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The radiolysis of poly(4-vinylpyridine) quaternary salt ion exchange resins

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Abstract

The radiation chemical yields of gaseous products, especially molecular hydrogen (H_2), have been determined in the radiolysis of different poly(4-vinylpyridine) quaternary salt ion exchange resins with up to about 30 wt% of absorbed water. Irradiations were performed with 5 MeV ^{4}He ions to simulate α-particle radiolysis and with γ-rays for comparison. The resins were quaternary salts of chloride and nitrate that are commonly used as matrixes in anion exchange and in plutonium recovery processes. An increase in H_2 yields with increasing water loading was observed for both types of ionizing radiation in all of the resins. The yield of H_2 for the nitrate-form was lower than that for the chloride and the yield of H_2 was lower when the pyridinium nitrogen atom is coordinated to a methyl group rather than to atomic hydrogen. Spectroscopic studies included UV/vis, IR, and Raman and suggested that all the resins exhibit a high radiolytic stability.

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1. Introduction

Ion exchange resins used in the reprocessing of radioactive materials are a vital link in the nuclear fuel cycle [1]. Even though some resins have been engineered for their selectivity and efficiency, their characteristics will constantly be changing as they undergo radiolysis in the separation of radioactive materials. Poly(4-vinylpyridine) quaternary salts under various forms have been used in nitric acid plutonium recovery processes [2]. Plutonium in the positive four charge state is stable in nitric acid, forming the divalent hexanitrate complex $Pu(NO_3)_6^{2-}$ [3–5]. The plutonium can be removed selectively from the nitric acid by Reillex™ HPQ and Reillex™ 402 anion-exchange resins (Reillex™ HPQ and Reillex™ 402 are registered trademarks of Reilley Industries, Inc.), which are based on poly(4-vinylpyridine) quaternary salts [6]. Reillex™ HPQ is a poly(4-vinylpyridine) resin cross-linked with divinyl benzene, which consists of a 1-methylpyridinium cation and chloride, Cl^-, or nitrate, NO_3^-, counterions. Reillex™ 402 is similar, except that a hydrogen atom is attached to the nitrogen. Fig. 1 shows the structures of the series of Reillex™ resins employed here. These resins are packed into a column through which the nitric acid solution of plutonium is flowed. The plutonium hexanitrate is retained by complexing with two positively charged nitrogen sites of the resin [2]. Radiolysis of the resin and associated water by emitted α-particles can lead to concerns in the management of the exchange columns. The production of molecular hydrogen, H_2, is especially important because its

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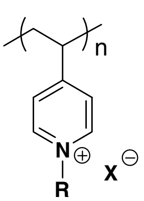

	R	X
HPQ	CH_3	Cl NO_3
402	H	Cl NO_3

Fig. 1. Structures of the pyridinium salts.

flammability and explosion potential can cause serious engineering and maintenance problems [7–10]. Molecular oxygen, O_2, formation from the water or nitrate radiolysis can exasperate the problem considerably.

The radiolysis of organic polymer materials leads to the production of gases, especially H_2, depending on the nature of polymers or the type of ionizing radiation [11–17]. The production of H_2 can be explained from simple radical chemistry (e.g., H atom–H atom combination, H atom abstraction, and disproportionation) following C–H bond breakage due to the energy deposited by the passage of ionizing radiation or from the unimolecular decomposition of excited singlet states [13,16]. In general, H_2 yields are found to increase with increasing LET (linear energy transfer $= -\mathrm{d}E/\mathrm{d}x$) of the incident radiation because of changes in the track geometry as defined by the local region where the energy is deposited. For instance, the yield of H_2 is fourfold greater with 5 MeV ^{4}He ions than with γ-rays for both liquid benzene and polystyrene [13]. Reillex™ resins carry a repeated unit of a pyridine analogue and the radiation chemistry is expected to correlate closely with the radiolysis of liquid pyridine, which also exhibits an increase in the yield of H_2 with increasing LET [13,18–20].

