by gamma radiolysis has been studied at various doses in different atmospheres (anaerobic, anaerobic with liquid water, and aerobic). The effect of these parameters on the degradation of ion exchange resins is rarely investigated in the literature. We focused on the radiolysis gases produced by resin degradation. When the resin was irradiated under anaerobic conditions with liquid water, the liquid phase over the resin was also analyzed to identify any possible water-soluble products released by degradation of the resin. The main products released are trimethylamine (TMA), molecular hydrogen (H_{2g}) and carbon dioxide (CO_{2g}). TMA and H_{2g} are produced in all the irradiation atmospheres. However, TMA was in gaseous form under anaerobic and aerobic conditions and in aqueous form in presence of liquid water. In the latter conditions, TMA_{aq} was associated with aqueous dimethylamine (DMA_{aq}), monomethylamine (MMA_{aq}) and ammonia ($NH^{+}_{4\,aq}$). CO_{2g} is formed in the presence of oxygen due to oxidation of organic compounds present in the system, in particular the degradation products such as TMA_{g}.

1. Introduction

Ion exchange resins are widely used in purification processes in the nuclear industry. After use, these resins are considered and managed as low- and intermediate-level nuclear wastes. During interim storage and after disposal, ion exchange resins are subjected to ionizing irradiation by radionuclides trapped in their structure or stored near-by, which causes their decomposition and modifies their chemical structure. In these conditions, the dose rates are expected to reach 100 Gy/h. The range of total absorbed dose varies from 5 MGy to 40 MGy for duration between 20 and 40 years. In use and especially in subsequent storage the resins may be exposed to gamma irradiation resulting in decomposition and modifying their chemical structure.

As reported in the literature [1–4], most gamma-induced decomposition of ion exchange materials is related to matrix aging, leading to the production and possible release of gases and other undesirable degradation products. The resins most widely used by the nuclear industry are nuclear grade commercial materials, constituted by sulfonic (cation resin) and trimethylammonium (anion resin) functional groups fixed on a polystyrene–divinylbenzene backbone, or a mixture of the two (mixed bed ion exchange resin). Most studies of ion exchange resins concerned radiation-induced modifications in their physical and chemical properties such as their total exchange capacity, pH and moisture content [2,5–7]. Changes in their chemical structure has been reported and were explained by radiolytic scissions of the functional groups taking place at different bond levels and by the deterioration of the resin matrix (cross-linking, oxidation, etc.). Few studies have focused on the gases or other species generated by gamma irradiation of anion exchange resins [1,2,4,8,9]. The comparison of the reported results was difficult because the studied resins were in various ionic forms and were irradiated under different conditions (doses, moisture content, presence of oxygen, etc.). For example, the dose rates used in these studies vary between few Gy/h to several kGy/h and doses between 5 kGy and up to 25 MGy.

Pillay [6] tried to summarize key findings of the experimental studies into a set of qualitative and semi-quantitative data concerning the radiation stability of ion exchange materials.

Concerning anion exchange resins with quaternary ammonium groups, earlier studies reported that these materials exhibit low gamma radiation stability even at low doses. Degradation began at 0.1 MGy by splitting off the functional groups from the organic backbone, according to a deamination process, generating radiolysis gases (trimethylamine and molecular hydrogen as major gases) and releasing water-soluble products (such as amines) when the resin was irradiated in the presence of water

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[4,6,9,10,12]. Swyler et al. (1983) [2] showed that gamma irradiation of these resins in OH^- and Cl^- form produced molecular hydrogen with relatively high radiation yields and trimethylamine gas in lower proportions. In these studies, carbon dioxide (CO_{2g}), carbon oxide (CO_g) and methane (CH_{4g}) formation was also observed in lower proportions. The significant production of molecular hydrogen gas could be explained by radiolysis of hydration water, degradation of quaternary ammonium groups and radiolysis products such as amines produced in gaseous or aqueous phases. Recent work by Baidak and Laverne (2010) [4] reported that the reactivity of an anion exchange resin depends on its ionic form (NO_3^-, Cl^-, etc.) and the percentage of water loading in the material. Enhanced H_{2g} production was observed with high water content and the radiolytic decomposition of the compounds released during irradiation (at a dose rate of 3.8 kGy/h) in the aqueous phase largely contributed to the generation of molecular hydrogen. Hall and Streat [9] revealed that primary, secondary and tertiary amines and ammonia were the main aqueous decomposition products released when these resins were irradiated in the presence of water. Other studies [13,14] also demonstrated that amine compounds γ-irradiated at room temperature in aqueous and gaseous phase, particularly trimethylamine, produced molecular hydrogen with yields depending on dose, pressure, hydrated electron and free radical scavengers. In the presence of oxygen and water in the irradiation environment, oxygenated compounds could be formed by oxidation of the resin during irradiation, which could accelerate the resin decomposition and consequently enhance gas generation [5,15]. Many attempts to explain such radiation damage by proposing degradation mechanisms have been reported [2,5,9,11]. It has been demonstrated that the deamination process by direct effect of radiation results from interaction of the resin with the e^-_{solv} resulting from the water radiolysis [5,9,11,16]. The mechanism of this reaction was studied in detail by Kabi and Clay [14] and Bobrowski [17] in the gamma radiolysis of aqueous solutions of arylalkylamines and benzyltrialkylammonium. They reported that the deamination process is very rapid and is controlled by e^-_{solv} diffusion. The backbone of these anion exchange resins, based on styrenedivinylbenzene copolymers, is known to be very stable under irradiation because of aromatic ring resonance. Very high doses are required to produce significant change in its chemical structure [18].

