Eutectic Molten Salt Thermal Storage System

GERRIT DEVRIES* AND H. EDMUND KARIG†
Naval Undersea Research & Development Center, Pasadena, Calif.

AND

GARY DRAGE‡
Ooyec Hill Air Force Base, Utah

An analysis of thermal storage materials indicated that a eutectic mixture of lithium hydroxide and lithium fluoride could provide relatively high heat capacity for a closed-cycle thermal propulsion system for deep-running underwater vehicles. In contrast with other high-heat-capacity lithium compounds, this mixture undergoes practically no expansion during fusion. It has a low melting point of 800°F. It does not react chemically with water, but does absorb small amounts if exposed to steam at high pressure. Tests with various metals, including 304 stainless steel and Inconel 600, indicated that corrosion may occur at random at temperatures above 900°F. From 900° to 1200°F, Inconel 600 indicated the least corrosion of the high-strength materials tested.

Introduction

A SYSTEM under investigation at the Naval Undersea Research and Development Center (NUC) requires an unmanned, deep-operating vehicle with long endurance. Although atomic energy could provide the necessary power, no such power source is likely to be available in the foreseeable future. As a result, an investigation of relatively short-endurance propulsion systems and energy sources was undertaken.

The investigation centered around systems capable of recharging or refueling from a surface vessel at sea within 6 hr or less. In addition, the system should meet other criteria: 1) operation at extreme depths without reduction of performance, 2) minimal change in buoyancy or center of gravity (to eliminate trim problems), 3) minimal hazards to the crew of the tending ship. Many possible energy sources were considered, and some of the available energy sources are compared in the following paragraphs.

Figure 1 is a nomograph of endurance vs specific energy for various energy sources considered for underwater powerplants in small submerged vehicles, which range from 200 to 600 ft^3 in size and require from 50 to 100 shaft hp. The vertical width of the band for each energy source indicates the penalty paid for the addition of material or containers to provide neutral buoyancy. The bottom line of each band represents the possible energy and endurance for each system, whereas the top line indicates the net available energy when buoyancy material and containers are included. On this basis, the eutectic thermal storage system applied to a Rankine cycle steam engine compares very favorably with rechargeable batteries, and the narrowness of the crosshatched area for the salts indicates the relatively small penalty incurred when neutral buoyancy is required.

Batteries

Conventional storage or rechargeable batteries are more favorable with respect to buoyancy control than the combustion engine. However, the available energy per charge of batteries is quite low, the number of times they can be recharged is limited, and their high negative buoyancy can impose a considerable penalty if additional material is required to provide neutral buoyancy.

Fuel Cells

Based on specific fuel consumption only, fuel cells appear to provide the greatest endurance. However, space requirements for auxiliary equipment appear too great for smaller vehicles, and many problems must be overcome before fuel cells can be seriously considered for small submerged vehicles.

Thermal Combustion Engines

A combustion engine has several disadvantages in deep-ocean operation. It is depth-sensitive if the products of combustion are exhausted directly overboard against high back pressures. In fact, additional equipment is required if the products of combustion are to be pumped overboard or stored. Furthermore, trim is a problem if the center of

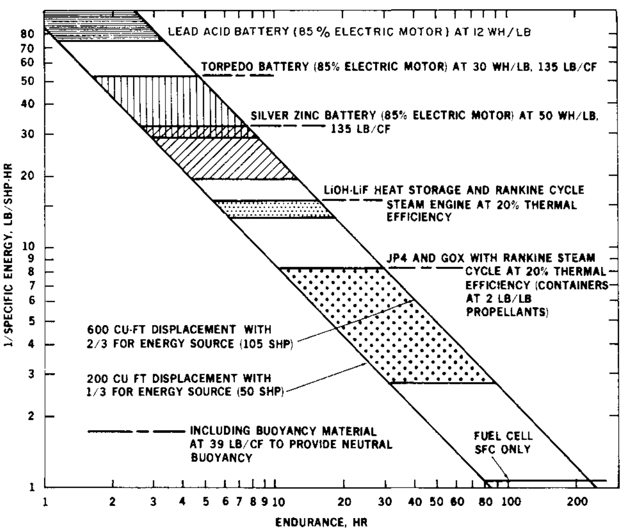

Fig. 1 Submerged vehicle endurance with various energy sources.

Received March 3, 1969; revision received July 7, 1969.

* Metallurgist.

