



Interactions Between an Organic Coolant and Drops of Molten Lithium

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***FUSION TECHNOLOGY INSTITUTE
UNIVERSITY OF WISCONSIN
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L.S. Nelson, J.D. Krueger, M.L. Corradini

Fusion Technology Institute
University of Wisconsin
1500 Engineering Drive
Madison, WI 53706

<http://fti.neep.wisc.edu>

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ABSTRACT

Twenty scoping experiments were performed to investigate the behavior of nominally 0.5 g molten lithium drops when released into 0.7 L of the organic coolant Therminol 66 at local atmospheric pressure using a vortex insertion technique. Diagnostics consisted of video and photographic imaging and a few chemical analyses. Temperature ranges were selected for the coolant and the Li drops to represent extremes of typical operating conditions being considered for nuclear fusion applications: $470\text{ K} < T_{\text{Li}} < 770\text{ K}$ and $300\text{ K} < T_{\text{c}} < 600\text{ K}$. In none of the experiments performed here was there any indication of (a) a vigorous, self-sustaining chemical reaction between the lithium and the organic coolant, or (b) the formation of water-insoluble debris, in particular, carbon. Our work confirms the benign behavior seen in several experiments reported earlier by others.

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INTRODUCTION

Organic heat transfer liquids have been proposed as cooling media for molten lithium in several breeder/blanket applications related to nuclear fusion (Gierszewski and Hollies 1987; Romero 1984; Trego and Miller 1980). Polyphenyl liquids have been used to cool nuclear fission reactors since their earliest days. There is extensive literature that describes such use of these coolants (Smee et al., 1976) especially related to the operation of the organic cooled WR-1 reactor for nearly 20 years in Canada (Turner 1974). The coolant used in this reactor was a commercial partially hydrogenated terphenyl mixture, a viscous straw-colored liquid at room temperature with a boiling temperature range of 339-353°C (612-626 K) at atmospheric pressure. This coolant was normally operated at 397°C (670 K) and 2.28 MPa in the WR-1 reactor.

There have been many investigations of this coolant including its physical, chemical, thermal, hydraulic and neutronic behaviors. Moreover, much is known about its toxicological properties from both animal and human studies. Because of this large information base, this coolant is now being considered as a secondary coolant in the Li-V design for ITER. There is considerably less information about the interactions that might occur if molten lithium were inadvertently to contact this organic coolant, for example, due to some leakage. Thermodynamics indicates that a reaction between the terphenyl coolant and molten lithium might produce an energy release per unit volume of coolant about one-third that of the reaction of Li with water (which is 28.8 kJ/g of Li). A few early tests suggest, however, that the reaction does not go to completion and is actually relatively mild (private communications cited by Gierszewski and Hollies 1987, and Romero 1984). Nevertheless, there also were indications that under certain conditions, these reactions might proceed exothermically and produce significant pressurizations. Because available pertinent data are very limited, new scoping experiments were performed to provide a broader and more systematic information base.

Because of the low density of the metal compared to the organic liquid, molten lithium cannot simply be dropped into the coolant to achieve good contact; that is, the lithium will float on the organic liquid unless some special procedures are used. To overcome this difficulty we have developed a vortex insertion technique that provides a way to place a drop of molten lithium beneath the surface of the denser coolant and to maintain contact between the two liquids.

Twenty scoping experiments were performed here to investigate the behavior of nominally 0.5 g molten lithium drops when released into 0.7 L of the organic coolant at local atmospheric pressure using the vortex insertion technique. The pairs of temperatures selected for the coolant and the lithium drops represented the extremes of typical operating conditions. Diagnostics consisted of video and photographic imaging followed by a few chemical analyses.

In none of the experiments performed here was there any indication of (a) a vigorous, self-sustaining chemical reaction between the lithium and the organic coolant, or (b) the formation of water-insoluble debris, in particular, carbon. Our work confirms the benign behavior seen in the earlier experiments cited by Gierszewski and Hollies (1987) and Romero (1984) that were performed by releasing metal into coolant at pairs of temperatures similar to ours.

Preliminary descriptions of our work have been presented previously in two informal interim progress reports (Nelson et al., 1993 a and b).

EXPERIMENTAL

Materials

The lithium was obtained in granular form from the Alfa Chemical Company. The coolant is a commercial organic heat transfer liquid known as Therminol 66 (sometimes designated alternatively as OS-84 or HB-40). It was obtained from the Monsanto Chemical Company, St. Louis, MO. Information about the physical and chemical characteristics of this material has been provided by Green (1993).

Vortex Insertion

To achieve good contact with the denser organic liquid we have investigated the release of single drops of molten lithium into a stable vortex several centimeters deep produced in the coolant with magnetic stirring. The downward flow along the centerline of the vessel that produces the vortex tends to pull the less dense material down into and levitate it below the surface of the denser liquid. Moreover, the flow of coolant around the vortex should subject the inserted material to forced convection conditions that qualitatively simulate those that might accompany a leak in a heat exchange situation.

Preliminary Vortex Insertion Experiments

Wooden Sphere Experiments

Simple scoping experiments were performed to test the vortex insertion scheme. The first was to produce stable vortices in water at room temperature contained in a standard one liter Pyrex beaker with a commercial combined magnetic stirrer and hot plate. A typical vortex is shown in Figure 1.

The behavior of a low density material released into a vortex is shown in Figure 2. Here we dropped a 16 mm-diameter maple sphere (density = $\sim 0.7 \text{ g/cm}^3$) into the vortex. It was immediately pulled down into the water and levitated on the centerline several centimeters beneath the vortex. The levitated sphere could be lowered and raised in the water by increasing and decreasing the stirrer speed.

Hot Wax Experiments

Scoping experiments were also performed to compare the behavior of the wooden sphere with that of a low density liquid released similarly into a stable vortex formed in water. As the liquid, we selected a wax used to make votive

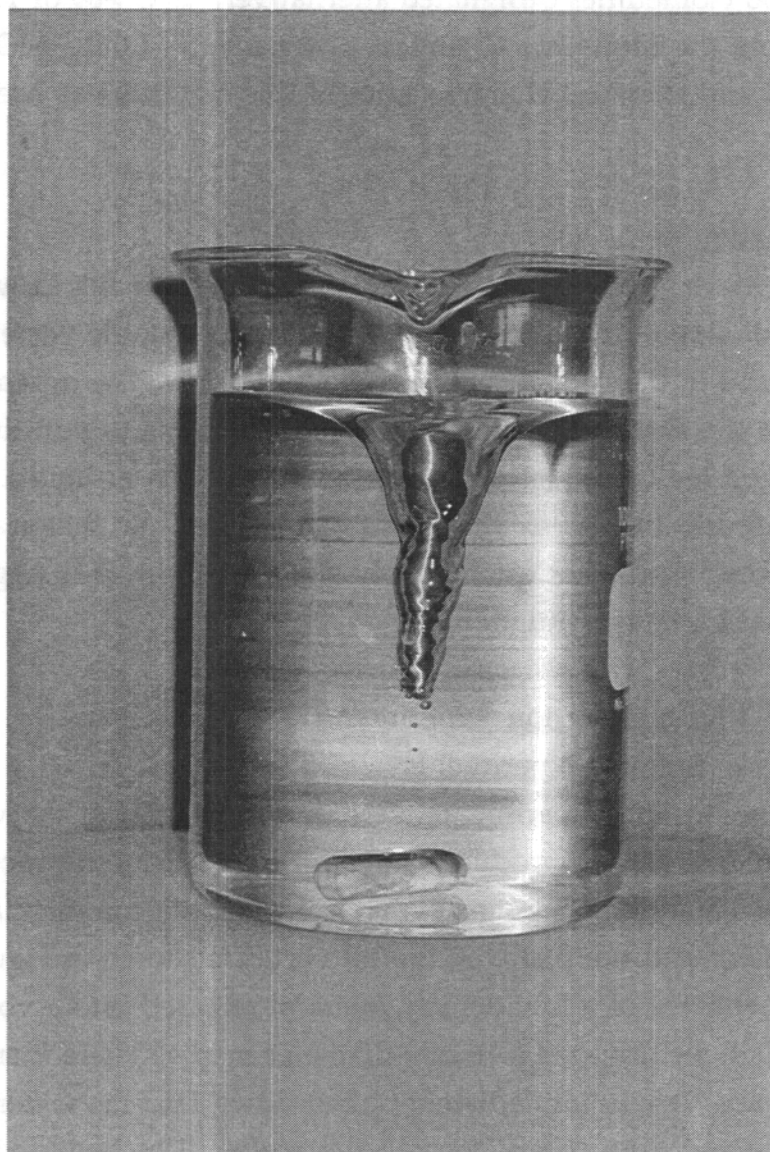


Figure 1. Stable vortex produced in 1 liter of water with a magnetic stirrer. (A-11-1)

