*AmBe Waste Minimization Activities
Annual Report*

September 30, 1998

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Issued: May 1999

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*Kent D. Abney
Zita V. Svitra
Michael R. Cisneros*

AmBe WASTE MINIMIZATION ACTIVITIES

ANNUAL REPORT

September 30, 1998

**Kent D. Abney, Zita V. Svitra,
and Michael R. Cisneros**

Nuclear and Radiochemistry Group, CST-11

**Radioactive Source Recovery Program
Los Alamos National Laboratory
Los Alamos, NM 87544**

TASK OBJECTIVE

The CST-11 objective for the Radioactive Source Recovery Project is to evaluate a nitric acid-based flowsheet and alternatives for dissolution, separation, and recovery of americium from AmBe neutron source materials returned from private and governmental institutions. Specific tasks performed during FY97 and FY98 included the experimental investigation of material dissolution rate and efficiency as a function of time and temperature for nitric acid as compared to hydrochloric acid. Alkaline dissolution reaction conditions using sodium hydroxide and ammonium bifluoride were also investigated. In both the acidic and alkaline dissolution conditions, the objective was to effect an initial separation of the americium from the beryllium or vice versa. The process solution and remaining solids should also be amenable to further processing and purification schemes. This work was performed on actual AmBe neutron source material in order to demonstrate the feasibility of ^{241}Am purification from dismantled neutron sources.

INTRODUCTION

Since the passage of the Atomic Energy Act, both private industry and US government agencies have owned neutron sources. These sources are used for a variety of applications such as calibrating instruments and measuring rock porosities for well drilling. Due to the economic downturn in the oil and gas industry and the downsizing of defense funding, many of these sources are now dispensable. Unwanted sources may contain either (1) ^{241}Am oxide and beryllium metal or (2) $^{239/238}\text{Pu}$ and beryllium metal alloys. The hardships of ownership of an unwanted neutron source and the lack of a national inventory of these sources increases the concern of risk to the public's health and safety and to the environment. Likewise, no disposal or material recycle mechanism currently exists. It is, however, the Department of Energy's (DOE) responsibility under law to provide these services.

Los Alamos National Laboratory, through DOE guidance, has undertaken the task of collecting the americium and plutonium neutron sources from the private sector. The Laboratory has also begun an investigation of the potential for recycling the actinides by separating radioactive from non-radioactive components. Presented here are potential dissolution, separation, and purification schemes for americium. We will also discuss the value of selective dissolution followed by subsequent precipitation of either the americium or beryllium.

EXPERIMENTAL

Sample Recovery and Physical Characteristics

AmBe neutron source material was obtained from the Actinide Process Chemistry Group (NMT-2) after cutting operations within the Plutonium Facility (TA-55) glove boxes allowed recovery of the sample. All experiments performed were taken from a single batch of this material. This material was free flowing and highly powdered. To date NMT-2 has opened numerous AmBe sources, including four within the past year. Of these four, three were similar to the material used here while one appeared to be a pressed sample. This unique sample appeared to contain a binder material which rendered the source into a ceramic form having a cylindrical shape. The dissolution experiments described in this report are representative of the powdered sample and thus have optimum reaction kinetics because of increased surface area.

Dissolution Experiments

The dissolution reactions typically used 10 mg of AmBe neutron source material that was weighed into a plastic 40 mL centrifuge tube equipped with a screw top. Before it was placed in the glove box, the centrifuge tube was covered with parafilm to prevent outer surface contamination of the tube. After addition of the powdered sample, 5 mL of dissolution reagent was added. The tube bottom was then cooled with ice before the reagent was added. Subsequently, 1, 2, and 2 mL aliquots of solution were added sequentially. After addition was complete, the sample was transferred from the glove box to the entry box where the parafilm was carefully removed. The outer surface of the centrifuge tube was then certified to be free from contamination and the tube was then transferred to a hood, bagged, and placed on a tube rotating wheel. The sample was then rotated and inverted at frequency of 12 rotations per minute. Aliquots of 1 mL were then removed and weighed at selected hourly intervals.

