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LITHIUM LITERATURE REVIEW: LITHIUM'S PROPERTIES AND INTERACTIONS

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ABSTRACT

The lithium literature has been reviewed to provide a better understanding of the effects of lithium spills that might occur in magnetic fusion energy (MFE) facilities. Lithium may be used as a breeding blanket and reactor coolant in these facilities. Physical and chemical properties of lithium as well as the chemical interactions of lithium with various gases, metals and non-metals have been identified. A preliminary assessment of lithium-concrete reactions has been completed using differential thermal analysis. Suggestions are given for future studies in areas where literature is lacking or limited.

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LITHIUM LITERATURE REVIEW: LITHIUM'S PROPERTIES AND INTERACTIONS

I. INTRODUCTION

Because of recent shifts in energy source policy, the application of fusion power for the production of electrical and thermal energy is considered desirable and has come to the attention of many. Increased emphasis and expansion of the Magnetic Fusion Energy (MFE) program is a result of continued progress in fusion power research and positive performance of Tokamak-type devices proving the feasibility of this type of energy source. The design of a MFE reactor is based on a continuous deuterium-tritium (DT) fuel cycle. Tritium does not occur naturally, therefore it must be bred. Inherent features of the reaction determine basic characteristics of DT fusion reactors:

- A special blanket of low atomic number material is required to convert a deuterium beam into (radioactive) tritium as well as provide a biological shield.
- The blanket region will become radioactive due to the breeding of tritium.
- The blanket may also act as a coolant for the reactor.

Liquid lithium has been found to be the preferred material to carry out these functions.

Lithium is not activated to long-lived gamma or neutron emitting isotopes by neutron capture.(1,2) It exhibits a low neutron-absorption cross-section (for the separated isotope ^{7}Li), low melting point, high boiling point, low vapor pressure, low density, high heat capacity, high thermal conductivity and low viscosity. All these characteristics support lithium as a desirable tritium breeder blanket and primary coolant for nuclear fusion reactors. However, alkali metals are expected to be corrosive in operating environments sustaining high temperatures and high fluid flow rates. Lithium is no exception, and exhibits undesirable corrosive properties especially if it contains non-metallic impurities.

In MFE reactors, tritium is expected to be bred by neutron absorption in lithium. Lithium is contained under high vacuum. Whatever gas is present in the void region is usually helium in which lithium is inert under most conditions. Temperatures during normal operation vary between 200 °C and 550 °C but may exceed these in some MFE applications.(3) Based on current technology stainless steel is the chief construction material, although refractory metals such as niobium, vanadium, and molybdenum are being considered as base metals for lithium containment. Potential alloying elements are titanium, zirconium and chromium.

Because of the large amount of hot flowing lithium required in MFE use, one must be aware of the hazards of lithium leaks and spills. Both literature research and actual small- as well as large-scale experimentation are necessary to increase the state of knowledge concerning lithium and the effects of spills. Information obtained will be directly applicable to the safety assessment of the MFE Fusion Materials Irradiation Testing Facility (FMIT) and other MFE facilities.

This report gives the literature survey results concerning physical and chemical properties of lithium including chemical interactions lithium may undergo with various materials possibly present in MFE facilities. The validity and applicability of these results for large scale, high temperature accident conditions must be verified by actual experimentation.

II. SUMMARY AND CONCLUSIONS

A literature review of lithium and its properties and interactions was performed. However, most such information upon which this report was based deals with lithium reactions in small-scale quantities at low temperatures and with lithium in the solid phase. Because of this, much information about actual accident conditions is lacking. Extrapolation of the results to accident conditions may not be possible in some situations if actual large-scale tests are not performed for verification. Information is lacking regarding the possibilities of reaction propagation, the ultimate end products for lithium reactions, the possibility of an increase in reaction rate with temperature, and the rate of increase for specific reactions.

Some conclusions drawn from the existing literature are these:

1. Chemical and physical characteristics of lithium, especially a large liquidus range, high heat capacity and high thermal conductivity, allow lithium to be used as an effective nuclear reactor coolant. However, the corrosive properties of lithium require precautionary handling.

2. The high boiling point of lithium compared to sodium (1347 °C vs. 883 °C) results in a much higher ignition temperature, with possible effects on structures.

3. Bulk solid lithium at room temperature does not burn spontaneously in water or air. In dry oxygen, carbon dioxide, air up to 250 °C, and dry nitrogen up to 160 °C, lithium metal dispersions are considered inert.

4. Oxidation of lithium in dry oxygen is low all the way up to the ignition temperature. The ignition temperature of lithium in pure oxygen is uncertain, cited at values as high as 630 °C.

5. Lithium is the only alkali metal that will react with nitrogen to form a nitride. Thus nitrogen cannot be used as a cover gas as it is in sodium systems. Ignition temperatures for lithium metal in nitrogen are quoted between 170 °C and 450 °C.

6. Rates, products and temperatures for lithium-air reactions are uncertain and contradictory. Values between 180 °C and 640 °C have been reported for the ignition temperature of lithium in air. Discrepancy is due mainly to purity and moisture conditions.

7. Lithium reacts readily with water (vapor and liquid) to form hydrogen gas, a hazard under some accident conditions.

8. Molten lithium is extremely reactive. It will burn on contact with the moist skin of personnel working with it. It also produces, upon burning, aerosols irritating to the respiratory system.

9. Molten lithium reacts noticeably with concrete, other materials containing moisture and with many ceramic insulating materials. Lithium attacks ceramics more aggressively than sodium does.

10. At high temperatures, molten lithium reacts with all known molecular gases but can be handled up to 200 °C in paraffin vapors. Trace amounts of moisture catalyze lithium-gas reactions.

11. No information was found on the aerosol properties of lithium combustion products (size, distribution, density, shape, chemical nature, or toxicity).

12. No information is included on the effects of radiation on lithium properties and interactions.

13. Purity of lithium and the materials with which it interacts play a significant role in the nature of most lithium reactions.

14. Small lithium fires have been extinguished with a graphite powder, MET-L-X (a commercial preparation), and a pulverized salt eutectic mixture. Liquid lithium drains and self-extinguishing sump systems have been demonstrated effective for controlling small quantities of burning liquid lithium.

15. Based on an abbreviated study, the following preliminary conclusions may be drawn regarding lithium-concrete interactions:

    a. The DTA studies of the magnetite aggregate concrete yielded inconclusive results.

    b. The basalt aggregate concrete materials showed the highest apparent heat evolution values of all samples studied.

    c. Limestone aggregate concrete samples provided the most reproducible heat evolution values and exotherms.

    d. The exotherms of the dry Portland Cement paste were attributed to the direct reduction of the silicates to silicides.

III. RESULTS AND DISCUSSION

A. CHEMICAL PROPERTIES OF LITHIUM

Lithium (Li) is a member of the chemical group known as the alkali metals. It is the least reactive of this group. Its binary compounds are more stable than those of the other alkali metals.(1,4) The single "s" electron in the outer shell of a lithium atom is easily removed to form a positive ion. Removal of remaining electrons is difficult. Thus lithium is exclusively monovalent and forms compounds with all anions, organic and inorganic.

Lithium has an atomic number of three and an atomic weight of 6.941 atomic mass units.(5) Having the smallest atomic radius of all metals (1.50-1.56 Å)(6), lithium is the lightest of these, with a density only about one-half that of water. Naturally occurring lithium contains two isotopes: 7.52 at.% lithium-6 (atomic mass 6.017) and 92.48 at.% lithium-7 (atomic mass 7.018).(1)

In its crystalline form, pure lithium is silver white and soft. In a vacuum (residual pressure = 0.04 mm Hg), lithium starts to evaporate above 600 °C.(7) Solid lithium at room temperature is not as dangerous as other alkali metals, since it does not burn spontaneously in water or air. Molten lithium is extremely reactive. It burns when it contacts moist skin. Its combustion products are irritating to the respiratory system.(1) Lithium imparts a crimson color to a flame. When the metal burns strongly, the flame is dazzling white. Special handling is required because of lithium's corrosive properties.

Commercial lithium contains appreciable quantities of carbon, oxygen and nitrogen. Other contaminants commonly dissolved in lithium or mechanically dispersed in it are lithium compounds of chlorine, hydrogen, calcium, aluminum, iron, silicon, and sodium.(8) Table 1 summarizes some properties of lithium.

TABLE 1
PROPERTIES OF LITHIUM

Feature		Reference
Name	Lithium	
Symbol	Li	
Atomic Number	3	5
Atomic Weight	6.941 a.m.u.	5
Isotopes	Li-6 Li-7	
Boiling Point	1347°C	5
Melting Point	180.54°C	5
Heat of Vaporization	4680 cal/g	9
Heat of Fusion	103.2 cal/g	9
Cube Edge Length of Unit Cell	3.51 Å	10
Number of Atoms Exposed upon Immersion in Water of 1 cm Unit Cube	26.1×10^{14}	10

B. PHYSICAL PROPERTIES OF LITHIUM

1. Melting Point

The melting point of lithium is 180.54 °C.(5) Other references have cited values from 179 °C to 186 °C.(7-12) This temperature is twice as high as sodium but is significantly lower than the melting temperature of most common metals and is one of the reasons why lithium may be used effectively as a reactor coolant and heat transfer medium.

2. Vapor Pressure and Boiling Point

The normal boiling point for lithium is given at values from 1317 °C to 1370 °C.(5,7-12) These values are slightly low and high respectively--the most reasonable boiling point is around 1347 °C.(5)

Normal operating temperatures of MFE devices range from 200 °C to 550 °C. Lithium does not boil at normal atmospheric pressure until it reaches a temperature well above those encountered in the MFE devices. This allows the system to be operated unpressurized, thereby reducing design strength requirements and the potential severity of any leaks that might develop.

The vapor pressure of lithium is low at the melting point (approximately 10^{-10} mm Hg). Various equations have been derived for calculating vapor pressure at different temperatures. One equation, whose results are in good agreement with others, allows vapor pressure calculations from 700 °C to 1400 °C(8):

$$\log_{10} P = 8.00 - 8143\, T^{-1}$$

P units: mm Hg
T units: °K

Table 2 and Figure 1 show the vapor pressure of Li in mm Hg from around 700 °C to 1300 °C.

TABLE 2

VAPOR PRESSURE OF LITHIUM

Temperature (°C)	Vapor Pressure (mm Hg)
745	1
890	10
1084	100
1156	200
1236	400

Ref. 8; 9, Table 14.6

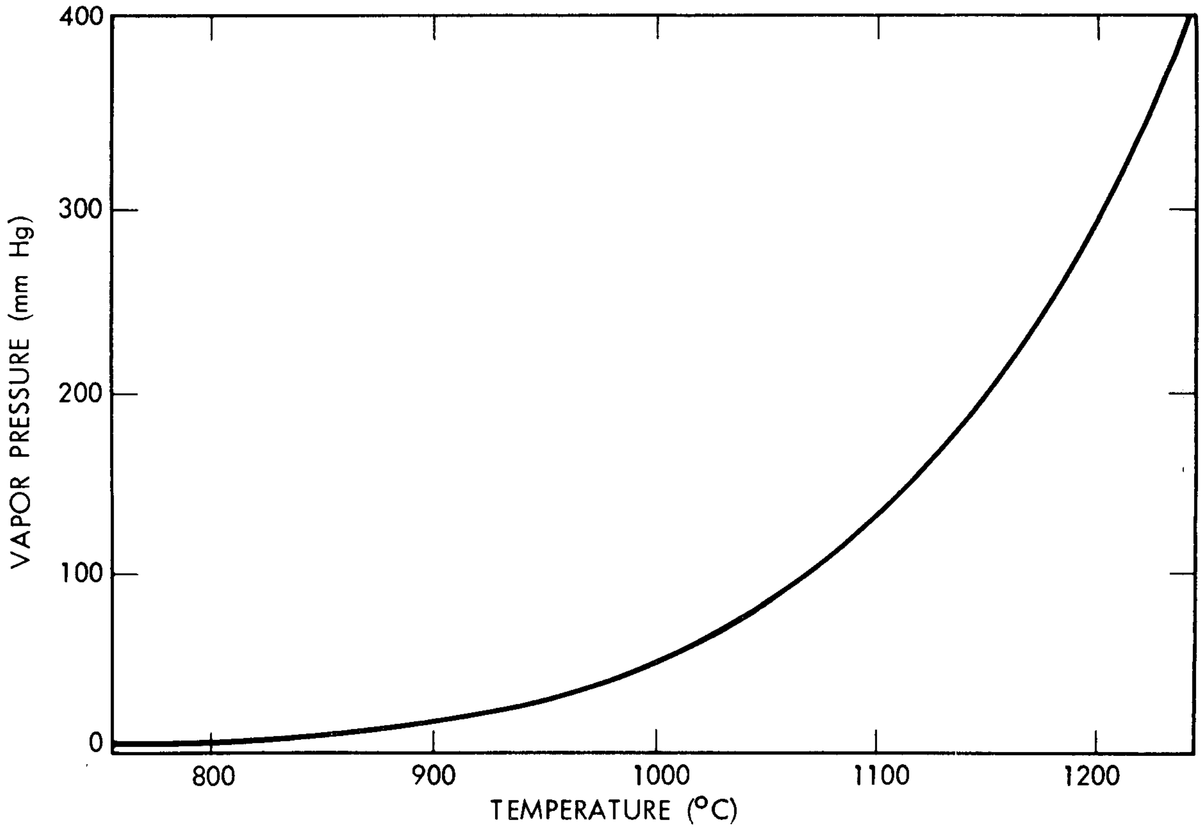

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FIGURE 1. Vapor Pressure of Lithium. Ref. 8, 9

3. Density

The following equation allows the calculation of density from 200° C to 1600° C with an accuracy of ± 0.3%$^{(13)}$:

$$= 0.515 - (1.01 \times 10^{-4})\ (T - 200)$$

T range: 200 °C-1600 °C
ρ units: g/cm^3
T units: °C

Table 3 and Figure 2 illustrate the results. The density of liquid lithium is a linear function of temperature and decreases with increasing temperature. Density decreases sharply with increasing temperature above 1600 °C.$^{(13)}$ Because of the low density, liquid lithium requires less pumping power for a given heat load than other liquid metals.

4. Viscosity

Two types of viscosity are defined. Dynamic viscosity is the resistance of a fluid to a change of form. This internal friction is a measure of how difficult it is to make the fluid flow. Kinematic viscosity is the ratio of the dynamic viscosity of the fluid to its density at the temperature under consideration. Two equations for calculating the dynamic viscosity of molten lithium are:$^{(14,15)}$

$$\log_{10} \eta = 0.4936 - 0.7368 \log_{10} T + 109.95\ T^{-1}$$

T range: 180.54 °C-1000 °C
units: centipoise
T units: °K

TABLE 3

DENSITY OF LITHIUM

Temperature (°C)	Density (g/cm^3)
200	0.515
400	0.495
600	0.475
800	0.454
1000	0.434
1200	0.414
1400	0.394
1600	0.374

Ref. 13, Table 2

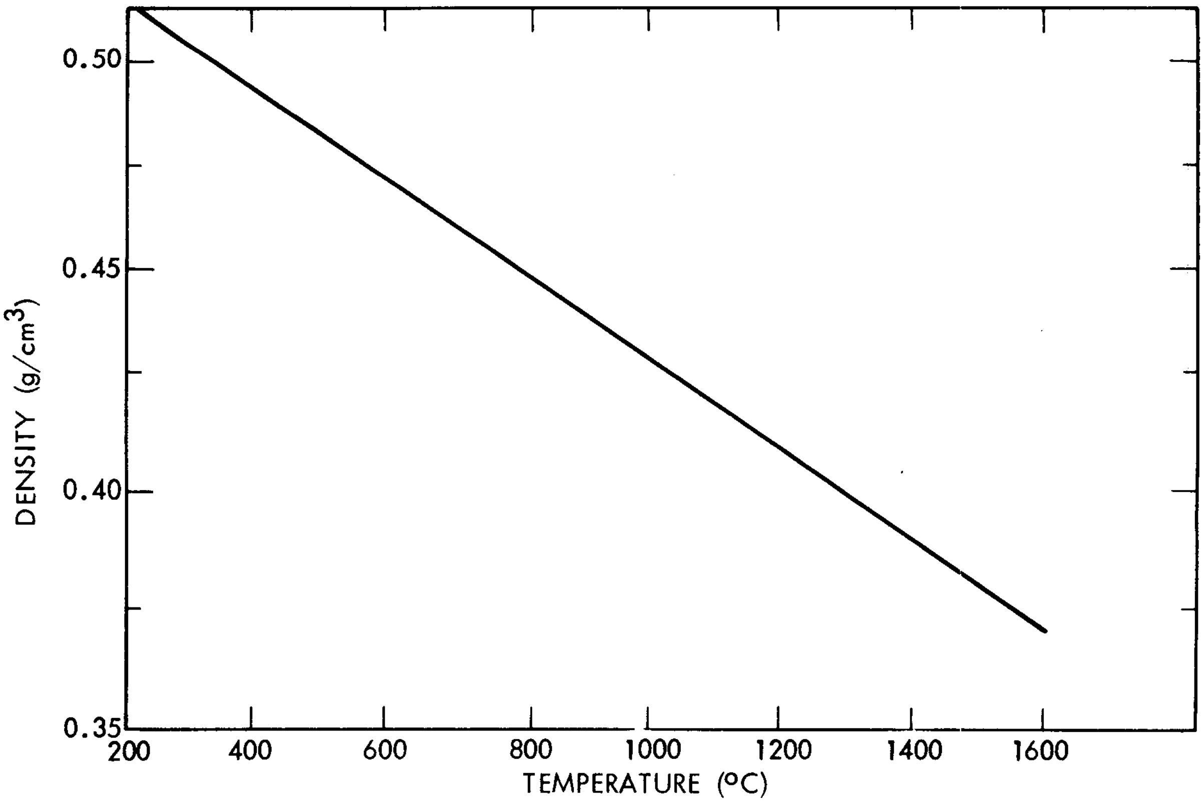

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FIGURE 2. Density of Lithium. Ref. 13

$\log_{10} \eta = 726.07\ T^{-1} - 1.3380$

T range: 600 °C-1200 °C
(especially for extrapolation to higher temps.)
η units: centipoise
T units: °K

Table 4 and Figure 3 represent dynamic viscosity of lithium as a function of temperature.

