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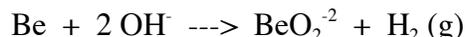
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1.0 Introduction

An inventory of Pu/Be metal mixtures derived mainly from machining chips and turnings has accumulated at Lawrence Livermore National Laboratory (LLNL) and other sites. Because of pyrophoricity, these materials need to be stored in argon atmosphere glove boxes until the Pu can be calcined to form PuO₂, which can then be put into long-term storage. Experience shows that if the Pu/Be mixtures are calcined without removal of the Be, the product mixture of oxides produces a high neutron dose rate, which results from the (α , n) reaction as a consequence of intimate contact between PuO₂ and BeO particles. Removal of the Be from Pu/Be mixtures by dissolution in concentrated NaOH solution prevents this subsequent high neutron dose rate problem. However, it was found that the Be dissolution process was accompanied by boil over out of the container when attempting to process samples greater than ~10 grams. A procedure is described here to process ~100 gram samples with NaOH without boil over by gradually increasing the NaOH concentration during processing.

Dissolving of Be in NaOH solution occurs by the reaction:



The reaction is thermodynamically favored and produces 8.8 kcal of heat for each gram of Be dissolved. The reaction can be followed by the generation of H₂ bubbles, and also by heating of the solution.

An advantage of the NaOH process is that Pu is insoluble in the NaOH solution, so that a clean separation from the Be can be accomplished. A disadvantage of the process is that the dissolution of Be may occur very rapidly, and the heat release can lead to boiling of the solution accompanied by a rapid release of H₂ gas. This combination leads to boil over of the NaOH solution out of the container. The main purpose of this procedure is therefore to control the rate of the dissolving reaction in order to avoid the boil over effect and at the same time prevent the unwanted rapid release of H₂ gas in the glove box.

This procedure is formulated for the treatment of ~100 gram samples of Pu/Be mixtures, in the presence of 1 liter of water. During processing, it is helpful to know how the solubility of Be increases with NaOH concentration. Table 1 gives the dependency in terms of grams NaOH added to grams Be dissolved in 1 liter of water at 30 °C. It is useful to generate a graph of this tabular data as a guide for following the amount of Be dissolved for the amount of NaOH added. The maximum

amount of NaOH addition is ~550 grams. If NaOH concentration is increased much further, precipitation of $\text{BeO}\cdot\text{NaOH}\cdot\text{H}_2\text{O}$ is expected to occur. The maximum concentration of NaOH for this procedure is actually limited to ~500 grams NaOH to 1 liter of water, because the amount of Be dissolving and the reaction rate increase rapidly with increasing NaOH concentration, and increasing the NaOH concentration past this region makes it difficult to control the boil over reaction.

Table 1. The grams of Be dissolved are given as a function of the grams of NaOH added to 1 liter of water at 30 °C.

Grams NaOH added	100	200	300	350	400	450	500	550(max)
Grams Be dissolved	0.3	0.9	3.0	5.0	8.0	13.3	19.9	26.2

2.0 Processing Equipment for Dissolving Be

Equipment used in this study for dissolving Be includes:

- VWR Hot Plate Stirrer, Model 575, 120V, 800W (VWR Cat # 14217-604)
- Temperature Probe Quartz Glass Sheath (VWR Cat # 33918-345)
- Stir-Pak Heavy-Duty Mixer Head, 115V (Cole-Palmer Cat # A-50002-20)
- Stir-Pak Controller, 115V (Cole-Palmer Cat # A-50002-20)
- R1389 Three-Blended Propeller Stirrer, PTFE Coated (VWR Cat # 33994-118)
- 3 Liter Pyrex Brand Double Scale Griffin Beaker (VWR Cat # 13912-342)
- SS Instrument Tray, 12" x 7 3/4" x 2 1/4" (VWR Cat # 62687-049)
- Long Handled Tin Snips

Comparable equipment from other vendors would also be acceptable.