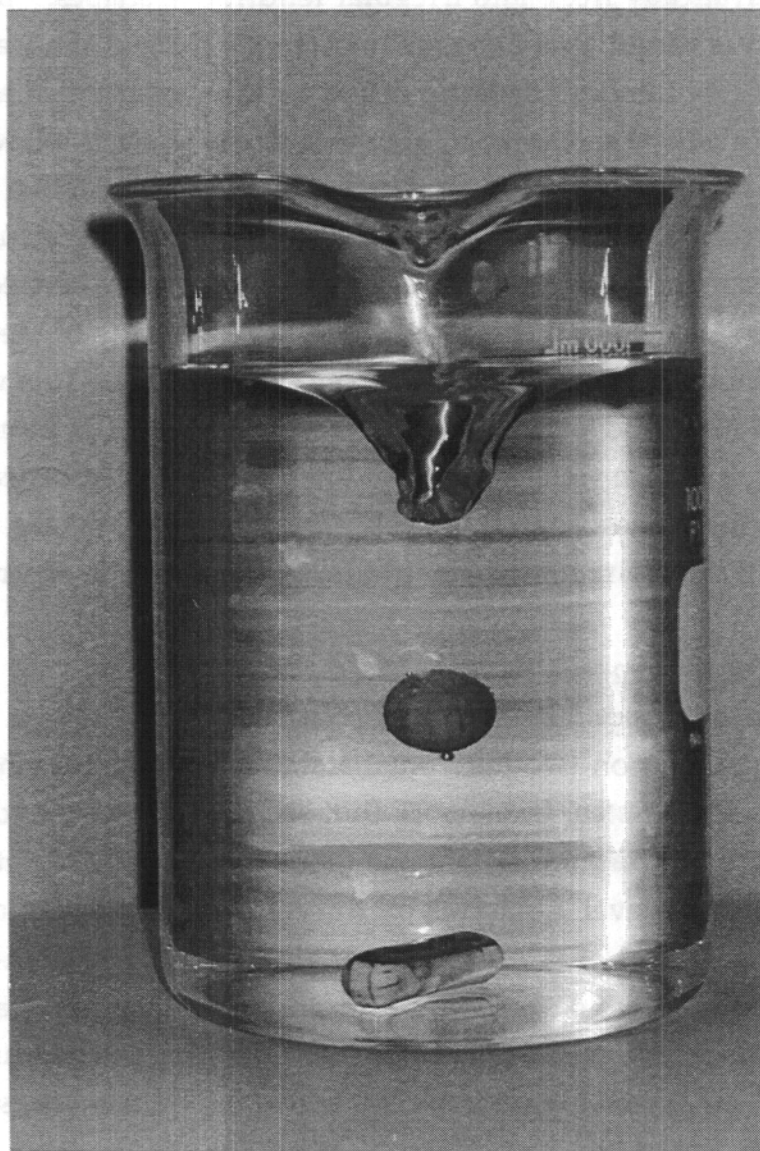


Figure 2. Maple sphere levitated beneath a stable vortex generated in 1 liter of water with a magnetic stirrer. Diameter of sphere is 16 mm. Density of maple is about 0.7 g/cm^3 . (A-11-3)

candles; it is colored red, has a density of $\sim 0.8 \text{ g/cm}^3$ and a fairly sharp melting temperature near 50°C (323 K).

We released 0.2 to 2.6 g globules of the molten wax into vortices formed in water as shown in Figure 1. When the water was at room temperature, the wax quickly and erratically froze into irregular tendril-like shapes. But when the water temperature was raised above the melting temperature of the wax, the melt descended quickly into the lower tip of the vortex and assumed a stable downward-pointing conical shape as shown in Figure 3. If the water is allowed to cool below 50°C (323 K), this shape is retained after the wax freezes. Unlike the wooden sphere, however, the conical wax shape was never pulled beneath the surface of the water, either while molten or after solidification. The difference between the wooden sphere and hot wax experiments is attributed to the ability of the melt to assume a shape that minimizes drag, not to the change in materials. This was tested by releasing a 14 mm solid wax sphere into a vortex formed in room temperature water. The wax sphere was also pulled down and levitated beneath the water just as the wooden sphere had been. It is likely that this drag-reducing adjustment of shape will also affect the levitation of the lithium globules in the organic coolant.

Construction of the Apparatus

A three-level apparatus has been constructed as shown in Figure 4. The three sections are mounted on two horizontal stainless steel plates which are in turn mounted on a sturdy steel framework (not shown) that surrounds the apparatus. Also attached to the framework is a one-piece stainless steel safety enclosure that surrounds the three-level apparatus on three sides, top and bottom (also not shown in Figure 4). The front of this enclosure is closed with a 9.5 mm-thick transparent Lexan sheet through which the video and photographic images are recorded. Commercial grade argon is flushed upward through this enclosure during the experiments. An exhaust hood is placed above the framework, safety enclosure and the three-level apparatus.

The bottom section of the apparatus is made from a 10.2 cm I.D. 15.1 cm-tall Pyrex pipe cap held with a bolted flange below the lower stainless steel plate. It will hold $\sim 0.7 \text{ L}$ of the organic coolant and a bar magnet for stirring to produce the vortex. The outside of the lower section is wound with a heating tape (Fisher Scientific Co., Catalog No. 11-463-52B). The tape is 13 mm wide and 122 cm long; this length was chosen to give about three turns around the Pyrex pipe cap. The tape will generate 312 W at 120 VAC AC. Its maximum working temperature is

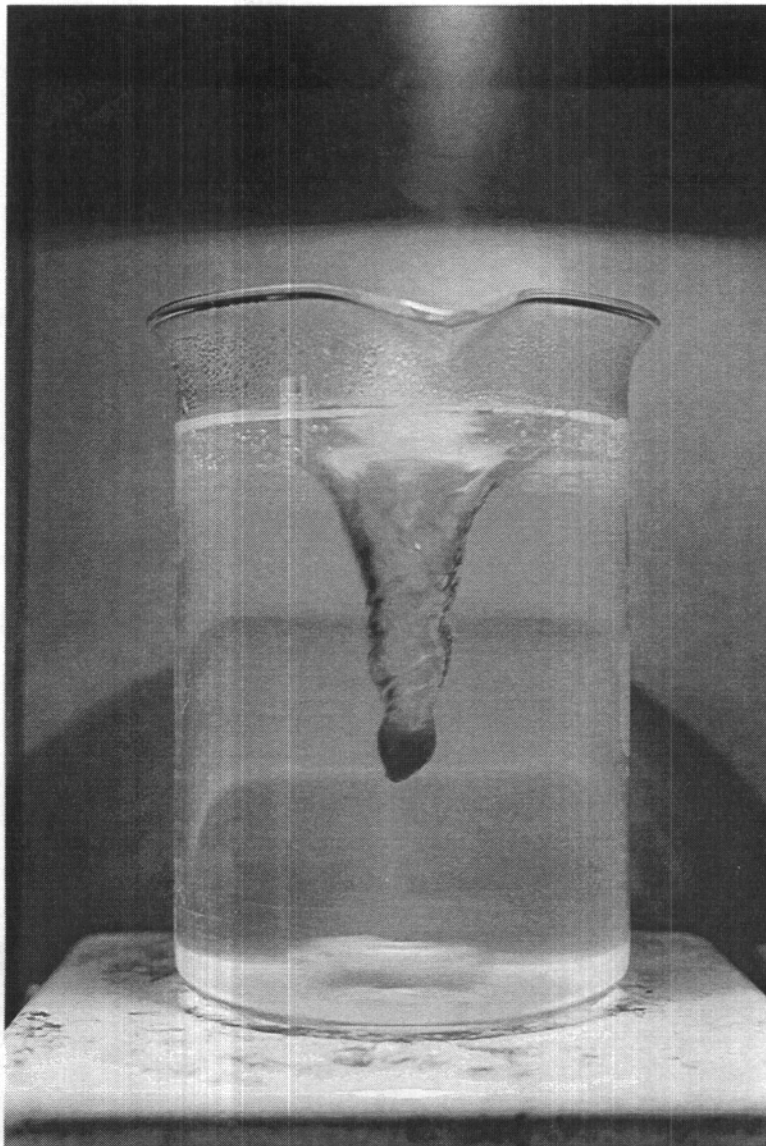


Figure 3. Preliminary vortex insertion experiment with 0.55 g of molten wax in about 1 liter of heated water. (A-22-1)

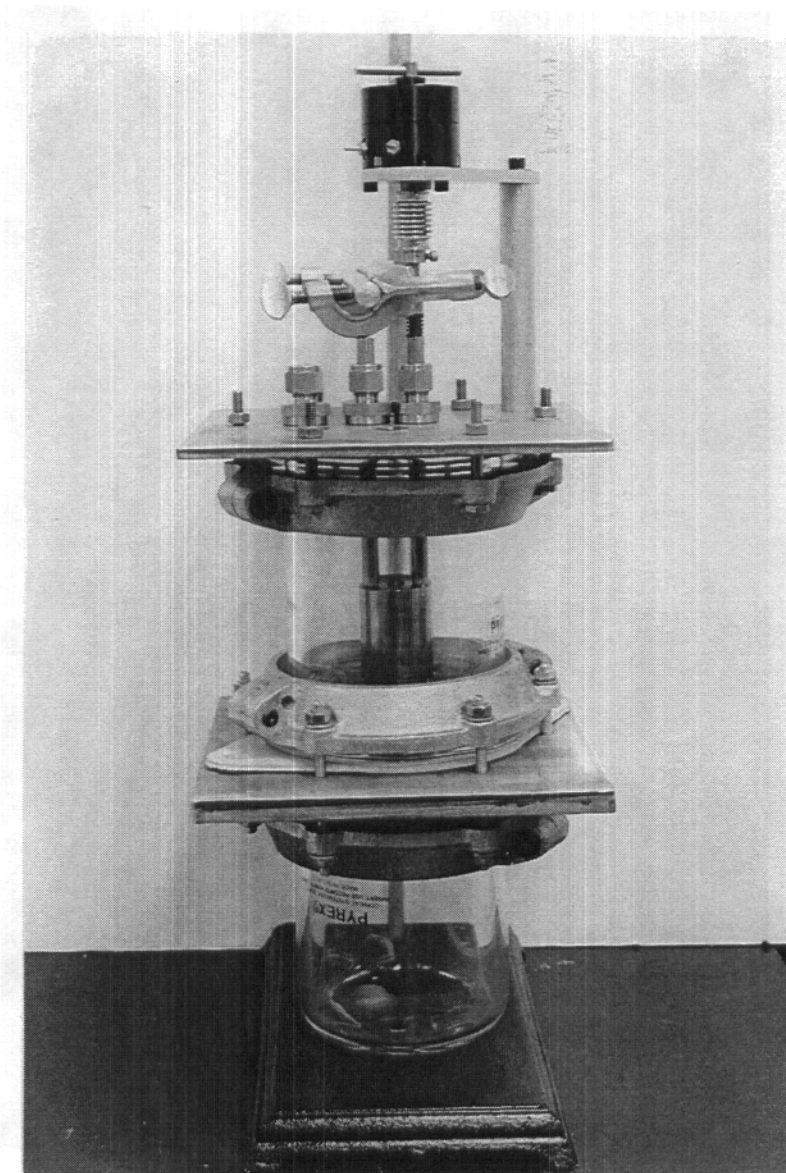


Figure 4. Apparatus used for vortex insertion experiments with molten lithium. Lower section holds ~0.7 L of organic coolant in which the vortex is formed by magnetic stirring. Lithium melting crucible is held inside a length of Pyrex pipe in the middle section. Several connectors and the air-driven actuator that releases the molten lithium are shown in the upper section. (A-32-1)

760°C (1033 K). The bottom section also contains a Type K thermocouple to measure the temperature of the coolant.