5. Surface Tension

The molecular forces holding matter together become conspicuous at surfaces of discontinuity, such as the interface between two fluids. At the surface of a liquid (lithium, for example), the absence of liquid molecules above it causes forces to behave as if a membrane were stretched over the liquid surface. This is due to the stronger attraction of liquid molecules to gas molecules (air, for example). The surface tension of the liquid lithium is a function of temperature. It was found during the course of experiments that liquid lithium could not be poured out of a container up to an inch in diameter even by inverting it. The combination of high surface tension and low density was sufficient to hold the metal in the container. Even vigorous shaking could not dislodge it.

An equation describing the surface tension of molten lithium from 200 °C to 1300 °C is given as:(16,17)

$\sigma = 0.16\ (3550-T) - 95$

σ units: dyne/cm
T units: °K

This is illustrated in Table 5 and Figure 4.

TABLE 4

VISCOSITY OF LITHIUM

Temperature (°C)	Viscosity (cp)	
	(Ref. 14)	(Ref. 15)
200	0.569	
400	0.374	
600	0.283	0.323
800	0.231	0.218
1000	0.196	0.171
1200		0.143

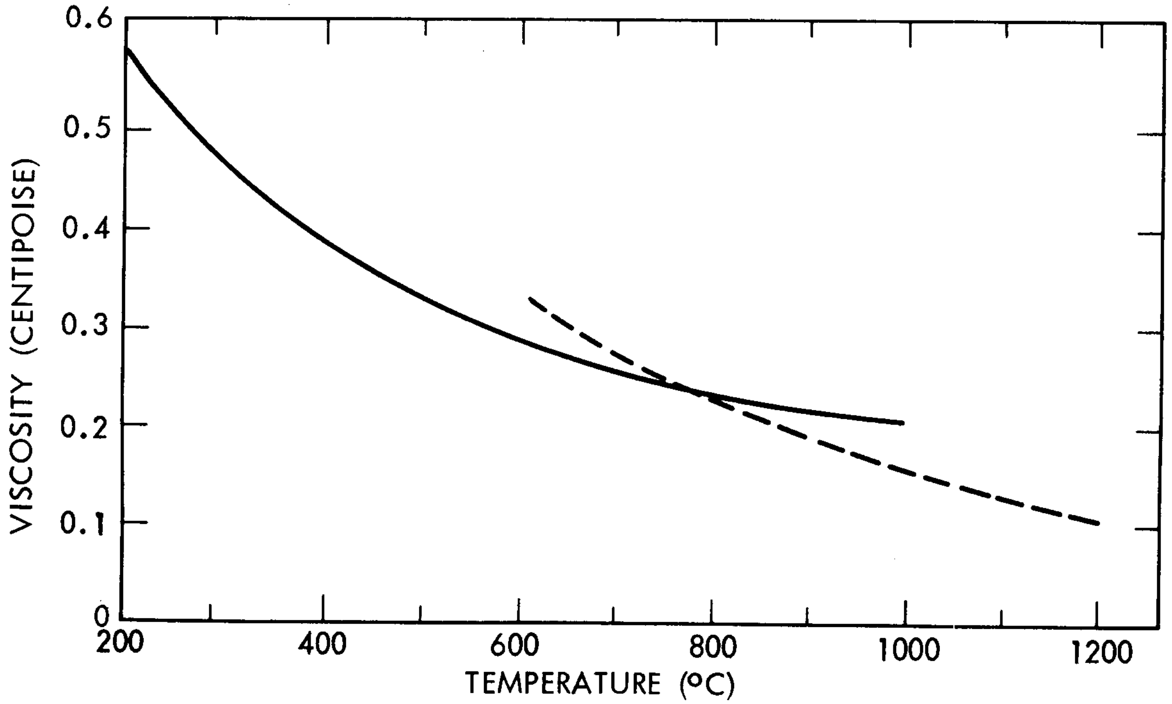

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FIGURE 3. Viscosity of Lithium. Ref. 14, 15

TABLE 5

SURFACE TENSION OF LITHIUM

Temperature (°C)	Surface Tension (dynes/cm)
200	397.3
400	365.3
600	333.3
800	301.3
1000	269.3
1200	237.3
1400	205.3

Ref. 16,17

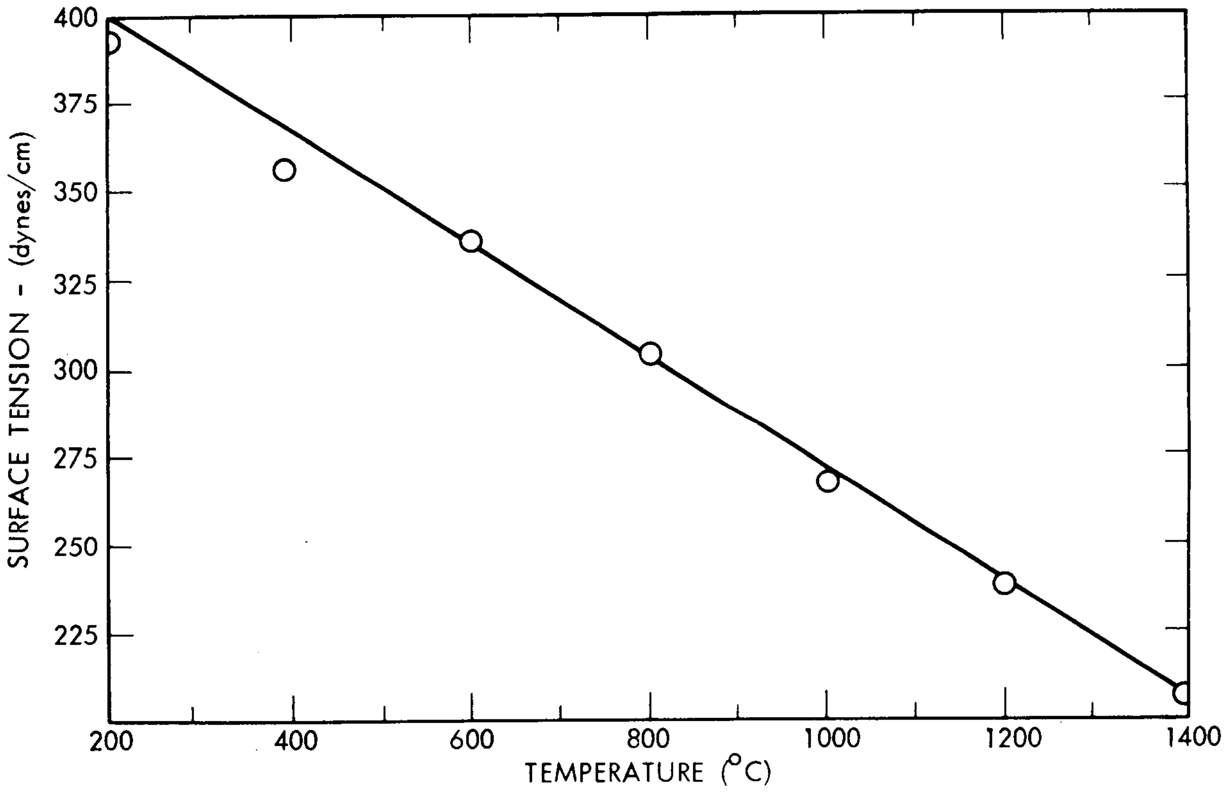

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FIGURE 4. Surface Tension of Lithium. Ref. 16,17

6. Wetting

Wetting describes the ability of a liquid to spread freely over the surface of a solid. Low surface tension usually accompanies higher degrees of wetting. Purified lithium reportedly will not wet stainless steel at 315 °C but does at 400 °C.(1) Impure lithium will not wet stainless steel at temperatures below 482 °C.(1)

C. THERMAL PROPERTIES OF LITHIUM

1. Enthalpy

The enthalpy or heat content (H_T) of a material is a thermodynamic function indicating the amount of internal energy plus pressure-volume (PV) work available in a system. Enthalpy can be determined by either of two equations:(14,18)

$$H_T = 270.4 + C_p\ (T-453.6)$$

T range: 190 °C-650 °C
H_T units: cal/g
T units: °K
C_p: Heat capacity (cal/g-°C)

$$H_T = -5.075 + 1.0008\ T - 5.173\text{x}10^3\ T^{-1}$$

T range: 500 °C-1300 °C
H_T units: cal/g
T units: °C

The experimental data verifying the first equation are represented in Table 6 and Figure 5.

2. Heat of Fusion

The heat of fusion for lithium is given as 103.2 cal/g(11,12,19) at 180.54 °C.

TABLE 6

ENTHALPY OF LITHIUM

Temperature (°C)	Enthalpy (cal/g)
185.75	270.40
213.78	303.65
286.90	379.15
357.16	449.00
428.28	521.94
456.50	549.32
492.75	584.09
525.95	618.19
585.05	677.62
593.79	688.06
620.41	713.41
628.61	722.49
647.71	742.34

Ref. 18; 14, Table 2

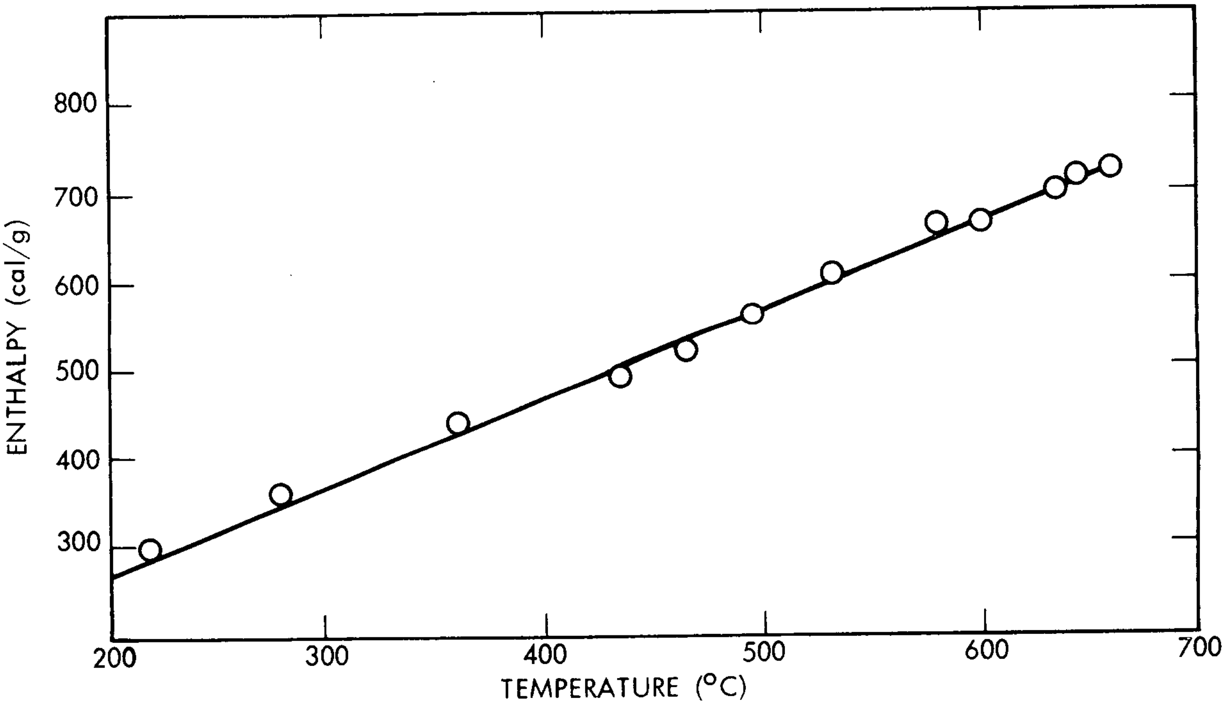

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FIGURE 5. Enthalpy of Lithium. Ref. 14,18

3. Heat Capacity

Table 7 and Figure 6 show the heat capacity in calories per gram-°C necessary to raise the temperature of lithium from 0 °C to 900 °C. Lithium has the highest heat capacity of any solid element, making it useful in heat transfer applications.

4. Thermal Conductivity

Three empirical equations for thermal conductivity (k) yield a scattering of experimental data (see Figure 4):(18,20,21)

$k = 10.1 + 2.94 \times 10^{-3}\ T$

T range: 250 °C-950 °C
k units: cal/sec·m· °C
T units: °C

$k = 10.48 + 4.98 \times 10^{-3}\ (T-180.6) - 0.58 \times 10^{-6}\ (T-180.6)^2$

T range: 300 °C-1100 °C
k units: cal/sec·m· °C
T units: °C

$k = 8.24 + 7.46 \times 10^{-3}\ T$

T range: 320 °C-830 °C
k units: cal/sec·m· °C
T units: °C

The best fitted equation obtained by method of least squares for the three above equations is:

$K = 9.59 + 4.55 \times 10^{-3}\ T$

k units: cal/sec·m· °C
T units: °C

This is represented by the dashed line in Figure 7.

TABLE 7

HEAT CAPACITY OF LITHIUM

Cp (cal/g-°C)	Temperature (°C)
0.784	0
0.844	50
0.905	100
1.012	180.6
1.058	200
1.040	250
1.020	300
1.015	350
1.010	400
1.000	450
0.998	500
0.997	550
0.996	600
0.995	650
0.995 ± 1%	650-900

