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PURIFICATION OF POLONIUM-210 USING PYROCHEMICAL EXTRACTION

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ABSTRACT

An efficient extraction process that does not utilize halides or organic solvents has been developed for the recovery and purification of ^{210}Po. Polonium-210, produced in bismuth metal by neutron irradiation, is extracted from molten bismuth metal into molten NaOH in an unique 3-compartment contactor under an inert atmosphere. At a temperature of 450±25°C, and at a NaOH/Bi weight ratio of 0.044, five successive 60-minute extractions remove >96% of the ^{210}Po.

Following phase separation and freezing, additional purification steps include dissolution of the solidified NaOH in HNO_3, recovery of ^{210}Po from this solution by MnO_2 carrier precipitation, dissolution of the precipitate by H_2O_2 in HNO_3, and, finally, electrodeposition of ^{210}Po onto platinum gauze.

INTRODUCTION

Polonium-210 is produced in bismuth by neutron irradiation according to the reaction

$$^{209}_{83}\mathrm{Bi} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{210}_{83}\mathrm{Bi} \xrightarrow[5.4\ \text{days}]{} {}^{210}_{84}\mathrm{Po}.$$

With a half-life of 0.38 years, ^{210}Po decays by emission of a 5.3 MeV alpha particle to stable ^{206}Pb. Polonium-210 is a valuable source of alpha radiation or of thermal energy for remote applications because of its high specific activity, high decay energy (144 W/g), and relatively low beta or gamma radiation. The concentration of ^{210}Po produced in a bismuth metal target depends on exposure time and reactor conditions, but is in the ppm range (15-20 ppm in the bismuth irradiated for the work being reported) because of the low neutron cross-section of ^{209}Bi.

Previous work on the recovery and purification of ^{210}Po from bismuth has involved:

1) Acid dissolution of the bismuth followed by spontaneous deposition of ^{210}Po onto unirradiated bismuth metal granules (1, 2). This is the process used at Mound Laboratory for large-scale recovery of ^{210}Po; repeated cycles were required for adequate concentration and purification.
2) Acid dissolution of bismuth followed by liquid-liquid solvent extraction for ^{210}Po concentration and electrodeposition for final recovery (3, 4).
3) Polonium-210 volatilization and vacuum distillation (5-8).

The processes involving dissolution of the bismuth suffer the disadvantage for large-scale applications that the bismuth cannot be directly refabricated into targets for return to the reactor. In the Mound process, the bismuth was dissolved in aqua regia, then the solution denitrated with formic acid prior to the succeeding spontaneous deposition of ^{210}Po.

The extraction of ^{210}Po from molten bismuth metal into molten NaOH was first reported by Barney (9). The concept was expanded, tested using kilogram amounts of irradiated bismuth, and proposed as a nonaqueous head-end process for polonium purification by Schulz, Schiefelbein, and Bruns (10, 11). Utilization of this pyrochemical extraction process in a unique contactor system, coupled with carrier precipitation and electrodeposition processes, for the purification of ^{210}Po is discussed in the following sections.

PROCESS DEVELOPMENT

Pyrochemical Extraction

The following processing conditions must be satisfied to successfully extract ^{210}Po from molten, irradiated bismuth metal with molten NaOH.

1. Oxygen must be excluded from the system to avoid oxidation of the polonium to the volatile oxide and to avoid formation of

bismuth oxide that would collect at the Bi/NaOH interface and disrupt transfer between phases.

2. The two phases must efficiently contact each other to establish equilibrium conditions between phases in a minimum time.
3. The molten bismuth must be contacted with a sufficient quantity of molten NaOH to effect the transfer of essentially all of the polonium from the bismuth phase. This can be accomplished by contacting both phases in a true counter-flow arrangement, or by contacting a batch of bismuth with several successive small batches of NaOH. The third alternative was used in the project being reported.

