Preparation of Kilogram Quantities of the 83 a/o Lead – 17 a/o Lithium Eutectic Alloy

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June 1995

UWFDM-971

FUSION TECHNOLOGY INSTITUTE

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ABSTRACT

Procedures are given for preparing several kilograms of the 83 a/o lead - 17 a/o lithium eutectic alloy for use in melt-water interaction experiments. Both cooling curves and inductively coupled plasma mass spectrometry are used to assess the composition of the alloy.

Because of the high purity of our starting materials and our careful melting procedures, we have determined that the eutectic temperature reported in the literature may be high by as much as 5 K.

ACKNOWLEDGMENTS

We are grateful to Mr. Sol Walsh for constructing key parts of the apparatus.

We are pleased to acknowledge the financial support of the U.S. Department of Energy's Office of Fusion Energy and the EG&G Fusion Safety Program provided via Dr. Kathy McCarthy of the National Engineering Laboratory, Idaho Falls, Idaho.

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INTRODUCTION

Because of its unique combination of breeding material with neutron multiplier and its relatively low melting temperature (230°C), the 83 a/o lead - 17a/o lithium eutectic alloy has been proposed for nuclear fusion blanket applications for over a decade (Sze et al., 1980). The alloy is not a commercially available material, however, and is normally prepared on individual bases as the needs arise. This report documents one set of procedures used at the University of Wisconsin (UW) in 1994 to prepare several kilograms of the alloy for melt-water interaction studies to be carried out later at both Prairie View A and M University and UW-Madison.

EXPERIMENTAL

Our preparative procedure is essentially the same as that used by Chopra and Smith (1984) in which they added small amounts of molten lithium (~ 10 ml, ~ 5 g) progressively to stirred molten lead (~ 6 L, ~ 60 kg) in a purified argon atmosphere. Our work differed from theirs by (a) preparing an order-of-magnitude less melt per operation (1 or 2 kg), (b) the addition of solid instead of molten lithium, and (c) the use of a pouring vessel instead of their more complex bottom drain vessel with valve to remove molten alloy from the reactor.

Reactors

Our reactors were constructed almost entirely from commercial Type 316 stainless steel NPT (American National Standard Taper pipe threads) pipe fittings obtained from the McMaster-Carr Supply Company, Chicago IL. We selected Type 316 stainless steel to construct these reactors because:

- The corrosion rate of Type 316 stainless steel in the molten eutectic Pb-Li alloy seems to be low, based on a brief comment by Jeppson and Muhlestein (1985) that "No measurable corrosion was observed for mild steel, 304 SS or 316 SS specimens suspended in the reacting alloy during the alloy-air reaction tests." Two tests were performed with the Pb-Li alloy, one at 450°C and the other at 700°C for unspecified times, probably about 8 hours for each test. Also, the corrosion rate of Type 316L stainless steel--similar in metallic composition to Type 316 but with lower carbon content--has been reported to be fairly low, ~ 100 µm/yr when in contact with flowing 83 a/o Pb - 17 a/o Li at 450°C (Sannier et al., 1991). We assume the corrosion rates to be similar for both Types 316 and 316L materials.
- It is readily obtainable in a variety of configurations from many suppliers.
- The recipients for whom our alloy is prepared will use apparatus in which Type 316 stainless steel will be in contact with the Pb-Li melt.

A photograph of one of our reactors is shown in Figure 1; sketches of the reactor as used in the first experiment are shown in Figures 2, 3 and 4.

Figure 1. Photograph of reactor used in the preliminary test, experiment A-123-1. After this experiment, the 1/4 in. pipe nipple at the left was changed to a 3/8 in. pipe nipple for the subsequent experiments.

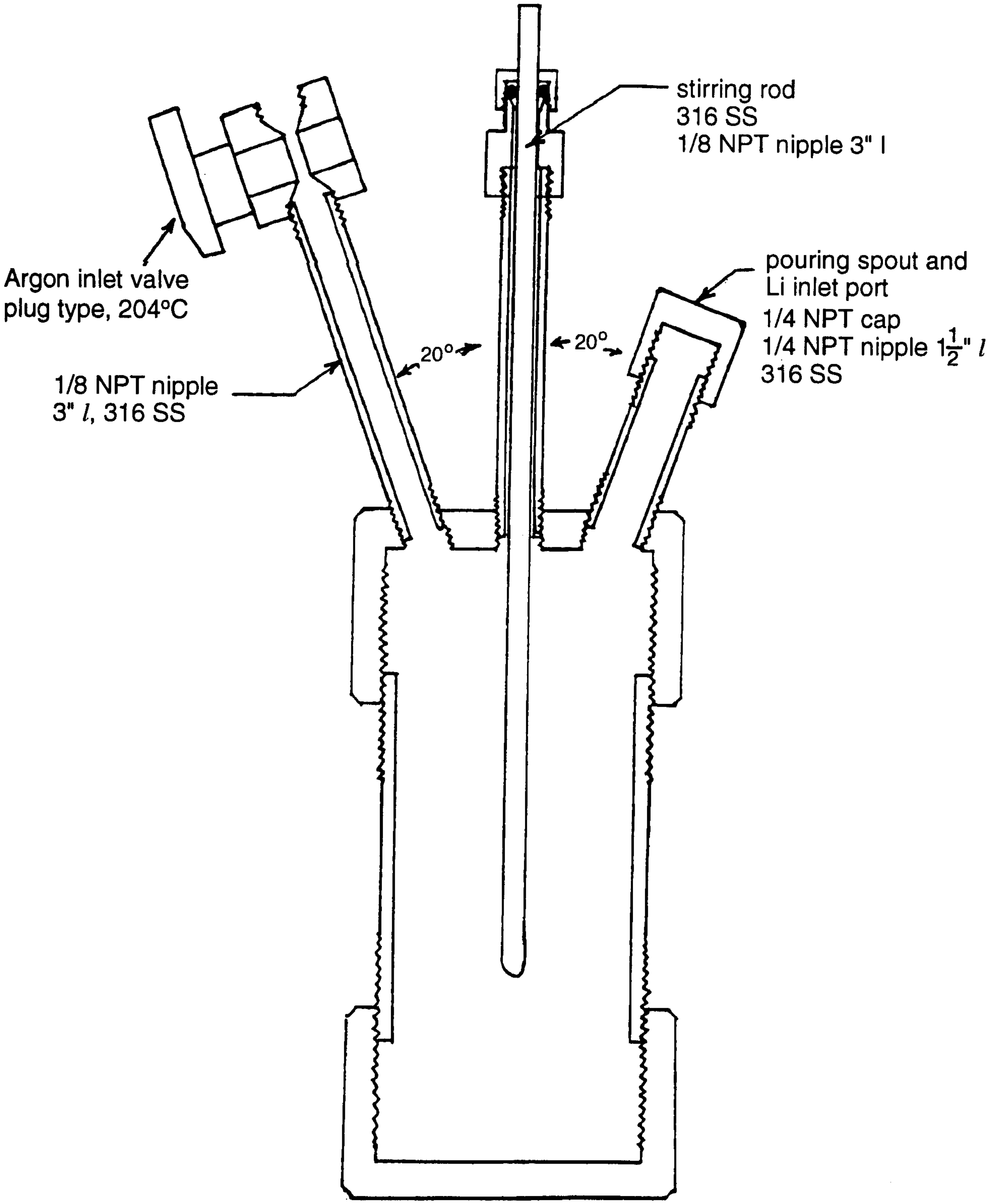

Figure 2. Schematic diagram of the reactor shown in Figure 1; sectional view from the front.

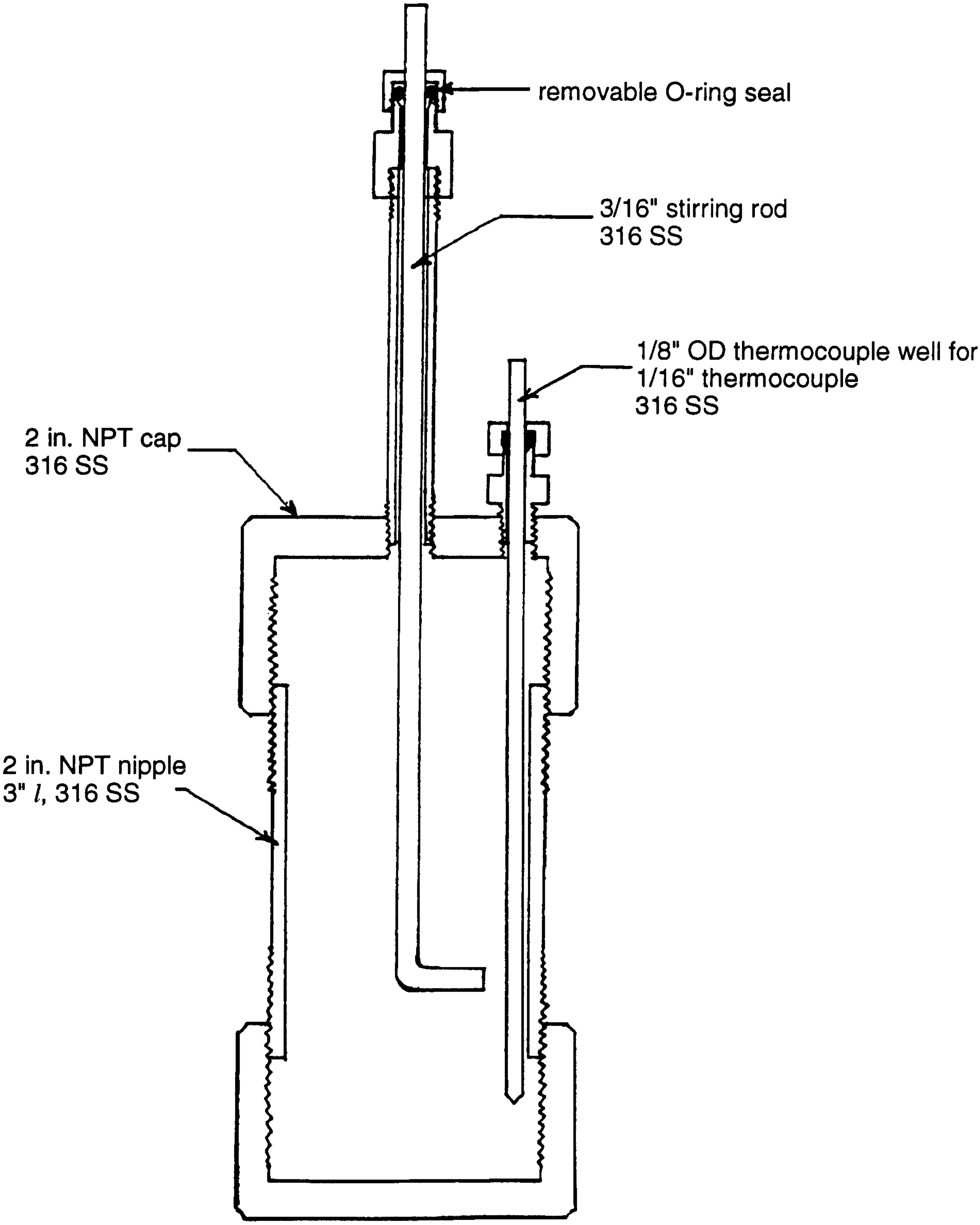

Figure 3. Schematic diagram of the reactor shown in Figure 1; sectional view from the side.

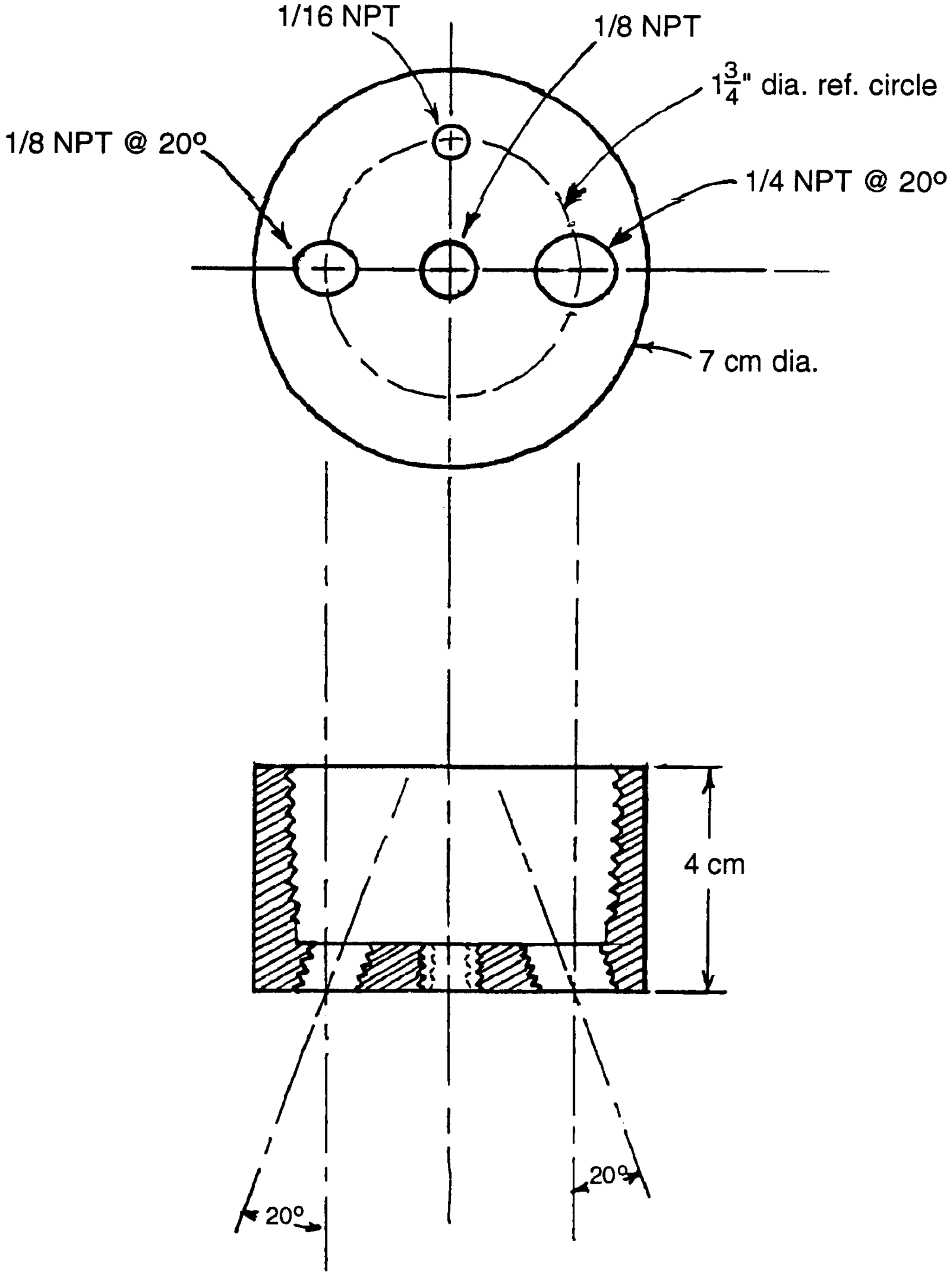

Figure 4. Schematic diagram of the reactor shown in Figure 1; pipe cap, top and side views.