In most of the previous studies realized on this kind of resin, the experimental conditions, especially the irradiation conditions, (dose rate and dose), were not always detailed.

To complete the anion exchange resins investigations reported in the literature, we have studied the gamma irradiation effects on the radiolysis gases produced by Amberlite IRA400 in hydroxide form. This resin is constituted of a polystyrene–divinylbenzene backbone with trimethylammonium functionality ($-CH_2N^+(CH_3)_3 \cdots OH^-$). Different irradiation conditions were investigated to determine the influence of liquid water and oxygen and relatively high doses (few MGy) on the evolution of gases and water-soluble products. In recent work [4], radiolysis gases were analyzed by gas chromatography coupled with mass spectrometry (GC–MS), but with this method interference may occur between some radiolysis gases such as hydrogen and nitrogen, which prevent identification and quantification of these latter. A mass spectrometry (MS) technique [19–21] was therefore used in our work to perform a full quantitative scan of released gaseous products. For irradiation under anaerobic conditions with liquid water, ion chromatography (IC) was employed for quantitative analysis of the water-soluble products such as amines and ammonia in the liquid over the irradiated resins. A kinetic study of the release of soluble decomposition products after resin radiolysis and spectroscopic analysis of the solid part of the irradiated resins were also conducted in parallel but will not be discussed in this paper [10].

2. Materials and methods

2.1. Resin

The resin used in this work is a strong base anion exchange resin, Amberlite IRA400 in hydroxide form (AmbOH), manufactured by Rohm and Haas Company (Philadelphia PA, USA). Its macroporous structure is formed by quaternary ammonium functional groups ($-CH_2N^+(CH_3)_3$) fixed in meta or para position on a polystyrene backbone cross-linked with 6.0% of divinylbenzene. This anion resin contains around 53% of hydrated water. Its chemical structure is shown in Fig. 1. AmbOH is used industrially in powder form. Supplied in bead form, it was then cryoground to powder with a mean particle size of 0.8 µm. Cryogrinding was carried out several times by a SPEX model device and it was used to avoid prior heat degradation. Each time, 2 g of resin were cryoground using the following number of cycles: 4; precool time: 2 min; cool time: 1 min; run time: 2 min; frequency: 11 chocks per second.

2.2. Gamma irradiation of AmbOH

2.2.1. Sample packaging

Three grams of resin were placed in a glass tube and conditioned under the appropriate irradiation environment. For the irradiations under anaerobic conditions with liquid water, 7 mL of liquid water was added to cover the resin. After conditioning, the irradiation tubes were emptied of atmospheric air by vacuum aspiration, then backfilled with the appropriate gas: argon for anaerobic conditions with and without liquid water and pure oxygen for aerobic conditions. The vacuum pressure was limited to 15–17 mbar to maintain the sample moisture content. This operation was repeated three times to eliminate the residual air before sealing the tube at slightly below atmospheric pressure. The sealing pressure under anaerobic conditions was limited to 800 mbar whereas in the presence of oxygen, it was around 1000 mbar to obtain the highest possible concentration of oxygen in order to ensure its presence throughout the irradiation period.

2.2.2. Irradiator and doses

Gamma irradiation was performed below 37 °C using a cobalt-60 irradiation source with a dose rate of around 3.5 kGy/h at different doses between 0.1 and 4 MGy. For the aerobic conditions, the maximum absorbed dose in this work was 3 MGy in order to ensure the presence of oxygen throughout the irradiation period. At this dose, gas analysis showed that 90% of the oxygen initially present in the sealed tubes was consumed.

The energy absorbed in the sample itself was measured by dosimeters with a known response to irradiation, proportional to the exposure time. These dosimeters based on Perspex films [23] (routine measurements with an error of 4% and a confidence

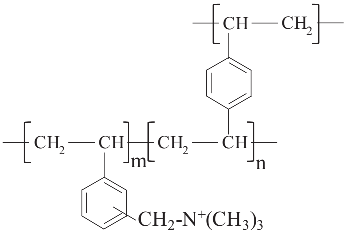

Fig. 1. Chemical structure of Amberlite IRA400 anion exchange resin (hydroxide form).