Stirring and vortex formation in the coolant are accomplished with a cylindrical Alnico magnet placed beneath the stainless steel safety enclosure just below the Pyrex pipe cap. The magnet is rotated with an air motor and drives the bar magnet in the coolant via induction through the walls of both the safety enclosure and the pipe cap.

The middle section of the apparatus is made from a 15.2 cm long piece of 10.2 cm I.D. Pyrex pipe mounted with bolted flanges between the upper and lower stainless steel plates. Centered near the bottom of the Pyrex pipe, a crucible is suspended from the upper stainless steel plate. This crucible, in which the lithium is melted, consists of a 38 mm O.D. cylindrical stainless steel block 51 mm tall, with a vertical central 9.5 mm hole closed at the bottom with a rotatable gate. The block is heated with a helical electrical resistance heater (a one-piece nozzle heater, Model No. HBA 32030, obtained from the Omega Engineering Co., Stamford CT). The helix has an I.D. of 38 mm and is 51 mm tall; it will deliver 300 W at 120 VAC. The temperature of the block is monitored with a second Type K thermocouple inserted downward into a vertical hole in the block.

The upper section of the apparatus consists of a second stainless steel plate held to the top of the Pyrex pipe with a bolted flange. The plate holds the following:

- (a) A gas line that leads flowing argon from a titanium chip purification furnace operated at 500°C (770 K) into the upper Pyrex chamber to provide a high purity inert atmosphere during melting of the lithium. This argon then passes downward into the lower chamber to inert the atmosphere above the heated coolant. It exits finally via a hole drilled horizontally through the lower stainless steel plate and eventually vents via an upward-pointing exhaust tube into the exhaust hood.
- (b) A 110 V electrical feed-through to power the lithium crucible heater.
- (c) Two fittings through which Type K thermocouples pass. One long thermocouple extends downward through the upper chamber, through the lower stainless steel plate and down into the lower chamber to measure the temperature of the coolant. The tip of the shorter thermocouple rests in the bottom of a hole drilled partway down into the crucible block. It monitors the temperature of the lithium during melting.

- (d) Two shafts, one to rotate the gate that releases the lithium globule from the crucible block, and the other to open and close a shutter that covers the hole in the lower plate during heatup of the coolant.
- (e) A tapped hole through which the lithium is loaded into the crucible block. This hole is closed with a threaded metal plug during heatup of the coolant and the crucible block.

As purified argon flushes through the center and lower sections of the three-level apparatus, a weighed quantity of granular lithium metal is placed in the preheated crucible via an L-shaped stainless steel sample tube. This tube is inserted into the center section through the open tapped hole in the upper stainless steel plate. After an appropriate melting time, the gate is rotated to release the molten lithium which falls as a globule into the stirred coolant through a 25 mm hole centered in the lower stainless steel plate.

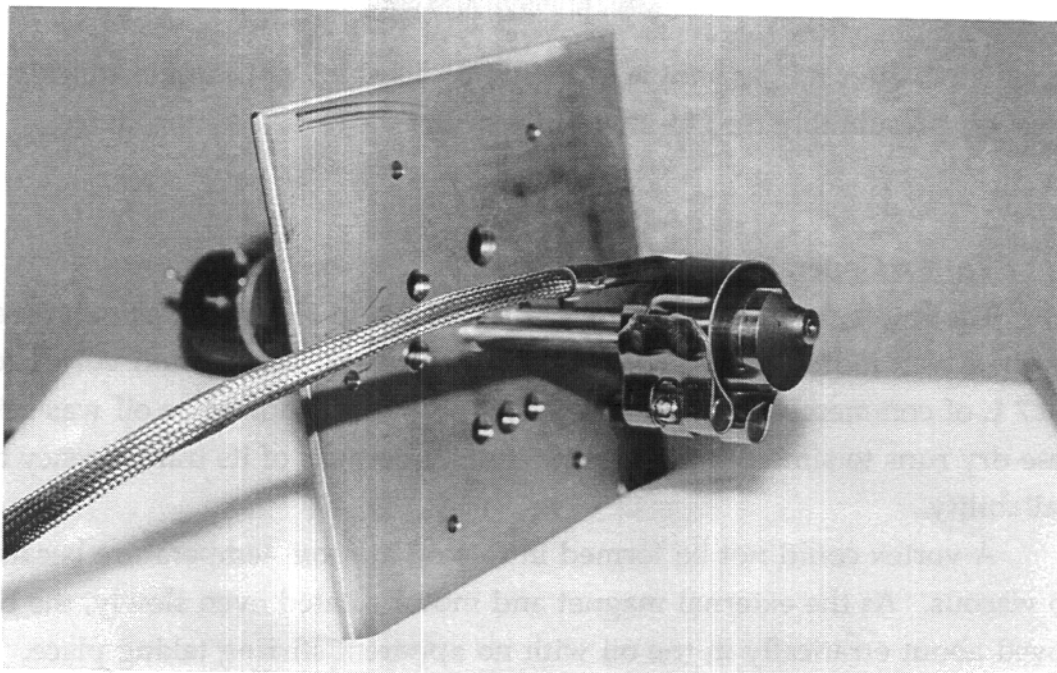
Rotation of the gate to open the bottom of the crucible for lithium release is accomplished with a pneumatic vane-type 90° rotary actuator (Swagelok 121 Series), the dark cylindrical unit at the very top of the apparatus shown in Figure 4. When air at a pressure of about 80 psig is admitted to the unit, it rotates a shaft that passes downward through the body of the crucible block and is attached to the gate. Construction of the crucible with gate closed and open is shown in Figures 5a and b.

Preliminary Testing

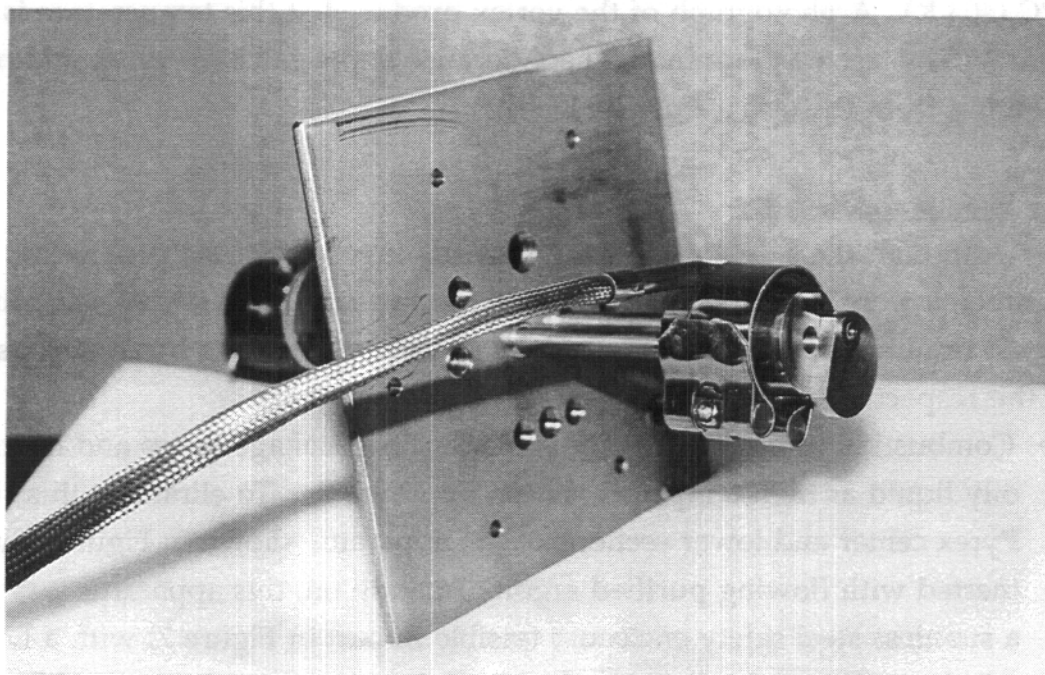
Lithium Drop Generation

We tested the heatup of the crucible block and rotation of the gate in air without lithium at temperatures up to 500°C (773 K), the maximum anticipated melt delivery temperature. Some seizing of the gate occurred above about 300°C (573 K); it was reduced significantly by coating the shaft and the edges of the gate away from the lithium with an automotive anti-seize lubricant (Anti-Seize Thread Compound 767 obtained from the Loctite Corp., Newington, CT).

We also performed two lithium melting and delivery runs in an argon-inerted glove box operated at a dewpoint of about -51°C (222 K). No coolant was used in these tests. We tried our lithium weighing, crucible loading, heating and melt release procedures with the two upper portions of the apparatus shown in Figure 4 mounted inside the glove box. Quantitative delivery of nominally 0.5 g drops of molten lithium at 200°C (473 K) into a stainless steel cup was achieved successfully. One of these drops was photographed through the glove box window



(a) Gate is closed (A-33-2)



(b) Gate is open (A-33-4)

Figure 5. Crucible for melting and releasing single drop of molten lithium in vortex insertion experiments.

immediately after fall, as shown in Figure 6. Its shiny appearance quickly darkened, however, presumably due to impurities in the glove box atmosphere.

Vortex Generation

The lower portion of the apparatus shown in Figure 4 was mounted above the air-driven motor and rotating magnet to test the stirring and vortex formation in 0.7 L of commercial heavy mineral oil (USP). This non-toxic oil was selected for these dry runs to simulate the organic coolant because of its transparency and easy availability.

A vortex could not be formed in this oil at room temperature because it was too viscous. As the external magnet and motor rotated even slowly, the bar magnet moved about erratically in the oil with no apparent stirring taking place. As the oil was heated, however, its viscosity fell rapidly until at about 80°C (353 K), good stirring set in and a shallow (~3 mm deep) stable vortex began to form. As heating continued while stirring at a constant rate, the vortex deepened to about 19 mm at 130°C (403 K). A photograph of the vortex produced at this temperature is shown in Figure 7. The test was terminated here because appreciable oil vapor and mist was emanating from the apparatus.