The body of each reactor consists of a 2 in. pipe nipple 7.6 cm (3 in.) long. The bottom and top closures are 2 in. pipe caps. Each bottom cap is used as received, while the upper cap has four holes drilled and tapped to receive NPT-threaded components. Two of the holes are drilled at an angle of 20° from the vertical centerline axis of the cap. Threaded into these four holes are:

- Centered hole, a 1/8 in. NPT nipple 7.6 cm (3 in.)-long that terminates in a Swagelok fitting to accommodate a 4.8 mm (0.188 in.) o.d. stirrer shaft.
- One angled hole, 1/8 in. NPT nipple 7.8 cm (3 in.)-long that terminates in a plug-type valve (Nupro Model No. B-2P4T4) to control argon flow.
- The other angled hole, a 3.8 cm (1.5 in) long, 1/4 in. NPT nipple (first experiment only) or a 3.8 cm (1.5 in.)-long, 3/8 in. NPT nipple (all subsequent experiments) that terminates in a pipe cap of appropriate diameter.
- The smaller hole, a 1/16 in. NPT Swagelok fitting to accommodate a 3.2 mm (0.125 in.) o.d. stainless steel tube closed at one end, used as a thermocouple well.

The total volume of each reactor is calculated from its dimensions to be 268 cm^3; the portion below the top edge of the 2-in. pipe nipple is 209 cm^3.

Each reactor is fitted with an air motor-driven stirrer that can be raised or lowered in the melt. It consists of 4.8 mm (0.188 in.)-diameter Type 316 stainless steel rod with its lower end bent 90° from the vertical. The horizontal portion of the rod is 20 mm (0.8in.) long. The stirring insures complete mixing when the very low density lithium is added to the high density molten lead, minimizes supercooling when the melt freezes and provides a sensor for melting and freezing of the alloy.

Heating

The reactor is heated with a helically wound 1.3 cm-wide X 1.3 m - long (1/2 in.-wide X 4 ft-long) heating tape (heavy insulated, Type STH 051-040, Omega Engineering Corp., Stamford, CT), as shown in Figure 5. The heating tape will deliver up to 313 W at 120V AC, and may be used in direct contact with metallic surfaces. Its maximum continuous operating

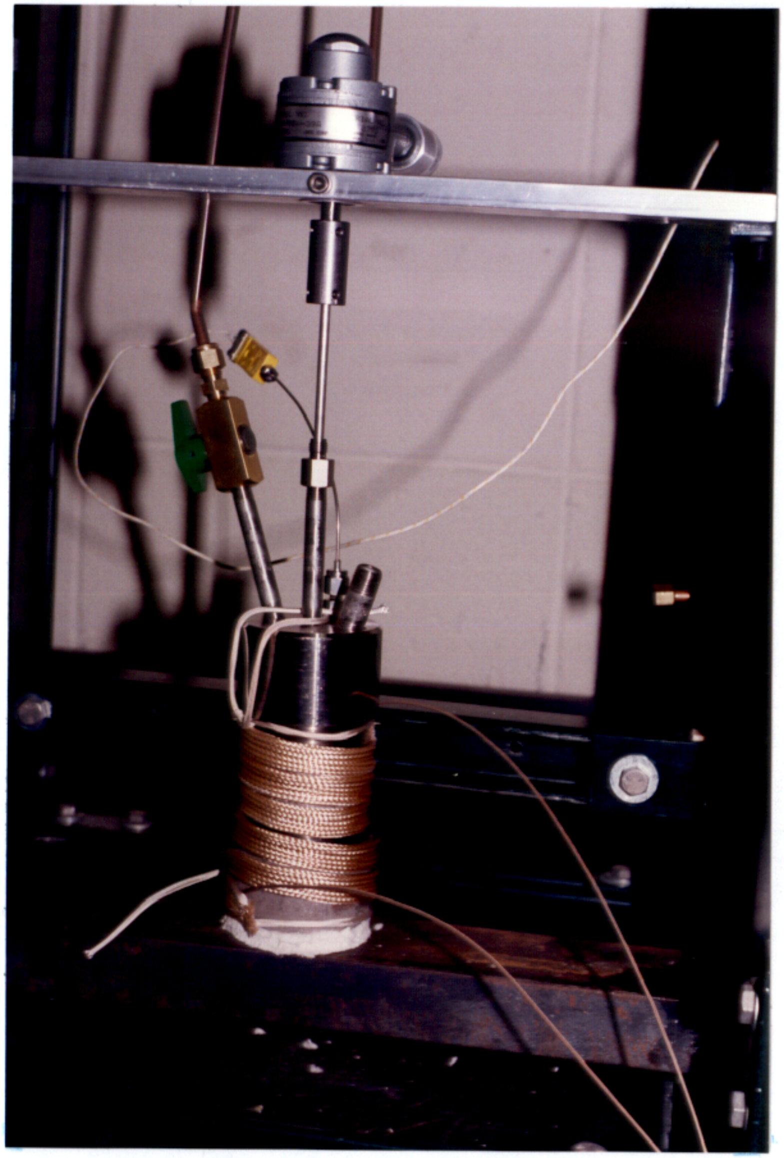

Figure 5. Reactor shown in Figure 1 with heating tape argon line and thermocouple added.

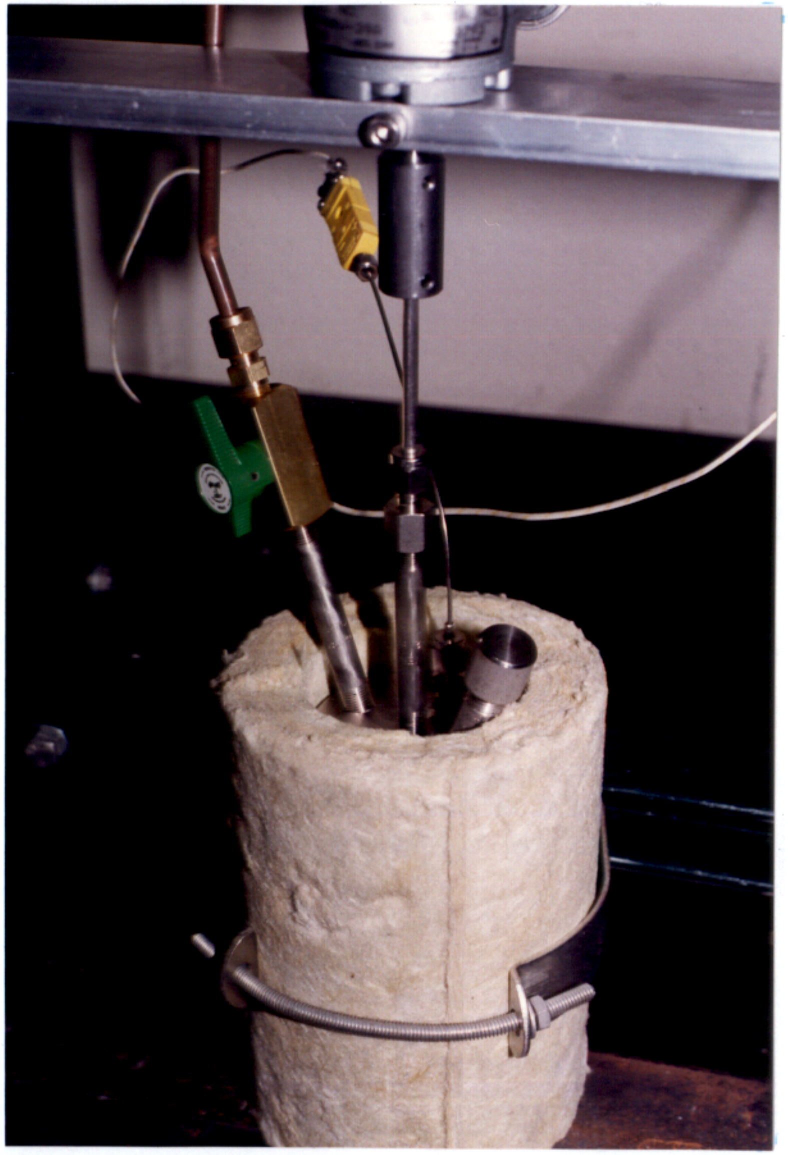

Figure 6. Reactor shown in Figure 1 with heating tape argon line and thermocouple added. Insulation has been put in place.

temperature is 760°C. The wall insulation is standard rock fiber pipe insulation, 7.3 cm I.D. X 2.5 cm-thick (2 7/8" I.D. X 1 in.-thick), obtained from the McMaster-Carr Supply Company, Chicago, IL. It is shown installed in Figure 6. The maximum safe operating temperature for this material is 650°C. The base of the reactor rests on a firebrick, while the top is insulated with alumina wool.

Temperature Measurements

The temperature of the metal is measured with a Miniature Digital Panel Thermometer, Model DP 371-KC5, that uses as a probe a Type K thermocouple, 1.6 mm-diameter X 30.5 cm-long (1/16 in.- diameter X 12 in.- long), Type KQSS--116V -12, both obtained from the Omega Engineering Corp., Stamford, CT. The output of the thermocouple is displayed as digital temperature readings in degrees Celsius. During heating, the thermocouple is slipped into the 3.2 mm (0.125 in.) - stainless steel tube that is immersed in the metal (see Figure 3). This tube is sealed at the bottom end by flame fusion to form a thin thermocouple well. Use of thermocouple wells allows us to make temperature measurements in each of the reactors with the same thermocouple, without concern for possible differences in calibrations or corrosive effects if the thermocouple were immersed directly in the melt.

The thermocouple and digital display were compared with a standard thermocouple by the University of Wisconsin's Electrical Standards Laboratory. Both thermocouples were placed together in a small resistance furnace. In the region of 225 to 235°C, our digital display coincided with the standard within 1°C. Also a duplicate digital display unit behaved identically when digitizing the output from the same Type K thermocouple.

Inert Atmosphere

An atmosphere of flowing argon is used to protect the lithium metal against oxidation and nitridation during cutting, weighing, melting and other operations. For lithium at room temperature, this is accomplished with industrial grade pressurized cylinder gas without further purification; it was obtained from the Liquid Carbonic Gas Corporation. Typical purity of this gas is 99.9992%, with < 5 ppm H_2, <10 ppm O_2, and < 10 ppm N_2, all by volume. This gas is purged through a VAC glove box and its antechamber for several hours sufficient to pass at least 0.8 m^3 (28 cubic feet) at atmospheric pressure. Mass spectrometer analyses of typical atmospheres sampled in this glove box indicate no detectable H_2O, O_2 or N_2 (the minimum level of detectability is ~ 1×10^{-9} mbar).

When the lithium is handled at elevated temperatures, the argon is purified by passage through a furnace packed with titanium chips held at a temperature of 500°C. The purified gas is passed through the reactor shown in Figures 1 through 6 at a rate of 1.4 liters per minute. This purified atmosphere allows us to perform the melting of the lead and the addition of the lithium on the bench top without the risks associated with high temperature operations in a glove box.

Materials

Lead

Two types of metallic lead were used as starting materials in this work:

- In our preliminary test only, experiment A-123-1, we used granular, lead metal, American Chemical Society certified, obtained from the Fisher Scientific Company, Catalog No. 246-500, Lot No. 926469A. The Actual Lot Analysis of this metal is presented in Table 1.

Table 1. Actual Lot Analysis of Lead Metal, Granular [ACS Certified, Catalog No. 246-500, Lot No. 926469A]

Sb and Sn (as Sn)	Passes Test*
As	0.2 ppm
Bi	1 ppm
Cu	0.6 ppm
Fe	0.0002%
Ni	0.0002%
Ag	0.4 ppm
Assay	100.3%

*Limit about 0.005%

This material is in a fine granular form that pours easily and can be weighed out almost exactly. When poured into a beaker, it appears as shown in Figure 7; notice the dark coloration of the massed particles.

- A round lead bar 5.08 cm (2.00 in.) O.D. obtained from Taracorp Industries, Inc., Granite City IL. It is 99.97% lead or purer, according to the supplier. The Certificate of Analysis is presented in Table 2. This lead was used for all subsequent experiments after the preliminary test.