† Consultant.

‡ Mechanical Engineer, Naval Undersea Warfare Center, Pasadena, Calif. (Naval Undersea Research and Development Center, Pasadena, Calif.); now Mechanical Engineer.

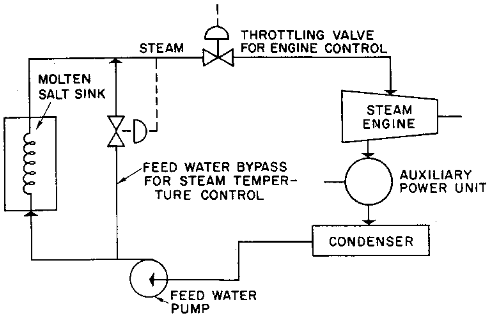

Fig. 2 Simplified flow diagram for a molten salt thermal energy propulsion system.

gravity or buoyancy changes as the fuel is consumed, so that a ballast or buoyancy compensation system is required. Trim is particularly critical for slow-moving submerged vehicles.

Thermal Energy Storage Systems

Several thermal storage systems have considerably higher specific energy storage capabilities than lead-acid or silver-zinc batteries,[1] and they provide constant buoyancy. Although thermal storage systems do not match the theoretical performance of some thermal combustion or fuel-cell systems, the one investigated by NUC has the advantage of being rechargeable in a simple fashion using superheated steam supplied from a surface vessel.

Proposed System

The proposed propulsion system uses thermal storage as the energy source for a Rankine or closed-cycle steam system with boiler tubing embedded in eutectic salts. A much simplified schematic is shown in Fig. 2. The tubing extracts heat from the salts by generating steam and reheats the spent eutectic salts with superheated steam from the tending vessel. Electrical heaters were not chosen for recharging because they add considerable extra weight. The boiler tubing, however, was investigated as possible resistance elements for electric heating, but was rejected because of excessive corrosion due to the conductivity of the salt and resulting electrolytic action. An advantage of a molten salt system is that the Rankine cycle used would be applicable also to a nuclear thermal system in the event that suitable nuclear power sources become available.

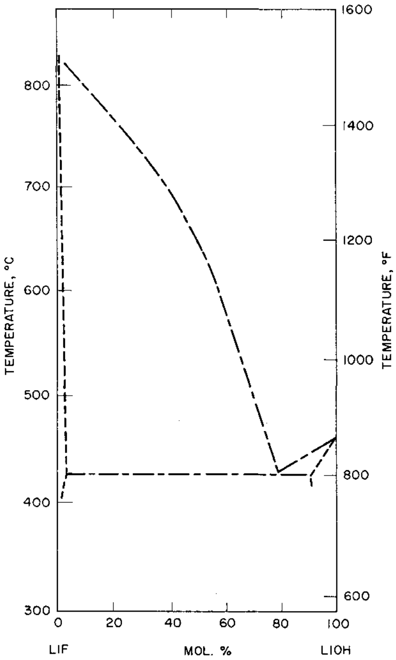

Fig. 3 LiF-LiOH phase diagram.

Several propulsion systems using a molten salt for thermal energy storage have been investigated for underwater vehicles with various missions. In general, they would provide much greater specific energy per charge than conventional storage batteries, and constant buoyancy for deep operation. However, most use either lithium hydride or lithium fluoride for energy storage and these have several undesirable features. Lithium hydride, which has the highest energy density of the lithium salts, was not considered satisfactory because 1) it is violently reactive in contact with water and hence a hazard to personnel during handling, 2) it has a 16–19% shrinkage during fusion, which might cause severe stresses within the heat exchanger when cycled repeatedly, and 3) its high melting point of 1256°F makes recharging with ship's steam difficult. Lithium fluoride was also discarded as sole energy source because of its high melting point (1556°F) and high shrinkage during freezing (25%).

Lithium hydroxide has a more favorable melting point of 884°F and low volumetric change during freezing. This volume change is unusual, in that it expands 3.4% on freezing, which is similar to water. Although this volumetric change of lithium hydroxide is comparatively low, there was apprehension that difficulty might be experienced in providing a vessel and heat exchanger to withstand stresses during repeated cycling. To minimize this expansion, lithium fluoride was added to the lithium hydroxide. With 20 to 30% lithium fluoride by weight, practically no change in volume was noted, and the melting point of the mixture was 800°F. The point of no volume change corresponds nearly to the eutectic of the mixture, as shown[2] in Fig. 3, and provides a salt with both low volumetric change and low melting point.

