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Abstract

As a continuation of previous work (Ref. [1]), an isotope generator column based on the ^{210}Pb decay chain has been made to produce highly radiopure ^{210}Po. Two replicate studies were performed on AG 50Wx8 columns with an average yield of 90.4 ± 1.9%. ^{210}Pb breakthrough was seen at the 6 month elution for both generators.

Keywords

Polonium, lead, isotope generator, cation exchange chromatography

Introduction

In recent years there has been increased interest in the chemical and physical behavior of ^{210}Po due to problems it poses in the operation of advanced lead-bismuth eutectic (LBE) cooled nuclear reactors as well as human radiation exposure from naturally occurring ^{210}Po [2] [3].

In LBE reactors, ^{210}Po is produced by neutron capture on ^{209}Bi producing ^{210}Bi ($t_{½}$ = 5.01 d), which decays to ^{210}Po ($t_{½}$ = 138.38 d) [4]. Polonium is highly volatile and readily evaporates from the LBE causing significant surface contamination of the primary cooling loop and collecting as a gas over the LBE [2, 5]. Since ^{210}Po is extremely toxic, this contamination poses a serious risk to worker health if it was to be released during maintenance or a coolant leakage emergency [4, 2].

Polonium contamination and potential for release is widely regarded as one of the major hurdles to overcome for the deployment of LBE reactors, and, therefore, understanding the behavior of ^{210}Po in LBE systems and the development of mitigation strategies for ^{210}Po contamination is an active field of research [5, 6, 7, 2, 8]. This is also a concern for other lead-alloy cooled reactors because bismuth is a common impurity in lead and is also produced by nuclear reactions on lead, which leads to ^{210}Po production [9].

^{210}Po is also of interest for public health and environmental reasons since it is a naturally occurring isotope from the ^{238}U decay chain and humans are regularly exposed to it in the environment [3]. The combined dose from ^{210}Po and ^{210}Pb account for 83% of the effective annual dose received by humans and studies have shown that ^{210}Po in tobacco may be a contributing cause to lung cancer [3] [10]. Therefore, the behavior and accumulation of ^{210}Po in the environment is widely studied to determine public health implications [3].

While ^{210}Po is often produced directly in LBE samples for reactor studies [5, 6, 7, 2, 8] or naturally occurring trace ^{210}Po is studied directly in environmental samples [11] [12], in many studies, both for reactor and environmental purposes, it is produced in accelerators with the irradiation of bismuth targets which are processed before use in experiments [4, 9, 13, 14]. However, there are many disadvantages to accelerator production of ^{210}Po: it is expensive and time-consuming, especially since the targets often require long cooling periods after the irradiation, and the separation of tracer amounts of ^{210}Po from the bulk bismuth target can be difficult [13, 4].

An alternative method of low level ^{210}Po production is an isotope generator that could produce highly pure ^{210}Po from commercially available ^{210}Pb at a fraction of the cost and time required for accelerator production. A cation exchange resin was chosen for the isotope generator because cation resins tend to be more radiation damage resistant than anion exchange resins [15]. Based on the results from previous work (Ref. [1]), AG 50Wx8, a strong cationic resin, is suitable for this purpose: ^{210}Pb and ^{210}Bi are absorbed on the resin with 0.2 M HCl and ^{210}Po is removed by elution with 0.2 M HCl [1].

When a ^{210}Pb sample is loaded on the column, it is in secular equilibrium with its daughter products and, therefore, all isotopes have the same activity. Once the equilibrium is broken by eluting the daughter products, they grow in according to the Batemann equations [16]. As shown in Fig. 1, it takes 2.3 years for ^{210}Po to re-establish equilibrium with ^{210}Pb and 53.5 days for ^{210}Bi. For the purposes of this experiment, the ^{210}Po is eluted every two months at which point it is at 23% of its equilibrium activity. The bismuth is not affected by the polonium elution and remains in equilibrium with the lead.