Table 2. Certificate of Analysis of Lead Rod [5.08 cm (2.00 in.)-diameter, Lab Number 16720, Lot Number CL82694A], in Weight Percent

Pb	99.97
Sn	-.001
Sb	.001
Cu	.003
As	-.01
Bi	.02
Ag	-.001
Ni	-.001
Al	-.001
Zn	-.001
Cd	-.001
Fe	-.001

We chose this less pure metallic lead in the bar configuration (see Figure 8) for the remaining experiments because it could be cut to an appropriate length (see Figure 9) that would fit snugly within the 2 in. stainless steel pipe nipple that forms the body of the reactor (see Figures 1 through 6). Samples in this compact form can be cleaned easily and offer a minimum surface area to collect

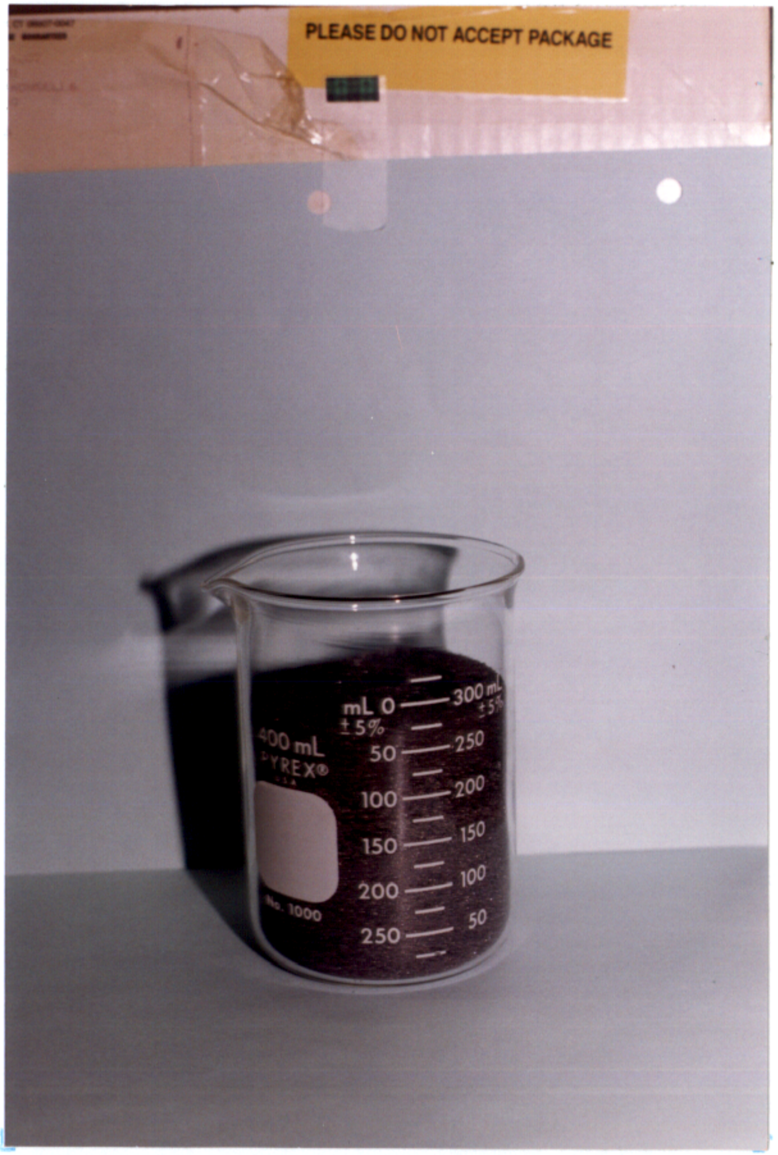

Figure 7. Granular lead ready for addition to reactor in preliminary test, experiment A-123-1.

Figure 8. Bar of precast lead as received.

Figure 9. Sample of lead bar prepared for a Pb-Li alloying experiment.

Figure 10. Container for lithium foil, as received.

surface oxidation; the bars melt to a pool of metal with a minimum of slag on the surface, compared to the granular material.

Lithium

The lithium was obtained from the Johnson Matthey Catalog Co. as Alfa Stock No. 10767, Lot No. J20D06. It has 99.9% purity (metals basis) in the Certificate of Analysis shown in Table 3.

Table 3. Certificate of Analysis of Lithium

[1.5mm (0.059 in.) thick X 100 mm (3.94 in.) wide, 99.9% (metals basis), Stock No. 10767, Lot No. J20D06]

Li	99.8%
Na	.0090%
N_2	.0015%
Ca	.0078%
Si	.0008%
Al	.0009%
Mg	.0005%
K	.0002%
Cl	.0020%
Fe	.0004%
Cu	.0020%

The lithium foil was received from the supplier in an argon-filled sealed metal can, as shown in Figure 10. Because the can is not strong enough to withstand significant pressure differentials, it was not possible to use a procedure that involved evacuation of the antechamber (pass through) before passing the can into the glove box. (Before this work, evacuation and refilling the antechamber several times with argon had been the standard method used for passing dense objects and materials in and out of the glove box.) Therefore, we developed the technique of flushing 0.8 m^3 (28 ft^3) of argon first through the glove box and then exiting via a vent line into the antechamber (with inner and outer doors closed). In this way, the antechamber and its contents could be maintained at atmospheric pressure as the gas composition in the antechamber approached that of the glove box interior. We estimated that 10 complete purges of the 0.08 m^3 (2.8 ft^3) antechamber volume would bring its composition sufficiently close to that of the glove box to permit opening the interior door to allow the inward pass through.

Once the can had been passed into the glove box, it was opened with an ordinary household can opener. When the cover was removed, the lithium foil was found to be wound on a metal spool that fit snugly inside the can (see Figures 11 through 13). We immediately removed the foil strip from the spool (see Figure 14), cut it in two across the 100 mm direction and placed each half loosely coiled in separate screw-top jars of about 1 L capacity. The metal was shiny and silvery when removed from the spool. It remained essentially unchanged throughout the experiments.

Preparation of the Lithium Samples

We used Type 304 stainless steel tubes about 15 cm (6 in.) -long and 10 mm (0.49 in.) -I.D. to hold about 8 mm (0.32 in.) - wide strips of lithium cut from the 100 mm (4 in.) - wide X 1.5mm (0.059 in.) - thick lithium foil. These tubes were individually stoppered with red rubber microanalytical stoppers (Fisher Scientific Company). The tubes with stoppers are shown in Figure 15. Both the tubes and their corresponding pair of stoppers were individually numbered to yield consistent tare weights. The tubes were passed into the glove box with stoppers removed.

In the first experiment, A-123-1, we cut the lithium foil with a 25 cm (10 in) Flex Broad Knife (a tool used in painting and spackling wallboard) pushed down against the foil backed with a 6 mm (0.25 in.) -thick polypropylene plate. Widths of the foil were estimated with a metric

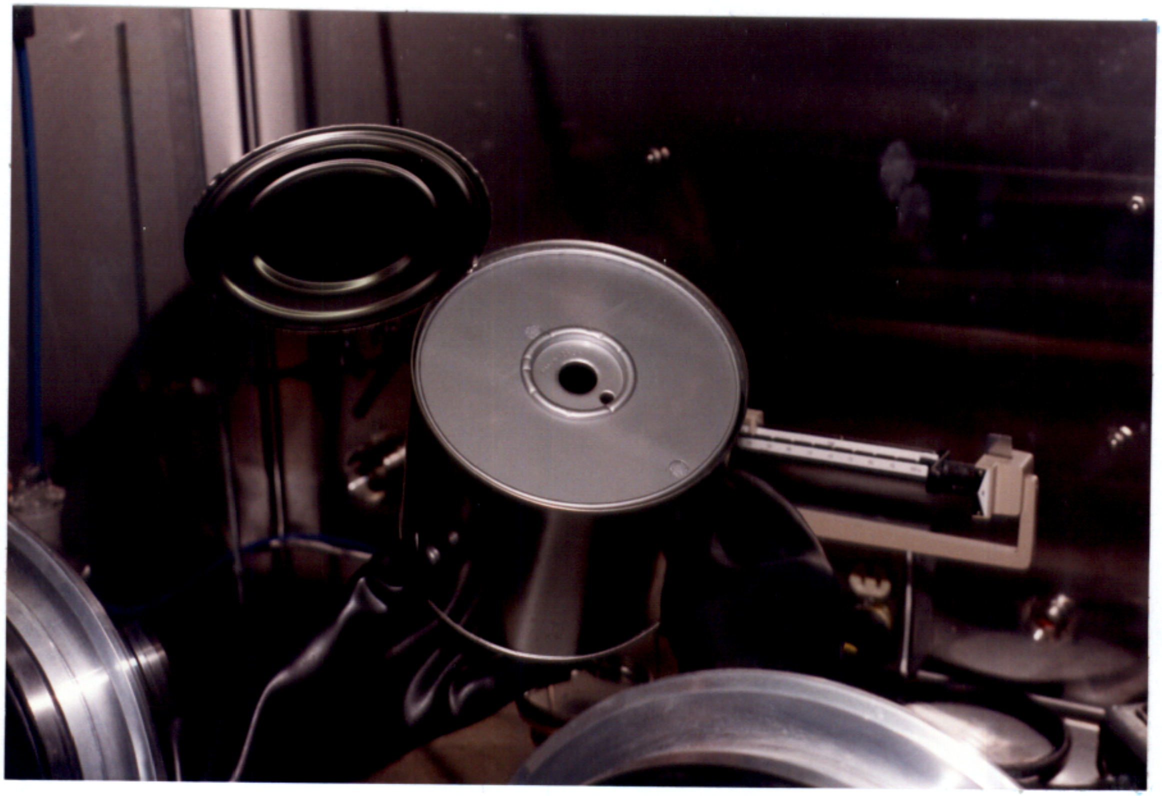

Figure 11. Container for lithium foil after lid was removed. One end of spool can be seen.

Figure 12. Spool of lithium foil after removal from container.

Figure 13. Lithium foil on spool, ready to be removed.

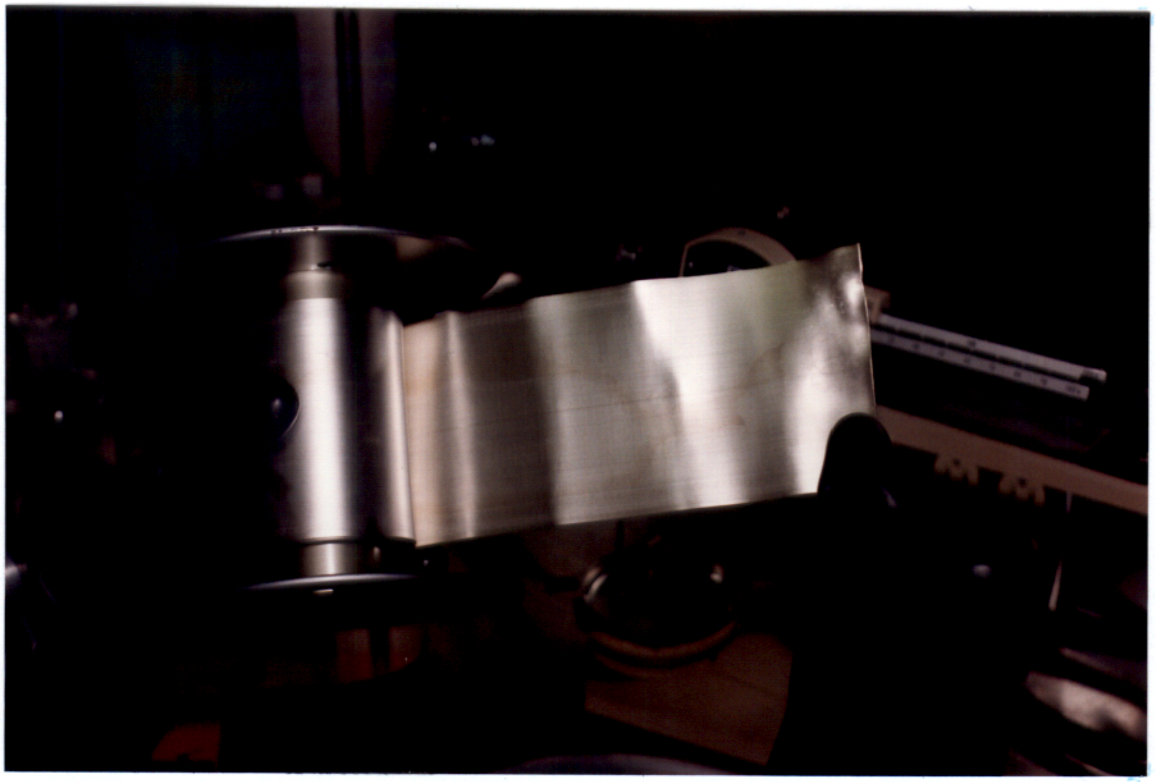

Figure 14. Lithium foil being removed from spool.

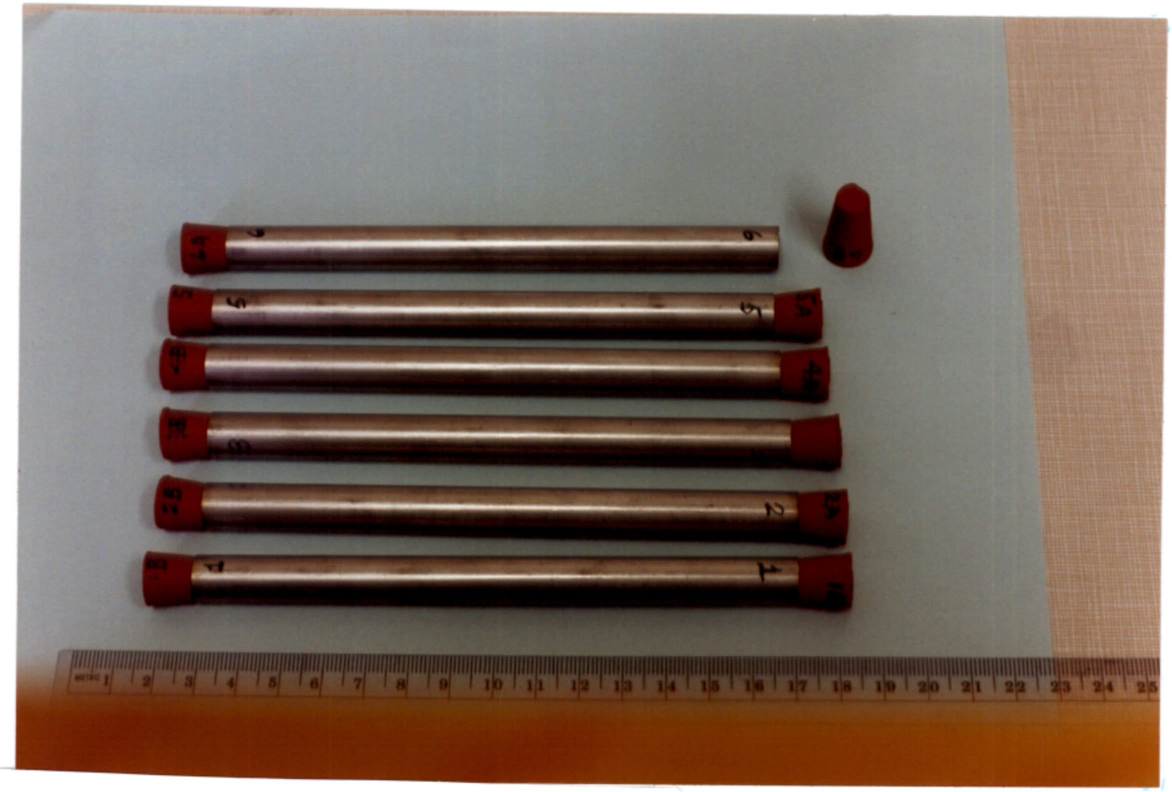

Figure 15. Tubes that hold strips of lithium foil.