Very little information was available on the thermodynamic properties of the eutectic or on chemical reaction with other materials. Therefore, some preliminary tests were made to reveal problem areas and to determine the feasibility of using this salt combination as a thermal storage medium.

Experimental Steam Boiler

A small heat-storage chamber was constructed to determine the practicality of generating steam from the hot salt. Also

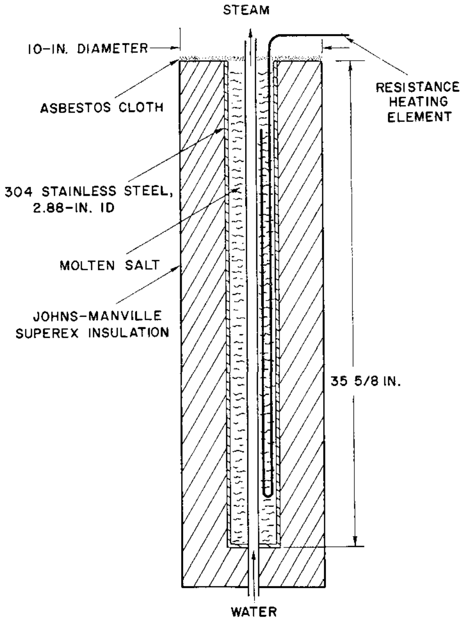

Fig. 4 Experimental molten salt steam generator; 12-lb salt capacity.

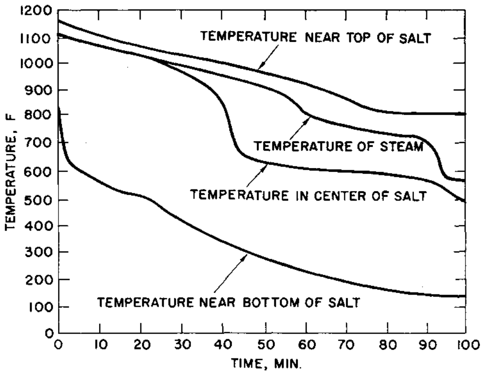

Fig. 5 Temperature-vs-time cooling curves for experimental 12-lb steam generator with a water flowrate of 4 lb/hr.

to be determined were approximate thermodynamic properties and the corrosivity or breakdown of the eutectic mixture during repeated cycling in contact with structural materials, such as stainless steel or Inconel. Figure 4 is a schematic of the test setup. The thermal storage container had a 3-in. i.d. and a length of 36 in. A heat-exchanger tube was positioned coaxially in the chamber. The tube was 0.5 in. in diameter with a wall thickness of 0.035 in. Both the tube and the container were type 304 stainless steel. The apparatus contained 12 lb of the eutectic mixture. Inconel-sheathed thermocouples were located at various elevations in the container and the steam tube. The outer shell was encased in high-temperature insulation (Johns-Manville Superex). An Inconel-sheathed resistance heating element was immersed in the salt to heat the mixture.

After heating the salts to the molten state, distilled water at pressures up to 1000 psig was introduced into the bottom of the steam tube by a Sprague pump. As the water flowed up the tube, it was converted to steam by absorbing heat from the hot salt. Initially, the majority of the heat was extracted from the lower part of the apparatus. As the run progressed, heat was extracted at higher and higher locations until, at the end of the run, the top of the salt had cooled below 800°F. A typical run record is shown in Fig. 5. Note that it is desireable to extract heat from the salt in a stratified manner. More, useful heat can thus be obtained, and steam can be generated at higher temperatures than if the salt cooled uniformly. The lower portion of the salt preheats the incoming feedwater at temperatures much lower than the fusion temperature; thus, the lower portion of the salt approaches the temperature of the feedwater and nearly all of the heat from this portion of the salt is extracted.

In one run, superheated steam was generated between 700° and 1200°F at 1000 psig for 1.5 hr at 4 lb/hr; in another for 4 hr at 1.5 lb/hr. A total flow of 8 lb of steam was possible at lower flow rates, which indicated that the available heat is approximately 1000 Btu/lb of the eutectic salt mixture. A third test run was made, in which the steam temperature fell from 1200° to 700°F in 17 min, with a flowrate of 15 lb/hr; an additional 4 lb of superheated steam was generated by lowering the flow rate.