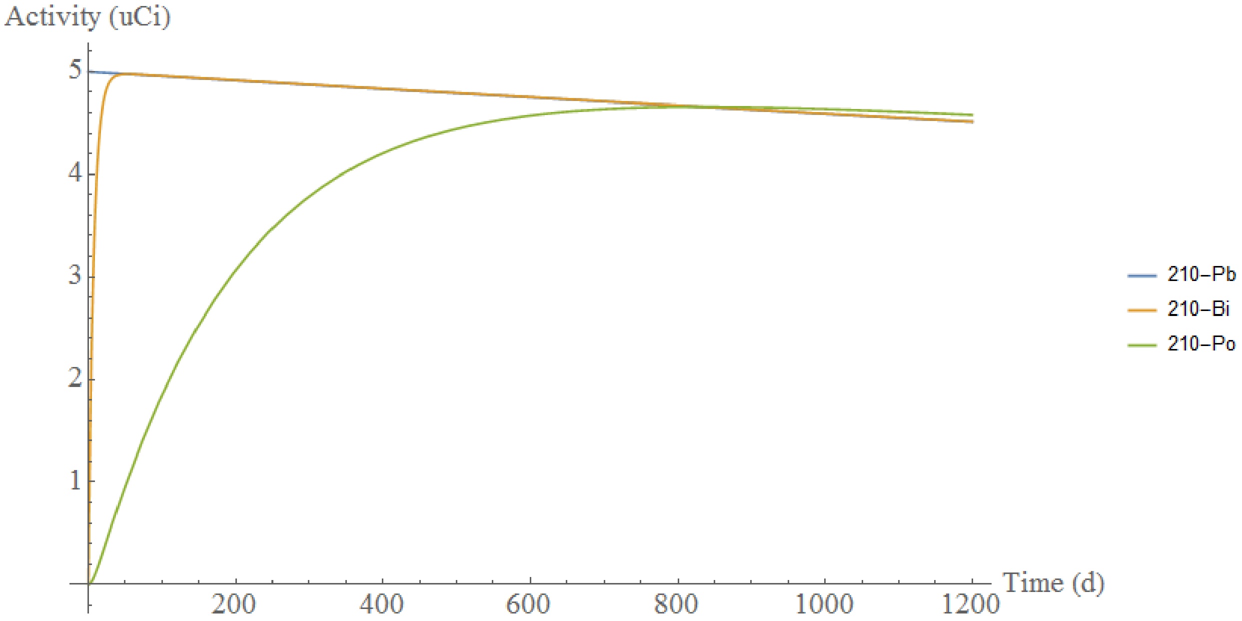


Fig. 1 Equilibrium behavior of ^{210}Pb decay daughters

Experimental

Two identical AG 50Wx8 columns (referred to as A and B) were prepared following the procedure in Ref. [1]. The ^{210}Pb was obtained from Eckert & Ziegler Isotope Products as $Pb(NO_3)_2$ in HNO_3. The concentration was 10 µCi/mL with 10 µg/mL of Pb carrier. The radionuclide purity was >99%. A stock solution was made from 1.5 mL of the ^{210}Pb nitrate solution. It was evaporated to dryness at 90 °C and brought up in 300 µL of 0.2 M HCl; this was repeated three times. The stock solution was then divided into three fractions of ~100 µL. Two of these were used as the load solutions for each of the columns while the third served as a standard. The standard was counted via gamma spectroscopy at the Nuclear Counting Facility at LLNL to determine the activity. The activities of ^{210}Po, ^{210}Bi and ^{210}Pb were determined from their highest intensity spectral lines: 803.10 keV (0.00121%) for ^{210}Po, 265.832 keV for ^{210}Bi and 46.539 keV (4.25%) for ^{210}Pb [17]. A high purity germanium (HPGe) gamma-ray spectrometer with an Ortec DSPEC multi-channel analyzer was used to measure the relative activity of the standard and load solutions. Maestro software (Ortec) was used to analyze the resultant spectra. All measurements were preformed relative to the standard using the same HPGe detector and in the same geometric configuration. The known activity of the standard was used to calculate the efficiency of the detector and the activities of the load solutions. The fractions were counted for ^{210}Po and ^{210}Bi in the same manner as the load solutions.