Figure 16. Paper cutter used to cut strips of lithium foil.

rule. Three or four approximately 8 mm (0.32 in.) -wide strips of foil were loaded into each of the six sample tubes. In several tubes, the lithium strips fit into the tubes quite snugly.

In the remainder of the experiments, the lithium foil was cut in the glove box with the office-type 25 cm (10 -in.) paper cutter (Premier Corp., Model P210) shown in Figure 16. The cutter had a guide with a metric scale that permitted square cuts of measured widths to be made easily; this was difficult with the knife and rule arrangement used for experiment A-123-1.

In these later experiments, the entire length of foil required to produce the proper alloy composition was cut and weighed. Its initial length was estimated somewhat high from the dimensions of the foil and its density; slight trimming with the paper cutter brought the strip to the exact weight desired. Then this piece of foil was cut into the appropriate number of strips desired. Photographs of the foil-cutting with the paper cutter in the glove box are shown in Figures 17 and 18. A minor inconvenience when the paper cutter is used is a gentle curl imparted to the lithium strips during cutting, as shown in Figure 18. The curl is easily removed by smoothing the strips with a (gloved) finger against the flat bed of the paper cutter.

In all experiments after A-123-1, only one strip of lithium was packed into each sample tube to assure easy delivery into the reactor. After stoppering both ends, each sample tube was shaken gently to make sure the lithium strip moved freely inside the tube. The stoppered tubes were then weighed individually inside the glove box and compared with the corresponding tare weights to determine the weights of each strip of lithium. Finally, the stoppered tubes were passed out of the glove box before an experiment was performed.

Safety and Health

Care was taken during handling, cutting and heating of the lead to prevent ingestion or inhalation of any form of the metal. The cutting (hacksaw) and cleanup of the sample is done with gloves as appropriate, followed by prompt washing of hands. The heating and melting is done with the reactor inside an efficient hood (see Figure 19) that exhausts vapors, smoke, aerosols or mists above the building.

Safety glasses are worn by all personnel that work near the apparatus.

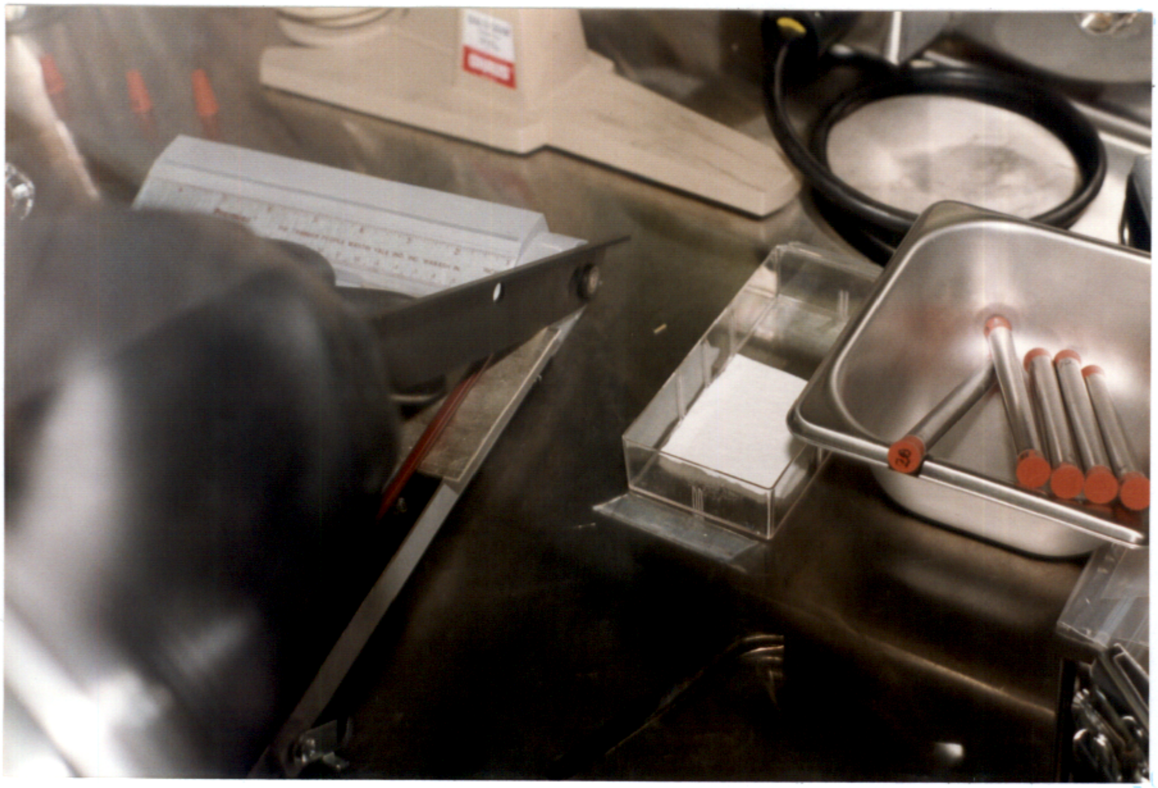

Figure 17. Start of cutting of strip of lithium foil in the glove box.

Figure 18. Nearly completed cutting of a strip of lithium foil. Note the curl imparted to the strip as it is being cut.

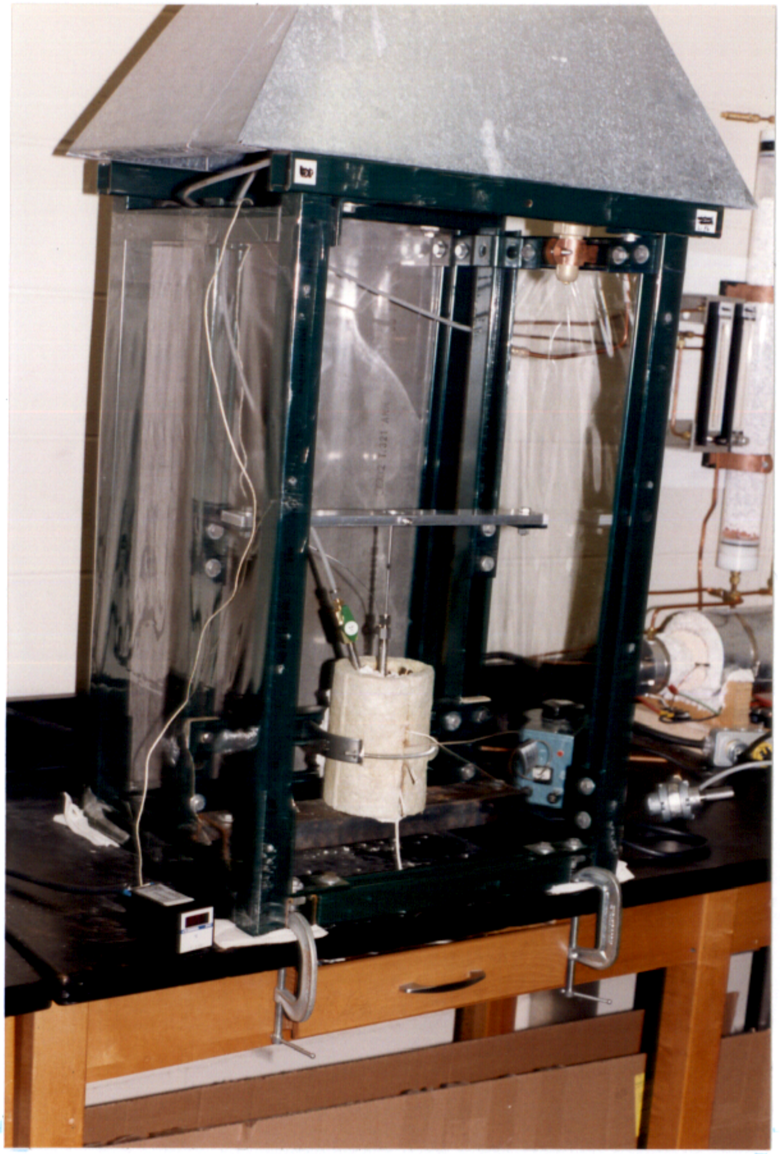

Figure 19. Overall view of the reactor as it is heated during preparation of a batch of Pb-Li alloy. Hood is above the apparatus; three sides of the framework are closed with metal or plastic sheets. Argon purifier (titanium chip furnace) is partially visible at the right of the photograph.

Figure 20. Body of the reactor used in the preliminary test A-123-1. Solidified alloy with flaky surface can be seen.

Lithium safety procedures involved maintaining the metal in an argon atmosphere in the glove box, during transit from glove box to the melting location, and during insertion into and reaction within the reactor. No more than 0.8 g of the metal was handled when the lithium in a given sample was added to the melt in the reactor. The lithium was always solid when handled.

RESULTS

The first experiment, A-123-1, is considered to be a dry run in which our procedures were tested. The next three experiments, A-133-1, A-146-1 and B-2-1, were conscientious runs that corrected or modified the mistakes and weak procedures identified during the initial run.

Preliminary Test

In experiment A-123-1, we used granular lead and lithium strips packed three or four to a sample tube. The reactor's entry/exit was a 1/4 in. Type 316 stainless steel pipe nipple which has a 13.7 mm (0.540 in.) O.D. and a 9.2 mm (0.364 in.) I.D. The sample tubes were 11.1 mm (0.438 in.) O.D. and 10.1 mm (0.398 in.) I.D. Thus the outer diameters of the sample tubes were somewhat larger than the inner diameter of the entry/exit nipple. This was compensated for by threading a 1/4 in. Type 316 stainless steel coupling onto the 1/4 in. nipple, thus providing an extension to the nipple with inner diameter of 13.7 mm (0.540 in.), adequate to accept the outer diameter of the sample tube, 11.1 mm (0.438 in.), and provide an in-line connection between the sample tube and the pipe nipple. Unfortunately, the inner diameter of the 1/4 in. nipple, 9.2 mm (0.364 in.), is slightly smaller than the inner diameter of the sample tubes, 10.1 mm (0.398 in.). Therefore, there was a small step between sample tube and nipple that prevented easy passage of the lithium strips into the reactor.

We were able to empty the lithium strips from Tube No. 1 into the reactor in spite of the step, although not without difficulty. But the second set of strips from Tube No. 2 hung up completely at the step. Pushing, pulling, heating to melt the lithium, etc., were all to no avail, causing us to terminate the experiment early with only a small fraction of the lithium placed initially in the six sample tubes actually added to the melt. We also terminated the experiment with a partial plug of solidified lithium at the inside of the inlet/exit nipple.

The solidification of the alloy upon cooldown began at about 290°C corresponding to an approximate composition of 91 a/o Pb - 9 a/o Li, estimated from the phase diagram (Hansen, 1958).

After the solidification and cooling to room temperature, the metal in the reactor was reheated to 300°C to allow us to remove the stirrer and thermocouple well from the melt. When solidified again, we were able to remove the upper cap and examine the frozen material and the intense components of the melter. We saw essentially no attack of the reactor interior or the stirrer by the melt, although conditions for viewing any attack were not ideal. The interior of the vessel and the head as removed are shown in Figures 20 and 21. The stirrer and the partially plugged 1/4 in. pipe nipple removed from the cap, viewed from both the inner and the outer sides of the reactor are shown in Figures 22 through 24.

Although we produced no usable alloy in experiment A-123-1, we took advantage of our experiences to make a number of improvements in the procedures for subsequent experiments. These are summarized in Table 4.

Table 4. Improvements to the Procedures for Preparing Lead-Lithium Alloys Based on Preliminary Test

Improvement Desired	Action to Take
Use block lead to minimize slag on surface of the melt	Seek supplier of cast lead
Provide larger orifice for Li addition; strips must pass through easily	Use larger entry/exit pipe nipple
Increase number of sample tubes; one Li strip per tube; strip must fall out freely	Procure more stainless steel tubing; cut more tubes
Improve cutting of Li foil	Obtain small paper cutter with guide and metric scale.

Subsequent Experiments

The three experiments performed after the preliminary test, A-123-1, were essentially identical. In these experiments we used the following improvements:

Figure 21. Dissembled reactor used in the preliminary test A-123-1. Upper pipe cap with retracted stirrer and thermocouple well rests on the body of the reactor shown in Figure 20.

Figure 22. Stirrer after removal from the upper pipe cap shown in Figure 21. Note slag-like coating.

Figure 23. Inside end of partially plugged 1/4 in. pipe nipple removed from upper cap of the reactor shown in Figure 21. Note deposit of metallic lithium.

Figure 24. Outer end of partially plugged 1/4 in. pipe nipple removed from upper cap of the reactor shown in Figure 21. Note deposit of metallic lithium.

- A 3/8 in. nipple as the entry/exit port, threaded into an enlarged, tapped hole in the cap of the reactor. Its I.D. is larger than the O.D. of the sample tubes and the widths of the lithium strips. Sample tube can be inserted into this nipple during loading of the lithium.
- A cylinder of solid lead precast to the 51 mm (2.00 in.) inner dimension of the reactor.
- Strips of lithium cut more precisely with a paper cutter.
- One strip of lithium loaded per sample tube in a way that allows freedom of motion when loading into the reactor. Freedom was checked by gentle shaking of each sample tube.

The four experiments, A-123,1, A-133-1, A-146-1, and B-2-2, are summarized in Table 5.

Observations During the Experiments

Each of the three subsequent experiments was started by cutting, deburring, cleaning and weighing the lead slug and placing it in the reactor. Each reactor head (pipe cap) was then put in place and tightened. The reactor was then wound with the heating tape and positioned on the insulating base and secured in the framework that supports it, the stirring motor and the exhaust hood (see Figure 19). The insulation was then positioned around the reactor, which then was ready for heating. When the upper cap was placed on the reactor, both the stirrer and the thermocouple well rested on top of the solid lead slug in the reactor.