Corrosion

About 30 test runs were made with the 12-lb unit, during which the salt mixture was molten between 800° and 1300°F for approximately 200 hr and in the partially molten state during reheat for several times that long. No deterioration of the salts or failure of the steam tube, Inconel-sheathed thermocouples, or of the heater exposed to the salts was detected during this period.

The 12-lb salt container was later cut into sections. Only the bottom portion of the salt column indicated deterioration, as shown by corrosion products accumulated there, and the upper portions appeared uncontaminated. The wall of the stainless-steel tube underwent some corrosion at the upper section, where high temperatures were sustained for greater periods of time. However, most of the corrosion was on the inside surface, which was exposed only to steam. These results were considered quite favorable, especially since the construction material was common 304 stainless steel.

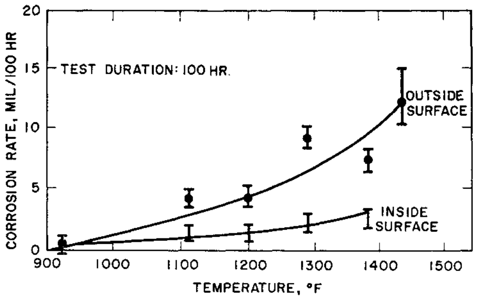

Fig. 6 Corrosion rates vs temperature of a section of $\frac{3}{16}$-in.-o.d. Inconel 600 tube in a molten LiF-LiOH environment.

Subsequent tests on samples with other metals indicated that rapid corrosion may occur. A contract to determine the best materials to withstand corrosion and the conditions that cause accelerated corrosion was therefore let to Atomics International, Division of North American Aviation, Canoga Park, California.[3]

Screening tests were made on nearly 50 different metals and alloys. Nickel, some nickel-base alloys, and the precious metals, silver, gold, and platinum proved to have the best short-term (3 hr) corrosion resistance. Longer-term tests of 550 hr were conducted on nickel and nickel-base alloys. The two most promising materials were nickel and Inconel 600, with average corrosion rates during the 550-hr test at 1200°F of 0.027 mil/day and 0.27 mil/day, respectively.

The effect of temperature on the corrosion rate is shown in Fig. 6. Corrosion increases considerably as the temperature is increased and is insignificant below 900°F.

Sulphate and silica impurities increase the corrosion rate of most container materials. Small amounts of sulphate ions in the melt increased the corrosion rate significantly in all cases. For some high-iron-content alloys, dissolved silica in the melt also increased the corrosion rate. For Inconel 600, however, silica had little effect. This is important because many insulating materials contain silica, and Inconel 600 appears to be the best containment material. Sulphur-bearing compounds in insulating materials are suspected of causing catastrophic failures of test containers on several occasions, perhaps because nickel is subject to attack by sulphur gases above 600° to 700°F. Reducing conditions are worse than oxidizing. Above 1190°F a eutectic of nickel and nickel sulphide forms. Being molten, the eutectic penetrates the grain boundaries and leads to disintegration of the metals.[4]

Salt Characteristics

A contract was let to the Dynamic Science Corporation, Monrovia, California, to determine the thermodynamic properties of the salt mixture. A parallel in-house effort was conducted to determine physical characteristics and to check the thermodynamic study. Table 1 lists the basic properties determined by these two studies.

An important feature is that the salt density is only 40% greater than that of water. Hence the space-weight penalty paid to make the system neutrally buoyant is not as great as for other rechargeable energy sources, such as lead-acid or silver-zinc batteries which require large quantities of flotation material.

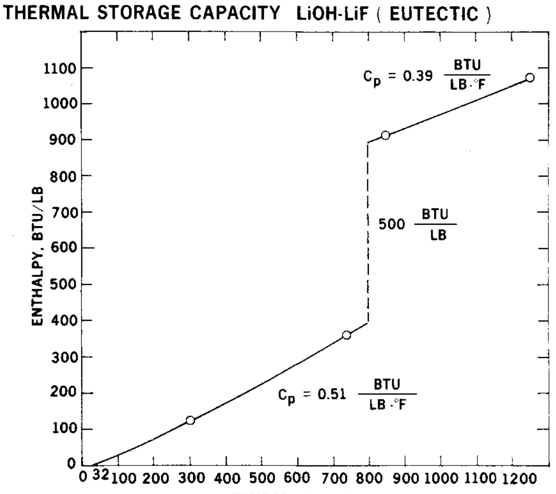

Fig. 7 Enthalpy distribution for the LiF-LiOH eutectic mixture.