Hydrochloric acid (4.0 M) was used to provide a reference standard for the americium gamma activity. Dissolution was virtually complete within two hours with heating in nearly all reactions, as evidenced by the disappearance of gray AmBe solid and the generation of clear solutions containing no solids. These dissolution reactions were typically very exothermic with gas evolution due to heat generation. Nitric acid reactions using 0.1, 1.0, and 8.0 M concentrations were typically less exothermic. Even after 24 hours a significant amount of solid remained, suggesting that total dissolution was not achieved.

Sodium hydroxide and ammonium bifluoride were used to investigate the feasibility of selective beryllium dissolution under alkaline conditions. For the sodium hydroxide, 5 and 10 M solution concentrations were used. In the course of these reactions, a significant amount of gray beryllium metal remained even after contact for 24 hours. Ammonium bifluoride concentrations of 0.5, 1.0, and 1.5 M were investigated. In all cases, cooling prevented vigorous boiling of the solution upon addition. Typically after one hour, the total disappearance of gray solid was evident with the presumed concurrent formation of white NH_4AmF_4 solid being generated.

Gamma Counting

The specific activity of the solutions and thus the extent of americium dissolution was determined using gamma counting techniques. A lithium drifted germanium (GeLi) detector was calibrated for geometry effects of the 3 mL polyethylene vial containing 1 mL of solution. The background activity was measured daily to determine the stability of the instrument using the ^{241}Am 60 keV peak in this low energy x-ray region. The samples were counted in the same position (shelf 7) in each instance with the Cd absorber in place, rendering the total efficiency of the counter at 60 keV to <10%. No absolute calibration was necessary since all dissolution experiments were either referenced to a series of totally dissolved AmBe standards (using hydrochloric acid) or else mass balanced by determining the amount of americium remaining in the residual solids. The residual solids were dissolved in 1 M HNO_3 and gamma counted.

Beryllium Measurements

Beryllium concentrations were measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES) or an inductively coupled plasma mass spectrometer (ICP-MS).¹ Calibration standard solutions of 10, 100, 250 and 500 ppm were prepared in either 0.1 M nitric or 0.1 M hydrochloric acids to determine the linearity of the instrument. All samples were diluted to below 1 M acid concentration and within this beryllium concentration range to make accurate measurements of beryllium without matrix effects.

RESULTS AND DISCUSSION

The major goal of this project was to effect the dissolution and initial separation of americium from beryllium in one step. In this manner we can minimize additional downstream processing and reduce the generation of secondary wastes from these steps. In order to accomplish this goal, dissolution and analytical protocols were established to quantify both the americium and beryllium. The methodology used in this study is described in Figure 1.

Figure 1. Dissolution and analytical measurement protocol.

AmBe neutron source material was obtained from NMT-2 after cutting operations allowed removal of this material from the stainless steel cylinder. The 3 Ci source weighed approximately 5 g in total with approximately 0.5 g being removed for this set of experiments. This material was highly powdered and expected to react vigorously with hydrochloric acid because of its high surface area in analogy to previous experience with PuBe

¹ All beryllium measurements were performed by the NMT-1 Analytical Chemistry Group. Both methods were used to cross check the analytical results.

samples. The AmBe source material is presumed to be a mixture of AmO₂ and beryllium metal. No efforts were made to determine if the beryllium had been converted to an oxide during the mixing, sintering, and pressing operations to form the commercially packaged AmBe neutron source.

The general procedure used involved weighing the powdered material in the glove box followed by addition of the dissolution reagent. The sample was then removed from the glove box and transferred to a hood. The sample was then mixed by rotation. After 1, 4, 6, and longer hourly intervals, the sample was centrifuged and 1 mL aliquots removed for analyses. Gamma counting was used for americium measurements and ICP-AES or ICP-MS for beryllium measurements. After the experiment was complete, the residual solid was dissolved and measured for both americium and beryllium to allow for total mass balance of the sample.