The Model 575 Hot Plate offered by VWR is a suitable hot plate, and comes with a thermocouple probe with feedback control of temperature. A quartz glass closed-end protection tube is also provided with the thermocouple probe. VWR also sells stainless steel instrument trays. The one used here is 12" x 7 3/4" x 2 1/4". A hole is drilled at the 2" level to reduce the maximum fill level in order to meet LLNL criticality safety requirements. The height of the Pyrex beaker has been reduced so that a complete fill is only slightly more than 3 liters. This is for the purpose of making it easier to maintain the total amount of aqueous solutions intermixed with Pu in the glove box to less than 4 liters for the purpose of criticality safety.

In preparation for a run, the stainless steel tray is placed on the hot plate and the 3 liter beaker is placed in the tray. The stainless steel tray is used to catch overflow of solution from the beaker if boil over accidentally occurs. When ready to operate, the sample to be processed is loaded into the beaker, taking care to arrange the sample to leave sufficient room in the center of the beaker for the stirrer. One liter of distilled or deionized water is added to the beaker. The hot plate temperature probe, which is inside of a closed end quartz glass protection tube, is then mounted inside of the beaker on one side near the bottom of the beaker. The mechanical stirrer is then mounted with the Teflon-coated blade in the center of the beaker and ~1/3 of the way down into the water.

3.0 Supplies for Dissolving Be

Sodium Hydroxide pellets, reagent grade. Expect to use 1 - 1.5 kg per run.

6N NaOH solution, reagent grade. Expect to use 250 ml as a rinse solution per run.

Nitric Acid, concentrated. Used for neutralizing NaOH solutions.

Wide-mouth polyethylene bottles. Two bottles are needed for NaOH pellets.

Anti-Foaming Agent. See text.

4.0 Beryllium Dissolving Procedure

4.1 Weigh Out a Sample

To begin the dissolving procedure, first weigh out an ~100 gram Pu/Be sample. Conduct the weighing in a glove box separate from the dissolving glove box. Estimate the amount of Be in the sample and make a note of it for future reference. The amount of Be in the sample will determine the number of dissolving batches that will be required to process the sample. Examples would be: (1) a sample of Pu/Be mixture with ~15 grams Be would need 1 dissolution batch requiring 500 grams of NaOH pellets (see Table 1), (2) another sample with ~30 grams Be would need 2 dissolution batches requiring a total of 1,000 grams NaOH pellets, and (3) still, another sample with ~45 grams Be would need 3 dissolution batches requiring a total of 1,500 grams of NaOH pellets. At LLNL, the Be weight must not exceed 50 grams in the dissolving glove box because of criticality control. Therefore, the development work here was for batches containing less than 50 grams Be. The estimate of the Be weight is given by the net weight of the sample minus the Pu element weight. If the estimated Be weight in a sample exceeds 45 grams (allows for 10 % uncertainty in the estimated weight of Be), the sample needs to be divided into two smaller samples, which are then processed separately. When sample weight and estimated Be weight are determined, transfer the sample to be processed into the dissolving glove box.

In addition to the amount of Be in the dissolving glove box, the amount of NaOH is also of concern. If 50 grams of Be were present in the dissolving box and sufficient NaOH was provided to dissolve the entire amount of Be and produce H₂ gas, a calculation shows that the H₂/air mixture would not reach the explosive limit for our glovebox system. By limiting the introduction of NaOH to 500 grams per batch, it reduces the possibility of an explosive mixture even further, and also helps to minimize the potential for boil over (see introduction). The potential for production of BeO·NaOH·H₂O is also avoided.

4.2 Cut up Machining Turnings

If machining turnings are present in the sample to be processed, the turnings need to be cut up into small pieces before loading them into the beaker. This is done to avoid entanglement of the turnings with the stirrer in the beaker, and to avoid a height of material above the liquid level in the beaker. In order to avoid the direct handling of sharps in the glove box, transfer the Pu/Be sample into an open can, and using the long handled tin snips, cut up the turnings into ~1/2" pieces.