Meanwhile, in the glove box, the required amount of lithium had been unwound and cut from the loose coil of 1.5 mm - thick foil that is stored in a screw top jar in the glove box. If needed, the large piece (about 15 cm long and 10 cm wide) was trimmed slightly to adjust its weight to form the alloy properly with the amount of lead already contained in the reactor. This parent piece of foil was then cut into nineteen 8 mm-wide strips with the paper cutter. The last two or three strips to be cut sometimes were somewhat narrower than the rest depending on the accuracy of each cut and the total length of the parent strip.

Each of these strips was then placed in its own sample tube, which was in turn stoppered at both ends, placed in a rack that holds up to 24 tubes (see Figure 25), and then passed out of the glove box through the antechamber maintained always at atmospheric pressure.

Table 5. Summary of Runs in Which Lead-Lithium Alloys Were Prepared

Expt. No.	Reactor No.	Empty Reactor Wt. (g)	Wt. of Pb (g)	Added Wt. of Li (g)	Wt. of Alloy(g)	T_{max} (°C)	T_{halt} (°C)	Remarks
A-123-1	0	-----	1709.6	-----	-----	453	-----	Li addition failed. Aborted at approximately 91 a/o Pb-9a/o Li
A-133-1	1	1963.4	1523.5	10.75	1534.3	422	230	Remelted to add final 0.62 g of Li; Tmax = 329°C during remelting
A-146-1	2	1938.2	1697.1	12.11	1709.2	450	231	
B-2-1	3	1845.2	1706.6	12.02	1718.6	450	230	

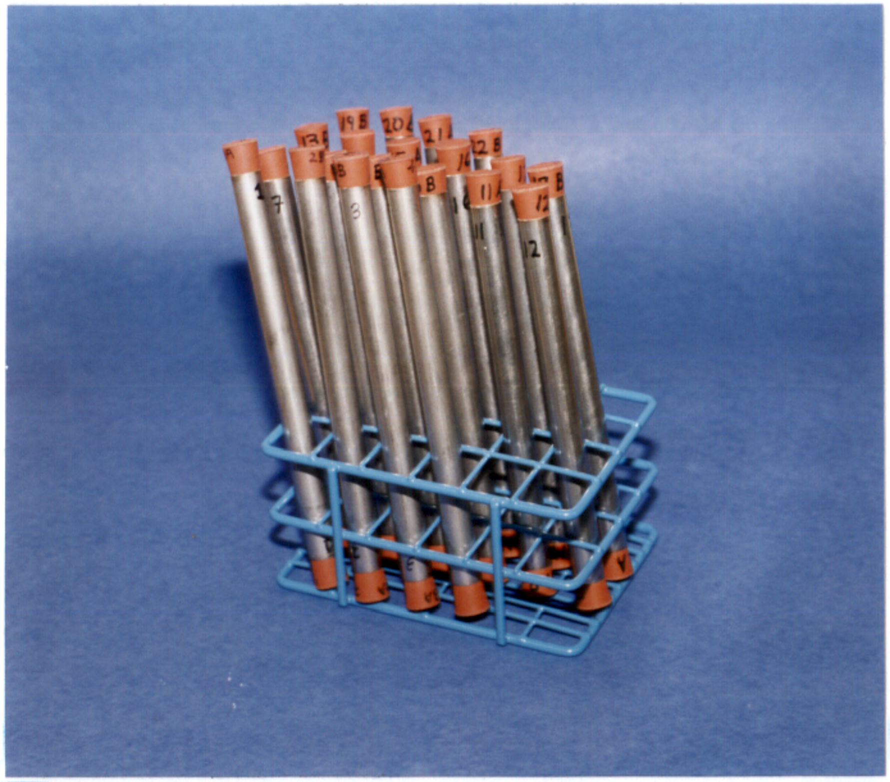

Figure 25. Lithium sample tubes in rack used for transport between glove box and reactor.

Figure 26. Lithium strip being added to the reactor during preparation of a batch of Pb-Li alloy. Air-driven stirring motor and stirring rod can be seen in upper portion of the figure.

After the lead and the lithium are ready, the purified argon flow is started through the reactor after the titanium chip furnace has reached 500°C. The purified argon enters the reactor through the open Nupro valve (see Figures 1, 2, 3, 5 and 6) and exits through the uncapped 1/4 in. or 3/8 in. pipe nipple. Some gas also exits around the untightened fittings around the stirrer and thermocouple well. The exiting gas and any vapors, mists, aerosols, and smoke are swept away by the action of the hood above the apparatus (see Figure 19).

Next, the reactor is heated to melt the lead. We discovered early on that this must be done fairly cautiously before melting is complete to prevent excessive vaporization of lead from the reactor. Apparently, the thermal conductivity of the lead is fairly low, allowing a thin layer on the outside of the slug to become quite hot and thus eject lead vapor which quickly condenses to a mist outside the exhausting exits. By heating fairly slowly (about two hours to reach 400°C) the mist formation is minimized.

There is a brief halt noticeable when the melting temperature of the lead, 320°C, is reached. Shortly afterward the stirrer and thermocouple well sink into the melting lead. The stirrer is then attached to the air-driven motor, and stirring begins. The thermocouple well is then lowered into position and fastened about 2/3 the depth of the melt (Note: The temperature readings before melting occurred must be taken with the thermocouple well resting on top of the solid slug of lead).

After melting was complete, the thermocouple well and stirrer were lowered into the melt. Also, the heating rate was then increased and the melt temperature brought to about 400°C. At this temperature we began to add the lithium strips one at a time into the reactor through the 3/8 in. pipe nipple. This was done by removing the stopper from the bottom end of each sample tube, quickly inserting the sample tube into the nipple and gently tapping to cause the strip of lithium inside the tube to fall into the stirred metal in the reactor (see Figure 26). Usually the strip fell in quickly, but occasionally it had to be helped in by removing the upper stopper on the sample (the argon purge gas now passes through the sample tube) and pushing the metal out with a stainless steel rod. The entire operation with or without the pushing normally required only a second or two per strip, with the lithium always bathed in the argon flowing from the reactor.

The addition of the lithium was an exothermic process, in which the temperature of the melt increased 5 or 10°C after each strip was added. Moreover, when we looked into the reactor with a flashlight, we could see the lithium strip being pulled down gradually into the vortex in the melt around the rotating stirrer. Then a few seconds after it had disappeared into the melt, a distinct small orange-red flame often formed above the vortex, perhaps 6 or 8 mm tall. It resembled a tiny candle flame in both behavior and appearance. (This flame is discussed in greater detail in Appendix A.) The flame appeared with almost every strip, both early and late in the addition of lithium. In a few additions of lithium, however, the flame did not form.

Occasionally, a brief, unusually vigorous orange-red flame formed that reached outside the entry/exit nipple. This sometimes produced a nebulous lime green flame in the air. This flame is rare and difficult to see. Both the orange-red and lime green flames are discussed in Appendix A.

Once all lithium strips have been added to the reactor, the temperature of the melt will have gradually increased from 400°C to about 425°C due to the exothermicity of the alloying. For uniformity between batches, the heater current is increased until the melt temperature reaches 450°C.

Cooling Curves

Once 450°C is reached, the current to the heater is cut off and the top and side insulation is removed to allow rapid cooling. The temperature of the stirred melt is then recorded once per minute during the cool down until it is a few degrees above the eutectic temperature of 230°C; at this point the temperature is recorded every 30 s until freezing is complete. After freezing the temperature is recorded then at minute intervals until about 200°C, at which point the gas exit nipple is capped and the argon flow is terminated by closing the Nupro valve. The experiment was considered complete at this temperature.

A plot of temperature vs. time for each of the last three runs is shown in Figures 27, 28 and 29. Note the well-defined plateau at 230-231°C that is observed as solidification proceeds. The plateau is about 10 minutes long for our conditions during which the stirrer begins to seize and slow down. The end of the plateau coincides with essentially complete freezing of the melt. It also coincides with the abrupt and complete stop of the stirrer.

Note also in Figures 27, 28 and 29 that no supercooling is detectable at the start of the plateau. This is attributed to the generation of nucleation sites during the continuous stirring of the melt during cooling.

In Figure 30, we have superimposed the cooling curves from Figures 27, 28 and 29. Note the excellent repeatability of the halts at 230 or 231°C (the precision of our temperature measurements is about 1°C). The phase diagram shows this eutectic to lie at 235°C (Hansen, 1958). Note also that the melt in experiment A-133-1 cools slightly faster and has a shorter halt than experiments A-146-1 and B-2-1. We attribute these differences to the smaller mass of alloy in experiment A-133-1, 1534.3g, compared to 1709.2g and 1718.6g in experiments A-146-1 and B-2-1.

Chemical Analysis: Inductively Coupled Plasma Mass Spectrometry

Samples of each batch of solidified alloy were taken by inserting a 30.5 cm (12 in.)-long 6.4 mm (1/4 in.) drill bit into each reactor through the pipe nipple entry/exit port, while cylinder argon purged the chamber through the Nupro valve. Slow rotation of the bit with an electric drill produces long turnings (see Figure 31) that were sent to the Soil and Plant Analysis Laboratory, Department of Soil Science, University of Wisconsin-Madison for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analyses. A brief summary of the results obtained is presented in Table 6; the complete analytical report is reproduced in Appendix B.

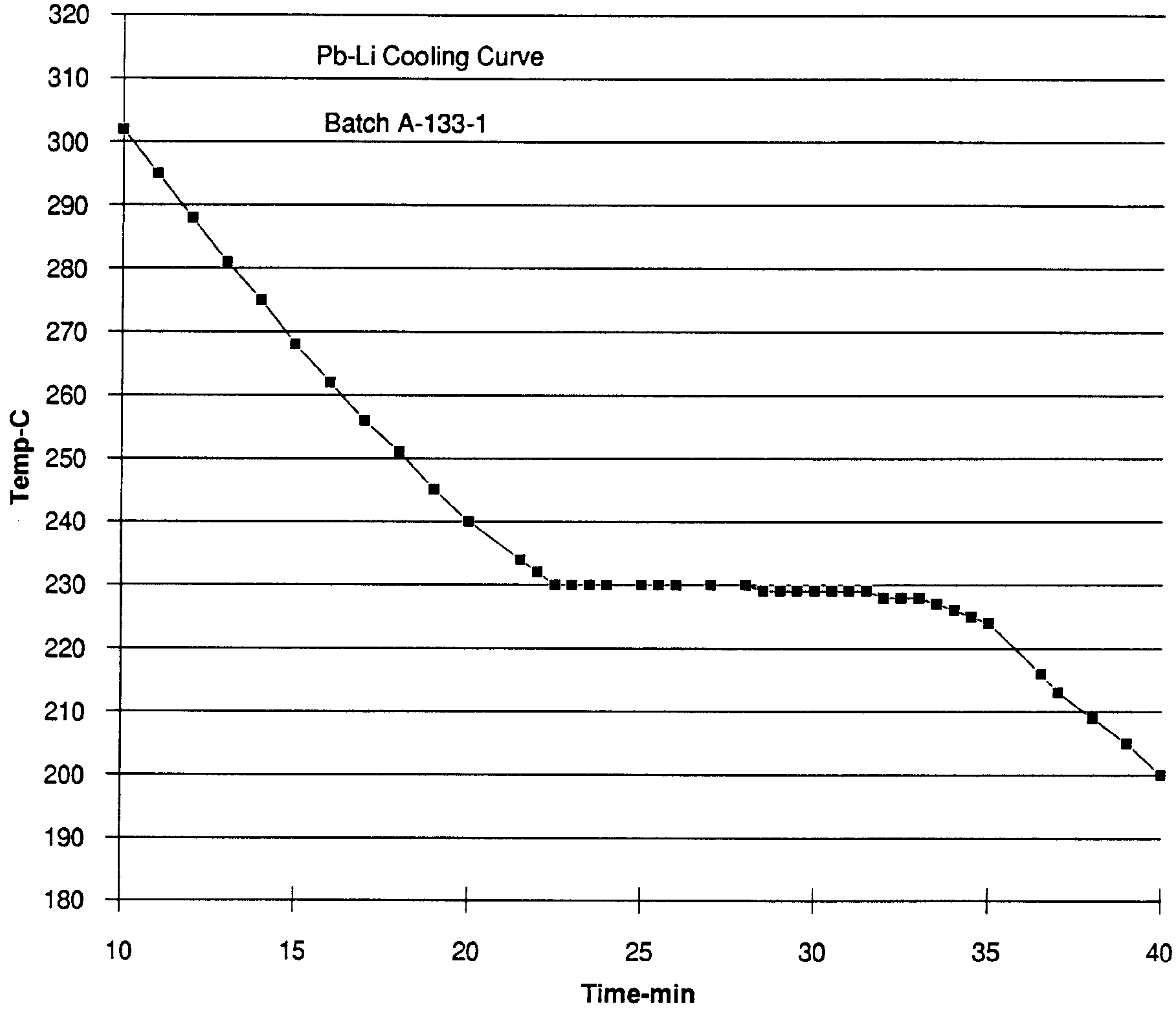

Figure 27. Cooling curve for experiment A-133-1.