Safety and Health

Although the safety and health hazards involved in the proposed experiments were not expected to be extreme, we nevertheless devoted considerable effort to minimize risks to personnel and surroundings. The hazards considered and the respective protective measures include:

- Combustion of the hot organic coolant. Both leakage drops and mists of the oily liquid at high temperatures can ignite in air. To eliminate this risk, the Pyrex center and lower sections of the apparatus shown in Figure 4 were inerted with flowing purified argon. In addition, this apparatus was placed in a stainless steel safety enclosure (visible in part in Figure 7) with a Lexan front window. The enclosure was also inerted with a second source of flowing argon. Buildup of combustible vapors or mists was minimized with an efficient exhaust hood. Moreover, both the stirring motor and rotary vane-type actuator were air-driven to eliminate potential spark ignition sources.
- Toxicity of the organic coolant. Care was taken when filling and transferring the organic coolant to prevent inhalation or contact with skin or eyes by use of

adequate ventilation, protective gloves, eye protection, and proper absorbents for spills and leaks. These absorbents were handled and disposed of as toxic materials. Transfer operations with the coolant while hot were avoided. Overflow pans were provided at several places in the apparatus to prevent spread of inadvertent leakages.

- Blast protection. Although explosive interactions between lithium and the coolant were not anticipated, the Lexan-windowed stainless steel safety enclosure was provided to mitigate unexpectedly vigorous interactions. Also, personnel remained 5 meters from the apparatus during each experiment.
- Lithium safety. Precautions required by the University of Wisconsin were followed carefully. The maximum permissible charge of lithium that can be handled during a given test is 0.5 g. Disposal of unreacted lithium was performed by slow water neutralization in an exhaust hood or by other safe procedure.
- Ventilation. A hood above the apparatus conducted smoke, oil mists and vapors and other airborne substances via a 30 cm-diameter flexible duct and strong exhaust fan to the outside atmosphere above the building.

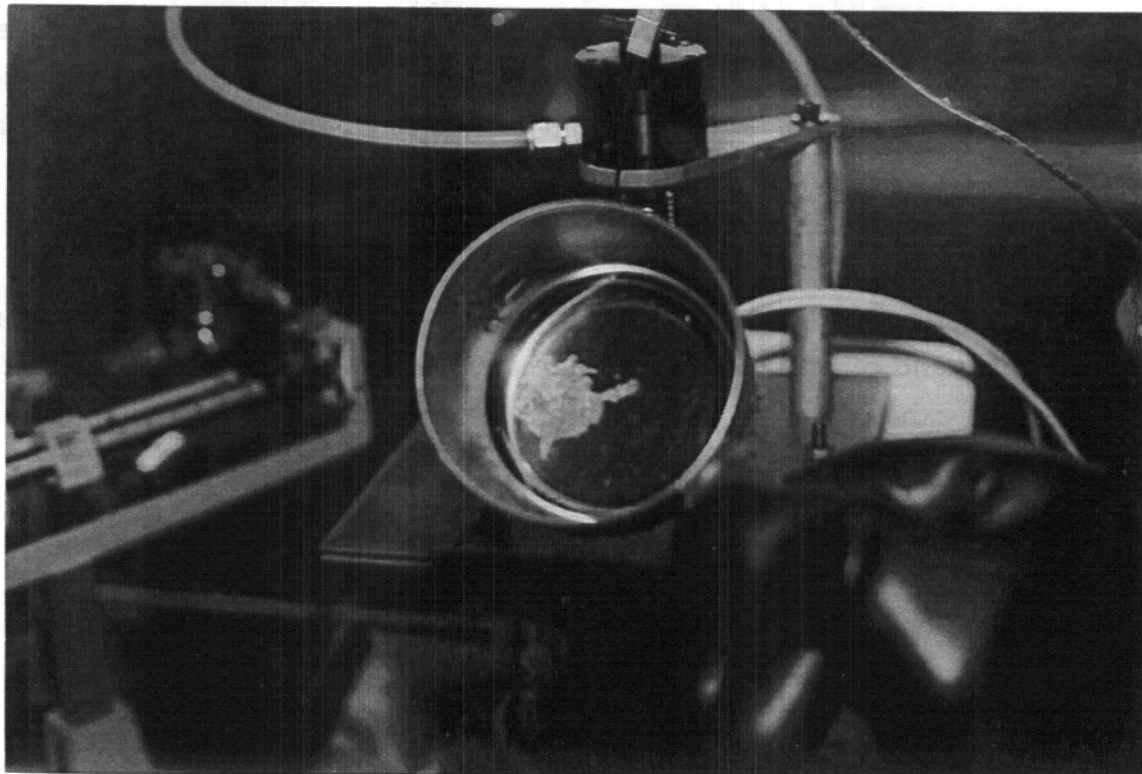


Figure 6. Globule of molten lithium (0.5 g) caught in stainless steel pan in glove box experiments. (A-43-1-1)

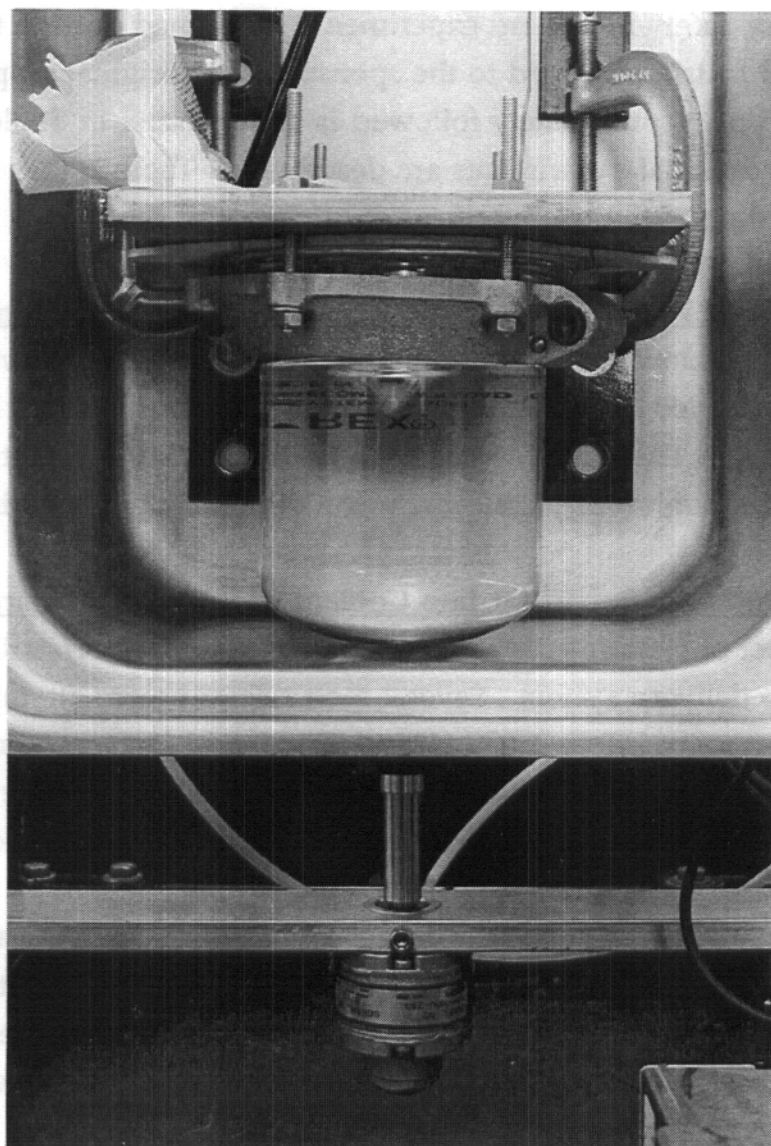


Figure 7. Stable vortex formed by magnetic stirring of mineral oil heated to 130°C (403 K). The air motor and portions of both the Alnico cylindrical magnet and the stainless steel safety enclosure are visible at the bottom of the photograph. (A-49-1)

RESULTS

Twenty experiments were performed in which lithium was released into vortices produced in Therminol 66 coolant. Several of these are considered either shakedown or safety-mandated experiments performed outside the basic experimental matrix proposed to the sponsor in the original scope of work. The experimental matrix ultimately followed is summarized in Table 1.

The individual experiments are described in Table 2; they will be discussed briefly according to the temperatures of lithium and coolant.

Solid Lithium at Room Temperature Into Coolant at Room Temperature

One shakedown experiment (A-64-1) was performed in which 0.5 g of lithium granules as received from the supplier were released all at once into a shallow vortex formed in Therminol 66 coolant. Both materials were at room temperature. There was no chemical or physical reaction detectable by video imaging.

Molten Li with Low Superheat Into Coolant at Room Temperature

This set of experiments was performed while we were still improving our lithium drop delivery system. Several melt releases were attempted at a nominal melt temperature of 200 to 250°C (473 to 523 K) with gravity alone to move the molten metal from the stainless steel crucible. The results were unreliable with either a tiny drop (A-54-1) and/or delayed release of the main globule (A-59-1) after the gate beneath the crucible was opened.

We then added a snug-fitting "pusher" gas tube to the heated stainless steel crucible after the lithium sample had been added, stirred and after about 10 minutes of temperature equilibration. Argon pressurization of the space above the molten lithium in the crucible promptly drove the melt through the open gate as an essentially single globule.

In our first test of this procedure (A-66-1), however, the gas pressurization inadvertently was applied before the gate had opened. This late opening caused molten lithium to be sprayed into the coolant as well as onto the upper surface of the lower stainless steel plate. Melt temperature was 250°C (523 K). No unusual or vigorous chemical or physical reaction between the droplets of lithium and Therminol 66 could be detected on the video imaging record. In addition to millimeter-sized spherical globules, there was some black material, both fibrous and fine powder, found floating on the coolant after the experiment. Although the black material looked very much like carbon, all debris recovered from this experiment by

Table 1. Experimental Matrix for Scoping Tests in which 0.5 g of Metallic Lithium is Released into 0.7 L of Magnetically Stirred Therminol 66 Coolant

Nominal Lithium Temperature (°C, K)	Nominal Coolant Temperature (°C, K)		
	20,300 (Room Temperature)	191,464 (Intermediate Temperature)	300,600 (High Temperature)
20,300 Solid	Granular Li (A-64-1a)	-----	-----
250,530 Molten Low Superheat	Li spray (A-66-1a) Li globules (A-59-1,A-69-1,A-70-1)	Li globule (A-73-1a)	Li globules (A-79-1,A-83-1-2,A-86-1)
500,770 Molten, High Superheat	Li globules (A-89-1,A-93-1, A-97-1,A-98-1)	-----	Li globules (A-100-1,A-105-1,A-110-1)

^a Shakedown or other experiment not in matrix originally proposed to sponsor.