Ref. 8, 19; 9 , Table 14.6; 18, Table 4

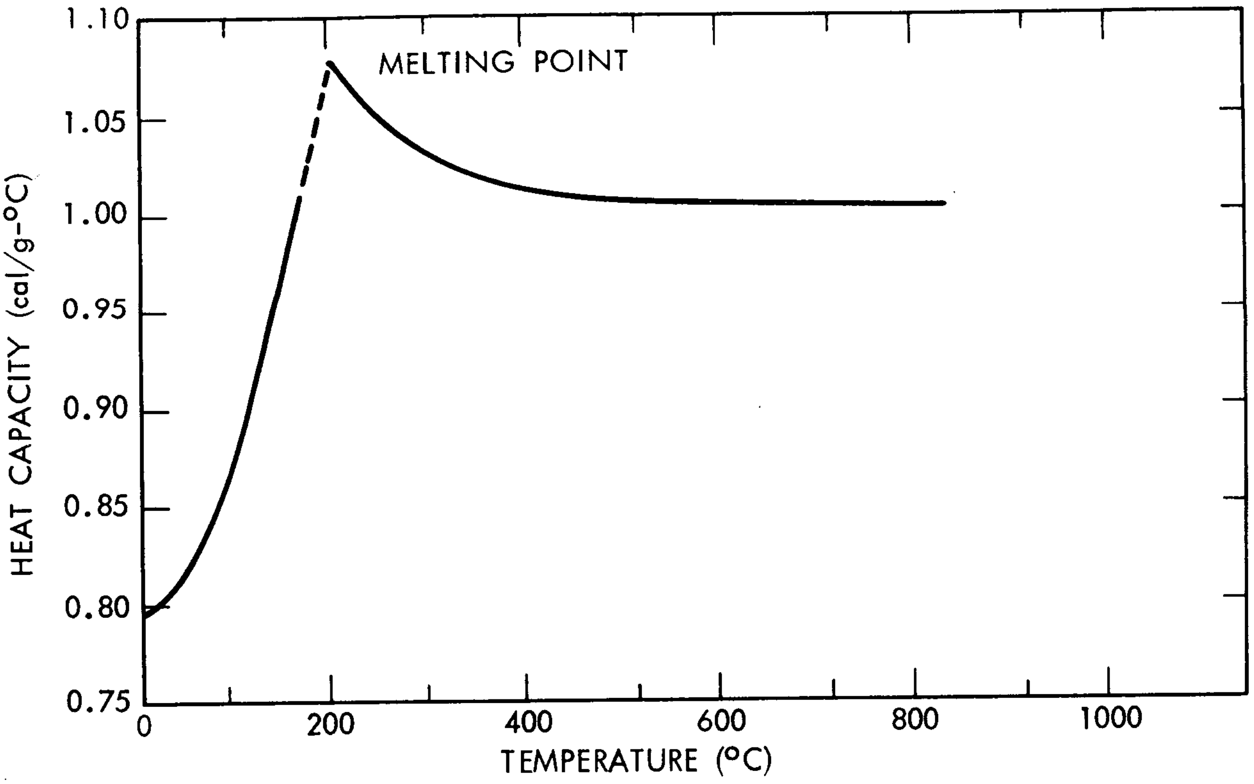

FIGURE 6. Heat Capacity of Lithium. Ref. 9,18,19,8

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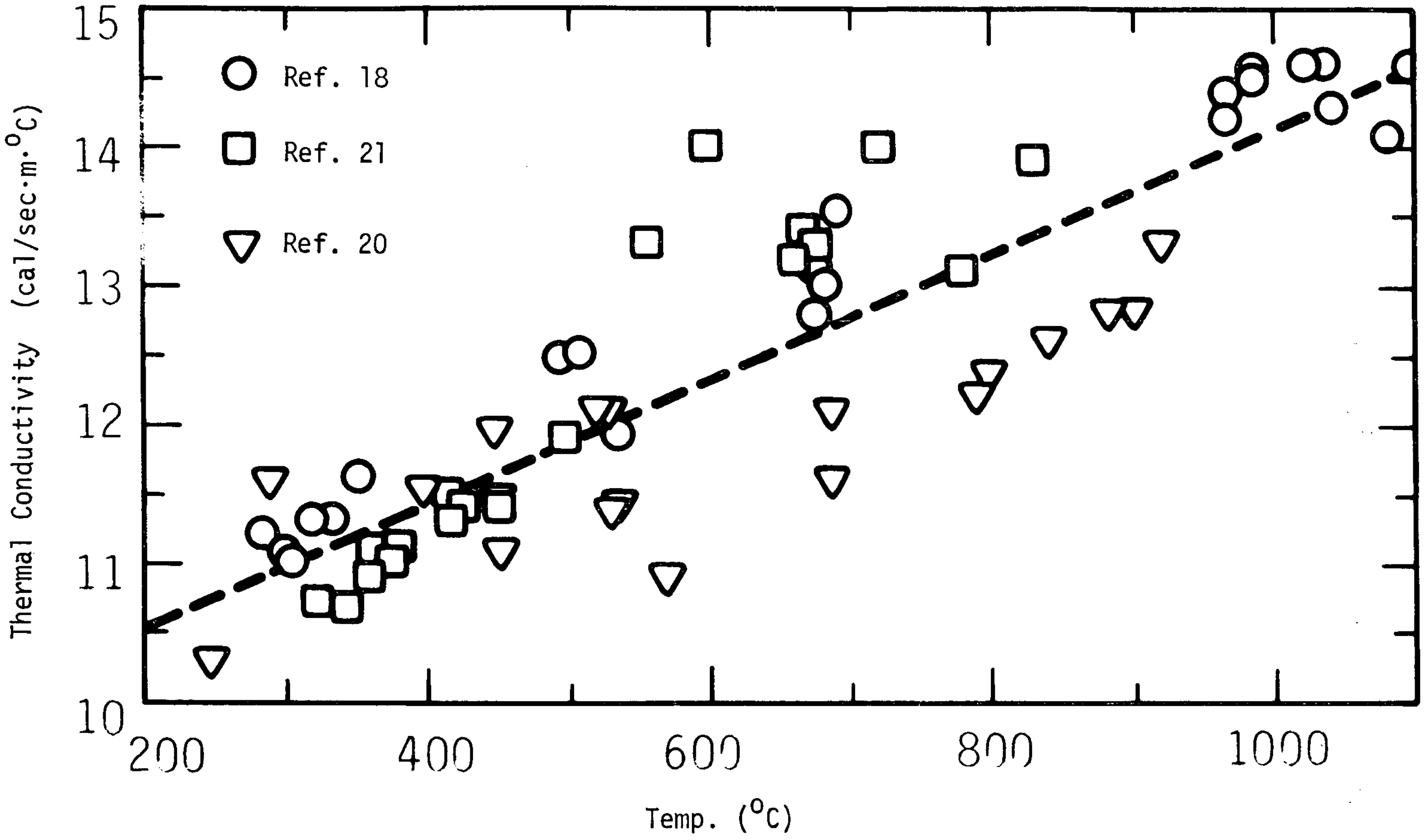

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FIGURE 7. Thermal Conductivity of Lithium. Ref. 18,20,21

D. CHEMICAL INTERACTIONS OF LITHIUM

1. General

Although lithium is the least reactive of the alkali metals, it still undergoes many chemical reactions and is not found naturally in the free form. Lithium reacts vigorously with the halogens, emitting light.(8) It reacts violently with most inorganic acids, but cold concentrated sulfuric acid attacks it slowly.(1,22) Molten lithium reacts vigorously with concrete and other materials containing moisture and rapidly with ceramic insulating materials.(1,23) At high temperatures, molten lithium reacts with all known molecular gases but can be handled up to about 200 ° C in paraffin vapors.(24) It is considered inert in helium under most conditions. Trace amounts of moisture catalyze lithium-gas reactions. Liquid lithium will not react with oxygen or carbon dioxide in air at its melting point in the absence of water; but 10 to 15 parts-per-million (ppm) moisture will cause lithium to react with air, nitrogen, oxygen and carbon dioxide at room temperature.(1) Lithium reacts readily with air and water and with traces of oxygen, carbon, nitrogen and hydrogen even in the inert fluids in which it is stored. Contamination with these materials promotes corrosion of metals by lithium. The stable binary compounds--lithium oxide, lithium nitride, lithium hydroxide, lithium hydride and lithium chloride are very corrosive.(8) Metallic impurities also catalyze lithium reactions.

Table 8 gives the enthalpies and free energies for various lithium reactions.(1) More negative values indicate a higher tendency for the reaction to proceed as written. The values are all taken at room temperature (25 °C).

TABLE 8

ENTHALPIES AND FREE ENERGIES OF LITHIUM REACTIONS

Reaction	ΔH° (25°C) kcal	G (25°C) kcal	References
$2\ Li(c) + 1/2\ O_2 \rightarrow Li_2O(c)$	-142.650	-133.950	80
$2\ Li(c) + O_2(g) \rightarrow Li_2O_2(c)$	-151.9	-138.1	92
$Li(c) + 1/2\ H_2(g) + 1/2\ O_2(g) \rightarrow LiOH(c)$	-116.589	-105.676	93
$Li(c) + 3/2\ H_2(g) + O_2(g) \rightarrow LiOH \cdot H_2O(c)$	-188.926	-163.437	93
$Li(c) + H_2O(\ell) \rightarrow LiOH(c) + 1/2\ H_2(g)$	-48.7	-48.99	6
$Li(c) + H_2O(\ell) \rightarrow LiOH\ (in\ H_2O) + 1/2\ H_2(g)$	-53.142		91
$Li(c) + 1/2\ F_2(g) \rightarrow LiF(c)$	-146.300	-139.650	80
$Li(c) + 1/2\ Cl_2(g) \rightarrow LiCl(c)$	-97.700	-92.500	80
$Li(c) + 1/2\ I_2(g) \rightarrow LiI(c)$	-64.790	(-62.200)	80
$3Li(c) + 1/2\ N_2(g) \rightarrow Li_3N(c)$	-47.500	-37.300	80
$Li(c) + 1/2\ H_2(g) \rightarrow LiH(c)$	-21.61	-16.72	75
$2\ Li(c) + 3/2\ CO_2(g) \rightarrow Li_2CO_3(c) + 1/2\ C(c)$	-148.6	-128.4	94
$2\ Li(c) + 3\ CO(g) \rightarrow Li_2CO_3(c) + 2\ C(c)$	-210.45	-171.38	94
$Li(c) + NH_3(g) \rightarrow LiNH_2(c) + 1/2\ H_2(g)$	-32.46		6
$2\ Li(c) + 2\ C(c) \rightarrow Li_2C_2(c)$	-14.2		75
$2\ Li(c) + Mo(c) + 2\ O_2(g) \rightarrow Li_2MoO_4(c)$	-365.25		95
$Li(c) + Al(c) + 2\ H_2(g) \rightarrow LiAlH_4(c)$	-24.67		96
$Li(c) + Sn(c) \rightarrow LiSn(c)$	-16.8		75
$Li(c) + Pb(c) \rightarrow LiPb(c)$	-14.6		75
$Li(c) + Tl(c) \rightarrow LiTl(c)$	-12.8		75
$Li(c) + Hg(c) \rightarrow LiHg(c)$	-20.8		75
$3\ Li(c) + 2\ Sb(c) \rightarrow Li_3Sb_2(c)$	-43.5		75
$3\ Li(c) + Bi(c) \rightarrow Li_3Bi(c)$	-55.2		75
$2\ Li(c) + H_2SO_4(\ell) \rightarrow Li_2SO_4 + H_2(g)$	-148.92		6
$Li(c) + CH_3OH(\ell) \rightarrow LiOCH_3\ (in\ CH_3OH) + 1/2\ H_2(g)$	-55.1		6
$Li(c) + C_2H_5OH(\ell) \rightarrow LiOC_2H_5\ (in\ C_2H_5OH) + 1/2\ H_2(g)$	-51.6		6

Ref. 1, Table 5

2. Lithium-Gas Reactions

TGA Studies(25) -- Thermogravimetric analysis was used to study lithium metal-gas reactions for wet and dry dynamic gases. Heating at a rate of 0.67°/minute, lithium metal dispersion samples held in small quartz cups were subjected to various dynamic gaseous atmospheres (argon, air, nitrogen, oxygen, carbon dioxide). Flow rates were around 150 ml/min at ambient conditions. For dry gas analyses, the high purity gases were passed through a column of anhydrous magnesium perchlorate. To achieve wet gases of 50% relative humidity at room temperature (partial pressure of water = 9.03 mm Hg at 20 °C), the gases were dispersed through a saturated solution of sodium dichromate dihydrate. The results are depicted in Figure 8. Conclusions drawn from this are:

- Dry carbon dioxide, oxygen and air up to 250 °C and dry nitrogen up to 160 °C appear inert with respect to lithium metal dispersions.
- With the presence of water vapor in each gas, continuous and significant weight gains were observed over the heating period indicating lithium-gas reactions.
- When exposed to all the moist gases, a black surface forms over the lithium metal. It is composed of anhydrous lithium hydroxide and a little lithium oxide.

Use of metal dispersions is characterized by a high available surface area. This tends to exaggerate reaction rates since the possibility of rate-controlling diffusion effects are minimized. The sequence of events is unchanged in nature but possibly accelerated in time. The results are specific for a given heating rate, gas flow rate and high purity of gases. Because of this, reaction rates and temperatures may be different in actual uncontrolled conditions.

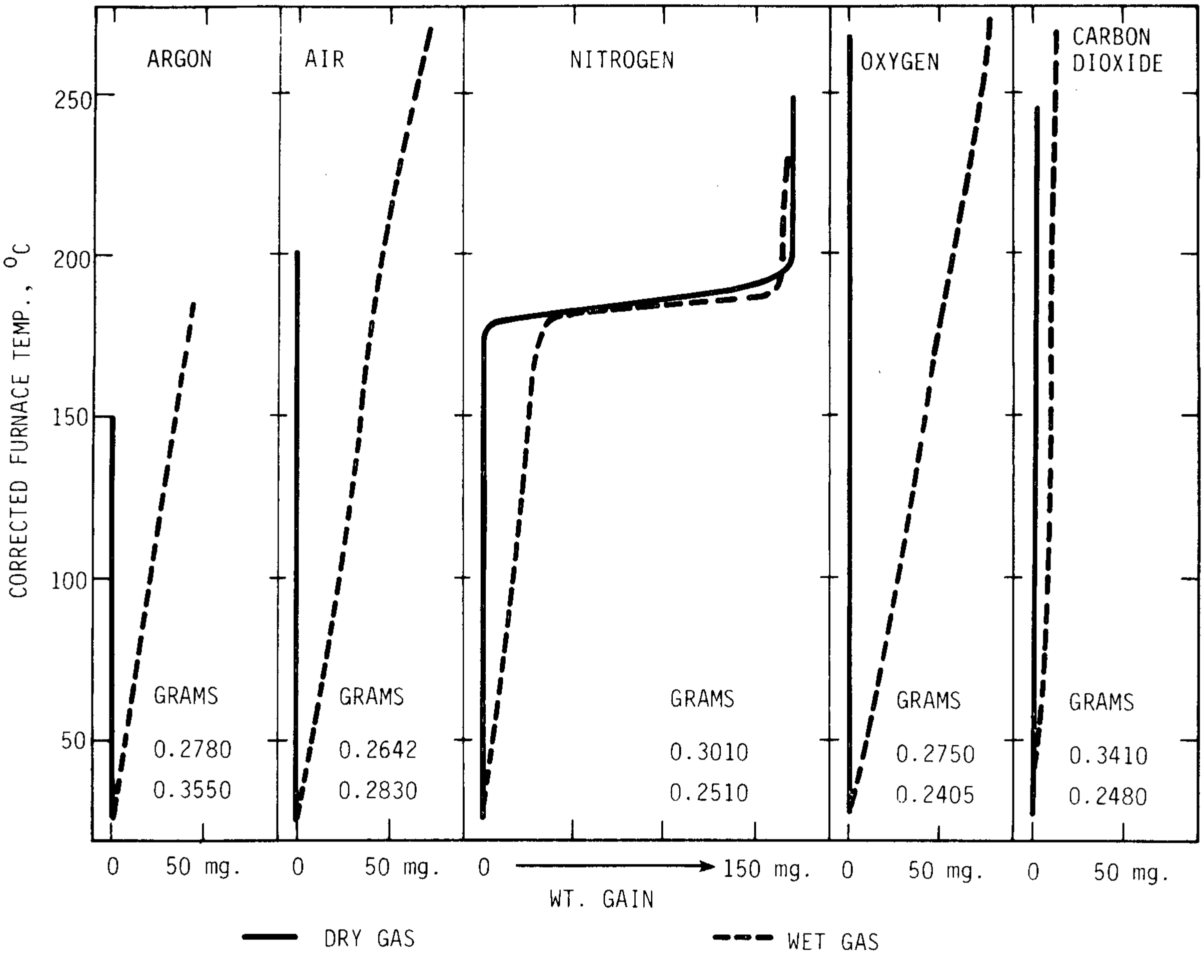

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FIGURE 8. TGA Curves of Lithium Metal Dispersions Exposed to Various Gases. Ref. 27, Figure 4

3. Lithium-Oxygen Reactions

Lithium is highly resistant to oxidation even at elevated temperatures in pure oxygen or even in dry air atmospheres.(10,25,26) The rate of oxidation of lithium is low all the way to the ignition temperature cited in one report as 630 °C.(26) No reaction of solid lithium in dry oxygen occurs below 250 °C. With moist oxygen, the reaction proceeds exothermically:(1)

$$2\ \mathrm{Li\ (s)} + 1/2\ \mathrm{O_2\ (g)} \rightarrow \mathrm{Li_2\ O\ (s)} \qquad \Delta H_{25\ ^\circ C} = -142.65\ \mathrm{kcal/mole}$$

1.152 grams of oxygen combine with 1.0 grams of lithium to produce 10.33 kcal of energy.(9)

The oxide coating that forms on the surface of solid lithium at low temperature may prevent further reaction of lithium with oxygen. A specimen of solid lithium in moist oxygen (partial pressure of water = 4.6 mm Hg) at 35 °C forms a white reaction product on the surface of the metal. If the specimen is then exposed to dry oxygen, the reaction rate drops to zero with no further oxide forming under these conditions.(27)

The reaction of liquid lithium with oxygen was carried out from 210°C to 640 °C with pressures of 130 mm Hg to 1.0 mm Hg.(28) The oxide film formed initially was observed throughout the entire experiment. Figure 9 illustrates the kinetic curves of reaction of liquid lithium with oxygen. From this, the reaction may be divided into three segments. The first represents non-steady-state reaction. The second is described by a logarithmic rate law and has an activation energy of 15.3 kcal/mole. The terminal segment indicates continuous growth of the oxide film and follows a linear rate law. The activation energy for this last segment is 15.6 kcal/mole.(28) Values may differ for flowing lithium containing different degrees of impurities.

Figure 10 shows the DTA curve of lithium metal dispersed in a flowing nitrogen atmosphere.