Equipment Description

The equipment used for the pyrochemical extraction is shown schematically in Figure 1 (12). The melter and contactor vessels were fabricated from Inconel 600 alloy pipe and plate for increased corrosion resistance. They were heated by high-temperature resistance heaters banded to the external surfaces. Vessel temperatures were monitored by thermocouples attached at the indicated locations. The extraction chamber was randomly filled with 6-mm long sections of 6-mm diameter Inconel 600 rod to increase contact efficiency. The packing was supported in place by a heavy perforated plate at the bottom of the extraction chamber. The three high-temperature transfer lines were electrically heated by heating cables, and the temperature was monitored by thermocouples. High-temperature stainless steel bellows valves were used for the three high-temperature transfer lines. A high-temperature silicone rubber gasket was used to seal the contactor lid in place. The gasket was replaced after each run. Other vessel, valves, and interconnecting tubing were fabricated from 304 or 316 stainless steel. The glovebox vacuum system (not shown in Figure 1) was properly trapped and filtered, and was capable of evacuating the system to a pressure of about 10 torr Hg. The two pressure relief valves were adjusted to vent the contactor or the dissolver at positive pressures in excess of 7 kPa.

The narrow connection between the extraction chamber and the molten bismuth reservoir provided for efficient separation of the molten NaOH phase from the molten bismuth phase, but at the same time defined the batch size of bismuth that could be processed per run, i.e., that amount of bismuth metal that would fill the reservoir and rise in the connecting chamber to the interface level shown in Figure 1 when the gas lift was