Table 2. Experiments in which 0.5 g of Metallic Lithium was Released into 0.7 L of Therminol 66 Coolant

<u>Exhibit No.</u>	<u>Date</u>	<u>Temperature at Release Time</u>				<u>Inter action^a</u>	<u>Remarks</u>
		<u>Lithium</u>	<u>Coolant</u>	<u>(°C)</u>	<u>(K)</u>		
A-54-1	10/12/93	~198	~471	~20	~293	No	Only a tiny (5 mm x 4 mm) drop fell
A-59-1	10/14/93	~265	~538	19	292	No	A tiny drop fell on first attempt; large chunk fell later
A-64-1-1	10/15/93	~20	~293	220	493	No	Solid lithium granules fell into coolant
A-64-1-2	10/15/93	-----	-----	-----	-----	-----	No drop fell
A-66-1	10/19/93	250	523	19	292	No	Crucible pressurized with Ar for 1st time. Li sprayed into coolant
A-69-1	10/20/93	250	523	20	293	No	Large globule fell
A-70-1	10/21/93	248	521	20	293	No	Large globule fell
A-71-1	10/21/93	-----	-----	172	445	-----	Stopped early because of excessive coolant vaporization. No Li dropped
A-73-1	10/22/93	249	522	191	464	No	New shutter isolated Li from coolant vapors during heatup
A-79-1	10/25/93	253	526	284	557	No	Satisfactory Li release
A-83-1-1	10/26/93	-----	-----	-----	-----	-----	Shutter failed to open. Li did not fall into coolant
A-83-1-2	10/26/93	255	578	283	556	No	Repeat of previous experiment. Large globule fell
A-86-1	10/27/93	258	531	286	559	No	Large globule fell
A-89-1	10/28/93	503	776	19	292	No	Coolant reused from A-86-1 effervesced. Large globule fell
A-93-1	11/1/93	508	781	22	295	No	Large globule fell, probably solid
A-97-1	11/2/93	496	769	22	295	No	Li fell as three globules
A-98-1	11/3/93	501	774	21	294	No	Li fell as three globules
A-100-1	11/4/93	499	772	292	565	No	Li fell as two globules. Globules turned red-brown on top
A-105-1	11/8/93	489	762	292	565	No	Large globule fell. Turned red-brown
A-110-1	11/9/93	499	772	299	572	No	Large globule fell. Turned red-brown in ~1s

^a "Interaction" is defined as an energetic, self-sustained chemical or physical reaction detectable by video or photographic imaging when lithium contacted coolant.

filtration immediately reacted with water and dissolved. We concluded that no carbon had been formed.

In each of the subsequent tests in this group at similar melt temperatures in which gas pressurization was used (A-69-1 and A-70-1), essentially the entire lithium charge was ejected as a single globule. Sometimes after an experiment a few tiny droplets of lithium were found on the upper surface of the lower stainless steel plate; their combined weights were estimated from photographs to be only about 1% of the total lithium in each major globule. Again, no unusual or vigorous chemical or physical reaction could be detected on the video imaging records.

Molten Lithium With Low Superheat into Coolant at an Intermediate Temperature

In the next set of experiments, we continued to release molten lithium just above its melting temperature (nominally at 250°C (530 K)) into vortices formed in Therminol 66. The experiments were performed as in the previous set except that we heated the coolant.

Two physical changes of the organic coolant significantly affected the experiments as we increased its temperature--a rapid decrease of viscosity and a steady increase of vapor pressure. At the intermediate temperature of 172° C (445 K) the viscosity decreases from approximately 100 cP at room temperature to 1.3 cP (water at room temperature is 1 cP), while the vapor pressure increases from essentially zero to 8×10^{-4} MPa (Green 1993). The two order-of-magnitude decrease in viscosity allowed us to easily produce very deep vortices in the coolant with only moderate stirring rates compared to the shallow vortices that could be sustained in the room temperature liquid with the most intense stirring rates (cf. the preliminary vortex generation tests with mineral oil described above; see Figure 7).

In the first experiment attempted with heated coolant (A-71-1) we learned that the increased vapor pressure caused oil mists and vapors to pass freely from the lower to the upper Pyrex sections of the apparatus and also to exit via the open plug through which the lithium sample was introduced into the preheated crucible. Significant mist also emanated from the argon exhaust tube into the hood above the apparatus. We stopped this experiment when the coolant reached 172°C (445 K), before adding the lithium to the crucible, in order to modify the apparatus. The vapor pressure of the coolant at this temperature had increased to almost 1.3×10^{-3} MPa, as noted above.

In our original apparatus, we had neglected to include ways to control the effects of oil vaporization. Our modifications accomplished this control reasonably well by:

- Placing a rotatable shutter plate over the holes in the lower stainless steel plate to minimize passage of oil vapor from the lower into the upper chamber in which the lithium is melted; this shutter could be opened and closed with a shaft that extended through the upper stainless steel plate (see Figure 4).
- Oil vapors also left the apparatus through the vertical argon exhaust line in quantities sufficient to condense as drops that fell back from the hood onto the apparatus and its surroundings. To minimize the hazards that might result from this uncontrolled formation of oil drops, the exhaust tube was bent in a smooth downward-pointing curve from its original vertical position. A graduated glass container was hung beneath the exit to collect the condensate, which amounted to as much as 100 ml during a normal experiment with the coolant at our maximum target temperature of 300° C (573 K).

After these modifications, our next experiment (A-73-1) was performed with the coolant at the intermediate temperature of 191° C (464 K) with the lithium released at 249° C (525 K). This coolant temperature was chosen to cautiously explore both the new modifications made to control the vaporization and the possibility of a vigorous interaction between the heated coolant and the molten lithium. There was no significant interaction detectable, however, and the modifications seemed satisfactory, giving us confidence to move to higher coolant temperatures.

Molten Lithium with Low Superheat into Coolant at High Temperature

We then performed three experiments (A-79-1, A-83-1-2 and A-86-1) with the coolant at a nominal 300° C (573 K) and the lithium with small superheat at nominally 250°C (530 K). In each experiment, there was again no indication of chemical or physical reaction detectable with video or photographic imaging. After each experiment, a single parent and perhaps several very tiny lithium drops were found floating on the surface of the coolant.

Molten Lithium with High Superheat into Coolant at Room Temperature

The next four experiments (A-89-1, A-93-1, A-97-1 and A-98-1) were performed by releasing 0.5 g drops of strongly superheated molten lithium at a nominal temperature of 500° C (770 K) into shallow vortices formed in Therminol 66 at room temperature. In each experiment, there was an immediate, intense generation of oil vapor and mist when the hot metal contacted the surface of the coolant. Moreover, as the heated melt cooled in contact with the coolant, there were clearly visible thermal refractive index discontinuities pulled down and dispersed into the stirred coolant. But in none of the experiments was there any sign on the video record or in the debris of a self-sustained chemical reaction during or after contact of the strongly superheated lithium with the coolant at room temperature.

There was an unanticipated result during the first experiment in this set (A-89-1), however. In this experiment, we inadvertently reused the coolant that had been heated to 286° C (559 K) and exposed to a lithium drop at 258° C (531 K) in the previous experiment A-86-1. The sample of coolant had cooled to room temperature overnight in contact with the debris in a static argon atmosphere. Before the experiment, the only apparent difference from the light yellow fresh coolant was a somewhat darker coloration.

When stirring began in experiment A-89-1, an opacity immediately began to develop in the coolant that grew progressively denser as the stirring continued. Close examination of the coolant during stirring indicated that the opacity was caused by myriads of tiny bubbles dispersed throughout the organic liquid. We had never seen these bubbles before when previously unheated cold coolant was stirred, with or without prior contact with molten lithium. After discussions with the coolant's supplier, we concluded that pyrolysis gases, e.g., H_2 and C_nH_x , where n and x are small numbers, had dissolved in the coolant as it cooled overnight from the previous experiment. These gases apparently had been nucleated by the mechanical stirring to form the tiny bubbles.

In spite of the opacity generated by stirring the used coolant, we continued with experiment A-89-1 as originally planned. Although viewing was significantly obscured, the video record was consistent with the absence of a vigorous or self-sustained chemical reaction in the other three experiments performed subsequently in this set (A-93-1, A-97-1 and A-98-1). The rapid vaporization when the drop of molten lithium fell into the coolant could be seen as clearly in experiment A-89-1 as in the other three subsequent experiments in which no opacity developed in the stirred (fresh) coolant.

The apparatus was not opened for three days after experiment A-89-1 had been completed; that is, after cooling to room temperature, the coolant had been in a static argon atmosphere and in contact with the debris for this time. When we revisited the apparatus the opacity of the coolant had disappeared completely, apparently due to re-solution of the pyrolysis gases.

Molten Lithium with High Superheat into Coolant at High Temperature

The final set of experiments, A-100-1, A-105-1 and A-110-1, was performed under the two extreme conditions--strongly super-heated lithium (nominally 500° C (770 K)) dropped into vortices formed in strongly heated Therminol 66 coolant (nominally 300°C (573 K)). Although we were pushing the apparatus to its maximum capabilities in these experiments, there still were no indications on the video records or in the debris of luminosity or other vigorous self-sustained chemical or physical reactions during or after contact between the hot lithium and the hot organic coolant. The only noticeable change during these three experiments at the temperature extremes was the development of a red-brown surface coloration on each originally silvery lithium drop within a few seconds of its release into the coolant as shown in Figures 8a and b (Experiment A-110-1). We attribute this coloration to the formation of a thin coating of lithium nitride, Li_3N , on the drops by the reaction of the clean metal with nitrogen-containing impurities in the purge gases and coolant. The formation of this coating will be discussed in more detail in Appendix A.