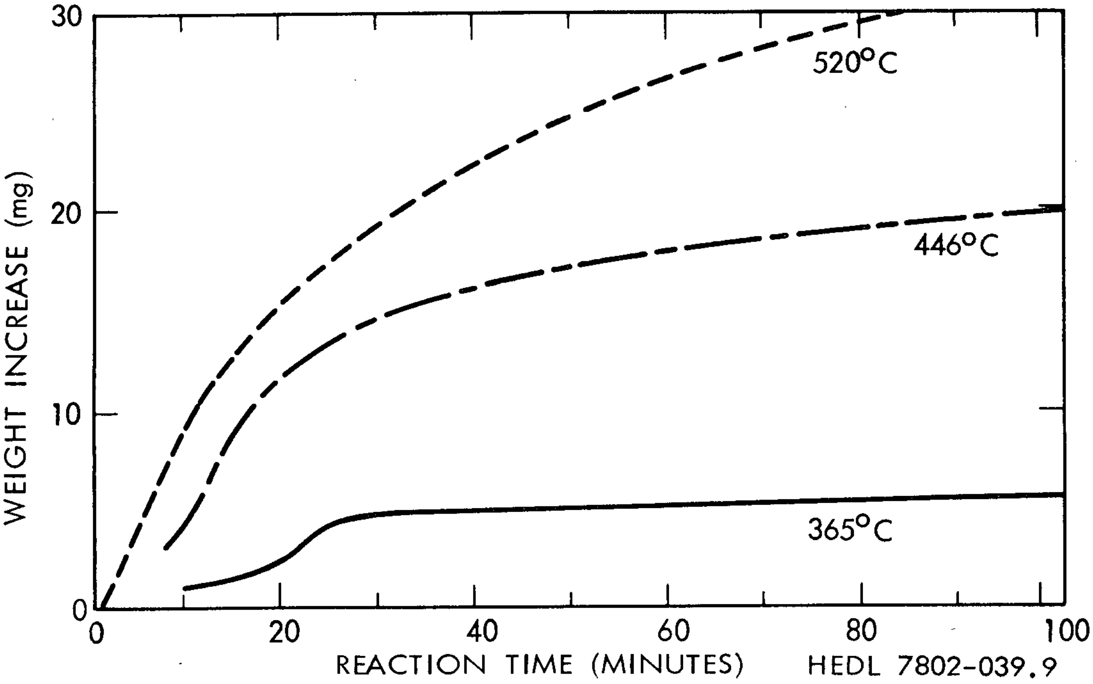

FIGURE 9. Kinetic Curves of Liquid Lithium Reacting with Oxygen. Ref. 28, Fig. 1

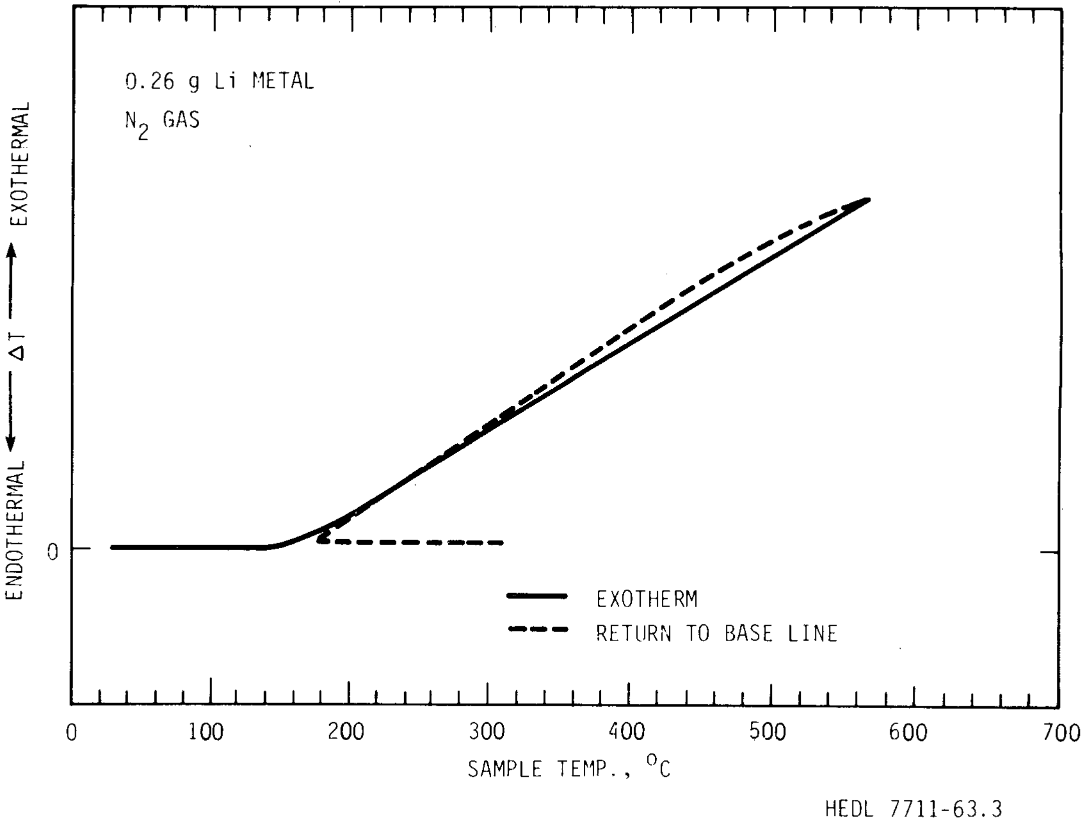

FIGURE 10. DTA Curve of Lithium Metal Dispersed in a Flowing Nitrogen Atmosphere. Ref. 25, Figure 6

Free energies of formation have been calculated for lithium oxide at different temperatures.(1) The results show an ultimate decrease in free energy with an increase in temperature. More negative values indicate a more exothermic, energetic reaction and therefore a release of more energy.

G (k cal/g-atom C)	T (°C)	Reference
-134	25	29
-177	527	30
-111	000	
-92	1227	30

4. Lithium-Nitrogen Reactions

Lithium is the only alkali metal that will react with nitrogen gas to form a nitride:(31)

$$6\ \mathrm{Li}\ (s) + \mathrm{N_2}\ (g) \rightarrow 2\ \mathrm{Li_3N}\ (s) \qquad \Delta H_{25\ ^\circ C} = -47.50\ \text{kcal/mole}$$

Greater than 10 ppm moisture or elevated temperatures will increase the rate and extent of reaction of lithium and nitrogen. Dry nitrogen will not react with lithium up to about 160 °C. At room temperature with moisture present, reaction proceeds exothermically, forming a thin protective coating of reddish-brown to black lithium nitride (LiN). The latter is hygroscopic, yielding ammonia in the presence of water. Lithium is more susceptible to nitridation than oxidation at moderate temperatures.(10,25) In a stream of dry nitrogen, the reaction between litihium and nitrogen is 10 to 15 times more rapid than in air.(7) Oxygen and hydrogen inhibit the interaction of lithium and nitrogen. Presence of oxygen in nitrogen greater than 14 volume % or hydrogen over 3.5 volume % may completely prevent reaction at lower temperatures.(7) With lesser amounts, the reaction proceeds much slower.

Powdered lithium (< 100μ particle size), when heated in nitrogen flowing at 100 ml/min in a tube furnace apparatus, ignited at 388 °C and 410 °C.(32) Other ignition temperatures have been quoted at 170 °C, 450 °C and dull red heat.(25,32)

A differential thermal analysis (DTA) was performed on lithium metal dispersions in dry dynamic nitrogen atmospheres at a heating rate of 5°/minute.(25) The reaction occurred around 170 °C and was rapid and exothermic. Figure 10 illustrates the results. Formation of appreciable quantities of anhydrous lithium hydroxide (18.6 wt.%) was requisite before significant formation of lithium nitride occurred. The velocity of the reaction increased to a maximum value, then dropped to zero.(7) Thus, the presence of a lithium hydroxide film on the metal surface is necessary for lithium-nitrogen reactions and explains lithium's susceptibility to low temperature nitridation under moist conditions.

High temperatures were encountered during the rapid nitridation of lithium. Upon ignition in nitrogen, temperatures around 600 °C were reached in less than one minute with a 0.26 gram lithium dispersion sample.(25) Ignition occurred without fusion and coalescence (mixing) of the metal implying that rapid diffusion of reactant nitrogen through a bed of porous, solid lithium and lithium nitride is possible. With a compact mass of liquid lithium, nitridation may be slower due to diffusion controlling of the reaction.

Reaction rates between dry nitrogen and lithium have been examined for stirred and stationary liquid lithium.(28) With stirring, three stages were observed in which the rate laws followed rectilinear, log-arithmic and parabolic laws successively and independent of pressure. Without stirring, the rectilinear stage was not observed. Reaction rates were strongly temperature dependent. Solubility of nitrogen in the lithium was also an important factor.

With stirring in the presence of nitrogen, liquid lithium spread over the total internal surface area of the containing vessel. Thus reaction rates were all influenced by dimensions. An activation energy of 33 kcal/mole was obtained at the stage in the reaction when rates obeyed the rectilinear law. This lasted approximately 35 minutes. As product accumulated, even stirring could not continually maintain a "fresh" surface for reaction and the logarithmic relationship took over.

This occurred in the region of 12 to 30% of the total reaction. The reaction was not inhibited by the surface films but proceeded with a parabolic rate law. Activation energy was measured at 1.5 kcal/mole for surfaces carrying a continuous nitride film. The final reaction product was a ruby-red crystalline lithium nitride.

Without stirring, the lithium-nitrogen reaction was completed in an average of 80 minutes for 0.5 grams of lithium. The region from 33 to 80% of the total reaction followed the parabolic law. Figures 11 and 12 illustrate the reaction curves of nitrogen with stirred and unstirred lithium at 400 °C. Figure 13 shows the kinetic curves for the reaction at different temperatures.

Free energies of formation have been calculated for lithium nitride at different temperatures.(1,29,33) The results show a decrease in free energy with increasing temperature:

ΔG (kcal/mole	T (°C)	Reference
-37.3	25	29
-20.1	527	33
+ 3.8	1227	33

5. Lithium-Hydrogen Reactions

Lithium readily reacts with hydrogen forming a stable but reactive, high-melting hydride. The reaction proceeds as follows:(1)

$$\text{Li (s)} + 1/2\ \text{H}_2\text{ (g)} \rightarrow \text{LiH (s)} \quad \Delta H_{25\ ^\circ C} = -21.61\ \text{kcal/mole}$$

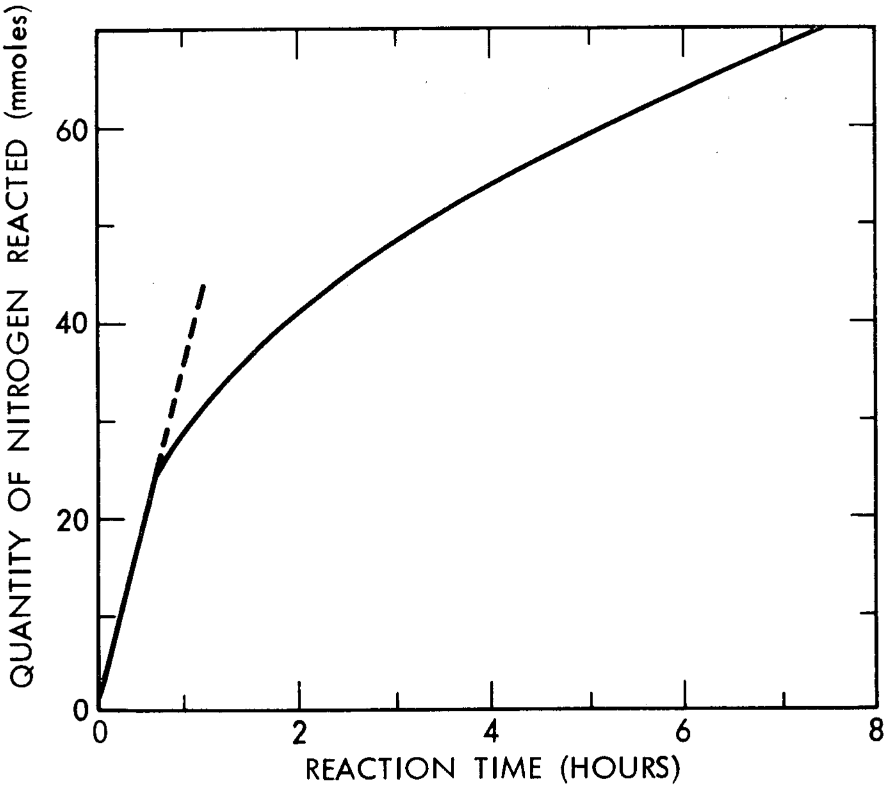

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FIGURE 11. Curves of Stirred Liquid Lithium Reacting with Nitrogen at 400°C. Ref. 31, Figure 6

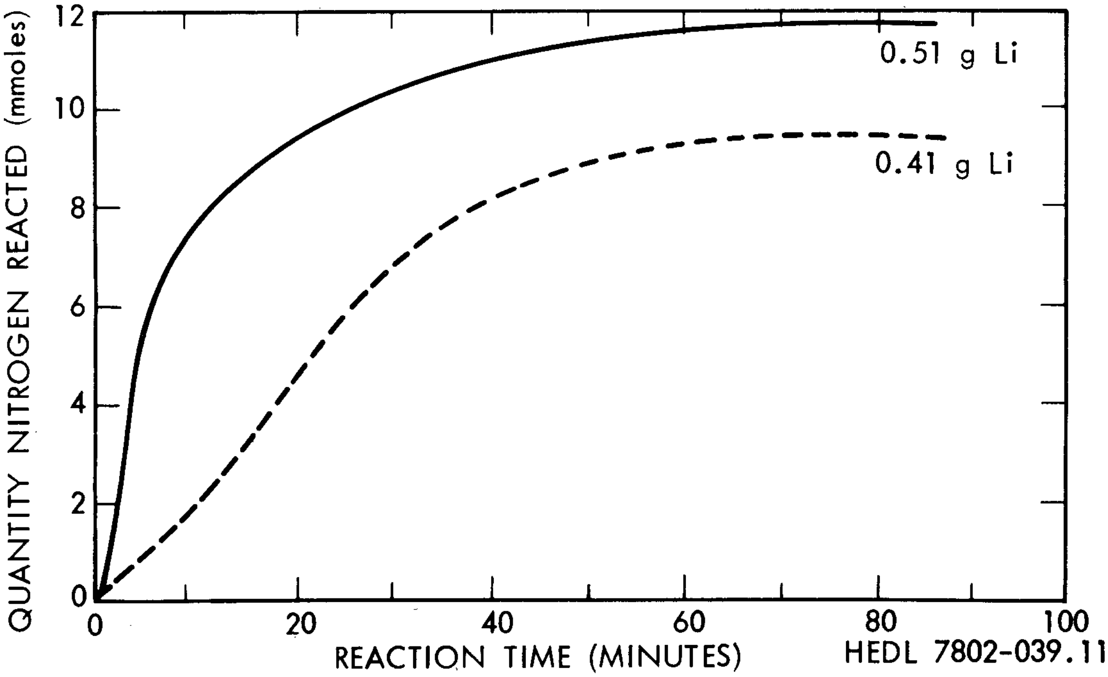

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FIGURE 12. Curves of Unstirred Liquid Lithium Reacting with Nitrogen at 400°C. Ref. 31, Figure 2

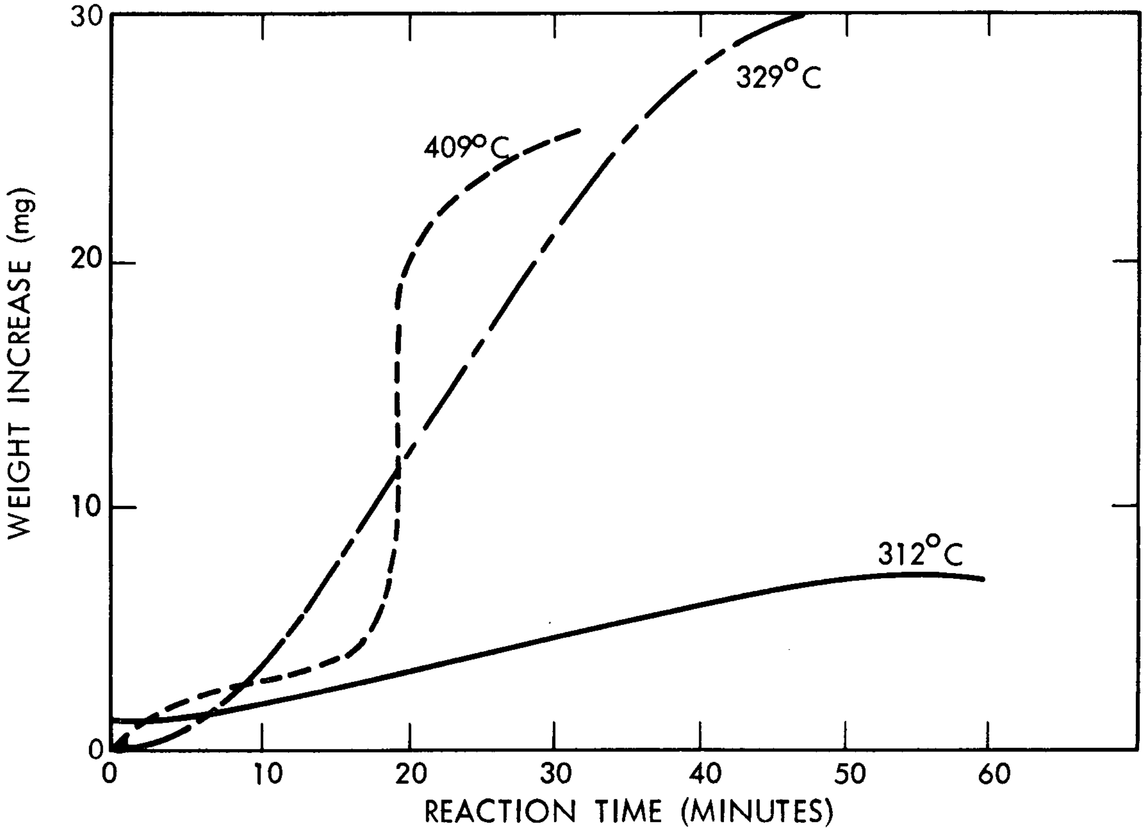

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FIGURE 13. Kinetic Curves of Liquid Lithium Reacting with Nitrogen. Ref. 28, Figure 5

Lithium hydride, depending upon formation conditions, is either white crystalline powder or needle-like crystals. The reaction rate of hydrogen with a clean liquid lithium surface is first order and linear with an activation energy of 12.6 kcal/mole.(34) This activation energy is less than both values for the reactions between hydrogen and sodium or potassium. The ratio of reaction rates at 250 °C for lithium, potassium and sodium is 43:4:1 respectively.(34) As expected, the rate of reaction increases with increasing temperature. Table 9 and Figure 14 show the effect of temperature on the absorption of hydrogen.

The reaction between molten lithium and purified gaseous hydrogen at high temperatures starts around 400 °C, terminating quickly at 710 °C.(7) Explosions and ignitions occur sometimes due to impurities in the initial products. The above values pertain to static, relatively pure systems. Other environments may yield different rates and temperatures.