Enthalpy

Figure 7 shows the enthalpy distribution for the salt. Heat capacities of the mixture were measured using an ice calorimeter. It is significant that 87% of the total enthalpy available in the range of 300° to 1200°F exists below 900°F. Thus, the salt could be used below 1200°F without a severe penalty in usable enthalpy. It is also significant that more than half of the thermal energy within this range is in fusion at 800°F.

Thermal Conductivity

Figure 8 shows the thermal conductivity of the solid salt. The conductivity of the eutectic is slightly lower than those of LiF, LiOH, or LiH. However, the net effective thermal impedance of the LiF-LiOH mixture may be lower because the eutectic adheres to the heat-transfer surfaces without forming the voids that often occur in salts that contract during freezing.

Change in Melting Point

When the molten salt is maintained at high temperatures for extended periods, some of it decomposes, due to breakdown of LiOH to Li_2O and H_2O (see Ref. 5). The rate of this breakdown is greatly increased by corrosion and by contamination of the salt by corrosion products. The breakdown occurs more rapidly in small containers because of the larger ratio of container surface area to salt volume.

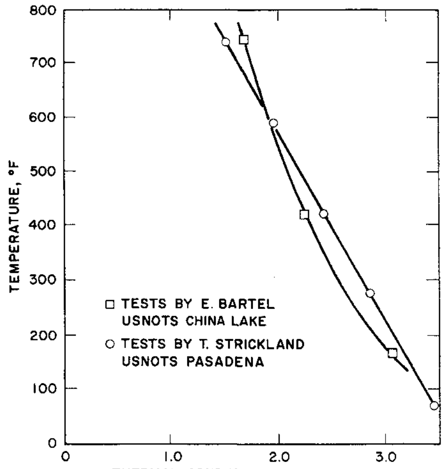

Fig. 8 Thermal conductivity for the LiF-LiOH eutectic mixture.

Table 1 Properties of salt used in heat storage

Composition	20% LiF-80% LiOH (eutectic mixture)
Melting point	800°F
Volume change (70° to 1200°F)	≈7%
Density	90 lb/ft³ at 1200°F, 97 lb/ft³ at 70°F
Average specific heat	
Solid	0.51 Btu/lb°F
Liquid	0.39 Btu/lb/°F
Heat capacity from 300° to 1200°F	
Solid	260 Btu/lb
Fusion	500
Liquid	170
Total	930 Btu/lb

Decomposition of the salt changes the melting characteristics and raises the temperature at which the thermal energy is released upon solidifying. As decomposition proceeds, portions of the salt solidify at temperatures above 800°F. Figure 9 shows an example of the effects of this decomposition when some of the salt was maintained for extended periods at 1200°F in a small container. At lower temperatures, corrosion and salt breakdown are greatly reduced. Tests conducted for long periods at 900°F yielded little or no change or distortion of the melting point even when 304 stainless steel was used as the container material.

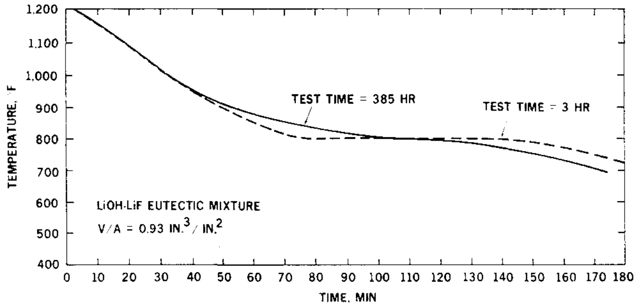

Fig. 9 Natural cooling curves showing distortion of the energy distribution resulting from extended test periods at 1200°F. Small test crucibles were used.

Water Solubility in the Eutectic Mixture

The system to which the salt was to be applied called for the pressure-balancing concept indicated in Fig. 10 to eliminate the need for a heavy pressure vessel. As the vehicle depth increases, water is forced into the inlet tube and converts to steam, until the pressure above the salt mass equals the ambient pressure. When the vehicle moves to shallower depths, the excess high-pressure steam is expelled from the salt tank and condensed. Thus pressure balance is maintained at all times.