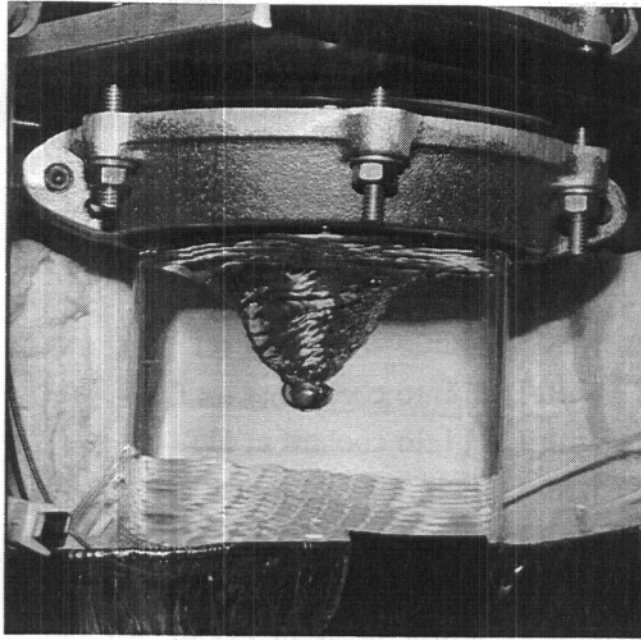


Figure 8a. Flash photograph taken 0.25 s after a nominally 0.5 g globule of molten lithium at 499°C (772 K) had been released into a vortex formed by magnetic stirring of 0.7 L of Therminol 66 organic coolant at 299°C (473 K). Note silvery appearance of the globule. (A-110-1-1)

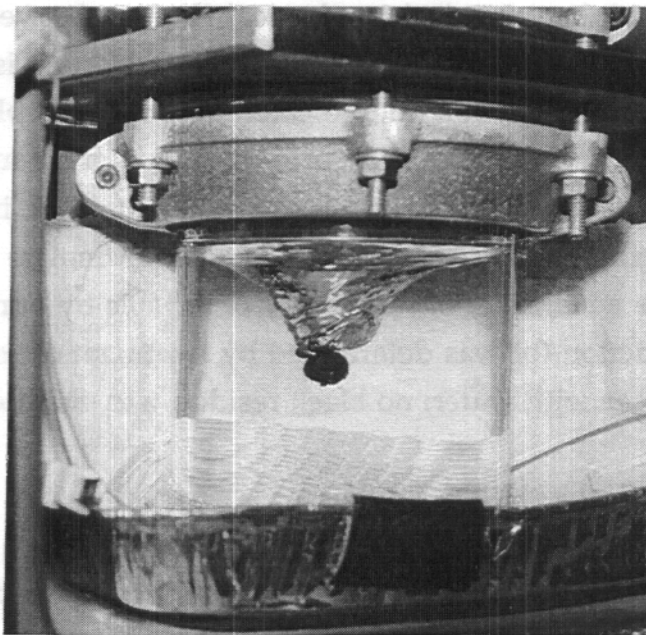


Figure 8b. Photograph similar to that in Figure 8a, but taken 5 min after the same globule had been released into the coolant. Note the dark red-brown coloration of the surface of the globule. (A-110-1-2)

DISCUSSION

Comments on the Experimental Results

In the scoping experiments described here, we investigated the interactions between 0.5 g samples of metallic lithium released into 0.7 L of strongly stirred partially hydrogenated terphenyl coolant, Therminol 66. Six basic sets of release conditions were studied:

- Solid Li at RT into coolant at RT.
- Molten Li with LSH into coolant at RT.
- Molten Li with LSH into coolant at an IT.
- Molten Li with LSH into coolant at HT.
- Molten Li with HSH into coolant at RT.
- Molten Li with HSH into coolant at HT.

where RT = room temperature = $\sim 20^{\circ}\text{C}$ (~ 293 K),

IT = an intermediate temperature of 191°C (464 K),

HT = a high temperature of $\sim 300^{\circ}\text{C}$ (~ 573 K),

LSH = a low superheat of ~ 75 K above the mp of 181°C (454 K), and

HSH = a high superheat of ~ 300 K above the mp of 181°C (454 K).

In none of the experiments performed here was there any indication of (a) a vigorous, self-sustaining chemical or physical reaction between the lithium and the organic coolant, or (b) the formation of water-insoluble debris, in particular, solid carbon. The absence of reaction (a), indicated by video and photographic imaging, includes the failure to observe rapidly propagating interactions that generate bubbles of coolant vapors, pyrolysis gases or other permanent gases, interactions that lead to molten metal fragmentation or deposition of fine particulate material (that is, vapor explosions), or the generation of luminosity detectable by our optical techniques. The absence of reaction (b) was determined by treatment of several debris samples on white filter paper with water; no black residue was ever detected visually.

Comparison with Earlier HEDL Studies

Release of Lithium into the Coolant

Several experiments similar to ours have been reported by workers at the Hanford Engineering and Development Laboratories (HEDL) (Gierszewski and Hollies 1987; Romero 1984). These experiments also involved the release of molten lithium into the same organic coolant. Their experimental conditions are summarized in Table 3. Compared to our experiments, there were several differences, however: their masses of lithium released were somewhat greater

while the masses of coolant were smaller than ours; their coolant was not stirred; their ambient atmosphere was air while ours was purified argon; and the maximum temperatures of the lithium and coolant were somewhat higher and lower, respectively, than our corresponding maxima. Both sets of experiments had similar results because no vigorous or self-sustained chemical or physical reactions were observed in either set. (There is some confusion in the first experiment listed in Table 3 because the lithium was burning in air at the time of contact with the coolant. The lithium fire was extinguished by the hot coolant, but it in turn ignited and burned in air. No chemical interaction between metal and coolant was reported, however.)

The results of both sets of experiments seem to indicate that no rapid energetic interaction occurs immediately (that is, within the first 0.5 s or so) upon contact of molten lithium at temperatures up to 537°C (810 K) with Therminol 66 coolant at temperatures between 20°C (293 K) and 300°C (573 K) in either HEDL's static or our fast flow (stirred) situation. Moreover, in our experiments, there were no signs that even a slow (many seconds) reaction occurs between the coolant at 20°C (293 K) and 300°C (573 K) and lithium at temperatures up to 300°C (573 K), our maximum quench temperature determined by the major thermal mass, the coolant. The only slow reaction at the higher lithium and coolant temperatures seems to be the formation of a dark red-brown coloration of the surface of the lithium. We attribute this to the formation of the lithium nitride, Li_3N , by reaction of the metal with nitrogen-containing impurities in the coolant and/or the ambient atmosphere (Schönherr et al. 1983, see Appendix A).

Table 3. Summary of HEDL's Experiments in which Molten Lithium was Added to Therminol 66 Coolant in an Air Atmosphere^a

Lithium		Coolant		<u>Remarks</u>
<u>Mass(g)</u>	<u>T(K)</u>	<u>Mass(g)</u>	<u>T(K)</u>	
2 ^b	810	13	500	Li extinguished, oil ignited
5	560	21	500	Oil vapor, no fire
20	700 ^c	21	500	Oil vapor, no fire

- Data are taken from Table 6 of Gierszewski and Hollies (1987).
- Lithium was burning when it contacted the coolant.
- In a separate private communication, R.F. Keogh of HEDL indicates that the temperature of the lithium was actually 700 K instead of 500 K as reported in Table 6.

Release of Coolant onto the Lithium

In a second set of experiments performed at HEDL (Gierszewski and Hollies 1987; Romero 1984), summarized in Table 4, there is some evidence that a relatively slow reaction may occur when the coolant is released onto the lithium when the metal is held at the higher temperature of 427°C (700 K). (Note that the normal boiling temperature of Therminol 66 lies in the range of 339°C to 353°C (612 K to 626 K); its "optimum use range" lies between -7°C and 343°C (266 K and 616 K) (Green 1993).) In these experiments, small amounts of the coolant were released onto somewhat larger amounts of molten lithium held in an insulated heated vessel. Here, the temperatures of the long term interactions were set by the combined thermal masses of the lithium and the vessel, not by the more massive coolant as in our experiments and the first set of HEDL's experiments summarized in Table 3.

In the experiments outlined in Table 4, there seems to be a distinct liberation of heat, an increased rate of coolant decomposition and carbon formation when lithium is present compared to the control experiment without lithium. Neither the number of experiments performed nor their documentation are extensive,

Table 4. Summary of HEDL's Experiments in which Therminol 66 Coolant was Added to Molten Lithium in an Argon Atmosphere ^a

Lithium		Coolant		<u>Remarks</u>
<u>Mass(g)</u>	<u>T(°C,K)</u>	<u>Mass(g)</u>	<u>T(°C,K)</u>	
3	287,560	1	227,500	Mild reaction; carbon film on Li
3	427,700	1	227,500	Rapid temperature increase, pressure surge after about 7 min. Carbon film 1 mm-thick formed on Li. Gas exit plugged with carbon.
Not given	427,700	1	Not given	Mild exothermic reaction. Decomposition of the coolant; 0.5 g of carbon formed
0	427 ^b ,700 ^b	1	Not given	Control for previous experiment. Little decomposition of the coolant

^a Data are taken from Table 6 in Gierszewski and Hollies (1987), augmented with information from private communications from R.L. Keogh of the Hanford Engineering and Development Laboratory.

^b Temperature of the vessel without lithium

however, suggesting the need for further study where the temperature of the lithium is maintained above the normal boiling temperature of the coolant (and, coincidentally, at temperatures above which the pyrolysis of the coolant may become significant).

It should be noted in closing that not all debris that appears black is necessarily carbon, as we discovered in experiment A-66-1. The pervasive formation of lithium nitride, Li_3N , which can appear black or deep red-brown, should always be considered because of its rapid generation in the presence of even very small concentrations of nitrogen-containing impurities (see Appendix A). Fortunately it may be easily identified and quantitatively determined because of its rapid conversion to the colorless oxide in the presence of oxygen and to the water-soluble hydroxide in the presence of water (with subsequent generation of ammonia in the latter reaction).