6. Lithium-Carbon Dioxide Reactions

Dry carbon dioxide will not react with lithium at temperatures up to 300 °C.(1) With moisture present, lithium and pure carbon dioxide react to form lithium carbonate:(1)

$$2\ \mathrm{Li}\ (s) + 3/2\ \mathrm{CO_2}\ (g) \rightarrow \mathrm{Li_2CO_3}\ (s) + 1/2\ \mathrm{C}\ (s)\ \Delta H_{25\ ^\circ C} = 148.6\ \mathrm{kcal/mole}$$

Lithium carbonate is comparatively insoluble in water in contrast to corresponding alkali salts.(9) Formation of the protective carbonate coating slows the reaction significantly. Powdered lithium (<100μ particle size), when heated in carbon dioxide flowing at 100 ml/min in a tube reactor, ignited at 330 °C.(32)

7. Lithium-Air Reactions

Lithium reacts slowly in dry air. In moist air it oxidizes more rapidly. Solid lithium becomes coated with lithium nitride, lithium hydroxide, lithium hydroxide monohydrate, lithium carbonate and lithium

TABLE 9

LITHIUM - HYDROGEN REACTION

Rate Constants (K)

Temperature (°C)	Pressure Range (kN M^{-2})	10^6K (mms^{-1}[kN M^{-2}]$^{-1}$)
217	23.7-8.9	4.683
244	23.5-4.9	8.030
257	23.1-1.9	12.488
270	17.8-1.2	16.400
295	18.5-1.2	27.919

Ref. 34, Table 1

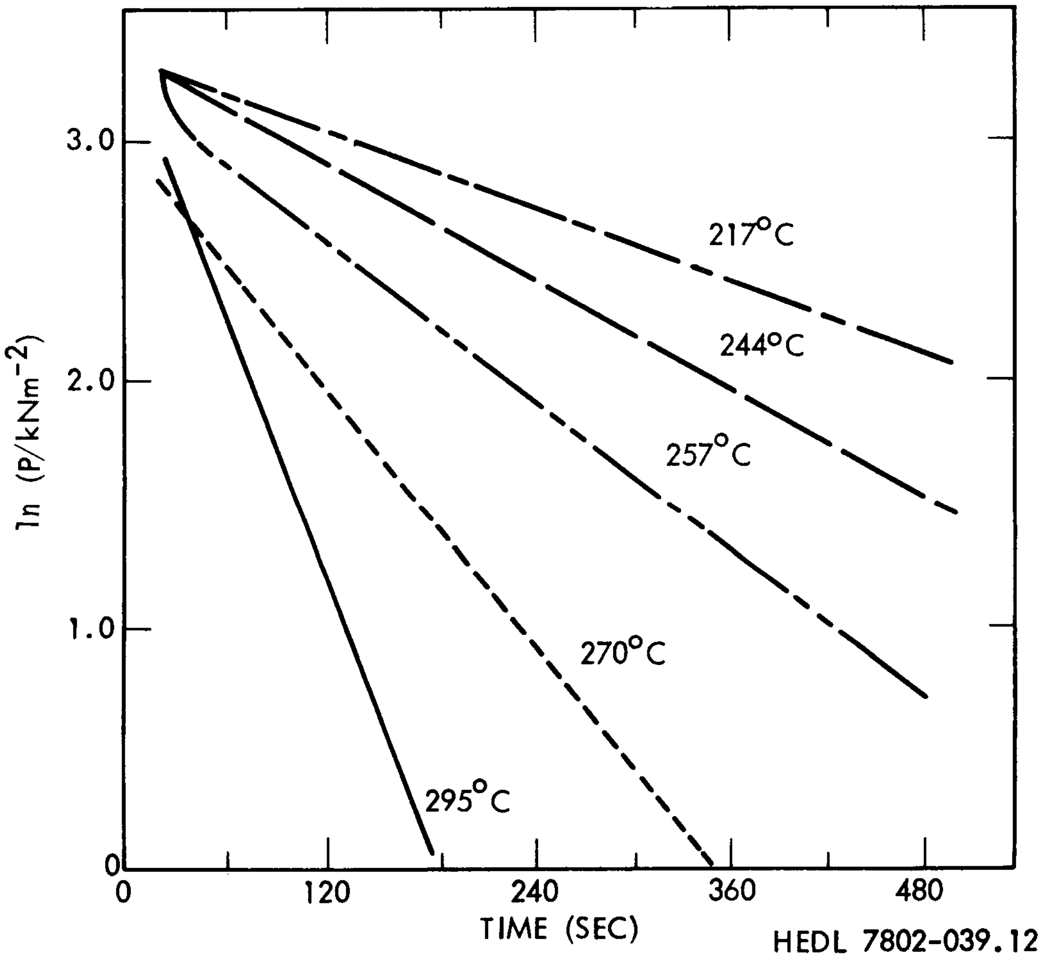

FIGURE 14. Reaction Curves Showing the Effect of Temperature on Liquid Lithium Absorption of Hydrogen. Ref. 34, Figure 1

oxide. Actual reaction rates, products, and temperatures are contradictory. Values between 180 °C and 640 °C have been reported for the ignition temperatures of lithium in air.(11) In one study, lithium metal dispersion samples were exposed to circulating air at 50% relative humidity and 27 °C. The ultimate reaction product was lithium carbonate. The temperature rise during the early period of atmospheric attack was noteworthy. Figure 15 illustrates these results. Information regarding liquid lithium-air reactions was lacking.

8. Lithium-Water Reactions (Liquid and Vapor)

Lithium reacts with water to form lithium hydroxide and hydrogen gas. It combines with water in both air and nitrogen atmospheres, with the lithium-water reactions taking precedence over the lithium-nitrogen reaction.(10) Bulk solid lithium reacts slowly with cold water. The hydrogen formed does not ignite in air. Very finely divided lithium (high total surface area per unit weight or high surface-to-volume ratio) greatly enhances the reactivity over a like weight of the bulk material. Lithium dispersions are quite reactive and ignite (hydrogen gas flames) if thrown into water at room temperature in either air or argon.(10)

The reaction proceeds as written with the heat of reaction measured at 25 °C as -53.142 ± 0.019 kcal/mole:(35)

$$\text{Li (s)} + 1001^{*}\ H_2O\ \text{(l)} \rightarrow \text{LiOH} \cdot 1000\ H_2O + 1/2\ H_2\ \text{(g)}$$

*Number represents concentration corrections related to heats of dilution.

The observed reactivity or rate of a reaction is often related to the rate at which heat is liberated during a chemical combination rather than to the total amount of heat evolved over a prolonged time period.(10)

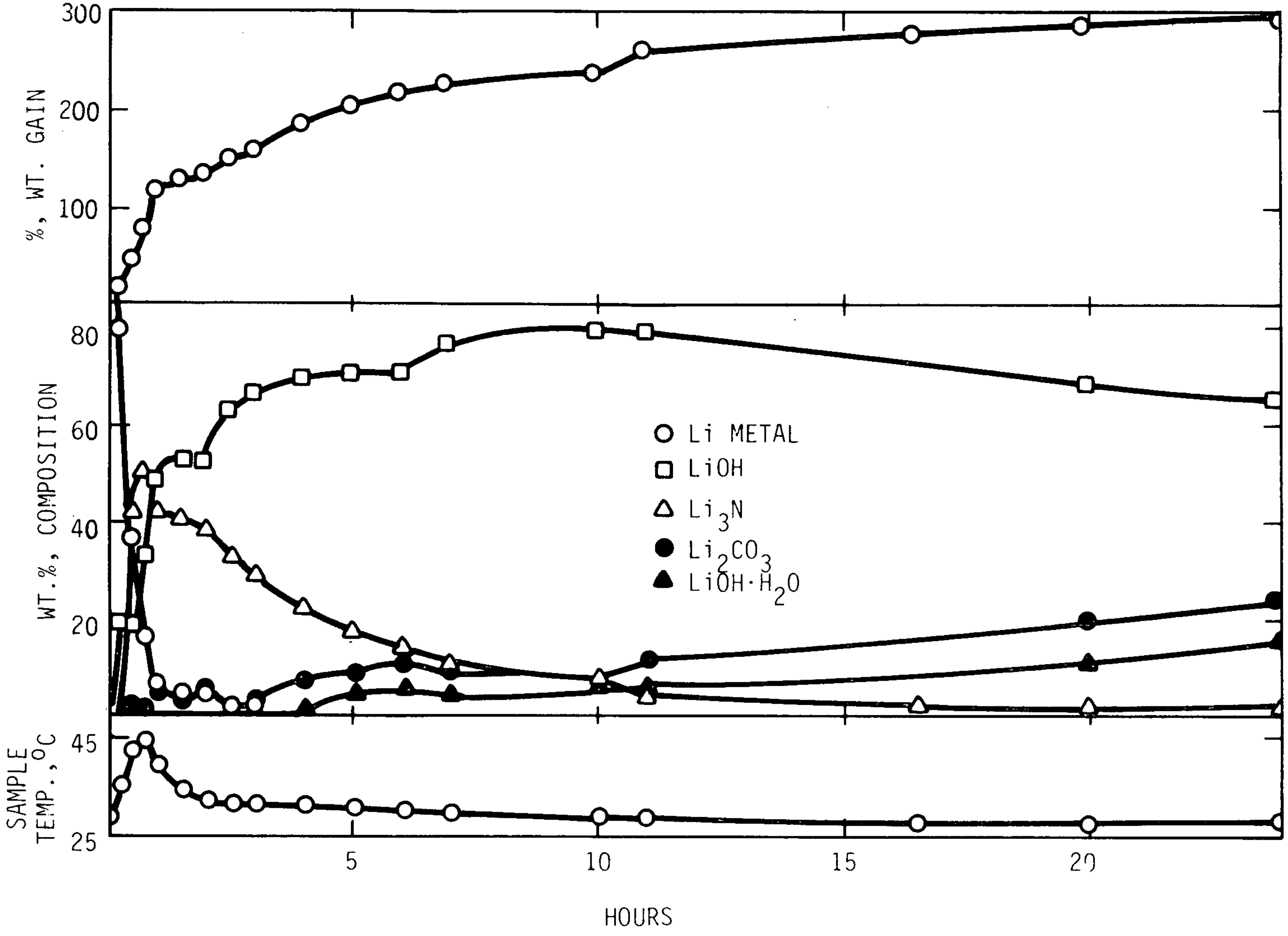

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FIGURE 15. Reaction Profiles of 100-125 Mesh Lithium Metal Exposed to Circulating Air. (50% r.h., 27°C) Ref. 25, Figure 2

Therefore, factors influencing the rate of heat evolution in an alkali metal-water reaction must be considered. The total amount of metal surface or the number of metal atoms exposed to water at any instant will primarily control the rate of heat released assuming relatively little hindrance of lithium metal-water contact due to hydrogen gas liberation. Two anomalies exist despite the tendencies just discussed:

- Solid lithium metal is considerably less reactive with water than sodium in air environments despite relatively small differences in the initial number of atoms exposed to water.

- Other alkali metals are known to be more reactive towards water than sodium or lithium despite larger unfavorable differences in the number of exposed atoms.

In reaction with liquid water at room temperature under an argon atmosphere, an irregularly shaped piece of solid lithium retained its original geometrical configuration when put in water. The reason for this phenomenon is that the water in contact with lithium metal acts as a heat sink to prevent fusion. A thermocouple embedded in a 3/8-inch sphere of lithium immersed in 250 cubic centimeters (cm^3) of room temperature water under argon or air indicated a maximum bulk temperature of only 98 °C to 103 °C.(10) Immersion of solid lithium in a slurry of ice and water exposed to air results in pronounced diminution of activity. The bulk temperature of a 3/8-inch sphere only reaches a maximum of 40 °C. This proves the effectiveness of the surrounding water as a heat sink. (Note: only valid when volume of water volume of lithium.) For large pieces of solid lithium in restricted volumes of water, the relative insolubility of the product (LiOH) may impede the reaction. Suitable coatings of lithium hydroxide may have some protective effects on the lithium metal. However, hydrogen and metal oxidation by air might increase the vigor of a water-initiated sequence of events.

In boiling water under an argon atmosphere, solid lithium reacts without combustion. If allowed to stand in flowing steam, a white coating forms consisting of LiOH, LiOH · H_2O and Li_2O. Within five minutes, the edges of the coating become incandescent. Liquid lithium metal flows through the cracks in the coating and starts to burn brilliantly.(10) The initial protective effects of the LiOH coating as it becomes thicker and develops cracks and strains, loses its protective character. It still functions like a thermal insulator to raise the metal to melting and ignition temperatures by retaining the heat of the lithium-steam reaction. At this point, the reaction tends to become quite vigorous. Hydrogen gas is one of the combustion products in this alkali metal-steam flame.

The reaction of solid lithium with water vapor (in moist argon and oxygen atmospheres) was studied from 20 °C to 45 °C and from 45 °C to 75 ° C.(27,36) Water vapor was present in partial pressures up to 100 mm Hg. Three reaction stages were identified:

- Formation at a constant rate of a lithium hydroxide film,
- Localized nucleation and growth by spreading of lithium hydroxide monohydrate at the outer surfaces of the hydroxide film,
- Simultaneous formation and hydration of the hydroxide at a constant rate culminating in the complete conversion of the metal to lithium hydroxide monohydrate.

Figure 16 shows the reaction curves using a moist oxygen atmosphere for the 25 °C to 42 °C temperature range. The initial step took approximately three to four hours with reaction rate remaining constant. The surface acquired a black glossy tarnish identified as partially formed lithium hydroxide. The intermediate step required one to four hours

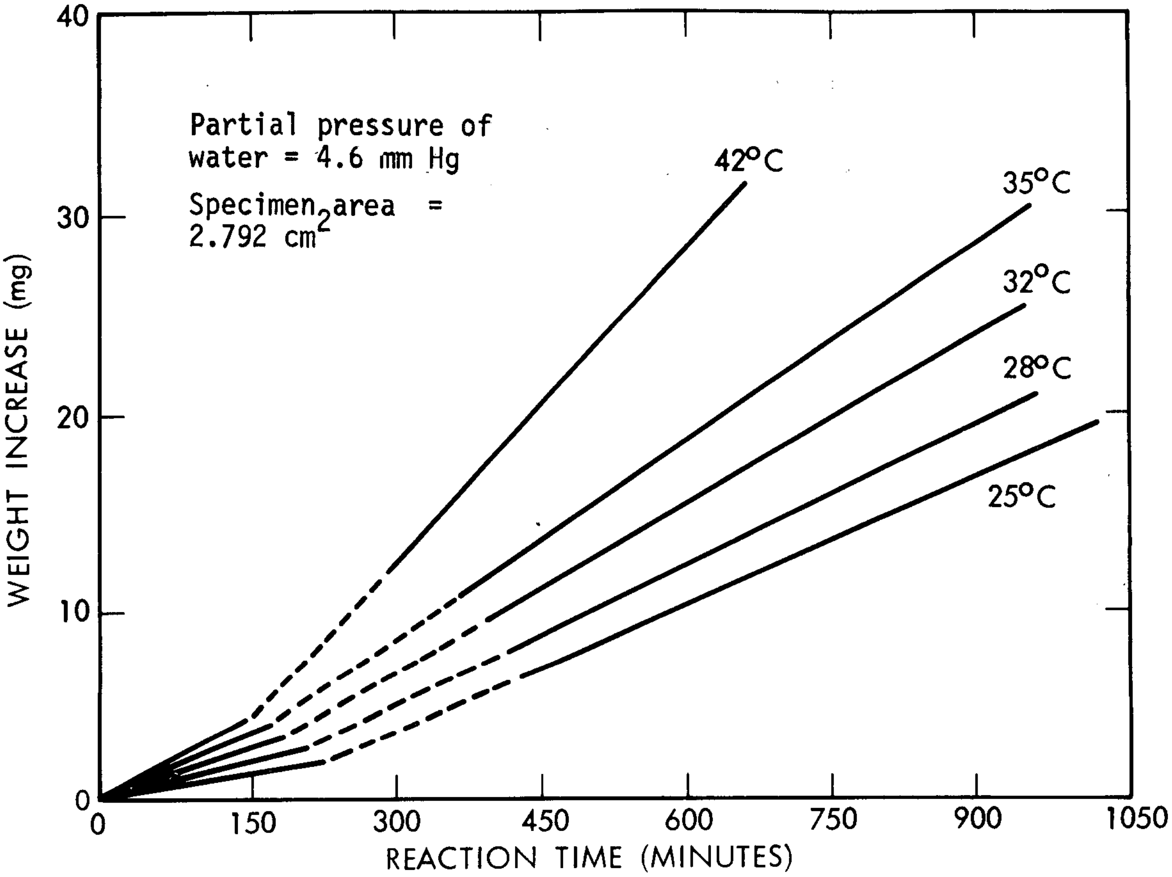

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FIGURE 16. Reaction Curves for Lithium Metal Specimens in Moist Oxygen at Various Temperatures. Ref. 27, Figure 1

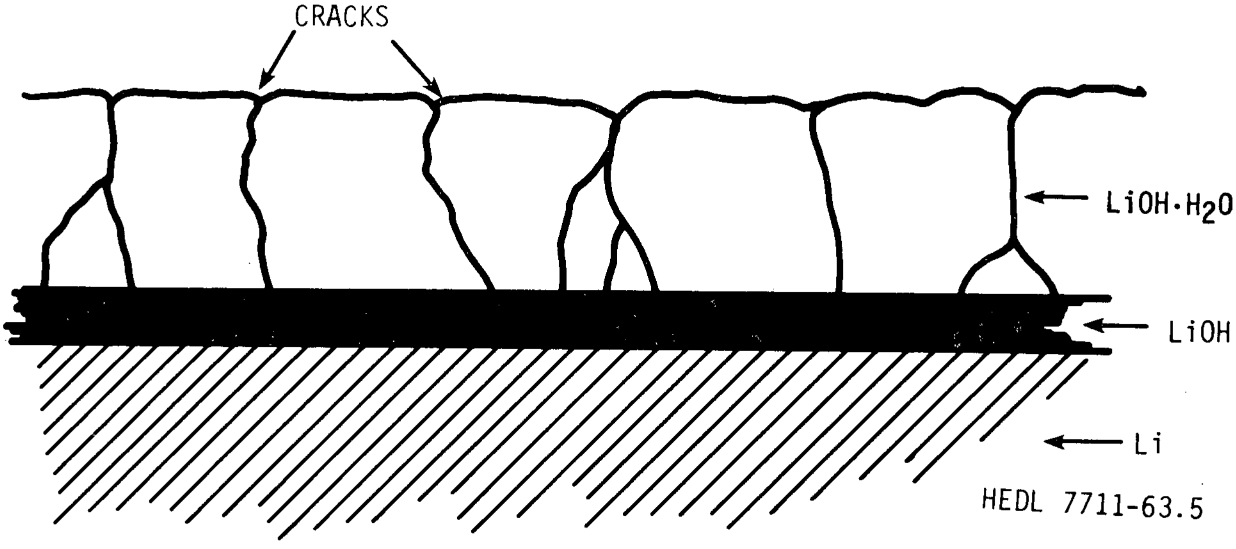

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FIGURE 17. Distribution of Lithium-Water Reaction Products. Ref. 27, Figure 5

(depending upon the temperature) during which the reacton rate increased continuously. White reaction product appeared at the edges of the lithium and grew laterally across the surface, confirming the presence of lithium hydroxide and lithium hydroxide monohydrate. Figure 17 illustrates the assumed distribution of reaction products. The final stage of the reaction proceeded at a constant rate approximately one and one-half times the rate of the first step. The actual range was between 1.3 and 1.9 times faster with the latter value holding for the low reaction temperatures.(27) The entire surface was white and uniformly thick. Lithium hydroxide monohydrate was the only product present. Activation energies encountered at the initial and final stages of the reaction were 11.7 ± 2.5 kcal/mole and 7.7 ± 1.8 kcal/mole, respectively, for the 20 °C and 45 °C temperature range.(27)

Figure 18 shows the dependence of the reaction rate at 35°C on water vapor pressure. Reaction rates for the initial and final stages of reaction increase rapidly with pressures between 2.9 and 4.6 mm Hg. A further increase in pressure causes a slower increase in the reaction rates.(27)

At temperatures between 45 °C and 75 °C and water vapor pressures between 22 and 55 mm Hg, the reaction rate constant is independent of pressure.(36) The reaction is diffusion controlled, dependent upon the diffusion of the reacting species across the developing hydroxide film. Activation energies encountered for vapor partial pressures of 50 and 100 mm Hg are around 6.2 kcal/mole and 5.5 kcal/mole, respectively.(36) At pressures greater than 55 mm Hg, reaction rate will again be pressure dependent.