Column A was loaded with 5.00 ± 0.18 µCi ^{210}Pb in equilibrium with its daughter products and column B with 4.38 ± 0.15 µCi; both had a 100 µL load volume in 0.2 M HCl. The load solution was absorbed on the resin, then 0.5 mL 0.2 M HCl was added to the top of the column and it was capped. The columns were eluted once every two months until lead breakthrough was observed, which occurred at about 6 months (177 days) after loading. Two months were chosen as the elution period to ensure enough ^{210}Po would grow in between elutions to provide reasonable counting statistics. Based on the results of the previous experiment, 6 mL was determined to be a sufficient elution volume to collect the ^{210}Po, which was increased to 8 mL for the second and third elutions to determine if bismuth would bleed off the column. Fractions were collected in 1 mL aliquots. The polonium activity in the elution fractions was measured using the procedure given by Ref. [1] with a silicon barrier detector with an Alpha Analyst system (Canberra) and the spectra were analyzed using the software Genie 2000 (Canberra). After lead breakthrough was observed, the columns were stripped with 2 mL 0.2 M HCl and 4 mL 2 M HCl.

The lead fractions stripped from the columns were evaporated to dryness and it was observed that they contained a considerable amount of organic material from the resin. To clean these fractions for further studies, two 0.5 mL AG 50Wx8 columns were prepared and conditioned with 5 mL 0.2 M HCl. The stripped fractions from columns A and B were treated separately: each was dissolved in 4 mL 0.2 M HCl then loaded onto the prepared columns and rinsed with 2 mL of 0.2 mL HCl. The lead was then eluted with 3 mL of 2 M HCl. This was evaporated to dryness and reconstituted in 1 mL 0.2 M HCl for counting. The recovery from the cleaning procedure was 97.0 ± 0 .04% from column A and 97.4 ± 0.04% from column B. No daughter products were detected. Once cleaned, each sample was evaporated to dryness and reconstituted in 100 µL 0.2 M HCl.

Results

The elution curves for columns A and B are shown in Fig. 2. During the third elution, after 6 months of generator use, lead breakthrough was observed in all fractions of both columns A and B. In the first elution, the decay chain was in equilibrium so the total activity of ^{210}Po on the column was equal to the total activity of ^{210}Pb on the column. For later elutions, the ^{210}Po activity eluted is much lower because it is solely from in-growth after the previous elution, which is only 23% of the equilibrium activity. The yields from the elutions are shown in Table 1. The yields were found by comparing the activity eluted from the column to the activity on the column at the time of each elution as calculated by the Batemann equations and accounting for the yield from the previous elution.