Initial acid dissolution experiments focused upon hydrochloric and nitric acid media. Hydrochloric acid reactions are typically quite vigorous even with cooling in ice. Slow drop-wise addition is made initially because of boiling and gas evolution from the heat of reaction. Once the sample was covered with liquid, the remaining 5 mL of acid could be added in 1, 2, and 2 mL aliquots. The sample was then removed from the glove box and intimately mixed on a tube rotating apparatus. In nearly all reactions total dissolution was not achieved after 2 hours at ambient temperature. The samples were then heated to approximately 60°C, which resulted in complete dissolution within minutes. Each sample was then gamma counted. In this fashion and using several samples, the specific activity and the heterogeneous nature of each of the samples could be evaluated. The results of four hydrochloric acid dissolution reactions are shown in Table 1. As can be seen the average specific activity is 1.02×10^8 cpm/g for this counting procedure. The standard deviation of this measurement is approximately 17%. Typical gamma counting methods show replicate counting errors on the order of 5–10%. Thus this data depicts the non-homogeneous nature of the AmBe source material. This result was also confirmed by the Be analytical results wherein a variability of approximately 21% was measured. More surprising was the result that the samples contained an average of 56% beryllium.

Table 1. Hydrochloric acid dissolution results of AmBe neutron source samples.

Sample Number	Sample Weight (mg)	Aliquot Volume (mL)	Activity (cpm)	Specific Activity (cpm/g)	Weight % Be
1	9.0	0.94	1.55×10^5	9.19×10^7	41.8
2	9.0	0.97	1.88×10^5	1.07×10^8	56.6
3	9.0	0.98	2.18×10^5	1.23×10^8	70.3
4	9.0	0.97	1.48×10^5	8.43×10^7	57.1
			avg =	1.02×10^8	56.5 %
			std dev =	16.9 %	20.6 %

The dissolution of AmBe neutron source material in nitric acid was investigated with the intent of selectively dissolving americium. Dissolution experiments on *nonradioactive beryllium metal* confirmed the possibility of this approach as shown in Figures 2 and 3. At ambient temperature the dissolution of beryllium is minimal (<2%) and nearly independent of nitric acid concentration. Heating to 60°C increases the extent of dissolution to only 10% after 5 hours of heat treatment. More importantly, the 60°C 1 M HNO₃ treatment resulted in merely 3% dissolution of the beryllium suggesting the possibility of a crude separation of americium from beryllium by selective dissolution of the americium oxide while leaving the

beryllium metal as a solid. Thus all of these experiments imply that if the beryllium in the AmBe neutron source material exists as metal rather than oxide, then simultaneous dissolution and separation of the americium fraction may be achieved. To this end we next investigated actual neutron source material.

Figure 2. Dissolution results of beryllium metal at ambient temperature.

Figure 3. Dissolution results of beryllium metal at 60°C.

The investigation of nitric acid dissolution on actual AmBe neutron source material reveals that at very dilute acid concentration (0.1 M), the dissolution rate for americium is slow (Table 2). After 24 hours the extent of dissolution is only 70%. Heating to 60°C increased the americium dissolution rate significantly and increased the extent of dissolution. This same effect is also observed when the nitric acid concentration is increased from 0.1 to 1.0 M. An increased nitric acid concentration combined with heating to above 60°C allows complete and rapid dissolution of the americium. As expected further increase of the nitric acid concentration slows the dissolution rate because of a decrease in the total ionic strength at these higher concentrations. The effect of heating at 8 M nitric acid also increased the extent of dissolution within one hour from 44 to 83%. Further experimentation of the heating effect was not performed.

The effects of time, acid concentration, and temperature on the extent of beryllium dissolution were also measured. While the measurement of beryllium dissolution using 0.1 M nitric acid was not performed, the results of 1 and 8 M nitric acid clearly demonstrate that higher acid concentrations do not significantly effect the extent dissolution. Only by allowing an ambient temperature solution to contact the sample for 24 hours is the beryllium dissolved. However, the increase of reaction temperature has a dramatic effect upon beryllium dissolution. Unfortunately within 4 hours using 1 M nitric acid and 1 hour using 8 M nitric acid, it is possible to achieve 100% dissolution of the beryllium. These results, when compared with the nonradioactive beryllium metal results shown in Figures 2 and 3, clearly

demonstrate that beryllium may in fact be in the form of an oxide or some other readily dissolved configuration but certainly is not metal.