Two separate and distinct types of explosions might occur when hot molten lithium and liquid water are brought into contact.(37) The first is a physical phenomenon--the sudden vaporization and overheating

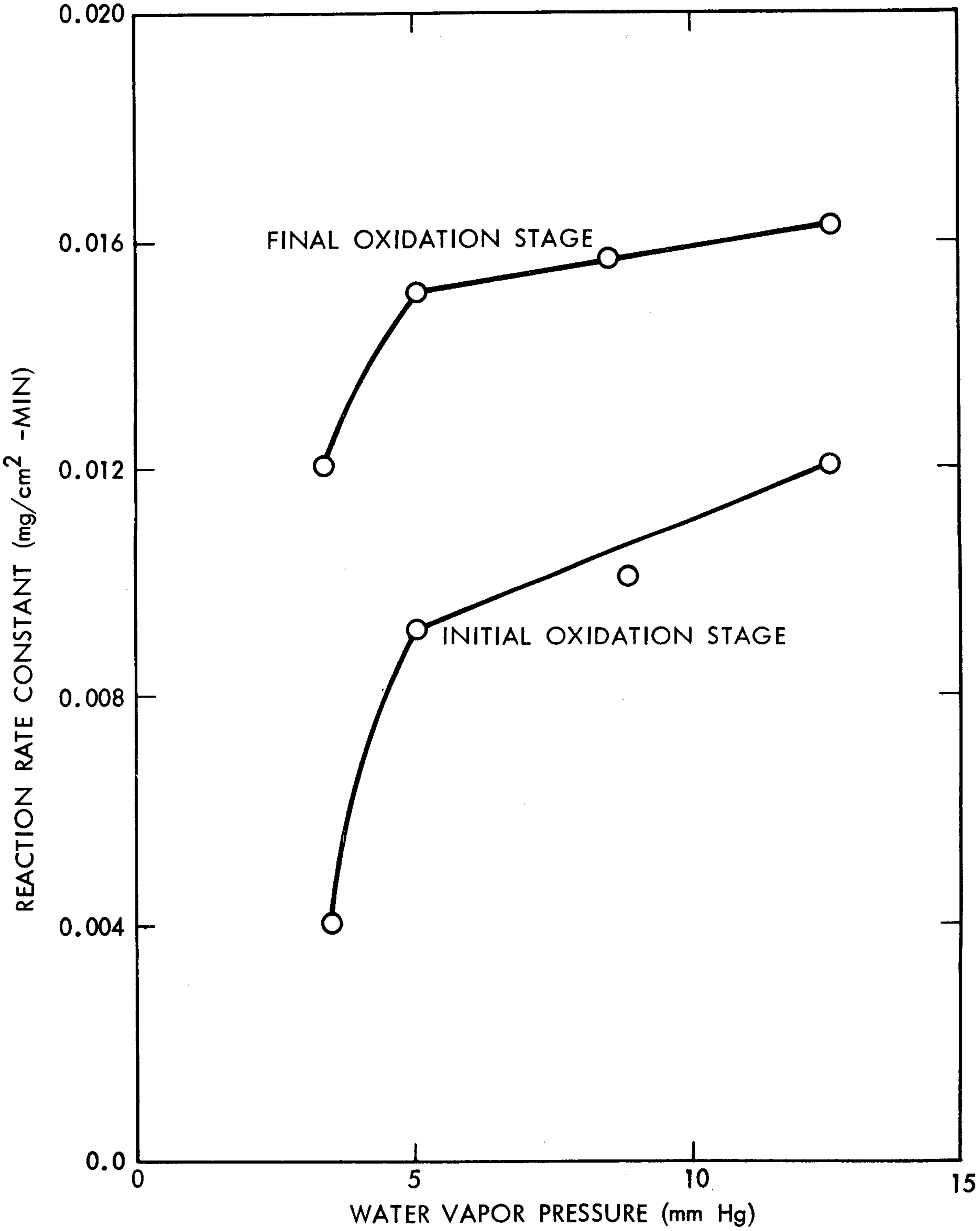

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FIGURE 18. Rate Constants of Lithium Metal Reacting with Moist Oxygen at 35°C. Ref. 27, Figure 4

of a mass of water resulting in the generation of high pressures and maybe a boiler type explosion. The second is a chemical reaction:

$$\text{Metal (1)} + n\ H_2O\ (1) \rightarrow \text{Metal}\ O_n + n\ H_2\ (g)$$

This may take place with extreme rapidity and violence accompanied by a release of heat. The reactive metal must be molten before contacting water for both results to occur. In the physical reaction, only relatively large masses are effective in producing an explosion. In the chemical reaction, a fine state of subdivision of liquid metal and large interfacial area between the two immiscible reacting phases are required. Most important, however, the metal must be capable of displacing two hydrogens from water molecules with great rapidity. With lithium, only one hydrogen is displaced with formation of lithium hydroxide as the preferred reaction product. Therefore, this chemical reaction should not be feasible for lithium.

It is postulated that to cause an explosion when a mass of hot lithium falls into a pool of water. The lithium must contact the bottom of the containing vessel while part of its mass is still fluid. If water is trapped between the molten metal and the bottom of the vessel, cooling of the metal will result in heating of the trapped water forming steam and causing dispersal. No evolution of hydrogen or any other chemical reaction occurs between the system's components.

The nature of the surface on which the metal rests is important. If the solid interface is not readily wetted by liquid water (hydrophobic), it is difficult to obtain the trapping necessary for sustaining an explosion. If the interface is hydrophilic (clings to water), an explosion can occur under conditions where none would occur, for example, with a smooth metallic bottom. Layers of rust, lime, gypsum, aluminum and iron hydroxide especially promote settling. Coating a surface with oil, grease, tar, paint and other surface finishes with little or no affinity for water tends to prevent trapping of water and thus explosions.

Most of the available information for lithium-water reactions pertains to solid lithium reacted on a very small scale. It is reported that for lithium, rate laws do not depend on whether the metal is liquid or solid but on the nature of the reaction films formed. Thus the laws may be extrapolated into the liquid range.(37) Whether this holds true for all temperatures and quantities of lithium and water is not known.

IV. LITHIUM COMPOUNDS

The four most predominant compounds formed from lithium reactions are lithium hydride (LiH), lithium oxide (Li_2O), lithium nitride (Li_3N), and lithium hydroxide (LiOH). Table 10 lists some properties and descriptions of these. All are stable but extremely reactive and corrosive compounds.

TABLE 10

PROPERTIES OF LITHIUM COMPOUNDS

Formula	LiOH (s)	Li_2O (s)	Li_3N (s)	LiH (s)
Molecular weight	23.95	29.88	34.82	7.95
Density (g/cm^3) at 15-20 °C	2.54	2.01	1.38	0.78
Melting Point (°C)	471.1	1427	840-850 275	688
Boiling Point (°C)	925	1527		
ΔG° (kcal/mole) at 25 °C)	-48.99	-133.96	-37.30	-16.72
ΔH° (kcal/mole) at 25 °C	-48.70	-142.65	-47.50	-21.61

LiOH:	Corrosive; no metal or refractory material can handle molten lithium hydroxide in high concentrations.
Li_2O:	Highly reactive with water, carbon dioxide, refractory compounds.
Li_3N:	Very reactive; no metal or ceramic has been found resistant to molten nitride. Hygroscopic-forms ammonia in the presence of water.
LiH :	Reduces oxides, chlorides, sulfides readily; reacts with metals and ceramics at high temperatures.

Ref. 1,5,9,38

V. CORROSION-RESISTANCE OF MATERIALS TO ATTACK BY LITHIUM

1. General(1,8)

Glasses, plastics and ceramics are all attacked by molten lithium near the melting point. Severe attack is due to formation of relatively stable but highly corrosive lithium oxide, nitride and carbide. Nonmetallic impurities in the liquid metal have a profound effect on the compatibility behavior of lithium and other materials. For example, molten lithium nitride, readily formed from liquid lithium-nitrogen reactions is highly reactive. No metal or ceramic material has been found resistant to it. Molten lithium hydroxide, a possible impurity since oxygen is present in solid lithium as hydroxide rather than the oxide, is very corrosive. No refractory material or metal can handle it at high concentration. Molten lithium chloride, found in commercial lithium, attacks iron and copper. Molten lithium hydride resulting from lithium exposed to hydrogen gas or moisture is reactive with metals and ceramics at high temperatures.

Armco steel shows good resistance at temperatures up to 600 °C. It is generally resistant to attack up to 1000 °C and higher. High purity molten lithium may be held in quartz containers up to 285 °C. However, commercial lithium readily attacks glass, quartz, porcelain and other silicate materials. Lithium attacks most oxides of structural metals, less stable metal carbides, silicides, rubbers and plastics. Figures 19, 20 and 21 show the resistance ratings of various materials to liquid lithium under different conditions.

2. Ceramics and Insulating Materials(1,39)

Corrosion resistance of ceramics is an extremely sensitive function of the impurity concentration, deposition of the reaction products on the ceramic surfaces in contact with lithium, and the size and distribution (porosity) of pores with respect to grain boundaries. From a

MATERIAL	TEMP. °C		
ALUMINUM	800		□
	600		▨
	300		▨
BERYLLIUM	800		▨
	600		□
	300		□
CHROMIUM	800		□
	600		□
	300		□
COPPER-BASE ALLOYS (WITH Al, Si, OR Be)	800		▨
	600		▨
	300		▨
COPPER-BASE ALLOYS (WITH Zn OR Sn)	800		□
	600		▨
	300		▨
COBALT-BASE ALLOYS	800		▨
	600		▥
	300		░
MOLYBDENUM, COLUMBIUM, TANTALUM, TUNGSTEN	800		░
	600		░
	300		░
NICKEL AND NICKEL ALLOYS (WITH Fe, Cr, Mo)	800		▨
	600		▨
	300		▥
NICKEL ALLOYS (WITH COPPER)	800		▨
	600		▨
	300		▨
PLATINUM, GOLD, SILVER	800		□
	600		▨
	300		▨

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░ GOOD RESISTANCE

▥ LIMITED RESISTANCE

▨ POOR RESISTANCE

□ UNKNOWN RESISTANCE

FIGURE 19. Resistance of Various Materials to Liquid Lithium. Ref. 8; 1, Figure 11

MATERIAL	TEMP. °C		
TITANIUM	800		▥
	600		☐
	300		☐
ZIRCONIUM	800		▥
	600		▥
	300		▒
ALUMINA (DENSE)	800		▧
	600		▧
	300		☐
GRAPHITE (DENSE)	800		▧
	600		▧
	300		▧
BERYLLIA (DENSE)	800		☐
	600		☐
	300		☐
MAGNESIA (CRUCIBLE)	800		☐
	600		☐
	300		▥
PORCELAIN/SILICATES	800		▧
	600		▧
	300		▧
PYREX GLASS	800		▧
	600		▧
	300		▧
FUSED QUARTZ	800		▧
	600		▧
	300		▧

HEDL 7711-63.7

▒ GOOD RESISTANCE

▥ LIMITED RESISTANCE

▧ POOR RESISTANCE

☐ UNKNOWN RESISTANCE

FIGURE 19. Resistance of Various Materials to Liquid Lithium (Cont'd)

MATERIAL	TEMP. °C		
PURE IRON	800		░
	600		░
	300		░
MILD CARBON STEEL	800		▧
	600		▥
	300		░
LOW-CHROMIUM STEEL (WITH V, Mo, OR Si)	800		□
	600		□
	300		░
2 TO 9% CHROMIUM STEEL (WITH Ti, Mo, OR Si)	800		□
	600		□
	300		□
FERRITIC STAINLESS STEEL (12 TO 27% CHROMIUM)	800		▥
	600		░
	300		░
AUSTENITIC STAINLESS STEEL (18-8 AND 25-20 Cr-Ni)	800		▧
	600		▥
	300		░
GRAY CAST IRON	800		□
	600		□
	300		□

HEDL 7711-63.8

░ GOOD RESISTANCE

▥ LIMITED RESISTANCE

▧ POOR RESISTANCE

□ UNKNOWN RESISTANCE

FIGURE 19. Resistance of Various Materials to Liquid Lithium (Cont'd)