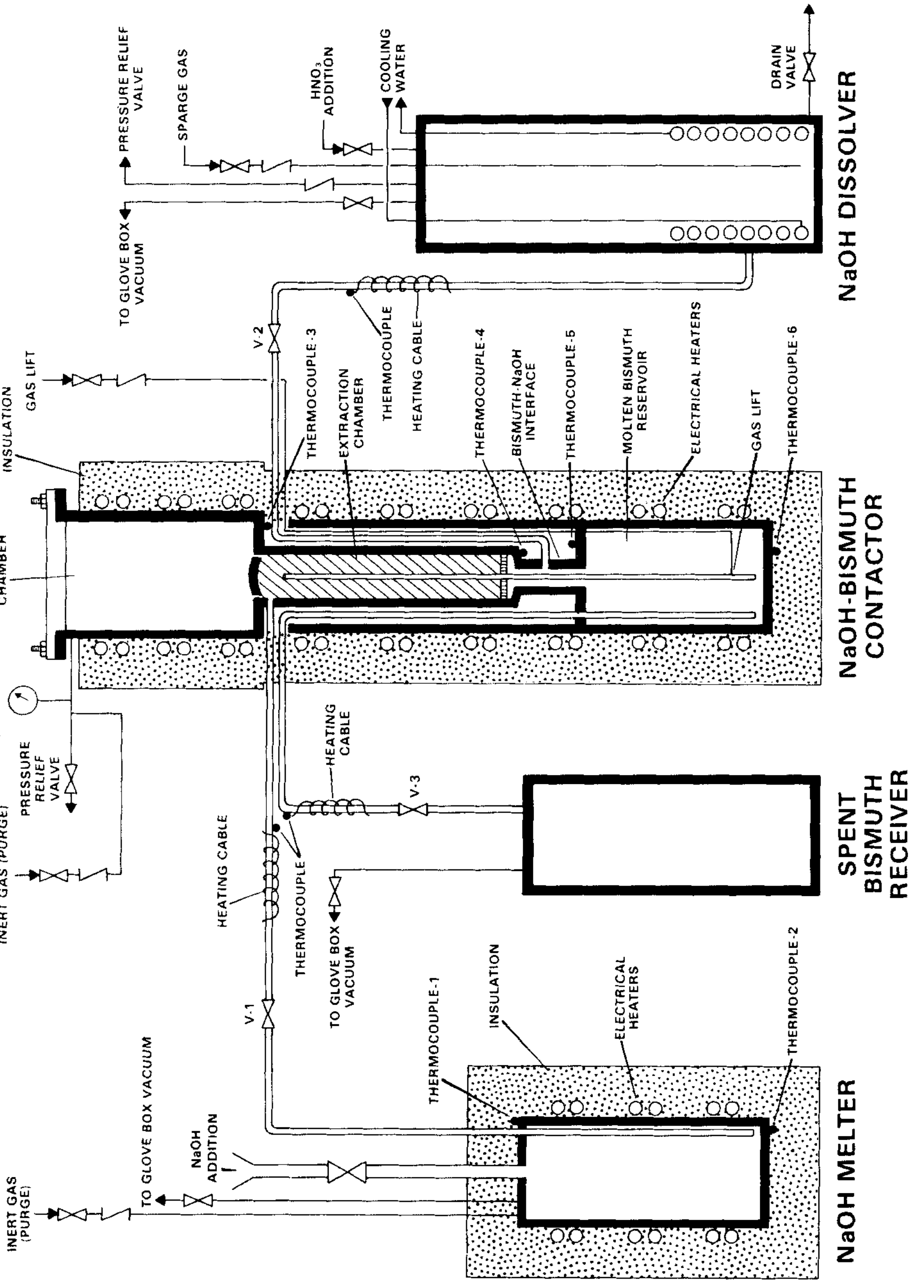

FIGURE 1: A Schematic View of the Pyrochemical Extraction Equipment

turned off, and the contactor was in the 450±25°C operating range. The contactor used for this project was sized to contain 20.45 kg of bismuth metal in the molten bismuth reservoir and 0.90 kg of NaOH in the extraction chamber. Extraction was achieved by turning on the gas to the gas lift which pumped a mixture of gas and molten bismuth from the bottom of the reservoir to the top of the extraction chamber. The lift gas was then disengaged from the bismuth, flowed into the melting chamber, and escaped from the contactor through the pressure relief valve. The molten metal globules percolated downward through the molten NaOH and Inconel packing in the extraction chamber to return to the top of the reservoir. The bismuth flow rate could not be directly measured, but based on simulated experiments with mercury and water, the gas lift was designed to pump at a rate that would give a bismuth batch circulation time of about 20 minutes with a gas flow of 0.08 to 0.1 m^3/h. Both 4% hydrogen in argon and 4% hydrogen in helium were used in the gas lift. No advantage was detected for either gas. The small addition of hydrogen was used to maintain reducing conditions in the contactor during extraction. Argon was used for the purging and sparging in the vessels.

Operational Description

The bismuth targets used in this project, 4.19 cm diameter by 29.2 cm long and weighing about 3.27 kg each, were canned in aluminum. After mechanical decanning and assay by gamma counting, five or six bismuth targets, plus sufficient unirradiated bismuth to bring the total charge to 20.45 kg, were placed into the melting chamber and the cover lid bolted in place. With valves V-1, V-2, and V-3 closed, the contactor vessel was evacuated and backfilled four successive times with the 4% hydrogen in argon or helium to remove most of the oxygen from the contactor. The argon purge to the top of the contactor was set at about 0.06 m^3/h, and the electrical power applied to the heaters to bring the system up to the operating temperature. The temperature was controlled by thermocouples-3 and -6 and monitored by thermocouples-4 and -5.

During the bismuth melting step, 0.90 kg of NaOH pellets were added to the NaOH melter through the addition funnel and the melter brought to a temperature of 450°C. When both bismuth and NaOH were melted and the respective vessels were heated to the proper temperature, transfer line V-1 was heated to 450°C, the NaOH addition valve closed, and the NaOH melter slowly evacuated to outgas the melted NaOH. The NaOH was transferred to the contactor by simultaneously applying a 103 kPa positive pressure of argon to the NaOH melter and opening transfer line V-1. After completion of the transfer, valve V-1 was closed, the argon purge to the melter was stopped, and the NaOH addition valve was opened to vent the melter and allow the melter to be recharged with a second 0.90 kg batch of NaOH pellets.

Extraction in the contactor was initiated by closing the argon purge line at the top of the contactor and starting the flow of lift gas. At the end of the extraction period, the gas lift was turned off, transfer line V-2 was heated to 450°C, and the NaOH dissolver was evacuated and backfilled three times with argon. Finally, the NaOH dissolver was evacuated, a small purge of argon was introduced into the dissolver through the drain valve to prevent plugging of the drain line with frozen NaOH, the argon purge to the top of the contactor was set at 0.7 m^3/h to avoid a vacuum in the contactor, and valve V-2 was opened to vacuum transfer the NaOH from the contactor to the dissolver. Valve V-2 was then closed, the argon purge turned down to 0.06 m^3/h, and a second cycle started. The temperature of the transfer lines was returned to ambient after each transfer to prolong the life of the heating cables.