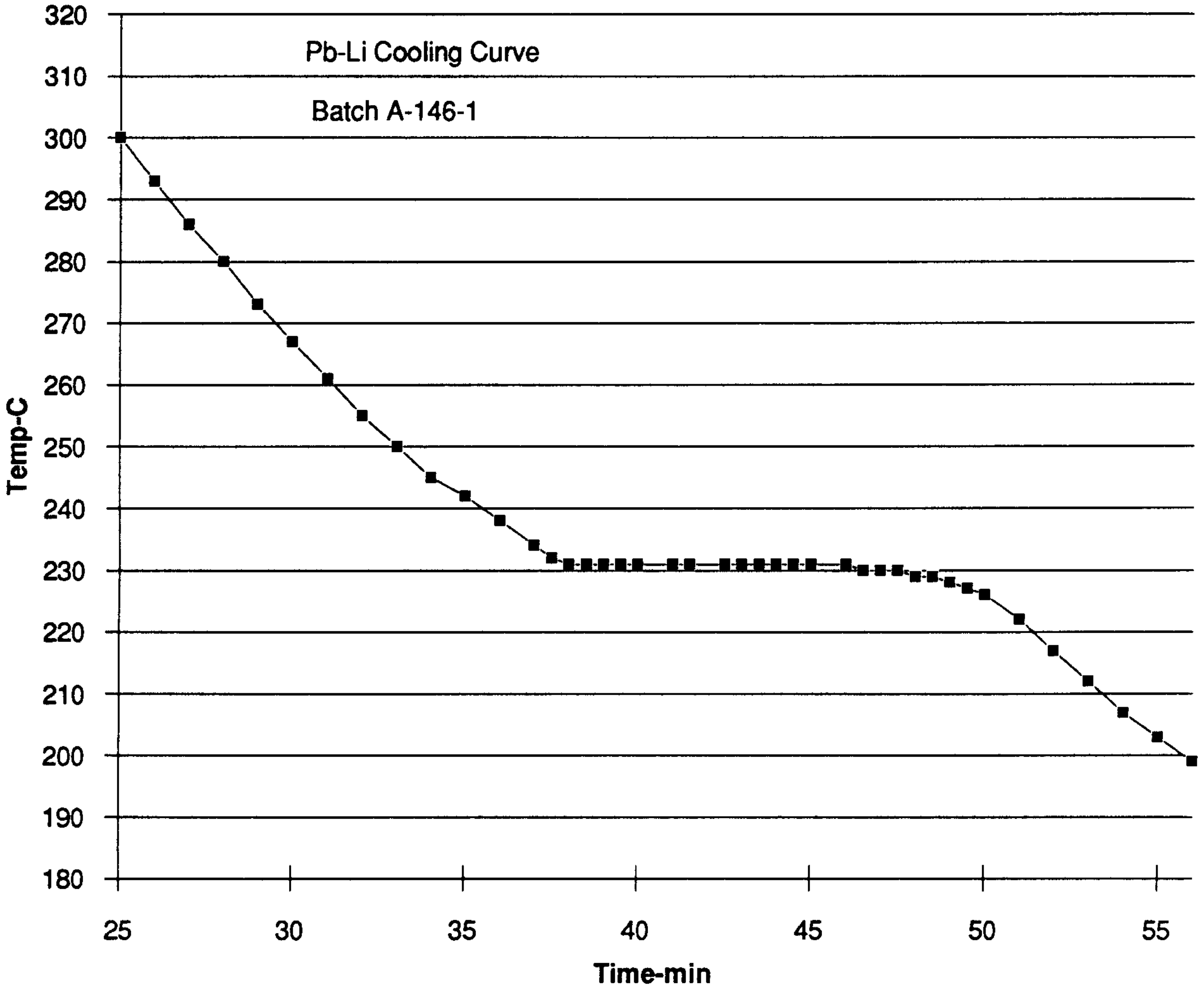

Figure 28. Cooling cure for experiment A-146-1.

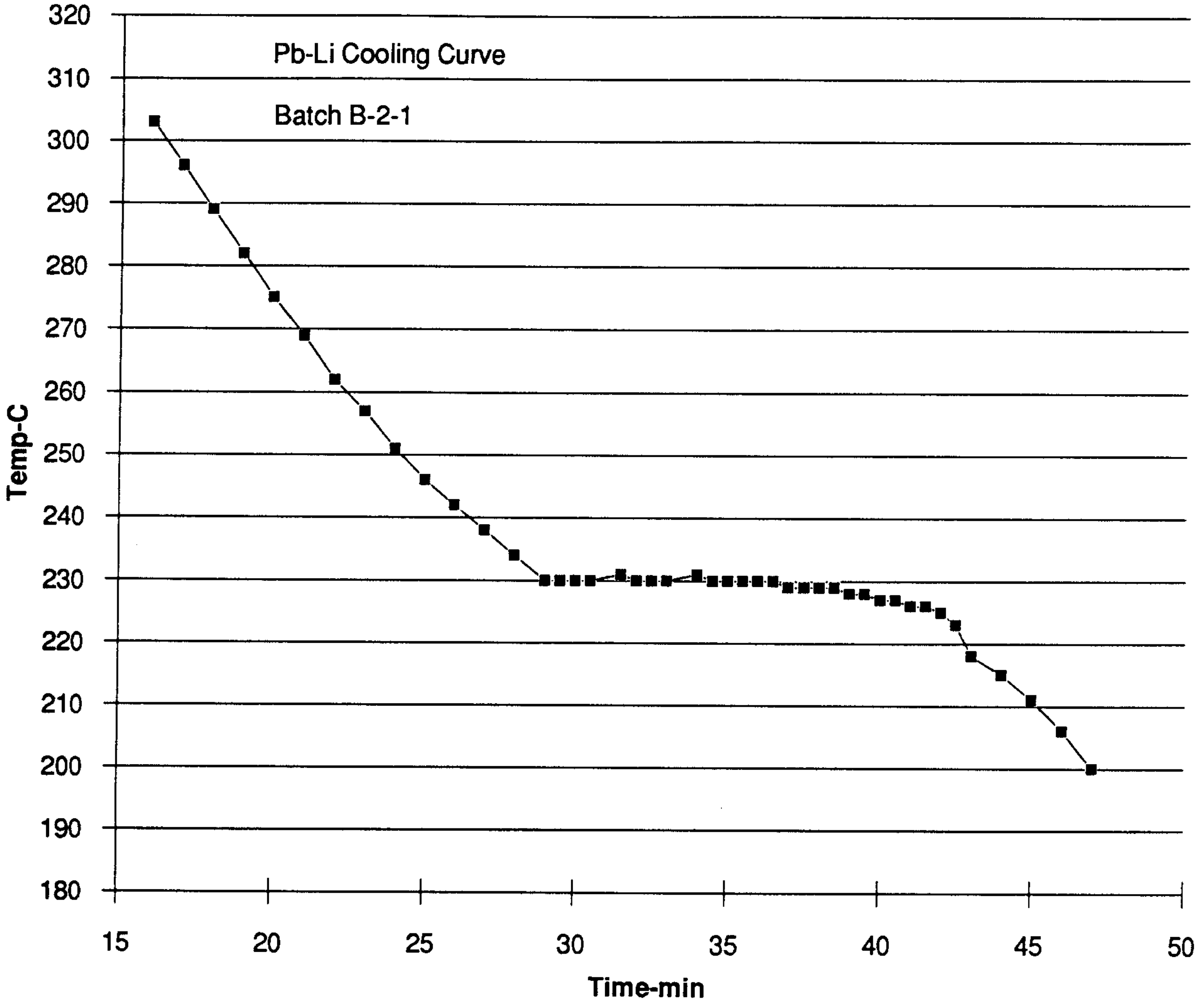

Figure 29. Cooling curve for experiment B-2-1.

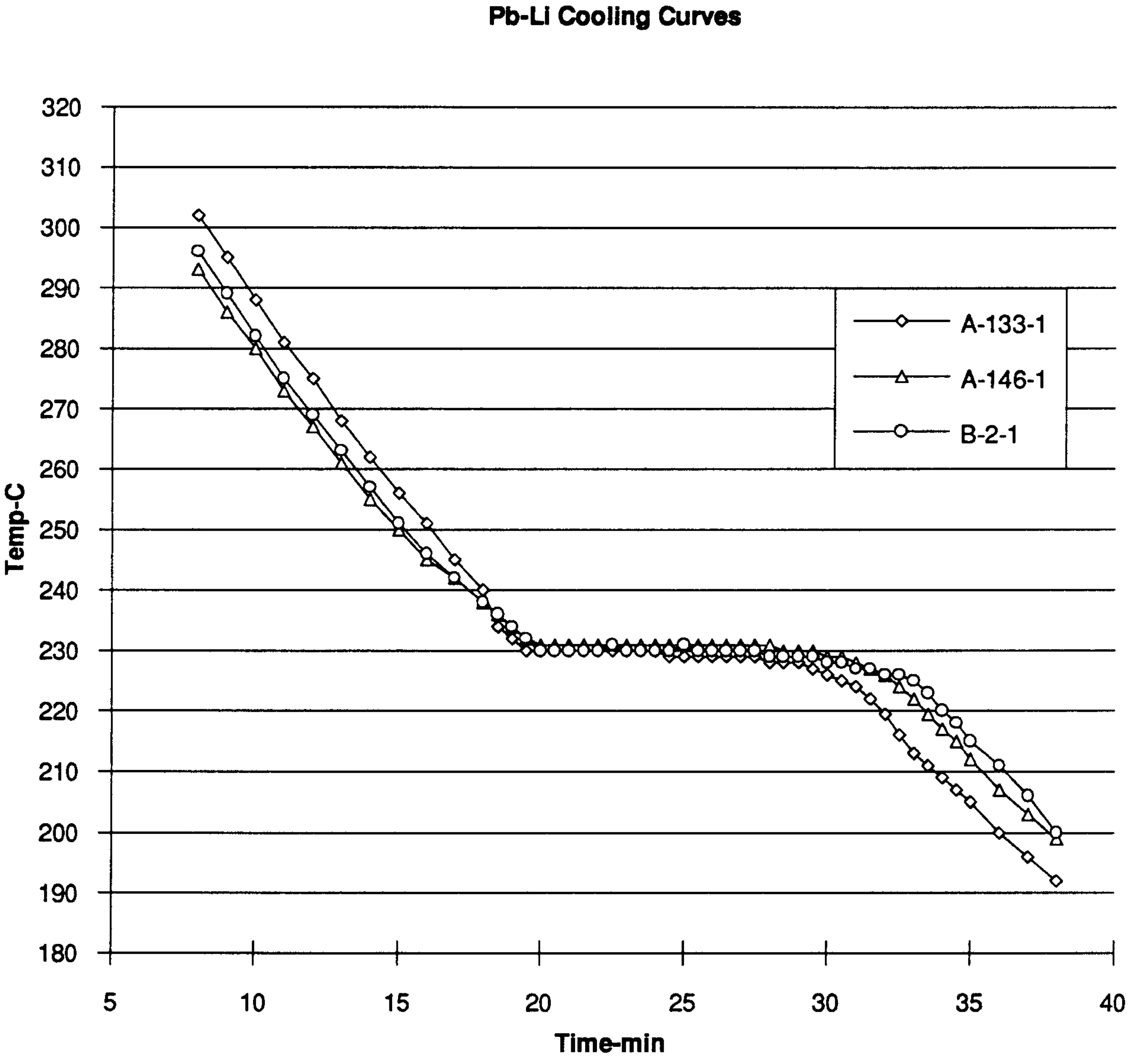

Figure 30. Superimposed cooling curves from Figures 27, 28 and 29.

Figure 31. Turning taken from Batch No. A-146-1.

Figure 32. Pouring rig prior to installation of outer insulation. Heating tape and argon line are in place.

Table 6. Summary of the Analyses of Pb-Li Alloys by Inductively Coupled Plasma Mass Spectrometry (a/o = atomic percent)

Sample No.	Li(a/o)	Pb(a/o)	(Li + Pb) (a/o)
A-123-1a	4.96	95.04	99.86
A-123-1b	5.21	94.79	99.79
A-123-1c	5.51	94.49	98.13
A-133-1a	16.98	83.02	99.45
A-133-1b	17.12	82.88	98.03
A-133-1c	17.00	83.00	99.97
A-146-1a	16.18	83.82	99.37
A-146-1b	17.55	82.45	98.01
A-146-1c	17.90	82.10	100.42
B-2-1a	17.27	82.73	100.26
B-2-1b	16.87	83.13	100.09
B-2-1c	16.97	83.03	100.00

The analyses show that the desired eutectic composition of 17 and 83 atomic percent for lithium and lead, respectively, in the three batches of alloy, A-133-1, A-146-1 and B-2-1, was achieved with accuracies of better than 1 a/o. Thus, use of these three batches interchangeably for melt-water interactions should present, at worst, only minimal chemical problems due to compositional inconsistencies.

Pouring and Casting the Alloys

We used a pouring rig based on a worm gear-controlled tilting tripod head, Geared Head, Model QHH-3 (Qikset International, Inc. Northbrook, IL). Photographs of the pouring rig are shown in Figures 32 through 34. Figure 32 shows the reactor held in place on a firebrick base with the heating tape wrapped around the reactor. In Figure 33, the outer insulation has been put in place. A pouring mold has been added; it is held in a graphite block heat sink. Figure 34 shows the heated reactor just after a sample of melt had been poured from Batch No. A-123-1, the material from the test experiment.

Four samples were poured successively from this batch at nominally 350°C into the stainless steel mold. Each sample froze quickly and, just as the metal came to about room temperature, it released spontaneously from the mold and could be tapped out. A photograph of a sample just after release from the mold is shown in Figure 35, along with the mold and the graphite heat sink. The four cast samples are shown in Figure 36.

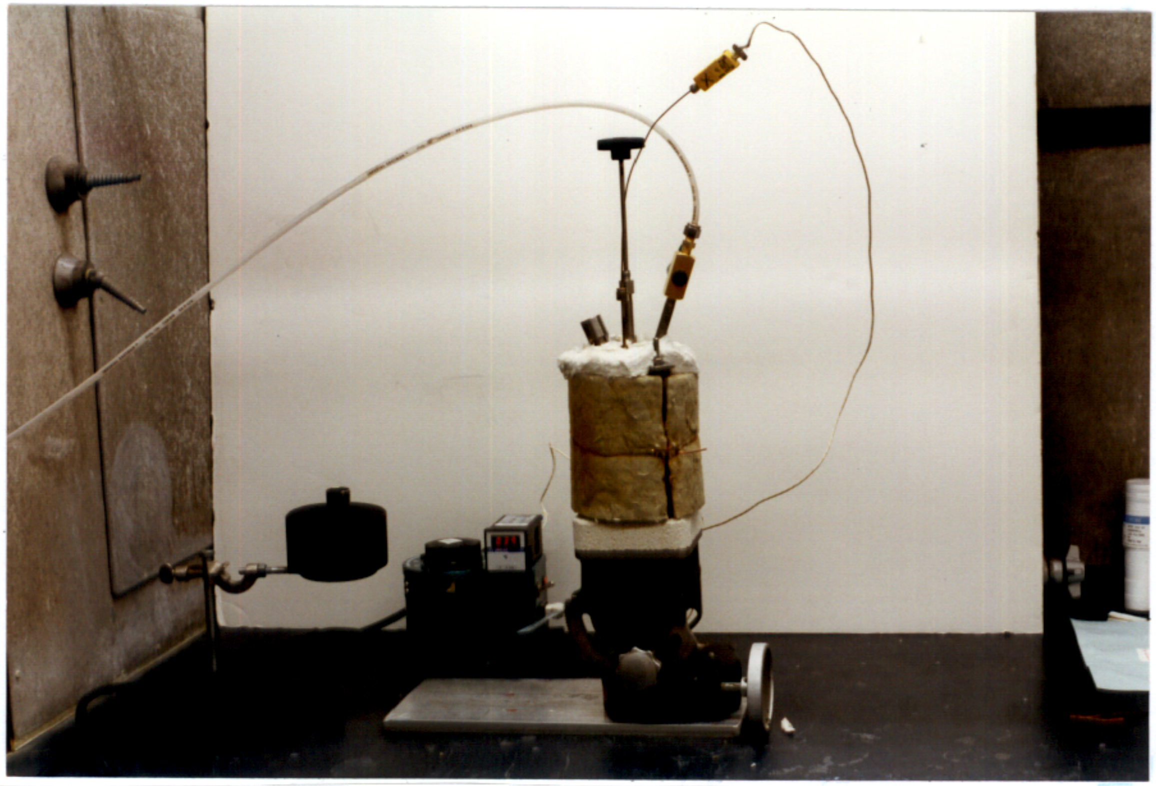

Figure 33. Pouring rig with outer insulation installed. Mold in graphite heat sink is in place. Variac and thermocouple with digital display are behind the rig.