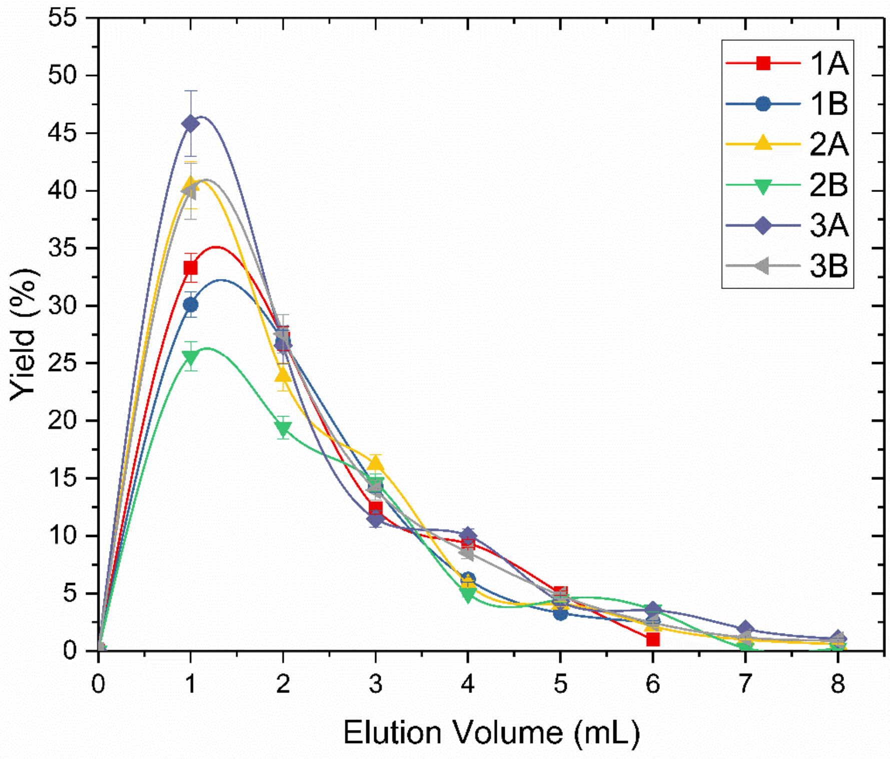


Fig. 2 Elution curves of replicate AG 50Wx8 isotope generators showing the first three elutions. Elutions are indicated by elution number and the column (A or B). Lines intended to guide the eye only. Errors presented are counting errors. Each elution was performed at two month intervals.

Table 1 Elution yields of AG50Wx8 isotope generators. Errors presented are counting errors.

Elution/ Column	Activity collected		Calculated activity on the column at the elution time		^{210}Po Yield	
	A (μCi)	Error (μCi)	A (μCi)	Error (μCi)	%	Error (%)
1A	4.39	0.02	4.98	0.18	88.2	3.2
1B	3.63	0.02	4.36	0.15	83.3	2.9
2A	1.560	0.008	1.66	0.08	94.1	4.8
2B	1.177	0.006	1.61	0.08	73.1	3.6
3A	1.585	0.008	1.51	0.09	104.7	6.5
3B	1.362	0.007	1.37	0.08	99.4	6.0

The radiopurity of the ^{210}Po fractions was confirmed by both α and γ spectroscopy; neither showed any detectable amount of ^{210}Pb or ^{210}Bi in the ^{210}Po fractions from the first two elutions. The minimum detectable activity (MDA) for all isotopes is of interest was calculated using the Currie formula [18], and was 0.083 cps for ^{210}Pb, 0.080 cps for ^{210}Bi and 0.023 cps for ^{210}Po. Furthermore, the ^{210}Po samples were counted twice, once immediately after elution and again two to three months later to confirm they were decaying with the half-life of ^{210}Po. This provided a secondary confirmation that the polonium fractions did not have bismuth contamination.

The lead breakthrough that was observed in elution three amounted to 0.04 ± 0.01% of the lead on column A and 0.07 ± 0.03% of the lead on column B. After the columns were stripped, the yield from column A was 89.3± 4.6% and the yield from column B was 79.9 ± 4.4%.

Discussion

The speciation of Po, Pb and Bi in this system is discussed in Ref. [1]. Previous work has shown that lead does not bleed off this column in 0.2 M HCl in normal conditions [1]. In addition, there was a significant amount of organic material eluted in the first fraction of each elution and when the columns were stripped. This is indicative of resin degradation over time, likely due to radiation damage. Since α radiation does more damage to the polymer matrix than the same dose of γ irradiation, the α particle emission from ^{210}Po (5.304 MeV) is suspected to be a major factor in the damage to the resin [15, 19].

Resins exposed to radiation, particularly α and γ radiation, show a decrease in strong acid capacity due to the sulfonic acid functional group splitting off from the polymer chain [15]. Radiation can also cause the formation of free radicals and radiolysis products that can also damage the resin [15]. This may lead to the lead breakthrough due to formation of neutral lead species that elute from the column.

Suspected mechanism of lead breakthrough

Dowex 50 is a strongly-acidic cation exchange resin with polymeric repeating units given by Figure 3 with a sulphite ion acting as the exchange media [20] [21].