4.3 Load the Sample and Initiate Sample Heat-up

Prior to transferring the Pu/Be sample into the dissolving glove box, take background gamma and neutron dose rate readings of the work area through the glove box window (note if the window is lead loaded). Set up the dissolving equipment as described in section 2.0 above and load the sample into the beaker. At this point, take gamma and neutron dose-rate readings of the sample through the glove box window, and note the distance to the sample (e.g., 20"). Now, making sure that the sample is not piled up in the center of the beaker, add 1 liter of deionized or distilled water to the beaker. Mount the quartz glass protected thermocouple probe in the Pyrex beaker, and mount the mechanical Teflon-coated stirrer into position (see section 2.0). Set the stirrer to a speed of 100 rpm. Turn on the hot plate and set it to heat the water to a set-point temperature of 65 °C. Heat up of the sample will be slow because of the presence of the stainless steel safety pan. This loading of the sample and start-up of the hot plate should be done first thing in the morning as it will take most of the day to complete the run.

4.4 Weigh out Two Batches of NaOH Pellets

While the sample is heating up on the hot plate, proceed to weigh out batches of NaOH pellets into the two wide-mouth polyethylene bottles. The first batch is 300 grams and the second batch is 200 grams. The bottles are kept closed except when removing pellets. They need to be kept closed to avoid moisture pickup, which makes the pellets stick together and to the container. The 300 gram batch will be added first using a faster feed rate, and the 200 gram batch will follow at a slower feed rate (see 4.5 below). The total of the two batches, 500 grams, is sufficient to dissolve 20 grams of Be (see Table 1).

4.5 Conduct First Be Dissolving Run

The concentration of NaOH in the beaker is built up slowly by a controlled addition rate of NaOH pellets, while stirring the solution at 100 rpm. There are three goals for controlling the NaOH addition rate in order to avoid boil over. The first goal is to maintain a low concentration of NaOH (e.g., <100 g NaOH per liter of water) until the Be dissolution reaction is initiated. The second goal is to maintain a moderate rate of reaction after the dissolution reaction is established. The third goal is to maintain the solution temperature below the boiling point.

4.5.1 Addition of 300 Gram Batch of NaOH Pellets

Begin addition of NaOH pellets from the 300 gram batch when the temperature during heat-up reaches 35 °C (or higher). Add ~20 NaOH pellets (4 grams) to the water. The pellets are fed by slowly shaking them out of the polyethylene bottle, and then visually estimating the number of pellets as they fall. The bottle should be kept closed when not feeding. It takes about 2 minutes for the pellets to dissolve, and 1 – 2 minutes to assess the degree of reaction that results. The degree of the reaction is assessed by the rate of H₂ bubble evolution and by the rate of temperature rise of the solution. Make successive additions of ~20 NaOH pellets frequently until the Be dissolving is definitely underway as

noted by H₂ bubble evolution. If the initiation of H₂ bubble evolution causes foaming of the solution and the head of foam rises rapidly up the beaker, it would be desirable to add a few drops (or more) of an antifoaming agent (e.g., n-octanol) to the foam to lower it to about the 1/2" level. Initiation of the reaction does not usually occur until the fifth addition of 20 NaOH pellets. In some cases, the reaction may not get underway until the temperature of the solution reaches 50 - 60 °C, i.e., after about 10 additions of 20 NaOH pellets. Normally, with 10 to 15 additions of NaOH pellets, temperatures greater than 65 °C and up to 95 °C are attained.

4.5.2 Complete the Addition of 300 Gram Batch of NaOH Pellets

Continue with the addition of ~20 NaOH pellets each time the H₂ bubble evolution drops to a low value. Make sure that the temperature of the solution is below 90 - 95 °C before the next NaOH pellet addition. Experience will show the right time to make the next drop of pellets. Too soon a drop will give too great a burst of H₂ gas evolution. If the H₂ bubble evolution causes foaming of the solution and the head of foam rises rapidly up the beaker at any time, add a few drops (or more) of an antifoaming agent to the foam. If the temperature of the solution remains high for some time, you will need to add water to regain the previous level. Even though the water is not boiling, water is lost because the evolving H₂ gas sweeps out water vapor at the high temperatures.