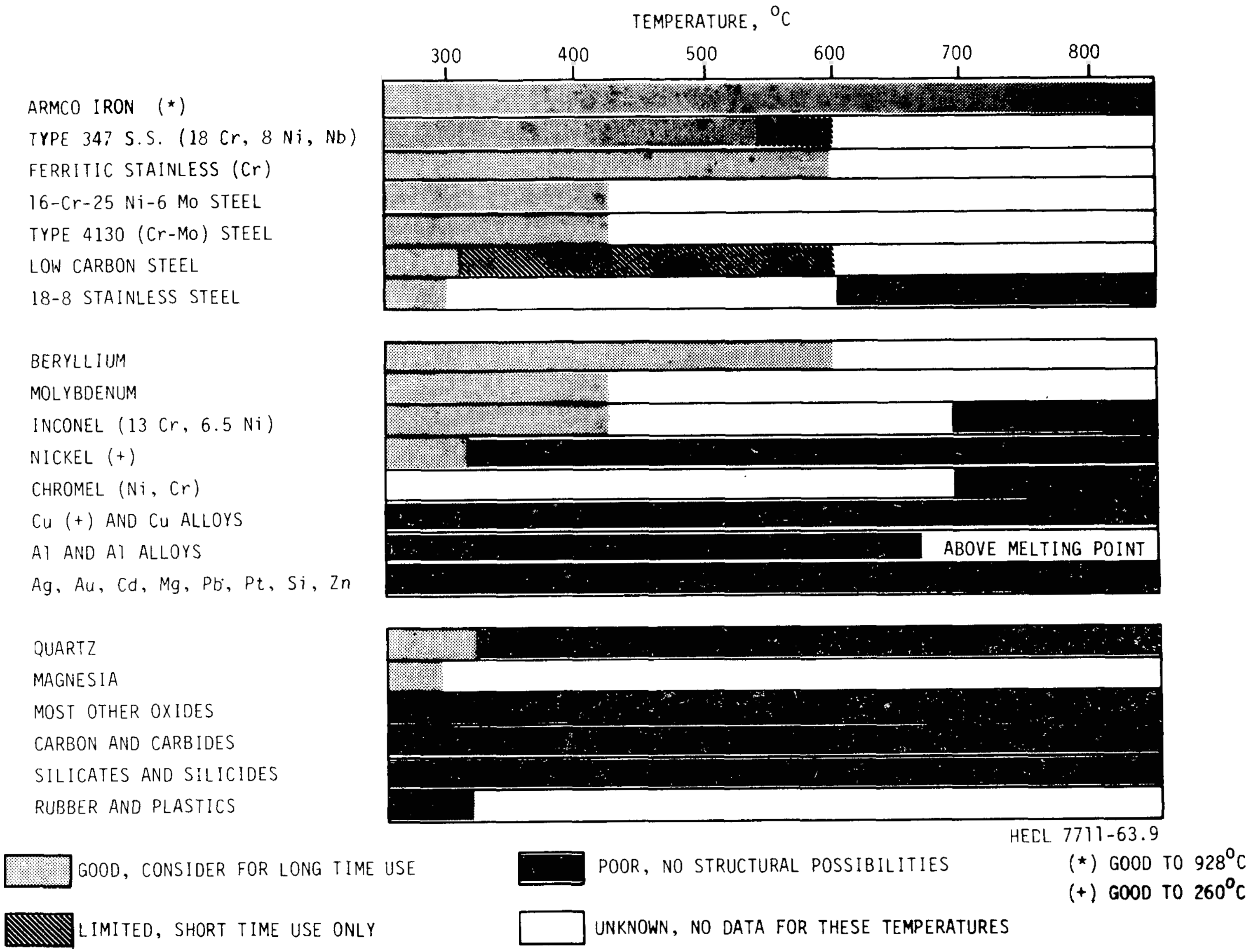

FIGURE 20. Resistance of Various Materials to Lithium. Ref. 1, Figure 12

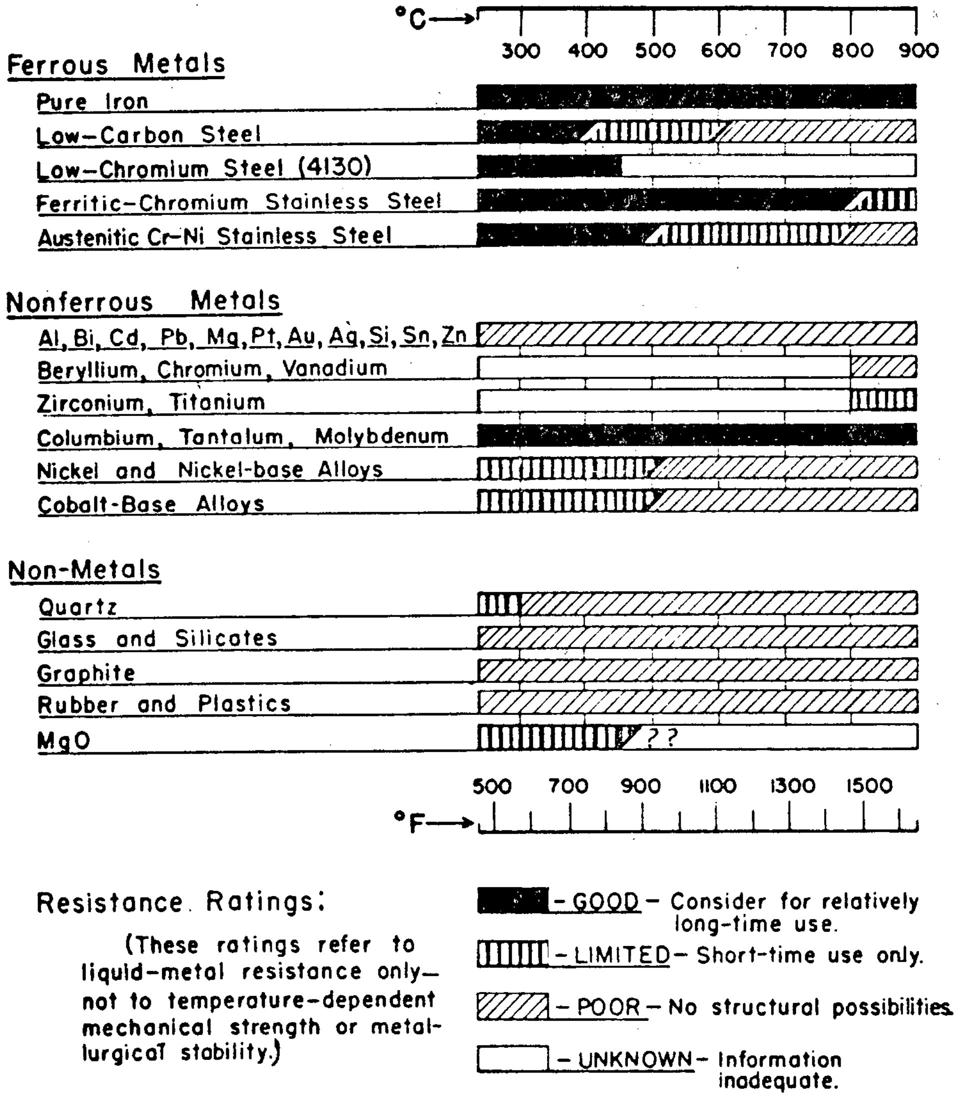

FIGURE 21. Resistance of Various Materials to Liquid Lithium. Ref. 8; 9, Figure 14.2

thermodynamic point of view, relatively higher levels of concentration of non-metallic impurities in liquid lithium are desired. With impure lithium systems, the oxide ceramics (ThO_2, BeO, Y_2O_3, MgO) are reported compatible with lithium only if the oxygen level in lithium is greater than a 10^3 ppm level. At an oxygen level less than or equal to 1 ppm in lithium, the following oxide ceramics are thermodynamically incompatible: Al_2O_3, $MgAl_2O_4$ (spinel), MgO, ThO_2, BeO, Y_2O_3, ZrO_2, TiO_2 (rutile), Li_2O, SiO_2. At a nitrogen level less than or equal to 10^{-3} ppm, all nitrogen ceramics (AlN, BN, Si_3N_4, Li_3N) are incompatible. AlN, BN, and Si_3N_4 are compatible if nitrogen levels are greater than 10^3 ppm. Figure 22 illustrates these results.

In conclusion, the compatibility conditions for oxide and nitride ceramics in a liquid lithium environment were found more severe than in a liquid sodium environment. Thermodynamically, only BeO, Y_2O_3, Si_3N_4, BN, AlN, ThO_2, and MgO are expected to be compatible with a liquid lithium environment from temperatures between 27 °C and 1427 °C. (These conclusions are subject to thermodynamic criterion only. Stability of a compound thermodynamically is a necessary but not sufficient condition for compatibility).(39)

A second set of compatibility test results were contradictory to the above. A series of tests run at 1093 °C were performed with the following results:(1)

- Light attack was observed on samples of Sm_2O_3 after 500 hours, ThO_2 after 1000 hours, TiC and ZrC after 2000 hours, and ThO_2-Y_2O_3 mixtures after 3000 hours.

- Samples of BeO, CuO, AlN, AlB_{12}, BN, MgO, and MgO-Al_2O_3 mixtures were very badly attacked at 1093 °C in less than 500 hours.

Tables 11 and 12 and Figure 23 show the results of other compatibility tests for the corrosion of ceramics by lithium.

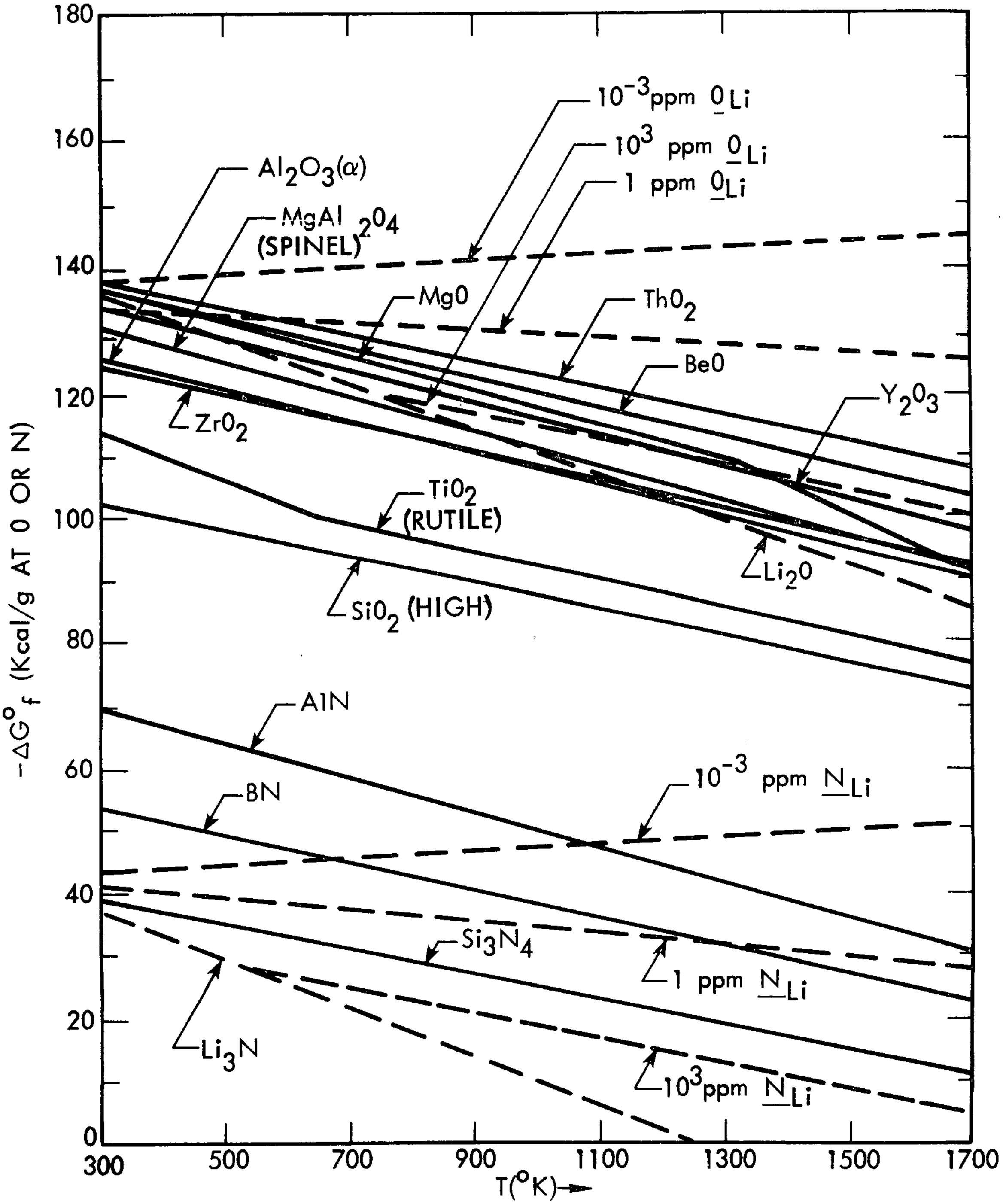

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FIGURE 22. Lithium-Ceramics Stability Diagram. The standard free energy of insulating ceramics formation and the chemical potentials of oxygen and nitrogen in liquid lithium (dotted line) vary as a function of temperature. Ref. 39, Figure 2

TABLE 11

COMPATIBILITY TEST RESULTS OF LITHIUM-CERAMICS INTERACTIONS

Material	Results
MgO, single crystal	Optical clarity retained; weight loss ~1%
MgO, hot pressed polycrystalline	Severe general attack
BeO	Some penetration of grain boundaries; loss of integrity
$CaZrO_3$	Integrity maintained; conductive layer formation
Si_3N_4 (Norton)	Cracked
Si_3N_4 (Westinghouse)	Destroyed
SiALON	Cracked
BN	Discoloration; substantial corrosion; loss of integrity
Y_2O_3	Little evidence of general attack; some grain boundary penetration
ZrO_2	Incompatible

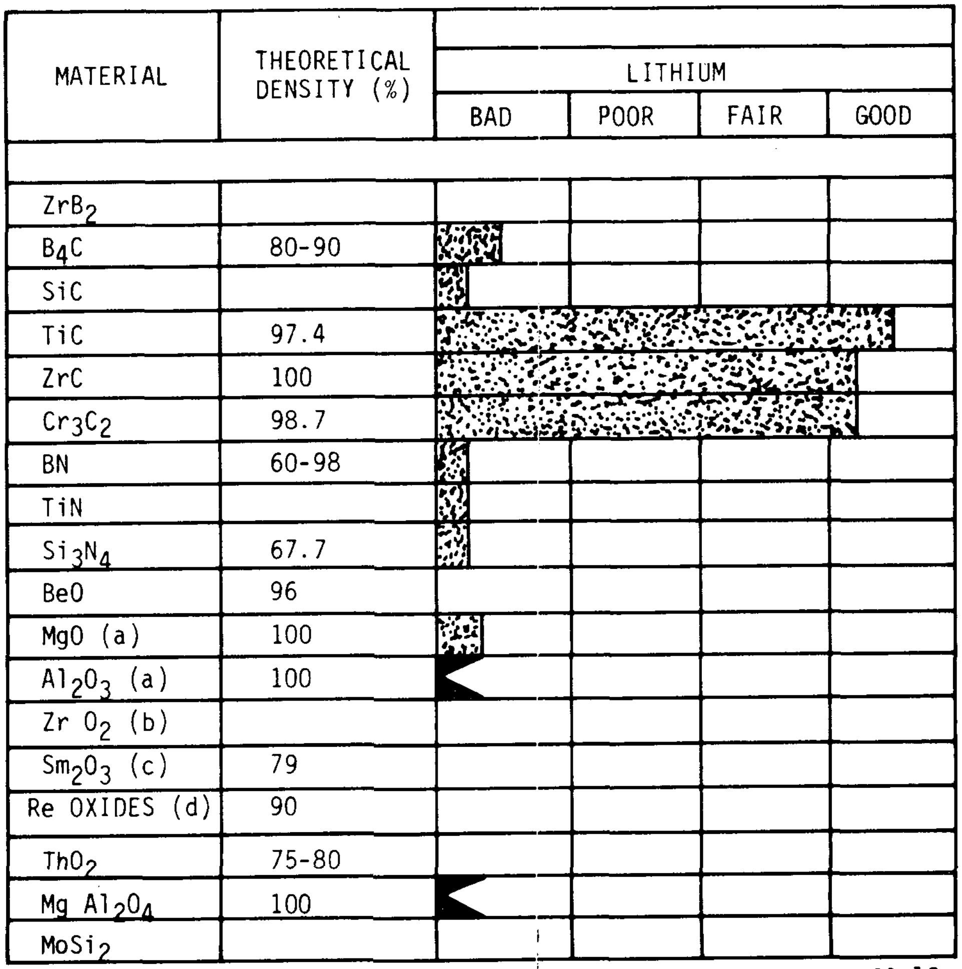
Ref. 40, Table 4

TABLE 12

STATIC 300-HR TEST OF LITHIUM INTERACTIONS WITH CERAMIC INSULATING MATERIALS AT 400 °C

Material	Possible Use with Lithium
Al_2O_3	No
MgO	Yes
BeO	Yes
ThO_2	Yes
Y_2O_3	Yes
ZrO_2	No
$MgAl_2O_4$	No
$CaZrO_3$	?
BN	Yes
Si_3N_4	Yes
SiALON	?

Ref. 40, Table 2



MATERIAL	THEORETICAL DENSITY (%)	LITHIUM			
		BAD	POOR	FAIR	GOOD
ZrB_2					
B_4C	80-90	▨			
SiC		▨			
TiC	97.4	▨	▨	▨	▨
ZrC	100	▨	▨	▨	
Cr_3C_2	98.7	▨	▨	▨	
BN	60-98	▨			
TiN		▨			
Si_3N_4	67.7	▨			
BeO	96				
MgO (a)	100	▨			
Al_2O_3 (a)	100	◀			
$Zr O_2$ (b)					
Sm_2O_3 (c)	79				
Re OXIDES (d)	90				
ThO_2	75-80				
$Mg Al_2O_4$	100	◀			
$MoSi_2$					

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▨ PIECES OF THE TESTED LITHIUM REMAINED

◀ NO VISIBLE TRACE OF THE TESTED SPECIMEN

(a) SPECIMEN FROM A SINGLE CRYSTAL
(b) CaO-STABILIZED
(c) A 1000-HOUR TEST
(d) A 500-HOUR TEST. (BODY COMPOSITION: 45.0 TO 49.5% Sm_2O_3; 22.5 TO 27% Gd_2O_3; BALANCE PRIMARILY OTHER RARE-EARTH OXIDES.)

FIGURE 23. Corrosion Resistance of Ceramics to Static Lithium for 100 Hours at 816 °C. Ref. 19; 1, Figure 14

3. Metals(1,3)

Stainless steels represent the primary containment material for lithium-cooled MFEs. Compatibility is highly dependent upon lithium purity, alloy treatment, flow rates and lithium handling procedures. Corrosion rates decrease with decreasing temperature in high purity systems and show less intergranular attack.