CONCLUSIONS

The twenty scoping experiments described here and the three experiments performed earlier at HEDL (see Table 3) in which small amounts of molten lithium were released into the partially hydrogenated terphenyl coolant, Therminol 66, strongly indicate that:

- Vigorous, self-propagating chemical or physical reactions between the organic coolant and molten lithium are unlikely, even at initial melt and coolant temperatures as high as 527°C (800 K) and 300°C (573 K), respectively.
- Slow reactions between molten lithium and the coolant are virtually nil as long as the temperatures of both materials remain (or are fixed) at 300°C (573 K) or below.

There is some indication that a relatively slow exothermic reaction with the coolant may occur when the molten lithium is maintained at a temperature of 427°C (700 K) for extended times of seconds or longer (see Table 4). This reaction may be mostly a thermal decomposition of the coolant, perhaps enhanced by the presence of the lithium. It is possible that this reaction could pressurize the system, increase its temperature and deposit a variety of pyrolysis products that range from hydrogen and low molecular weight hydrocarbon gases to polymers and solids such as carbon. Unfortunately, the experimental data base for this slow reaction is very limited and our experiments shed little light. Clearly, further studies are needed at these higher operating temperatures with more instrumentation to eliminate concerns of a lithium-coolant interaction.

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APPENDIX A

Surface Nitridation of Lithium

Throughout the work reported here, the surfaces of our shiny metallic lithium, either molten or solid, have taken on a black or dark red-brown coloration. This occurred after our preliminary molten lithium dropping tests in a glove box flushed with carefully dried commercial cylinder argon and also after all our releases of molten metal into Therminol 66 coolant; these latter experiments all were carried out in an atmosphere of argon purified by passage over titanium chips heated to 500°C (773 K). Perhaps the most striking and most rapid surface color formation was observed during the drop releases into the coolant when the temperatures of both the lithium and the organic liquid were at their maxima--nominally 500°C (773 K) and 300°C (537 K), respectively. Our video and photographic imaging indicated color formation in this latter situation to begin within about 0.5 s and to be complete within the next few seconds (see Figures 8a and b).

To learn more about this coloration, we cut one of the intensely colored globules recovered from experiment A-110-1 in half with a sharp blade. The coloration was found to be only on the surface, certainly less than a millimeter thick. When a tiny piece of the lithium with the surface coloration was dropped into water, it reacted completely to form only soluble and gaseous products; no solid materials (e.g., carbon) remained.

A striking aspect of the surface coloration was its reaction with air. In most of our lithium drop releases, the colored solidified globule remained floating on the surface of the coolant overnight or longer in either a static or a very slowly flowing atmosphere of argon. The surface coloration seemed unchanged from the previous day, coating both the top and bottom of the globule equally. But within several hours after the colored globule was transferred to a covered jar that contained either a small amount of the coolant or mineral oil, the top portion of the globule exposed to the air atmosphere lost its color while the lower portion retained its color unchanged. This change in coloration can be seen in Figures A-1a and A-1b.

After a search of the handbook listings of inorganic compounds of lithium (Weast 1974) indicated only two colored materials, lithium chromate (see Appendix B) and lithium nitride (the listing describes it as "black amorphous or red-brown crystalline"), we concluded that the formation of the nitride was the likely cause of the surface coloration observed in our experiments.

Lithium nitride, Li_3N , is a thermally stable crystalline material with a sharp melting temperature of 813°C (1086 K). It forms readily by the reaction of metallic lithium with gaseous nitrogen, and may be recrystallized in this atmosphere by the Czochralski technique to form shiny red-brown boules several centimeters in length and diameter (Schönheer et al, 1983). The exothermic nature of this reaction between lithium and nitrogen and its relationship to nuclear fusion safety has been studied by Kazimi and coworkers (e.g., Barnett et al. 1989). This reaction has been used to remove nitrogen from gas streams (Mellor, 1967). It can also be used to "fix" nitrogen, that is, to convert neutral gaseous nitrogen to the more reactive ammoniacal nitrogen. (Lithium nitride will react with water to produce ammonia, NH_3 , and lithium hydroxide (Mellor, 1967).)

Although we have done no specific chemical analyses of the intensely colored surface layers that form on our fresh lithium surfaces other than the water dissolution tests, we feel confident that reaction with nitrogen-bearing impurities in either the gaseous atmospheres or the coolant or both are the cause. Moreover, the relatively rapid discoloration of the upper surface of the colored globule as it floats in mineral oil or coolant with an air atmosphere above is consistent with the rapid reaction of lithium nitride with oxygen or moisture to form lithium oxide or lithium hydroxide, respectively, both of which are colorless. Impurities in the atmosphere may be the most significant contaminant because (a) when fresh titanium turnings were placed in the purification furnace for our last experiment (A-110-1), the buildup of the colored layer seemed to proceed more slowly than in the previous similar experiments (A-100-1 and A-105-1), and (b) the manufacturer believes the level of nitrogen-bearing impurities in the coolant to be very low as the result of their synthetic procedure, which involves the pyrolysis of benzene followed by partial rehydrogenation (Green, 1993).

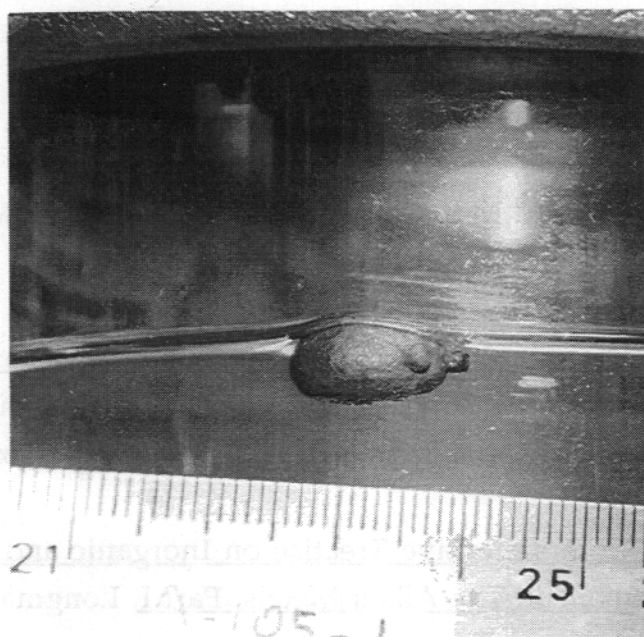


Figure A-1a. Globule of lithium floating on Therminol 66 coolant after having cooled in an argon atmosphere overnight. Release temperature was 489°C (762 K) and coolant temperature was 292°C (565 K) at time of interaction. Note dark coloration over entire surface of the globule. Small divisions = 1 mm. (A-105-1-3)



Figure A-1b. Same globule as in Figure A-1a, except that it had been transferred to a sample bottle half-full of mineral oil. Atmosphere in the jar above the oil was air. Note change in coloration of the surface of the globule that had been exposed to air above the oil. Small divisions = 1 mm. (A-105-1-19)

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APPENDIX B

Design and Performance of the Lithium Drop Generator

In this work, we developed a device new to our laboratories for preparing and dropping single nominally 0.5 g globules of molten lithium at temperatures up to 500°C (770 K). Inclusion of a few comments on its design and performance seems in order.

The construction of the stainless steel crucible and its rotatable bottom closure (gate) has been described in the experimental section and is shown in the photographs in Figures 4 and 5. The design is quite simple, basically a cylindrical block of Type 304 stainless steel with an axial hole drilled through it. The block is mounted with axis vertical. Its flat bottom is closed with a gate that can be rotated open by turning a shaft that passes through a smaller second vertical hole in the block parallel to and to one side of the larger axial hole. A second smaller hole is drilled vertically partway downward into the block on the other side of the block; it holds a Type K thermocouple for temperature measurement. The outside vertical surface of the block is heated with a helical resistance heater clamped firmly to it.

To prepare a molten globule, 0.5 g of coarse granular lithium is poured into the central hole in the preheated block with bottom gate closed. Purified gaseous argon passes over the furnace and charge throughout the heating. After 5 min, the lithium charge is stirred with a thin stainless steel rod to break up any surface skins on the individual granules and to assure coalescence of the molten globules. After another 5 min, the lithium globule is released when the bottom gate is swung to one side by rotating the vertical shaft 90°. The molten globule then is free to fall by gravity into the coolant below through a centered vertical hole in the lower stainless steel plate.

Recommendations for Improvement

Pusher Gas Tube

Early in the program, we realized that because of its low density and relatively high surface tension, the molten lithium charge did not fall reproducibly from the hole in the crucible block when the gate opened; sometimes only a small fraction of the metal fell. We remedied this by inserting a snug-fitting stainless steel tube into the top of the crucible from above through the same hole in the upper stainless steel plate (see Figure 4) through which the lithium charge was added previously. Gentle pressurization of this tube with argon after the shuttering gate opened pushed the

lithium downward in the crucible and ejected it as an essentially single globule into the lower chamber of the apparatus. (If the pressurization is applied before the gate opens, the lithium will be ejected not as a single globule but as a spray, as in experiment A-66-1.)

The installation and operation of the "pusher" gas tube could be improved. As we used it here, we hard plumbed the tube in place after the lithium was added. This prevented us from flushing the tube prior to its installation and operation. Even though the tube was later pressurized with argon through a line a meter or so long, it is possible that air had not been swept completely from the line. When the tube was finally pressurized this air might have been driven into the carefully argon-flushed lower chamber where the lithium and coolant were interacting. This might have provided some or most of the nitrogen that caused the surface nitridation (coloration) of the lithium globule during the interaction.

To minimize this source of contamination, we recommend use of a flexible line on the pusher gas tube so it could be purged with argon until just before its insertion into the crucible hole. We also recommend addition of a stainless steel fitting to the pusher gas tube to attach it gas-tight through the upper stainless steel plate. This would eliminate or minimize one possible source of contamination, namely the inward diffusion of air into the upper chamber around the pusher gas tube. In the current design, we rely on the outward flow of purging argon around the tube inserted into the threaded hole in the upper plate to prevent the entry of air into the apparatus. (We rely similarly on this outward flow to prevent the entry of air when the L-tube that contains the lithium granules is inserted into the crucible hole during charging.)