Table 2. Nitric acid dissolution results of AmBe neutron source samples.

Experiment Number	Nitric Acid Concentration (M)	Temperature (°C)	Time (h)	Percent Am Dissolved	Percent Be Dissolved
1	0.1	25	1	47	NP
1	0.1	25	4	54	NP
1	0.1	25	24	70	NP
2	0.1	60	1	87	NP
2	0.1	60	4	100	NP
2	0.1	60	18	100	NP
3	1.0	25	1	47	0.88
3	1.0	25	4	58	0.86
3	1.0	25	24	100	2.70
4	1.0	60	1	100	20.3
4	1.0	60	4	100	100
4	1.0	60	24	100	100
5	8.0	25	1	44	1.24
5	8.0	25	4	57	2.57
5	8.0	25	24	97	35.5
6	8.0	60	1	83	100

NP = Not Performed

Alkaline dissolution reactions using either sodium hydroxide or ammonium bifluoride were also investigated as a function of time and temperature. Hydroxide-based reactions afford the possibility of selectively dissolving beryllium by utilizing the amphoteric nature of beryllium hydroxide and the subsequent formation of $[\text{Be}(\text{OH})_4]^{2-}$. One nonradioactive experiment was used to test the feasibility of this process. Approximately 10 mg of beryllium metal powder was reacted with 5 M sodium hydroxide to determine the extent of reaction. Dissolution appeared to proceed nearly to completion albeit very slowly (>18 hours) as evidenced by gas evolution from the sample. Similarly both 5 and 10 M sodium hydroxide solutions were evaluated on AmBe material. In all reactions a continuous evolution of gas suggested the desired reaction was occurring. As expected, little or no dissolution of the americium occurred by addition of the base as shown in Table 3. Unfortunately, copious quantities of black beryllium metal remained in these solutions suggesting the formation of americium hydroxide on the surface of the beryllium metal. As a result this may have prevented effective dissolution of the beryllium metal. This result is also supported by the low concentrations of

beryllium in solution as also shown in Table 3. These data show that only at high concentrations of sodium hydroxide is the beryllium significantly dissolved and this requires at least 24 hours. The effect of heating did not dramatically increase the percent americium dissolved and is believed to have not changed the percent beryllium dissolved.²

Table 3. Sodium hydroxide dissolution results of AmBe neutron source samples.

Experiment Number	Sodium Hydroxide Concentration (M)	Temperature (°C)	Time (h)	Percent Am Dissolved	Percent Be Dissolved
1	5.0	25	1	0.01	0.07
1	5.0	25	4	0.01	1.21
1	5.0	25	24	0.01	20.52
2	5.0	60	1	0.01	NP
2	5.0	60	4	0.01	NP
2	5.0	60	18	0.01	NP
3	10.0	25	1	0.63	14.64
3	10.0	25	4	1.18	77.68
3	10.0	25	24	1.27	100
4	10.0	60	1	0.70	NP
4	10.0	60	4	1.51	NP
4	10.0	60	24	2.09	NP

NP = Not Performed

Ammonium bifluoride (NH_4HF_2) was also investigated as a means to selectively dissolve the beryllium fraction. During these reactions it was generally observed that initially the reaction was quite vigorous. In analogy to the hydrochloric acid dissolution reactions, the samples were normally cooled to 0°C to prevent loss of sample because of boiling. Once the samples were completely covered with solution, the dissolution proceeded without caution. Reagent concentrations of 0.5, 1.0, and 1.5 M NH_4HF_2 were investigated at ambient temperature and at 60°C . Our previous investigations showed that the dissolution reaction of nonradioactive beryllium metal powder in virtually any NH_4HF_2 concentration at ambient temperature is complete within minutes. However the commensurate AmBe neutron source material experiments visually showed significant amounts of starting material remaining after 3 hours of reaction time. Increasing the reaction temperature to 60°C reduced the dissolution time considerably. After 1 hour only a small amount of undissolved beryllium metal remained after contact with 0.5 M NH_4HF_2 . Increasing the reagent concentration also reduced the amount of undissolved beryllium. The tabulation of this data is shown in Table 4. The extent of beryllium dissolution for all of these experiments suffered from our inability to obtain rapid