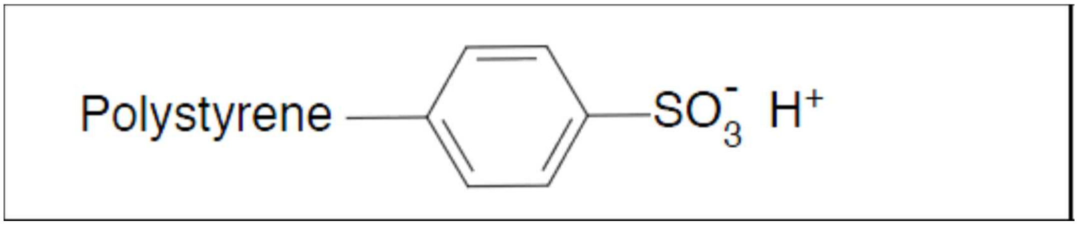
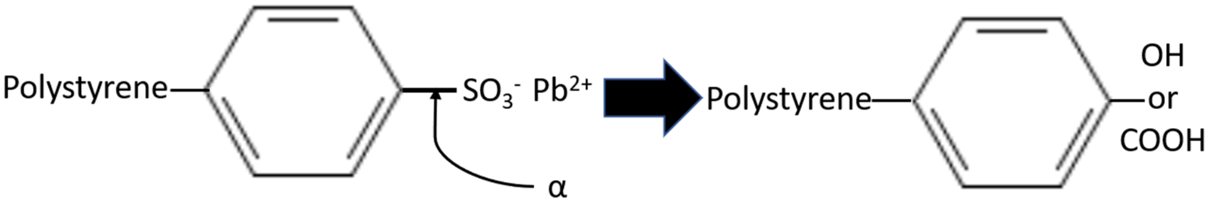


Fig. 3 Repeating unit of Dowex 50 [20] [21].

As mentioned previously, when radiolysis occurs one of the major decomposition pathways is the cleaving of the SO_3^- unit off the resin backbone [15] [22]. This leads to new functional groups on the resin backbone such as OH and COOH (Fig. 4).



Note: Cl or another resin unit to balance Pb charge

Note: may just be benzene

Fig. 4 Proposed degradation of Dowex 50 by alpha particle irradiation.

Lead(II) sulphite ($PbSO_3$) has some stability: it is the only naturally occurring sulphite mineral (Scotlandite) [23]. But it is easily oxidized and decomposed by acids and heat, which convert it into a mixture of sulfides, sulphates, and oxides [24]. The radiolysis caused by α-decay of ^{210}Po, a well-known heat source (1.1126 ng ^{210}Po/5 μCi), and the fact that this is occurring on an infinitesimally small area gives rise to the potential for these decomposition products of $PbSO_3$ to form as well as the potential for some of the Pb^{2+} to locate itself on undamaged resin lower down the column. The probable formation of $PbSO_3$ initially along with the stability of the $PbSO_4$, PbS (solid, molecular compound) and PbO (solid, molecular compound) can give rise to Pb^{2+} being unable to recombine with undamaged resin and a small amount bleeding off the resin as one of these Pb compounds.

Performance of higher crosslinked resins

AG 50Wx12 was also tested as an alternative resin for the generator because higher crosslinked resins tend to have greater chemical stability when exposed to radiation, which could extend the lifetime of the columns [15, 25]. However, preliminary data shows that while the elution behavior of ^{210}Po on AG 50Wx12 is similar to AG 50Wx8, the polonium peak is significantly broadened, and the yield is far lower, which makes this resin impractical for an isotope generator.

Comparison between isotope generator and accelerator production

Ref. [13] presents a method of ^{210}Po production via α particle irradiation of a ^{209}Bi target to produce 0.27 μCi of ^{210}Po in a one hour irradiation. After a seven day decay time, the target was processed and the ^{210}Po extracted with an 82.5 ± 4.5% total recovery [13]. The AG 50Wx8 ^{210}Pb/^{210}Po isotope generator described in this experiment is able to elute 1 μCi of ^{210}Po with an average yield of 90.4 ± 1.9% in 80 minutes once every two months. This is a significant improvement in time, activity and yield as compared to the accelerator method of production.

Conclusions

The AG 50Wx8 ^{210}Pb/^{210}Po isotope generator performs consistently over a period of about 4 months, eluting ^{210}Po at activities of 1 to 4 μCi with no detectable lead or bismuth. However, after four months lead breakthrough begins due to the radiation damage sustained by the resin. Therefore, for continual use the generator should be fully eluted every four months, the lead fraction cleaned and then loaded onto a new column. Due to the levels of activity produced, the isotope generator method of ^{210}Po production is particularly suited for studies of Po bonding or as an environmental tracer and the ^{210}Pb/^{210}Po isotope generator presents a compelling alternative for accelerator production as it can produce more activity with a better yield and is far less expensive and time consuming.

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