Although this pressure-balancing system offers a very simple approach to some buoyancy and structural problems, the solubility of water in the salts imposes problems. Data from one water solubility experiment, conducted by Atomics International, are given in Table 2. In general, water is

Table 2 Solubility of water in the eutectic mixture of LiF-LiOH

Phase	Temperature, °F	Pressure, psig	Solubility, g/100 g of salt
Solid	800	1000	2.4
Liquid	806	800	4.7
Liquid	1382	2000	0.6

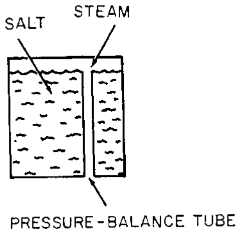

Fig. 10 **Sketch of pressure-balancing concept.**

more soluble in the molten salt than in the solid, but the solubility decreases as the temperature is increased above the melting point. Several hours was required to reach equilibrium water solubility. Upon freezing the dissolved water was expelled rapidly from the melt, which caused the salt to expand. When the melt was saturated with water immediately above the melting point, the expansion often exceeded the original volume of the melt.

This expansion also occurred, but to a much lesser degree, when there was no steam or high pressure above the salts, presumably due to the release of dissolved gases in the salt. The expansion depends upon the rate of cooling. It was never witnessed when the salt was allowed to cool slowly, but was easy to reproduce under rapid cooling conditions. Figure 11 shows a specimen that expanded when molten salt, which had not been exposed to high pressures or a steam atmosphere, was poured into a cold iron mold.

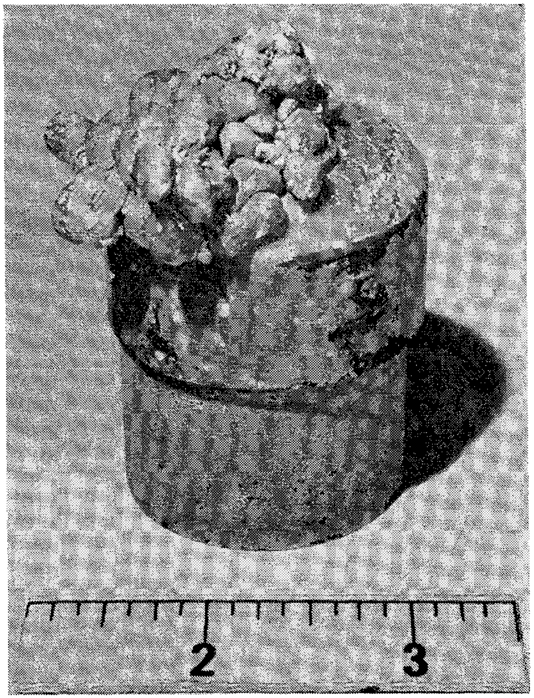

Fig. 11 **Expansion of the salt mixture resulting from the release of dissolved gases when the salt was cooled rapidly.**

Conclusions

Work conducted at the Naval Undersea Research and Development Center has yielded data on a eutectic salt mixture with novel characteristics that should prove useful in thermal storage applications, both underwater and elsewhere. The significant characteristics of the lithium fluoride-lithium hydroxide mixture are as follows: 1) little or no volume change during fusion and only about 7% volume change from room temperature to 1200°F, 2) low melting point of 800°F, 3) good thermal capacity, 4) relative safety (except for normal high-temperature hazards), 5) no chemical reaction with water, 6) corrodes most container materials above 900°F, but provides 800 Btu/lb of useful heat capacity at temperatures below 900°F.

References

[1] Flynn, G., Jr. et al., "Power From Thermal Energy Storage Systems," Paper 6088, 1962, Society of Automotive Engineers, Philadelphia, Pa.

[2] Levin, E. M., Robbins, C. R., and McMurdie, H. F., *Phase Diagrams for Ceramists,* The American Ceramic Society, Columbus, Ohio, 1964, p. 484.

[3] DeVries, G. and Grantham, L. F., "Corrosion of Metals in the Molten LiOH-LiF-H_2O System," *Electrochemical Technology,* Vol. 5, No. 7–8, July–Aug. 1967, p. 335.

[4] "Nickel and Nickel Base Alloys," Technical Bulletin T-13, International Nickel, Huntington, W. Va.

[5] White, W. D., "Thermodynamic Analysis of the Lithium-Water System as Applied to Chemical Power Generators," Navord Report 1202, April 1950, Naval Ordnance Test Station, Pasadena, Calif., Fig. 1, p. 4.