² The percent beryllium dissolved was not measured in the heated samples. However an extensive amount of dark gray solid remaining in these samples leads us to this conclusion.

analytical results. All ICP-AES and ICP-MS measurements indicate the beryllium content to be greater than the theoretical amount, based on our hydrochloric acid measurements. We believe this to be an artifact of the samples sitting for several months waiting for instrument repair and calibration. The result was evaporation of the liquid sample, thus rendering the Be concentrations high. Thus in all samples the high final beryllium concentration suggests that beryllium dissolution was complete and rapid.

The chemical behavior of the americium in ammonium bifluoride differed substantially from the beryllium and was unlike the sodium hydroxide experiments as well. Initially the americium also dissolved rapidly when mixed with the ammonium bifluoride. However, within 2 hours a white precipitate, presumably white NH_4AmF_4 resulted from these reaction thus agreeing with the measurement of little or no americium in the supernatant solutions at the conclusion of the experiment. Total americium mass balances were achieved by dissolving this solid in 1 M HNO_3 after completion of the NH_4HF_2 reaction.

Table 4. Ammonium bifluoride dissolution results of AmBe neutron source samples.

Experiment Number	Ammonium bifluoride Concentration (M)	Temperature (°C)	Time (h)	Percent Am Dissolved	Percent Be Dissolved
1	0.5	25	4	19.75	>100
1	0.5	25	90	0.01	>100
2	0.5	60	1	11.71	>100
2	0.5	60	3	0.08	>100
2	0.5	60	4	0.01	>100
3	1.0	25	1	30.69	>100
3	1.0	25	3	14.17	>100
3	1.0	25	19	0.52	>100
4	1.0	60	1	38.24	>100
4	1.0	60	3	13.34	>100
4	1.0	60	4	1.82	>100
4	1.0	60	19	0.00	>100
5	1.5	25	4	18.47	>100
5	1.5	25	90	0.00	>100
6	1.5	60	1	43.92	>100
6	1.5	60	3	21.90	>100
6	1.5	60	4	7.82	>100
6	1.5	60	19	0.01	>100

SUMMARY AND FUTURE DIRECTIONS

The primary goal of this project was to evaluate potential americium and beryllium separation strategies in a single dissolution step. The use of hydrochloric acid results in the rapid and complete dissolution of both the americium and beryllium components of neutron source material. The goal of simultaneous dissolution and separation of americium from beryllium may be achieved using low concentrations of nitric acid without heating. Likewise, the use of ammonium bifluoride represents an alternative means to dissolution and separation wherein the americium component remains as a solid while the beryllium is dissolved. Finally, the use of high concentrations of sodium hydroxide to effect the selective dissolution of beryllium shows promise but is difficult to handle due to the americium hydroxide precipitate remaining.

Future experiments involving this constrained investigation would include process scale-up to determine dissolution efficiencies and technical hurdles. For instance, other cations to replace the ammonium ion may be an alternate approach. The overall purity of the americium for potential resale to the private sector should also be determined. The combination of advanced separation methods (e.g., extraction chromatography or ion exchange) with these dissolution techniques should also be investigated.

ACKNOWLEDGMENTS

This project was funded jointly by DP-22 and EM-36 of the Department of Energy and directed through the Nuclear Materials and Stockpile Management Program Office as well as the Environment Management Program Office at Los Alamos National Laboratory. Many thanks to Mark Dinehart (NMT-5), Sammi Owens (NMT-2), and Vance Hatler (NMT-2) for guidance in directing this work.