Figure 34. Pouring rig just after casting of a sample of alloy from Batch No. A-123-1

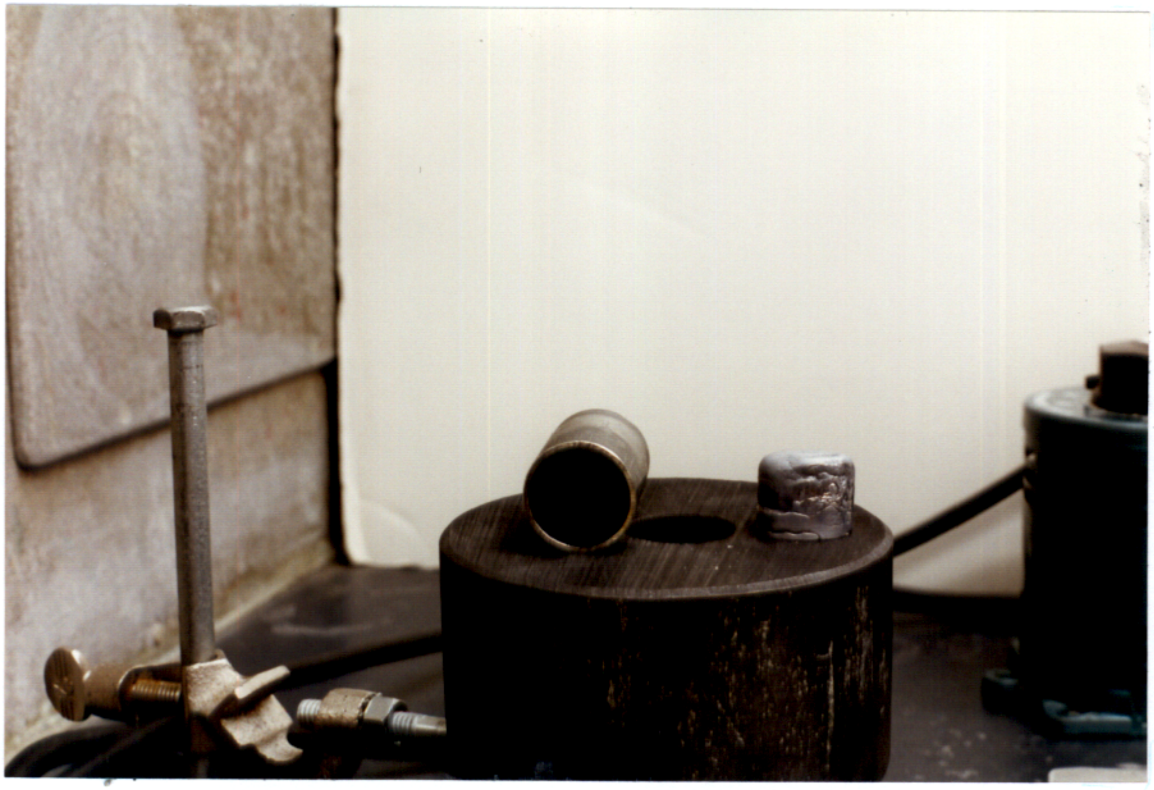

Figure 35. Sample of alloy from Batch No. A-123-1 resting on graphite heat sink. Also shown is the stainless steel mold.

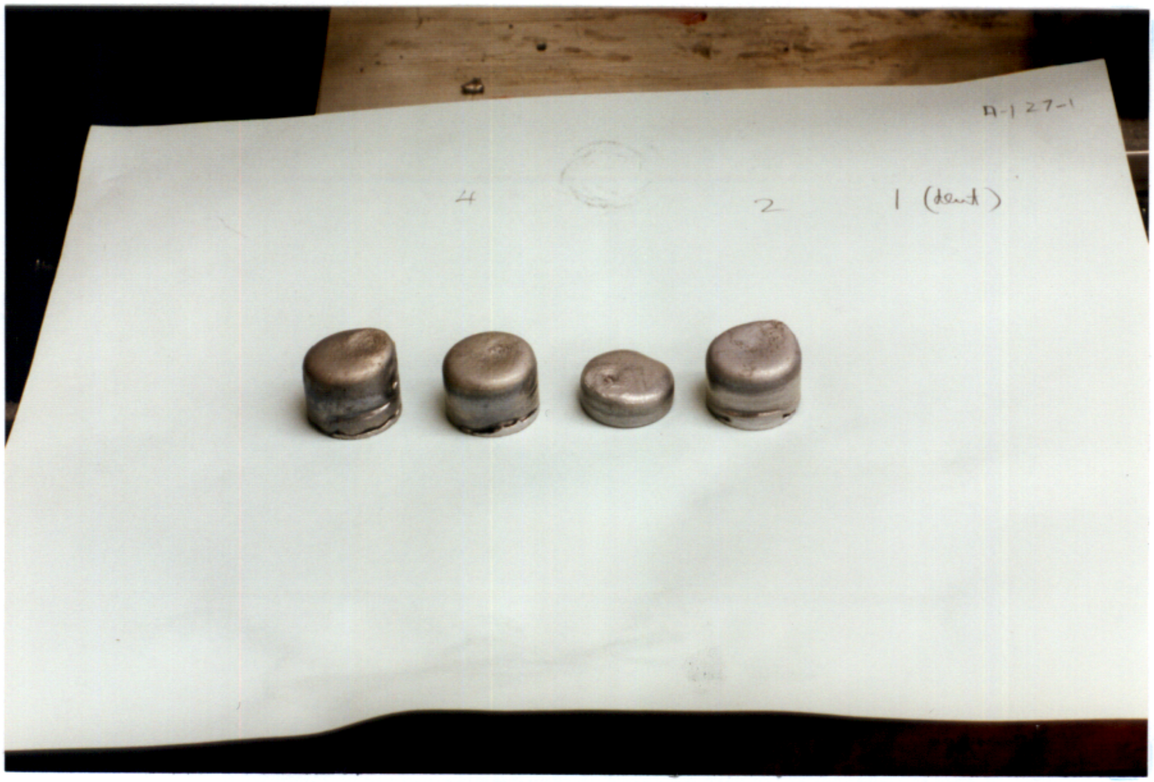

Figure 36. Four samples of alloy cast from Batch No. A-123-6.

DISCUSSION AND CONCLUSIONS

In this report, we have recorded procedures for preparing kilogram quantities of the low melting lead-lithium eutectic alloy with 83 atom percent lead and 17 atom percent lithium. We have shown that relatively pure massive bar stock lead can be melted under argon with only minor slag formation. Also, while stirring it can be reacted with a number of small amounts of solid lithium to produce a homogeneous alloy with a sharp horizontal temperature plateau during cooling and freezing.

The plateau for the eutectic occurred at 230.3°C, nearly five Kelvin degrees below the eutectic temperature of 235°C reported in the literature (Hansen 1958). We attribute the lower temperature to our pure starting materials (99.9% Li, 99.97% Pb on a metals basis, see Tables 2 and 3), careful attention to the purity of the atmospheres used for cutting and handling the lithium metal and during the preparation of the alloy, and perhaps a better and more precise method of preparing and weighing the metals (namely, the saw cutting of bar stock lead and the cutting board procedure for measuring out desired amounts of the thick lithium foil).

In addition to the favorable cooling curves, we also checked the composition of the three batches of alloy with ICP-MS. The desired atomic percentages of 83 and 17 for the lead and lithium, respectively, were achieved and confirmed to better than one percent for each batch of alloy. Moreover, each batch seemed to be homogeneous according to the analyses, although this aspect of the preparations was not investigated very extensively.

We also tested a rig for pouring and casting the test alloy (~ 5 a/o Li) in a stainless steel cup to form small ingots that can be used later for melt-water interaction experiments. Although we melted under argon, we cast a low lithium test alloy in air without appreciable slag and with no sign of chemical reaction with air on the crucible. Moreover, the relatively small amounts of alloy per reactor (~ 1.5 kg) make for easy handling. This bodes well for future efforts to cast the 83 a/o Pb-17 a/o Li alloy similarly in an argon atmosphere.

REFERENCES

(1) Chopra, O., and D. Smith, 1984, "Corrosion of Ferrous Alloys in Eutectic Lead-Lithium Environment," J. Nucl. Mater. 122 and 123, 1219-1224.

(2) Hansen, M., 1958, Constitution of Binary Alloys, 2nd Edition, McGraw-Hill Book Company, Inc., New York.

(3) Jeppson, D.W., and L.D. Muhlestein, 1985, "Safety Considerations of Lithium Lead Alloy as a Fusion Reactor Breeding Material," Fusion Technol. 8, 1385-1391.

(4) Sannier, J., M. Broc, R. Flament and M. Terlain, 1991, "Corrosion of Austenitic and Martensitic Stainless Steels in Flowing Pb 17 Li Alloy," Fusion Eng. Des. 14, 299-307.

(5) Sze, D.K., Clemmer, R., and Cheng, E.T., 1980, LiPb, A Novel Material for Fusion Applications, University of Wisconsin, UWFDM-378.

APPENDIX A

Flames Observed During Preparation of the Lead-Lithium Alloys

In each of the experiments in which the solid lithium could be observed as it reacted with the molten lead or lead-rich alloy (that is, in all experiments except A-133-1, where we had difficulty moving the lithium through the entry/exit port), we noticed very pronounced orange-red flames inside the argon-purged reactors. These flames resembled small "sooty" candle flames in air, but less luminous.

Phenomena similar to these were observed by Chopra and Smith (1984) when they added molten lithium to molten lead or lead-rich alloy. They reported only that "the reaction produced an orange-red flame-like color" at the interacting interface. They also mention release of intense heat by the reaction, but provide little further information.

We conclude that the luminosity is generated by heat released during the alloying process, and that the flames are probably generated by the reaction between the vapors of lead and lithium. We further suggest that since the reactors are purged with oxygen-free argon the luminosity is generated by a hot, condensing aerosol of the newly formed alloy. This aerosol produces the "sooty" appearance of the flame, not unlike that of the hot carbon aerosol that provides the luminosity of the candle flame.

We also observed that the flames occurred after each addition of lithium, ranging from the earliest (e.g., sample tube no. 2) to the latest additions for a given batch (e.g., sample tubes Nos. 15 through 19). We can conclude then that the heat generated by the alloying reaction remains high over the range 100a/oPb to 87a/0Pb 17a/oLi.

We also noticed a more ephemeral flame when an unusually large burst of the orange-red flame pushed out of the entry/exit pipe nipple into the surrounding air. This flame had a faint lime-green luminosity, difficult to see in a well lighted room. Because the large bursts of orange-red flame were rare, our observations of the lime-green luminosity were both sporadic and uncertain. We believe these greenish emissions may be caused by the burning of the alloy vapors or the aerosol in air.

We have tried to relate these colors to those imparted by the addition of the elements Li and Pb to gas flames. According to the Handbook of Chemistry and Physics (55th Edition, 1974-1975), Li imparts a carmine red color, while lead produces a light blue. It is likely that the greenish hue we see is related to the light blue color produced in the presence of lead.

Reference for Appendix A

(1) Chopra, O., and D. Smith, 1984, "Corrosion of Ferrous Alloys in Eutectic Lead-Lithium Environment," J. Nucl. Mater. 122 and 123, 1219-1224.

APPENDIX B

Analysis of Pb-Li Alloys by Inductively Coupled Plasma Mass Spectrometry

In this Appdenix, we reproduce the memorandum in which the results of the analyses of our three alloys were transmitted.

University of Wisconsin–Madison/Extension

Soil & Plant Analysis Laboratory
Soil Science Department
5711 Mineral Point Road
Madison, Wisconsin 53705-4453
Phone (608) 262-4364
FAX (608) 263-3327

College of Agricultural and Life Sciences

OCT 24 1994

Date 10/20/94
Acct # 900
Lab # S326

To: Lloyd Nelson
Dept of Nuclear Energy

From: Soil & Plant Analysis Lab
Sherry Combs, Director

Subj: Results of analyses on 4 Li-Pb alloy samples.

Please find enclosed results of Li and Pb by fully quantitative and rapid scan ICP-MS analysis for 4 Li-Pb alloy samples submitted 10/13/94.

The samples (about 0.2 - 0.5 g for one sub-sample) were dissolved in 10 ml of 10% HNO_3 and diluted to 100 ml with water. The sample solutions were further diluted by 10 times before ICP-MS measurement. The results are listed on p.1 and p.2.

W (g): Weight of sub-sample.
Li(ug/L) or Pb(ug/L): Li or Pb in solution.
Li(%) or Pb(%): Li or Pb in alloy in unit of weight percent.
Avg(%) or STD(%): weight percent.
RSD(%): Ratio of STD to Avg in percent.

Precision: RSD is one index to indicate precision. E.g. RSD of B-2-1-a is 0.85%, which is the percent ratio of STD (0.0059 weight percent) to Avg (0.6961 weight percent).