After transfer of the NaOH, the cooling coils were activated, the sparge turned on, and 5 L of 7 $\underline{M}$ HNO_3 were slowly added to dissolve the NaOH and the extracted ^{210}Po. The dissolver solution was then sampled and transferred to a storage tank. Prior to removing the spent bismuth from the contactor, a receiver vessel was connected, as shown in Figure 1, and the transfer line heated to 450°C. The argon purge to the top of the contactor was increased to full scale, a vacuum drawn on the receiver, and valve V-3 opened to permit the transfer. After cooling, the spent bismuth vessel was disconnected, removed from the glove box, and assayed for ^{210}Po by gamma counting.

Carrier Precipitation

The solution accumulated from dissolution of five batches of caustic had the approximate composition of 50 Ci ^{210}Po/L, 2 $\underline{M}$ HNO_3, 4 $\underline{M}$ $NaNO_3$, and contained a significant amount of very fine particles. Filtration proved to be difficult, but the solution was clarified by allowing the suspended solids to settle over a period of 3 to 4 days.

A manganese dioxide carrier precipitation was found to be effective for concentrating the ^{210}Po and removing it from the sodium nitrate. In this procedure, 2-4 L of clarified solution was heated to 50°C and adjusted to 0.017 $\underline{M}$ Mn^{2+} by the addition of 50% $Mn(NO_3)_2$ solution.

With continuous stirring, sufficient 0.3 M $KMnO_4$ was slowly added to first oxidize the trace impurities present and then to produce a stable MnO_2 precipitate. After 30 minutes at 50°C, the slurry was filtered and the precipitate washed with 0.1 M HNO_3 on the filter. The precipitate was then suspended in 3 M HNO_3 and dissolved by the addition of a few drops of 1.5% H_2O_2. By controlling the volume of HNO_3 used to dissolve the precipitate, a concentration factor of 2 to 10 could readily be achieved. The polonium recovery across this step was found to exceed 99.5%.

Electrodeposition

Final purification of the polonium was accomplished by electrodeposition from 3 M HNO_3 onto 0.4 cm wide x 4.4 cm long platinum gauze strips. The 45 mesh gauze was woven from 0.02 cm diameter wire. A cathode potential of +77 mV was maintained with respect to a silver-silver chloride reference electrode immersed in the plating solution. A platinum wire anode surrounded two suspended cathode strips and the reference electrode in the glass plating tank. Normally, 20 to 50 Ci ^{210}Po would be deposited on each strip in 24 hours. Deposition densities ranged up to 40 Ci/cm^2 of exposed gauze. When removed from the bath, the gauze strips were rinsed with distilled water and acetone, then inserted into a nickel sheath and sealed inside a Pyrex ampule backfilled with argon. For final product use, the polonium was dissolved from the gauze strips by HCl. When depleted to less than 10 Ci ^{210}Po/L, the plating solution was recycled to the carrier precipitation step.

PROCESS DEMONSTRATION

During twelve pyrochemical extraction runs performed in the equipment shown in Figure 1, 16,700 Ci of ^{210}Po were extracted from 222 kg of irradiated bismuth metal. A summary of the data taken during these runs is given in Table 1. A comparison of the total accountability of extracted ^{210}Po with the assayed content of the irradiated targets shows that the extraction is consistent and sufficiently complete to meet process demands.

After the completion of each run, the dissolver was cleaned out with 1 to 2 L of 8 M HNO_3 heated to 80-90°C with a heating tape temporarily attached to the bottom of the tank. In each case, NO_x fumes were observed, and material not dissolved in the more dilute HNO_3 was recovered. In