Shutter Gate Shaft

We had some trouble with the shaft that opened the shutter gate to release the lithium globule, particularly in the experiments at 500°C (770 K). The shaft, which passes snugly through a vertical hole in the heated crucible block, tended to seize during operation, and in some cases to freeze after cooling if molten lithium seeped into it along the upper surface of the shutter door. Some typical freeze-ups caused by lithium seepage are shown in Figures B-1 through B-3.

The seizing was alleviated to some extent by applying an automotive anti-seize lubricant, Loctite A, to the sliding or rotating surfaces keeping this material as far from the lithium as possible.

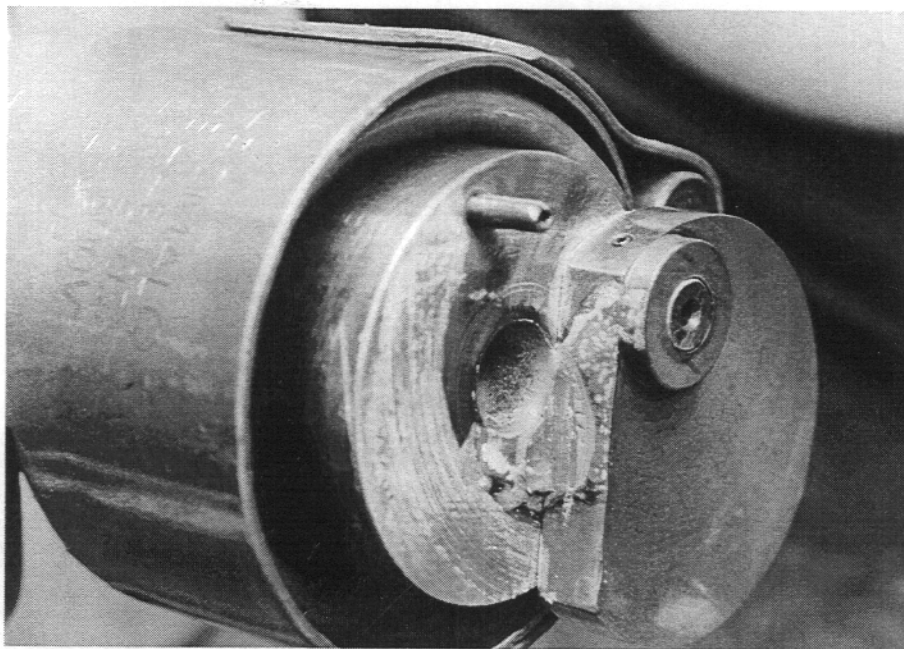


Figure B-1. Photograph of bottom of stainless steel crucible from which lithium globule had been released in Experiment A-100-1. Gate is shown in open position with some frozen lithium on the walls of the crucible and also on the gate. (A-100-1-16)

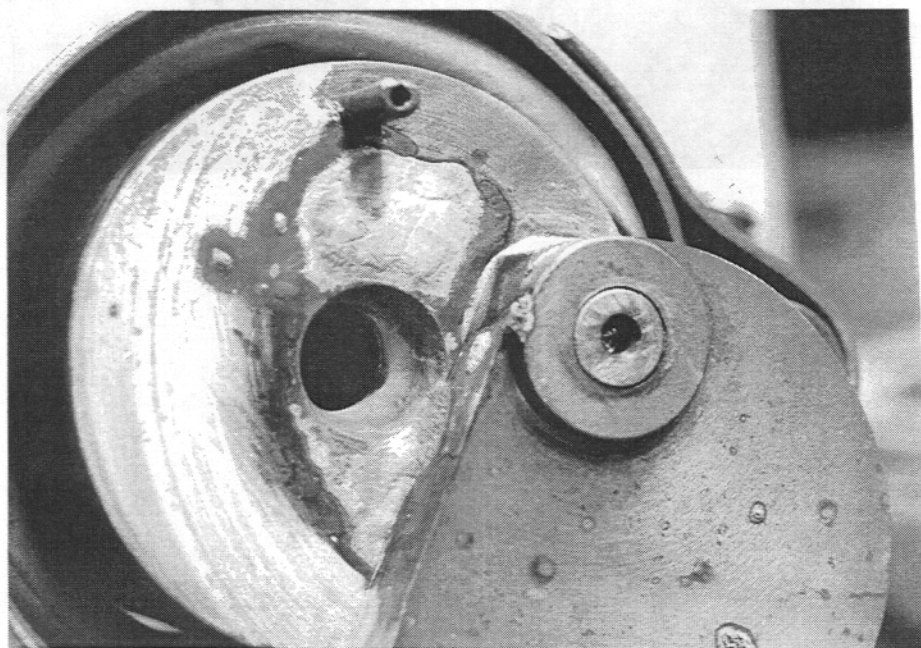


Figure B-2. Photograph of bottom of stainless steel crucible from which lithium globule had been released in Experiment A-105-1. Gate is shown in open position with some frozen lithium on the walls of the crucible and also on the gate. Some yellowish color is visible in the frozen lithium. (A-105-1-15)

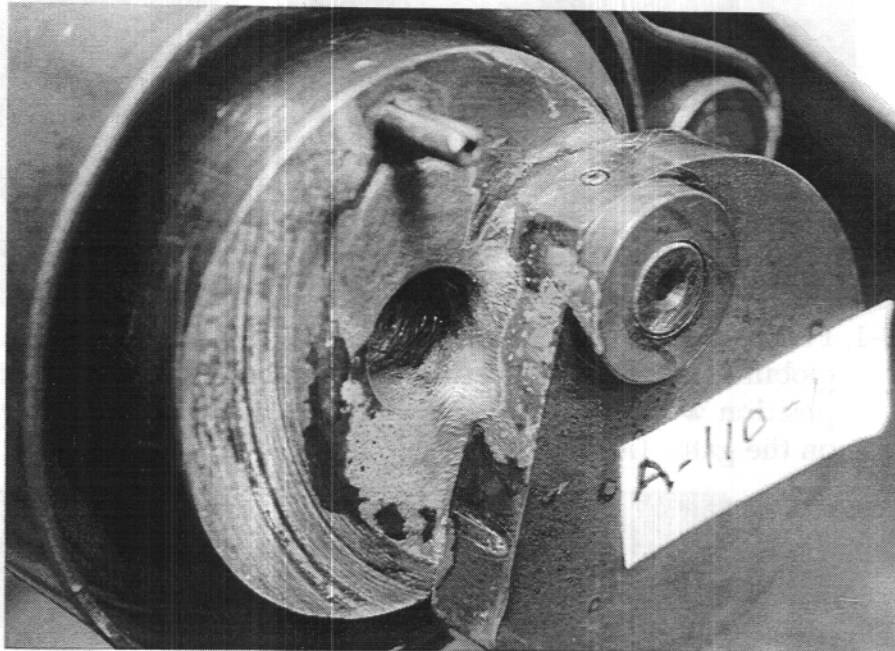


Figure B-3. Photograph of bottom of stainless steel crucible from which lithium globule had been released in Experiment A-110-1. Gate is shown in open position with some frozen lithium on the walls of the crucible and also on the gate. An amount of yellowish color larger than in Figure B-2 is visible in the frozen lithium. (A-110-1-15)

Sometimes the freeze-up of the shaft and shutter gate in the open position could be released simply by immersing the (cold) crucible with heater in place in water for several hours. The lithium would react away from the stainless steel parts and dissolve in the water. This procedure did not always succeed, however; the shaft then had to be freed by mechanically disassembling and reassembling the crucible, a procedure that required several hours.

The shutter gate rotation scheme could be improved significantly by a new crucible block design in which the shaft and its bearings could be removed from the heated zone and away from contact with the molten lithium. This might be accomplished by adding extensions to one side of the crucible block in which the shaft and its bearings could be located to keep them cooler and avoid contact with the molten lithium. Better bearings, e.g., ball bearings, might also improve operation of the gate.

Materials of Construction

Because of its high chemical reactivity and tendency to alloy with many metals, molten lithium is difficult to contain, especially at high temperatures. Mellor (1961) cites stainless steels as showing good resistance toward molten lithium at temperatures below 538°C (811 K). We constructed our apparatus on the basis of this statement as well as anecdotal information from other sources.

Although we had no serious difficulty with attack of the crucible block, shutter gate and shaft materials, all made from Type 304 stainless steel, we did have a minor spot attack at the bottom of the crucible block where friction with the shutter gate occurred. We saw a golden coloration in the frozen lithium at this point that steadily grew larger during the last three experiments, A-100-1, A-105-1 and A-110-1, all performed at release temperatures of 500°C (770 K). These colored spots are visible in Figures B-1, B-2 and B-3. These spots and their surrounding frozen lithium readily dissolved in water to reveal visibly smooth stainless steel surfaces beneath. We attribute the color to reaction of the lithium with some local chromium-containing imperfection in the stainless steel at this point to form the colored lithium chromate (Weast 1974).

Mellor (1961) reviews studies of the resistance of many pure metals and alloys to molten lithium at high temperatures, mostly as related to its use as a coolant in various nuclear applications. One of these studies (Hoffman and Manly, 1957) reports temperatures below which both static and dynamic systems may be operated with lithium for 1000 hr with less than 127 μm attack on iron, low-alloy steel, ferritic

stainless steel, austenitic stainless steel, nickel, "Inconel," cobalt, "Stellite," copper, copper-base alloys, refractory metals (molybdenum, niobium, tantalum, zirconium, titanium, tungsten and vanadium) and precious metals (silver, gold and platinum).

On the basis of Mellor's review, we suggest that, in addition to the Type 304 stainless steel used in this work, the lithium-resistant ferrous alloys and pure metals cited in the above quotation be considered for future experiments, particularly at temperatures higher than 500°C (770 K). While the Type 304 stainless steel performed satisfactorily in the limited number of experiments performed here at temperatures up to 500°C (770 K), we feel that its resistance toward molten lithium was indeed being pushed to its limit. Other constructional metals and alloys might provide a wider margin of stability, yet still be readily obtained and fabricated.

REFERENCES FOR APPENDIX B

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