If one wants to leave for a break (e.g., lunch), the best time is near the end (or at the end) of the 300-gram addition phase. To take the break, make sure that the H₂ evolution has slowed down, and leave the hot plate set to 65 °C and the stirrer going at 100 rpm. After the break, continue with the addition of NaOH pellets until the 300-gram batch is used up, and then proceed to **4.5.3**. However, if the estimated Be content of the sample is very low, i.e., less than 3 grams (see Table 1), the dissolution of Be might be completed with the addition of the 300 gram batch of NaOH pellets. To check for completion of the reaction, note if the H₂ bubbling has stopped. If it has stopped, be sure that the temperature is at ~90 °C (heat with the hot plate, if necessary), then add ~20 NaOH pellets. If no further reaction occurs, turn off the hot plate and stirrer, raise the stirrer out of the solution, allow the solution to cool and the solids to settle out overnight, and proceed to step **4.5.4** below.

4.5.3 Addition of the 200 Gram Batch of NaOH Pellets

If H₂ evolution continues after addition of the complete 300-gram batch in **4.5.2**, proceed with NaOH pellet additions in increments of ~10 pellets per addition. Smaller increments of NaOH additions are used because the solubility of Be and the evolution rate of H₂ are increasing more rapidly with increasing concentration of NaOH in this regime. It is desirable to maintain the dissolution reaction temperature in the 80 - 95 °C range, while closely watching and suppressing the formation of foam from H₂ evolution by using an antifoaming agent. Also, add make-up water as needed. Toward the end of the 200-gram addition of NaOH, the solution level should be at ~1.2 liters. If H₂ evolution stops during addition of the 200-gram batch, the reaction might be complete (check Table 1 for estimate of the amount of NaOH needed for completion). To check

for the reaction completion, with the temperature at 90 °C, add ~10 pellets of NaOH. If no further H₂ evolution occurs, turn off the hot plate and stirrer, raise the stirrer out of the solution, and allow the solution to cool down and the solids to settle out overnight, and proceed to step **4.5.4** below. If addition of the 200-gram batch has been completed with H₂ evolution occurring until the end, an additional dissolving run needs to be made. Turn off the hotplate and stirrer, raise the stirrer out of the solution, and allow the solution to cool down and the solids to settle out overnight, then proceed to section **4.6** below.

4.5.4 Filtration of the NaOH Solution

After the solution in the 3 liter beaker has cooled overnight and the solids have settled out, decant off the NaOH solution taking care to avoid solids carryover. About 100 ml of solution will be left behind in the beaker. The material left behind in the beaker will be processed in **4.5.5** below. At LLNL, the decanted solution is filtered because it is found that 1 – 2 grams of Pu are carried over as fines during the decanting, and are picked up on the filter paper. To conduct the filtration, use a vacuum filtration system with either bottle-top or Buchner filter funnels with two Whatman grade no. 42 ashless filter papers for each filter funnel (a single filter paper will be breached by the concentrated NaOH solution). The filtration of the NaOH solution will be slow because the concentrated NaOH has a high viscosity. It is therefore recommended that the NaOH solution be split between two filtration units to shorten the filtration time. Filtration time will still be about 16 hours.