TABLE 1: Summary of Pyrochemical Extraction Demonstration Runs

	Pyrochemical Extrction Run Number											
	1	2	3	4	5	6	7	8	9	10	11	12
Assay of Irradiated Bismuth (Ci ^{210}Po)	965	1194	1408	1275	1434	1432	1449	1647	1351	1467	1625	1595
Assay of Dissolved NaOH (Ci ^{210}Po)												
1st extraction	198	741	492	286	661	721	766	327	578	861	771	592
2nd extraction	209	270	440	450	379	332	388	533	408	233	270	493
3rd extraction	161	92	190	200	143	133	93	407	166	119	139	292
4th extraction	172	50	68	80	44	97	34	195	32	43	56	57
5th extraction	85	8	33	40	36	25	13	100	65	--	--	66
6th extraction	35	--	--	--	--	--	--	--	--	--	--	--
Assay of Dissolver Cleanout Solution (Ci ^{210}Po)	182	29	107	140	162	105	104	72	121	115	109	80
Assay of Spent Bismuth (Ci ^{210}Po)	<5	<10	30	<20	24	<10	<20	<20	<20	105	<20	41
Total Accountability (Ci ^{210}Po)	1042	1190	1360	1196	1449	1423	1418	1654	1370	1476	1365	1621
Percent of Available ^{210}Po Extracted In Each Contact												
1st extraction	23	63	39	27	51	55	58	21	46	63	61	38
2nd extraction	31	63	58	57	61	56	71	42	59	47	56	52
3rd extraction	35	58	59	59	58	50	58	56	59	45	65	64
4th extraction	58	74	52	57	42	73	51	62	27	29	74	35
5th extraction	68	44	52	67	60	71	39	83	76	--	--	62
6th extraction	88	--	--	--	--	--	--	--	--	--	--	--

run No. 1, the dissolved caustic from the 6th extraction was assayed immediately after the dissolution and cooling had taken place. The solution was left in the dissolver overnight and was assayed again the next day. During this 20 hour period, the ^{210}Po content dropped from 35 to 13 curies. These facts indicate that some bismuth metal was carried over into the dissolver with the caustic transfers, and also that some autodeposition took place. The amount of bismuth metal charged per run was reduced by 0.11 kg for all runs subsequent to the first, but the problem persisted. It seems reasonable to expect a small amount of molten bismuth to remain trapped in the packing after the gas lift is turned off and to be flushed out with removal of the NaOH. Such behavior would be random and could account for the fluctuations in the amount of ^{210}Po recovered during the cleanout.

The ^{210}Po recovered during cleanout was not included in calculating the percent of the available ^{210}Po extracted in each contact because of the uncertainty of its origin. In several runs the first extraction was significantly low; indicating, perhaps, the presence of an interfering impurity which was removed during the first extraction. Discounting the first run, which was abnormal because of equipment problems, the average percent of available ^{210}Po extracted in the second, third, fourth, and fifth extractions are 57, 57, 52, and 62, respectively, across the eleven runs. The fourth extractions are biased low by the poor extractions in runs 9 and 10. If these are discounted, the average for the fourth extractions is 58%, in good agreement with the others. Under the conditions used in this work (0.044 kg NaOH/kg Bi), extraction of 58% of the available ^{210}Po corresponds to a mass distribution coefficient (D_m) of 32, where

$$D_m = \frac{\text{Ci } {}^{210}\text{Po in NaOH phase}}{\text{kg NaOH}} \div \frac{\text{Ci } {}^{210}\text{Po in Bi phase.}}{\text{kg Bi}}$$

No investigation was made of the route of impurities through the processing steps. Very pure bismuth (99.999%) was used to avoid high dose rates from neutron activation products. Silver is the most common impurity in very pure bismuth. Some ^{110m}Ag was present in the irradiated bismuth targets but did not extract into the NaOH. During the first six runs, two hour extraction times were used. Starting with run seven, the extraction time was reduced to one hour with no effect on extraction efficiencies. The extraction kinetics appear to be reasonably fast, but the other processing operations did not allow a significantly shorter extraction cycle.

At the conclusion of the electrodeposition step, the ^{210}Po concentration in the plating solution ranged from 1 to 10 Ci/L. This material was recycled to the carrier precipitation step. A discard-to-waste limit of <0.5 Ci ^{210}Po/L was imposed on the filtrate solution from the carrier precipitation, but most of the waste discarded contained <0.1 Ci ^{210}Po/L. In all cases, the carrier precipitations and electrodepositions were routine and uneventful.

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