Accuracy: Accuracy is the closeness of measured value to "true" value. E.g. at atom ratio of Li:Pb = 17:83, the "true" weight percent of Li would be 0.681 weight percent. The accuracy of B-2-1-a is 0.6961/0.681 = 1.02 or 102%.

If the atom ratio is allowed to vary between 16.8 and 17.2 (17.0 +/- 0.2), the range of weight percent would be 0.673 and 0.689, or the accuracy requirement would be 98.83% and 101.17%.

If you have any questions concerning these analyses, please feel free to contact us.

Enclosure(s)

University of Wisconsin–Madison/Extension provides equal opportunities for admission and employment

Sample	W (g)	Li (ug/L)	Li (%)	Avg (%)	STD (%)	RSD (%)
B-2-1-a	0.4944	3465.0	0.70085	0.6961	0.0059	0.851
B-2-1-a	0.4944	3450.4	0.69790			
B-2-1-a	0.4944	3408.6	0.68944			
B-2-1-b	0.4085	2761.2	0.67594	0.6759		
B-2-1-c	0.4272	2904.2	0.67983	0.6798		
A-146-1-a	0.5040	3227.4	0.64035	0.6383	0.0018	0.288
A-146-1-a	0.5040	3210.1	0.63692			
A-146-1-a	0.5040	3213.0	0.63750			
A-146-1-b	0.4440	3082.0	0.69413	0.6941		
A-146-1- c	0.3913	2848.9	0.72807	0.7281		
A-133-1-a	0.3313	2240.1	0.67615	0.6769	0.0023	0.333
A-133-1-a	0.3313	2236.6	0.67511			
A-133-1-a	0.3313	2250.9	0.67943			
A-133-1-b	0.2604	1753.9	0.67355	0.6735		
A-133-1-c	0.3280	2234.8	0.68135	0.6813		
A-127-1-a	0.2514	442.3	0.17595	0.1743	0.0023	1.319
A-127-1-a	0.2514	440.4	0.17520			
A-127-1-a	0.2514	431.5	0.17164			
A-127-1-b	0.3114	571.6	0.18356	0.1836		
A-127-1-c	0.4016	768.2	0.19128	0.1913		
	W (g)	Pb (ug/L)	Pb (%)			
B-2-1-a	0.4944	493056.7	99.728	99.5564	0.4903	0.492
B-2-1-a	0.4944	489472.4	99.003			
B-2-1-a	0.4944	494091.2	99.938			
B-2-1-b	0.4085	406123.9	99.418	99.4183		
B-2-1-c	0.4272	424287.2	99.318	99.3182		
A-146-1-a	0.504	497623.3	98.735	98.7348		
A-146-1-b	0.444	432084.3	97.316	97.3163		
A-146-1- c	0.3913	390096.2	99.692	99.6924		
A-133-1-a	0.3313	327219.0	98.768	98.7682		
A-133-1-b	0.2604	253517.4	97.357	97.3569		
A-133-1-c	0.328	325681.6	99.293	99.2932		
A-127-1-a	0.2514	250610.9	99.686	99.6861		
A-127-1-b	0.3114	310164.3	99.603	99.6032		
A-127-1-c	0.4016	393334.6	97.942	97.9419		

	W (g)	Li (%)	Pb (%)	Li+Pb (%	Li (atom)	Pb (atom)
B-2-1-a	0.4944	0.69607	99.5564	100.25	17.27	82.73
B-2-1-b	0.4085	0.67594	99.4183	100.09	16.87	83.13
B-2-1-c	0.4272	0.67983	99.3182	100.00	16.97	83.03
A-146-1-a	0.5040	0.63825	98.7348	99.37	16.18	83.82
A-146-1-b	0.4440	0.69413	97.3163	98.01	17.55	82.45
A-146-1-c	0.3913	0.72807	99.6924	100.42	17.90	82.10
A-133-1-a	0.3313	0.67689	98.7682	99.45	16.98	83.02
A-133-1-b	0.2604	0.67355	97.3569	98.03	17.12	82.88
A-133-1-c	0.3280	0.68135	99.2932	99.97	17.00	83.00
A-127-1-a	0.2514	0.17426	99.6861	99.86	4.96	95.04
A-127-1-b	0.3114	0.18356	99.6032	99.79	5.21	94.79
A-127-1-c	0.4016	0.19128	97.9419	98.13	5.51	94.49

$$Li(atom) = \frac{\frac{Li(\%)}{6.941}}{\frac{Li(\%)}{6.941} + \frac{Pb(\%)}{207.2}} \times 100$$

$$Pb(atom) = \frac{\frac{Pb(\%)}{207.2}}{\frac{Li(\%)}{6.941} + \frac{Pb(\%)}{207.2}} \times 100$$

APPENDIX C

Preparation of Two Additional Batches of the 83a/oPb-17a/o Li Alloy for Use in Shock Tube Experiments at the University of Wisconsin

by

Joseph D. Krueger

In December of 1994, two extra batches of the lead-lithium alloy were prepared, repeating the procedures outlined earlier in the body of this report. These new batches are intended to be used in melt-water experiments to be performed at the University of Wisconsin in the shock tube apparatus described by Raz (1991).

Two entirely new reactors were constructed as described here. The starting materials were the identical materials, prepared in the same manner. The procedures were repeated carefully in order to produce samples as nearly identical as possible to the three batches of alloy prepared for the studies performed at Prairie View A and M University. The primary differences between the two samples prepared here and the three prepared earlier are that the maximum preparation temperatures were somewhat lower and detailed chemical analyses have not yet been performed on the later pair of samples.

The metal weights and important temperatures for the two runs, JK-121994-01 and JK-122294-02, are presented in Table C-1, while the cooling curves are shown in Figures C-1 and C-2. Note the similarities of these data and figures to the analogous information presented in Table 5 and Figures 27 through 30 in the main portion of this report.

The consistency between the cooling curves shown in Figures 27 through 30 and Figures C-1 and C-2 should be noted. The temperatures of the halts in these five figures lie well within the accuracy of the temperature measurements, namely ±1°C.

Table C-1. Summary of Additional Runs in Which Lead-Lithium Alloys Were Prepared

Experiment	Reactor No.	Empty Reactor Wt.(g)	Wt. of Pb(g)	Added Wt. of Li(g)	Wt. of Alloy(g)	T_{max} (°C)	T_{halt} (°C)
JK-121994-01	4	2175.3	1682.6	11.8	1694.5	415	229
JK-122294-02	5	2267.0	1690.7	11.9	1702.6	419	229

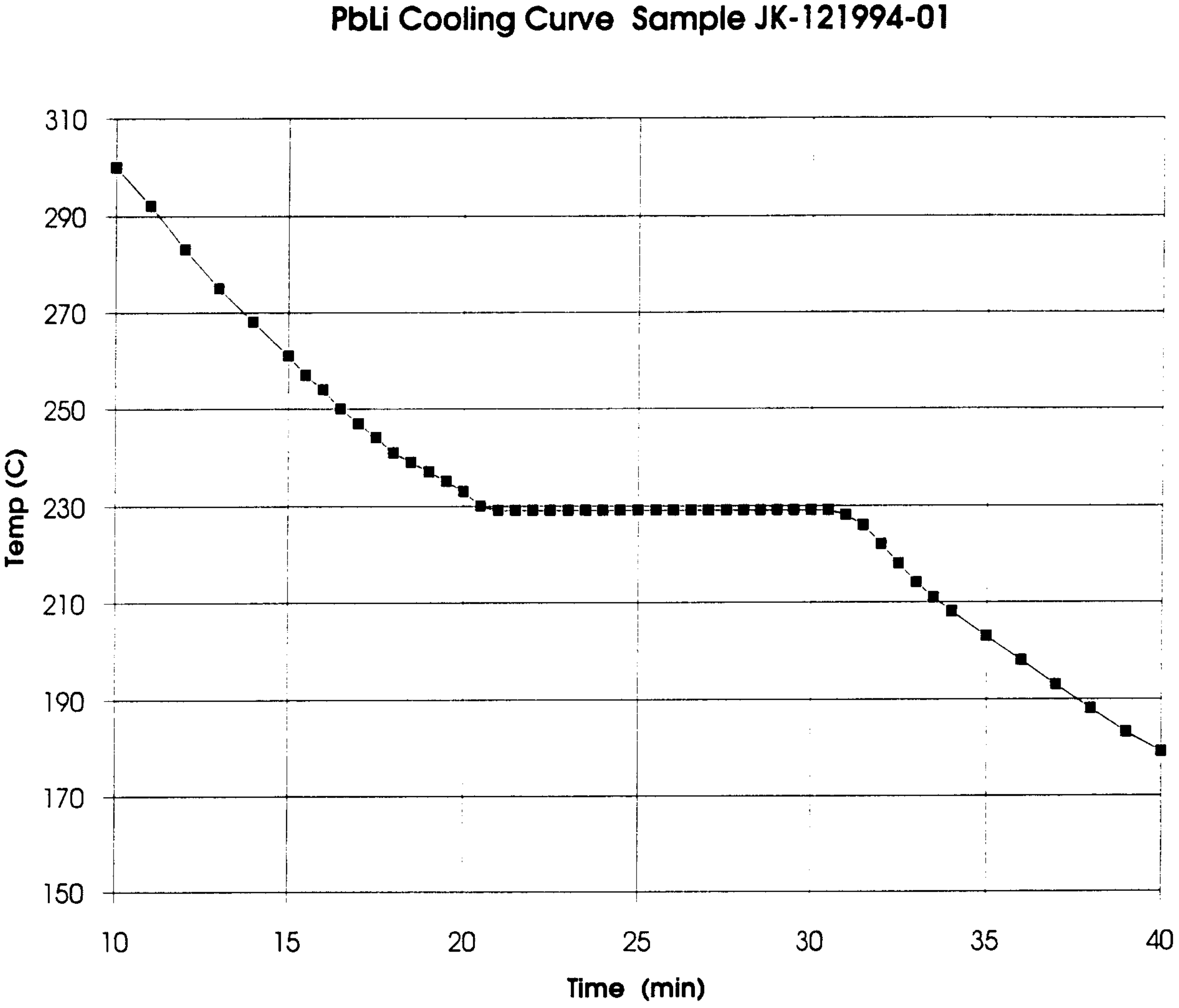

Figure C-1. Cooling curve for experiment JK-121994-01.

Reference for Appendix C

(1) Raz, M., 1991, Vertical Shock Tube Mechanical Design for Liquid Metal/Water Interactions, University of Wisconsin Reactor Safety Research Report UWRSR69.

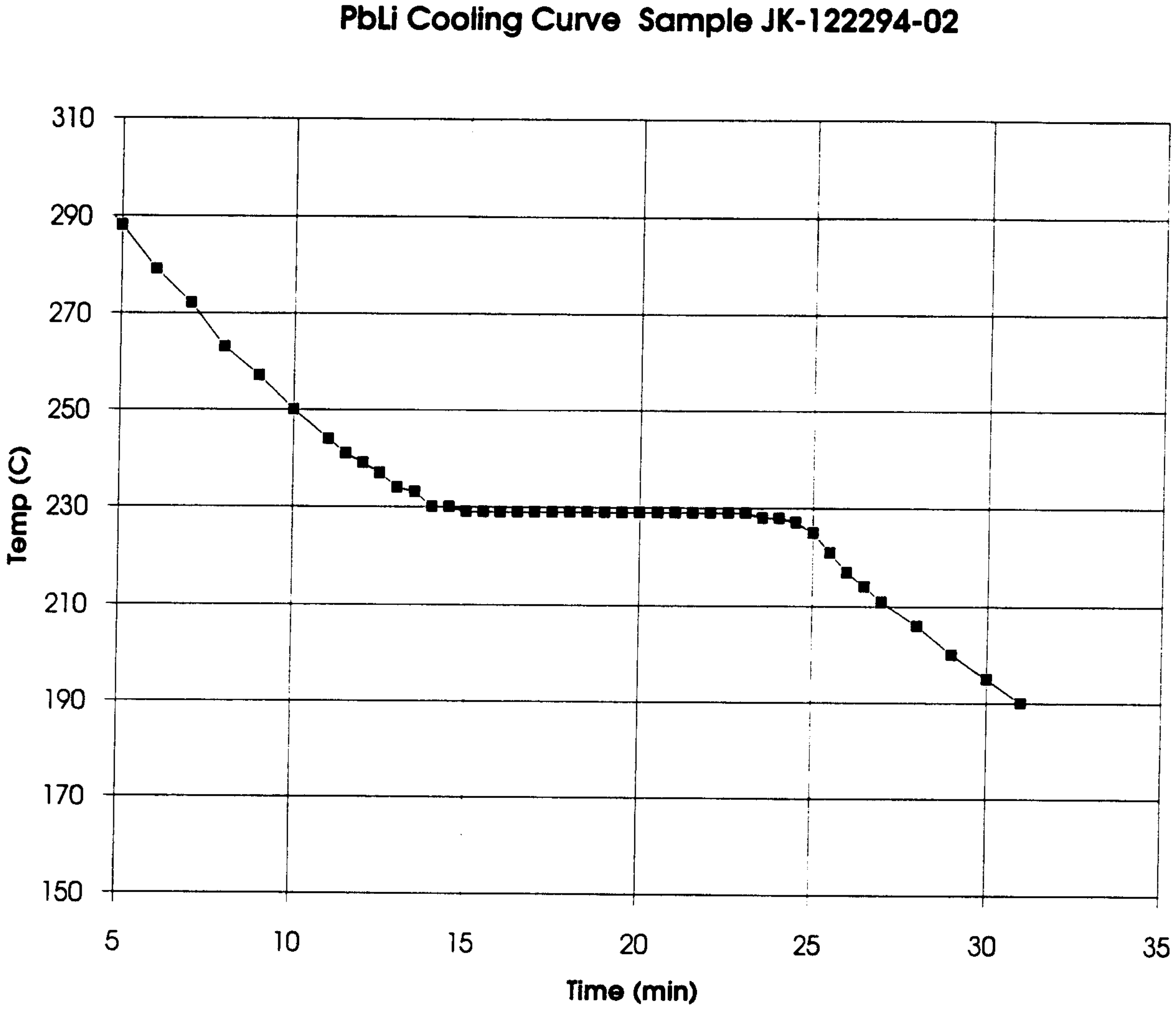

Figure C-2. Cooling curve for experiment JK-122294-02.