4.5.5 Rinsing of the Pu Material left behind in the Beaker

When filtration of the NaOH solution is completed, add 250 ml of 6N NaOH solution to the Pu material left behind in the beaker, manually stir it well, then wait an hour for the solids to settle out. Now decant the solution equally into the two filter funnels used in **4.5.4** above. Filtration will require about 4 hours. While waiting for filtration to be completed, add 500 ml of water to the beaker to rinse out the NaOH from the Pu material. Manually stir it well for 5 minutes, then allow the solids to settle. When filtration of the 6N NaOH is completed, decant the 500 ml of water into the two filter funnels. Filtration will take about an hour. When filtration of the water is complete, add a second rinse of 500 ml of water to the Pu material, stir well and immediately pour out the water and the Pu materials into the two filter funnels. Use a small rinse of water in the beaker and with the assist of a spatula pour out the residual Pu materials into one of the filter funnels. Filtration of the last 500 ml water addition will need an additional hour for completion. The purpose of the two rinses of 500 mls of water are made to ensure that the Pu material has been cleared of NaOH prior to a calcining step that will follow. When filtration is complete, allow the filter papers and Pu material to dry and then proceed to **4.5.6** for calcining. Neutralize the NaOH filtrates with concentrated HNO₃ solution and send them to another glove box for solidification with Aquaset and disposal in a TRU waste drum.

4.5.6 Calcining of Filtered Pu Materials

The recovered Pu materials and filter papers from **4.5.5** above are calcined in an air furnace at 800 °C for 8 hours. In order to assure that the Pu material has been fully oxidized, the calcined material is ground up in a Micromill coffee grinder to about -50 mesh and the calcination is repeated at 800 °C for 8 hours. A weight check is made to assure less than 1 % weight change. Calcination is repeated as necessary to assure a less than 1 % weight change. Gamma and neutron dose rate readings are taken on the product through a similar glovebox window and at the same distance as prior to the run. A neutron dose rate reading of < 2 mR/h is expected with a successful run.

4.6 Conduct Additional Be Dissolving Runs

In many cases, a second run is required in order to completely dissolve out the Be. In a few cases a third run may also be required. The material requiring an additional run comes from section **4.5.3** above, and consists of Pu material that has a portion of the Be dissolved away, and is contained in the 3 liter beaker with about 1.2 liters of NaOH solution present. The additional processing proceeds as follows.

4.6.1 Filtration of the NaOH Solution

After the solution in the 3 liter beaker (from **4.5.3**) has cooled overnight and the solids have settled out, decant off the NaOH solution taking care to avoid solids carryover. Conduct the filtration of the decanted NaOH solution as given in **4.5.4**, and conduct the rinsing of the Pu materials and the treatment of the filtrates following the procedures given in **4.5.4**. Save the filter papers for calcining later in **4.5.6** together with the bulk of the Pu material. Proceed now to **4.6.2** to initiate an additional Be dissolving run.

4.6.2 Initiate an Additional Be Dissolving Run

Return the 3 liter beaker with the Pu material requiring additional processing, to the hot plate assembly. Add 1 liter of deionized or distilled water to the beaker. Mount the thermocouple and stirrer into position. Set the stirrer to 100 rpm, and turn on the hot plate with a set-point temperature of 65 °C. Weigh out two batches of NaOH pellets: the first batch is 275 grams (this is less than 300 grams because some residual NaOH solution is present in the Pu material), and the second batch is 200 grams. When the temperature reaches 35 °C, go to section **4.5.1** (noting that 275 grams of pellets are used in place of 300 grams) and follow the procedures in **4.5.1** and succeeding sections until the completion of the run. If an additional run is needed, you will be routed again to section **4.6**.

5.0 Authorization Basis Requirements

For DOE sites other than LLNL using this procedure, it is recommended that they perform safety analyses and accordingly adjust the procedure given here in order to meet their authorization basis requirements.

6.0 Summary

During development of the procedure described here, ten ~100 gram batches of Pu/Be samples were studied. One boil over occurred and another one nearly boiled over. The neutron dose rate after calcining was < 2.5 mR/h for 7 samples, and 12 mR/h, 7 mR/h, and 5 mR/h for the remaining samples. After development of the procedure, eight ~100 gram Pu/Be samples were processed to test the procedure. There were no boil over problems. The neutron dose rate after calcining was < 2 mR/h for all of the samples, and usually about 1 mR/h. This procedure should give a well-controlled operation with good cleanup of Be and a minimal loss of Pu.