Since separation processes include an aqueous phase, the radiolytic decay of water must also be considered. The hydrated electron, e^-_{aq}, and its precursors are major contributors to the production of H_2 in the radiolysis of liquid water [21–25]. H atoms are also expected to play an important role, especially in acidic solutions [26]. The yield of H_2 in water is 0.45 molecule/100 eV with γ-rays and a strong LET dependence is observed [21,26]. Water radiolysis may be different when it is present in the adsorbed state on the resin surface than in the bulk, but water is still expected to contribute to the overall decomposition mechanism. Experimental studies on the radiolytic decomposition of these systems may lead to models for predicting radiation damage allowing for the better management of nuclear waste materials and reprocessing systems.

In this work, the radiation chemical yields of gaseous products, especially H_2, have been determined in the radiolysis of poly(4-vinylpyridine) and various Reillex™ resins with different amounts of adsorbed water. Irradiations were performed with 5 MeV ^{4}He ions to simulate α-particle radiolysis and with γ-rays for comparison. Optical analysis included obtaining IR, Raman, and UV/vis spectra of the irradiated resins to determine bulk degradation and to identify product formation.

2. Experimental section

2.1. Materials

Poly(4-vinylpyridine) (P4VP), poly(4-vinylpyridine) methylammonium chloride (Reillex™ HPQ), and poly(4-vinylpyridine) ammonium chloride (Reillex™ 402) resins were purchased from Aldrich and used without further purification. (Reillex™ HPQ and Reillex™ 402 are registered trademarks of Reilley Industries, Inc.) The latter two compounds are referred to in this work as Reillex™ HPQ and Reillex™ 402, respectively. The manufacturing lots were 04719PC, 04411PC, and 08227PI, respectively. Reillex™ HPQ chloride-form, lot no. 80302MA, was obtained directly from Reilley Industries and is referred to in this work as LANL HPQ. These resins are in the form of beads with diameters of about 100–1000 μm.

2.2. Anion exchange

Reillex™ resins in the chloride-form were anion exchanged using aluminum nitrate (Aldrich), $Al(NO_3)_3$, to give the nitrate-form. Two slightly different methods were used at the two laboratories to check for nitrating effects. At Notre Dame, the chloride-form resin from Aldrich (5.0 g) immersed in high purity water was transferred to a column of Pyrex ($\phi \sim 1$ cm, $L \sim 50$ cm) containing a plug of glass wool to support the resin bed. An aqueous solution 100 mL of 0.1 M $Al(NO_3)_3$ was allowed to flow through the column at a rate of 1 mL/min. The treatment was repeated three times, a total of 300 mL solution, until the column effluent showed no traces of chloride ion using an ion chromatography (Dionex Ion Chromatograph). The resin was then rinsed with water, filtered, and dried under vacuum. The apparatus is more of a commercial scale at Los Alamos where the Reillex™ HPQ resin was placed in a Pyrex column and covered with 0.6 M $Al(NO_3)_3$ for 24 h. The resin was then rinsed twice with 0.2 M HNO_3 followed by four rinses of deionized water and transferred using a peristaltic pump for storage under water in a carboy. Part of the resin was removed and dried under vacuum. A portion of the LANL HPQ nitrate-form was further heat treated to give LANL HPQ LTE according to a procedure reported by Crooks et al. [27]. This latter treatment is meant to remove any residual ethylbenzene pendant groups from the polystyrene copolymer.

2.3. Water loading

Prior to radiolysis, the resins were dried under vacuum, weighed, and placed in constant humidity chambers at room temperature. Three different relative humidity chambers were used. One chamber with drierite (calcium sulfate) was used to simulate “dry” conditions. Another chamber contained $Mg(NO_3)_2$ salt slush to obtain a relative humidity of 53% [28,29]. The final chamber contained water alone to obtain a relative humidity of about 95%. The resins were