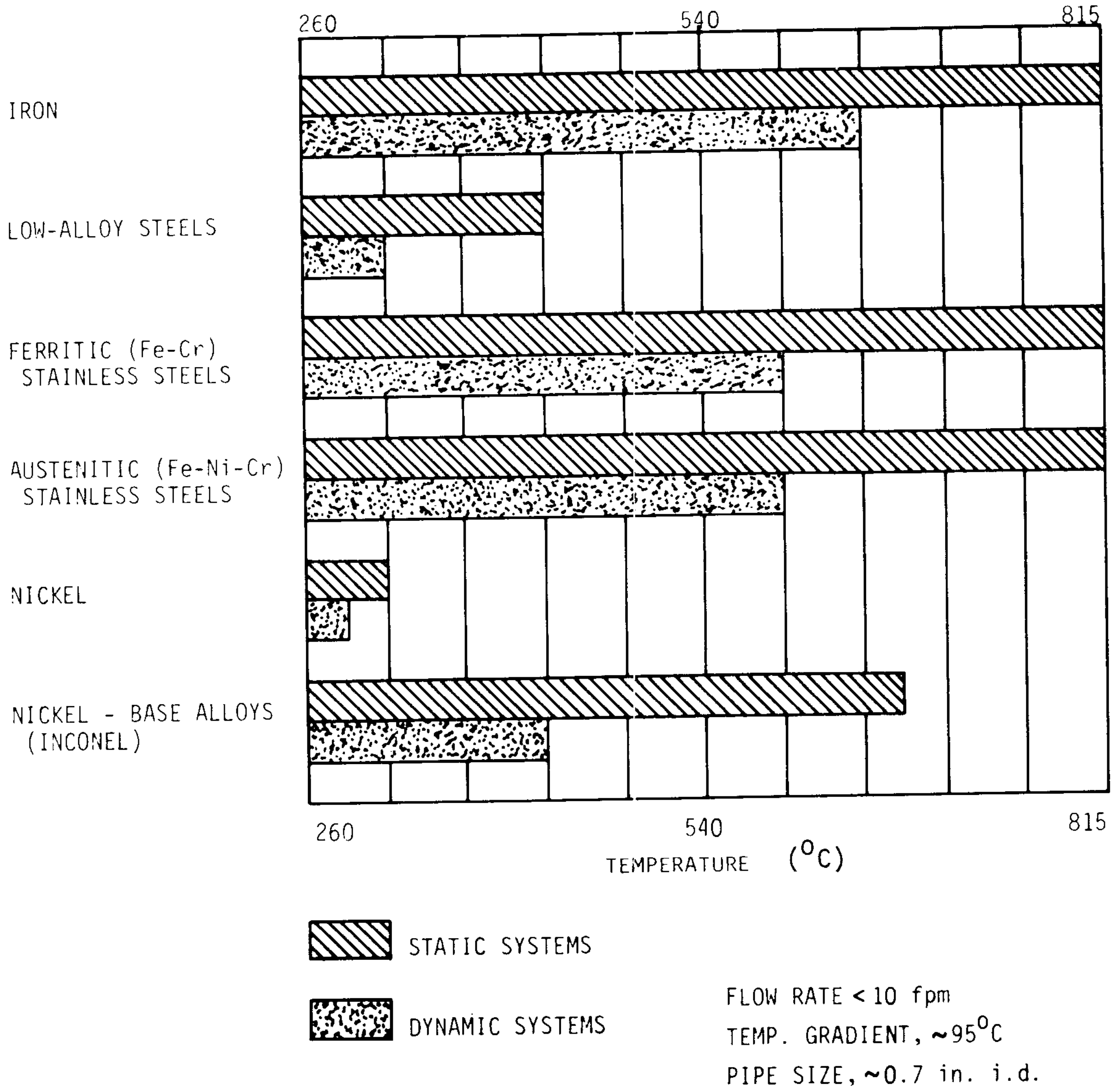
Austenitic and ferritic stainless steel with less than 0.12 wt.% carbon exhibit good resistance to lithium attack. Stainless steels of the austenitic types 302, 303, 304, 316, and 347 are resistant to corrosion by molten commercial lithium up to 315 °C for 7 days and 480 °C for 3 days. Low carbon steels (SAE-1020) have good resistance to attack at 300 °C and limited resistance at 600 °C. Of the refractory metals, columbium, tantalum, and molybdenum are relatively stable at 1000°C, zirconium and titanium are fair, but vanadium, beryllium and chromium are severely attacked. High temperature attack due to oxygen, carbon and nitrogen impurities in either the refractory metal or lithium itself is especially bad with respect to corrosion in refractory metals. Nickel shows good resistance at 225 °C, limited at 300 °C, and poor at 600 °C.

Aluminum, barium, bismuth, calcium, cadmium, gold, lead, magnesium, platinum, silicon, silver, strontrium, thallium, tin, zinc, and their alloys all react with molten lithium yielding products of no structural usefulness. Copper and copper alloys such as aluminum bronze show poor resistance. High temperature cobalt-base alloys are also attacked.

Figure 24 illustrates the results of corrosion resistance of various metals and alloys to lithium.

4. Lithium-Concrete Interactions

DTA measurements to determine lithium-concrete reaction temperatures, heats of reaction, and to identify reaction products for three types of concrete aggregates and Portland cement have been recently completed (attached as Appendix).



Bars indicate approximate temperatures below which a system might be operated for 1000 hours with less than 0.005 in. of attack or container surface removal.

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FIGURE 24. Corrosion Resistance of Various Metals and Alloys in Lithium. Ref. 42; 1, Figure 12

VI. LITHIUM HANDLING, SAFETY, AND FIRE CONDITIONS

Lithium-cooled controlled thermonuclear reactors require large quantities of hot flowing lithium. The reactive nature of lithium coupled with the radioactive content of the coolant after use demand special consideration of the hazards associated with lithium, especially leaks or fires. Major hazards result from vigorous reactions or fires due to contact with water, air, chlorinated hydrocarbons or other reactive agents, or personnel injury from direct contact with lithium or lithium reaction products. To accommodate for the reactivity of lithium, areas in which it is to be used should be dry, without sprinkler systems, fire-resistant and appropriately ventilated.(1)

A. LITHIUM CONTAINMENT

Lithium should be packaged in metal containers holding up to 200 pounds of solid lithium, with a protective atmosphere of helium, argon or hydrocarbon fluids.(1) In the presence of an inert atmosphere of paraffin vapor, lithium can be handled at temperatures up to 200 °C--it can be melted and poured without great difficulty.(24) Stainless steels and irons contain lithium up to 700 °C; heat resistant refractory metals to over 1500 °C.(1) Care should be taken to uphold the purity of the lithium since contamination increases lithium reactivity.

B. LITHIUM IGNITION

Combustion reactions involve carbon dioxide, oxygen and nitrogen of the atmosphere. The final product is essentially all oxide.(11) There is much disagreement in the literature as to the actual ignition temperature of lithium. Measurement of the spontaneous ignition temperature of a pool or spray of liquid lithium depends on metal purity, humidity of the heating gas used, pressure, sample size, different treatments undertaken, apparatus, and techniques used. Therefore, reproducibility and verification of results is difficult. Ignition occurs when the quantity of heat produced by the oxidation reaction is greater than the loss of heat from the lithium to the system. It is often determined by the character of the oxide crust formed by the oxidizing reaction.

Solid lithium is not easy to ignite. Even a small piece must be heated for some time before a sustained reaction takes place.(11) Molten lithium will not spontaneously ignite in dry air at temperatures up to 400 °C.(11)

One study reported an ignition temperature of 445 °C.(43) At temperatures above 445 °C, nodulation appeared. The surface of the metal transformed slowly, looking warped where it displayed yellow oxide particles. Ignition occurred at this spot on the surface, spreading to the whole mass of metal. A very hard residue in the form of cauliflower remained.

Other studies(11) make reference to a porous, coral-like growth of lithium oxide and lithium nitride which floats on the hot molten metal and acts as a wick and catalyst for the combustion reaction. In the presence of this coral (or lithium corrosion products), ignition can occur at temperatures around 200 °C. Combustion begins promptly if a piece of cold coral-like residue is dropped into molten lithium. This seems to be a specific effect since other materials (asbestos, sand, iron oxide) do not initiate combustion likewise. Without the coral-like compound, hot liquid lithium may be stirred, poured and handled in air without igniting. At temperatures over 600 °C (around 640 C(7)), spontaneous ignition will take place with pure metallic lithium.

Once initiated, combustion slowly spreads across the molten metal surface through a laterial growth until the entire exposed surface is taken up by the combustion process. Expansion from a pea-sized fire to a burning area of 2 to 3 square feet takes around 10 minutes, starting with molten metal at 200 °C with a depth of 3 to 4 inches. In still air, the temperature of the molten metal rises to an asymptote around 400 °C. A large temperature gradient exists across the burning layer since surface temperatures around 800 °C were observed. The rate of combustion with respect to lithium oxide formation appears to be strongly diffusion controlled. Very slight drafts of air accelerate combustion extensively. This is not true for lithium nitride formation. A stream of nitrogen directed onto a burning surface did not accelerate combustion appreciably. The proportion of oxide to nitride formation occurring may therefore be expected to increase as convection above a burning surface increases, with both the temperature of the fire and rate of heat generation increasing. The heat of formation of oxide is around three times that of nitride.

In this study(11), it was emphasized that very different rates of fire propagation can be observed if molten metal is suddenly dumped at a high temperature (around 800 °C) into a metal catch pan.

Combustion is accompanied by emission of dense, white and opaque fumes, tending to mask the seat of the fire. This is very similar to that seen with sodium. Splattering of hot metal, accidental contact of hot lithium with water, or other highly reactive materials, radiation to and ignition of nearby combustible materials, escape of molten metal and the production of large volumes of irritating fumes are all principle dangers of large lithium fires.

C. LITHIUM FIRE EXTINGUISHMENT

Lithium fires are hard to control and extinguish Fire control consists of cooling the reacting mass, preventing diffusion of reacting gases to the combustible surface and prevention of evolvement of combustible vapor or aerosols. Metal catch pans, dump tanks for rapid draining of the system if leaks develop, and flooding with inert atmosphere all aid in containing spills and diminish the possibilities for large lithium fires. A few studies have been made examining the effectiveness of different extinguishants on lithium fires. The results are subject to carefully controlled testing conditions and may vary in an actual accident situation.

In one study, both powdered sodium chloride (NaCl, also known as MET-L-X) and graphite were found effective in extinguishing lithium fires. Other possible extinguishants were cited as zirconium silicate, potassium chloride (KCl), and lithium chloride. A powdered carbon preparation, LITH-X, was also recommended. Conventional fire extinguishing agents were strongly discouraged since lithium readily reacts with the water, carbon dioxide, sodium carbonate, aqueous foams, soda acid mixtures and carbon tetrachloride (CCl_4) found in these agents.(1) One to two pounds reagent per pound of burning lithium sufficed to extinguish the fire. For dispersions of burning lithium in organic liquid, extinguishment was accomplished by application of sodium bicarbonate followed by MET-L-X. Fumes were reduced by use of electrostatic precipitators and scrubbers. For floors with steel drainage troughs, an angle with at least a 7° slope leading to a sump was necessary to help prevent serious lithium fires.(1)

The results of a second study(11) were quite comprehensive and are illustrated in Tables 13 and 14. The most effective of the extinguishants tested was a ternary inorganic eutectic: $NaCl\text{-}KCl\text{-}BaCl_2$. The MET-L-X mentioned above was also found to be good. The following conclusions were drawn from the study:

- The ternary inorganic eutectic is ineffective when applied from a pressurized extinguisher.

- The effectiveness of any extinguishant is influenced by the application rate. Thus for any given size and type of fire, an optimum application rate exists which permits attainment of fire control in minimum time.

TABLE 13

EXTINGUISHANTS FOR SMALL LITHIUM FIRES

Effect of various agents on small quantities (1.3 g) of burning lithium.

Extinguishing Agents	Reaction			Effectiveness			Comments
	Explosive	Vigorous	Little/None	Good	Fair	Poor	
1. Lead (shot)			X		X		Good quenching but extinguishing action not complete.
2. Lead (powder)	X	X				X	Small explosion occurred third trial-possibly a contaminant.
3. Brass (granular)			X		X		Good quenching action; extinguishant if lithium is completely blanketed.
4. Sodium bicarbonate		X				X	Acted as fuel rather than extinguisher.
5. Lithium chloride			X	X			Too hygroscopic for storage.
6. Potassium chloride		X				X	Moderate sparking occurred.
7. Lithium and potassium chlorides (50-50)		X			X		Effective cooling; sparking more vigorous than with KCl alone.
8. Celite 545		X				X	Appeared to be combustible.
9. Graphite			X	X			Complete extinguishment if entire burning surface well covered.
10. Pyrene G-1 Powder			X	X			Same as above.
11. Sodium Chloride		X				X	Much sparking; poor quenching properties.
12. Lith X			X	X			Lithium must be covered completely for extinguishment.
13. Boric acid		X		X			Secondary fire develops - is of short duration. Coating of oxide blankets lithium.
14. Graphite in #30 motor oil		X-burns		X			May be too viscous-thins out when in contact with burning lithium. Very little oil fire.
15. Celite and #30 motor oil		X-burns			X		Same as above.

Ref. 11, Table I

TABLE 13

EXTINGUISHANTS FOR SMALL LITHIUM FIRES (Cont'd)

	Reaction			Effectiveness			
Extinguishing Agents	Explosive	Vigorous	Little/None	Good	Fair	Poor	Comments
16. Pyrene G-1 and #30 motor oil		X				X	Resulted in more of an oil fire than graphite in motor oil.
17. Graphite and lubricant LB650X		X-burns			X		Viscous dispersion; oil did not lose viscosity on application to burning lithium.
18. G.E. Silicon oil 9996-1000 and graphite			X	X			Viscosity not lowered when in contact with burning lithium. Very little oil fire.
19. Sand		X				X	Violent sparking.
20. Trimethoxyboroxine (liquid)			X	X			Easy to apply; secondary fire burns with green flame for only a short time.
21. Saf (Fire retardant paint) (liquid)		X				X	Burns giving off heavy black smoke.
22. Unicel ND (blowing agent)			X		X		Some frothing observed.
23. Petroleum oil			X-burns		X		Loses viscosity at high temps.; flows away; secondary oil fire.
24. Boric acid anhydride		X				X	Poor results due to lack of flow and coverage.
25. Unicel ND 1 Petroleum oil 5		X-burns			X		No more effective than oil alone.
26. Celogen (blowing agent)			X	X			Excellent frothing-smothered fire rapidly; ineffective in petroleum oil and TMB.
27. Lead and tin alloy			X		X		Good flow properties. Fairly good smothering action.
28. Ternary eutectic salt mixture 25% BaCl, 35% NaCl, 40% KCl			X	X			Very effective.
29. Ternary eutectic plus celogen			X	X			Very effective. Forms liquid crust, Some blowing effect.

TABLE 14

EXTINGUISHANTS FOR MODERATE LITHIUM FIRES

Effectiveness of selected extinguishants on moderate-sized lithium fires.

Extinguishant		Fire conditions						Remarks
(amounts exting. used shown in center columns)	Area,(in)	64	64	64	110	81	346	
	Metal depth,(in)	0.4	0.6	0.8	1.0	3.5	3.0	
	Pounds metal	1/2	3/4	1	2	5	14	
ABC		-						Highly dangerous; secondary fire, spark shower, explosions.
CaF_2			7					Not effective.
Celogen				2.8				Secondary fire; black smoke.
20% celogen, 80% MET-L-X				4.7				No foaming or flotation effect observed. Did not appear to offer any advantage over straight MET-L-X.
Powder chemical concentrates				4.2	6.5			Smoke; secondary yellow flames. Relatively large amount required.
Lith-X		2.5		6				As above.
Lube oil		-						Fierce secondary fire; uncontrollable.
MET-L-X			0.8	1.5	3.5	5.1	14	Very effective. Did not sink in these experiments. Some suggestion of sodium formation.
Pyrene G-1			3.5	4.2				Smoke; secondary flames; slow after-cooling. Carbon glows after lithium extinguishment.
Salt ternary eutectic		2.5		2.5	2.2	1.5		Very effective. Sinking prevented by coral formation.
TMB		1.6						Not effective.
		2.8						Secondary flames.
		3.0						Dangerous fumes.

Note: Extinguishants applied by shovel.

Ref. 11, Table II

- There is no difficulty in keeping extinguishants from sinking below the molten lithium surface despite the low density of liquid lithium. This is due to the relatively high surface tension of liquid lithium and low apparent density of lithium oxide, coupled with its wetting properties.

- Different results may be obtained if the burning lithium is at higher temperatures.

- The results of the manufacturers of MET-L-X's tests on their own product are considered erroneous. During the latter tests, applied MET-L-X sank beneath the burning lithium surface while that remaining on the surface appeared to react, yielding free sodium. In effect, a sodium fire was substituted for a lithium fire. The reasons for this discrepancy are that the manufacturer's tests used larger areas of burning lithium and higher temperatures. Also the amount of MET-L-X used by the manufacturer was large. Therefore the sheer weight of it alone may have caused sinking below the molten lithium surface. Instead, it was found that no sinking occurred when MET-L-X was applied to a lithium fire 3 inches deep. The light, porous, coral-like growth mentioned before acts as a flotation layer, sufficiently buoyant to support the agent. The effect is aided by the high surface tension of molten lithium.

The most efficient agent--a pulverized fused salt eutectic mixture (melting point: 640 °C) is composed mainly of barium chloride (25%), sodium chloride (35%) and potassium chloride (40%). The preparation procedure is outlined in Table 15. Its extinguishing action depends on a blanketing effect since no chemical reaction was found between the salt mixture and burning lithium. Only the presence of the original agent components plus lithium oxide and lithium nitride were found in x-ray studies of the fire residue. The possibility of free sodium or potassium formation still exists.

TABLE 15

LITHIUM FIRE EXTINGUISHANT PREPARATION

Ingredients of Ternary Eutectic Salt Mixture (100 lb)

Barium Chloride	25% by Weight
Sodium Chloride	35% by Weight
Potassium Chloride	40% by Weight

Procedure

The crystalline salts were purchased as Technical Grade at 80 to 100 mesh grain size. Five 20-pound batches were made. Each lot was tumbled in a five-gallon glass jar rotated on a set of ball mill rolls turning at about 44 rpm for 30 minutes. The mixture of salts was distributed into six or seven 4-liter Pyrex glass beakers set inside one-gallon paint cans or steel beakers. The charges were heated for 2 hours at 720 °C. At this temperature, the salt mixture was completely liquid. After stirring to insure uniformity, the masses were allowed to cool and the glass beakers broken away.

The entire 100-pound lot of solid fused salt was broken up by hammer and ground to pass a 200 mesh sieve. During the milling operation, 2.5 pounds of magnesium stearate were added to prevent caking of the product and to assure easy flow.

Ref. 44; 11, Appendix B

Met-L-X was found good on fires from 0.75 to 14 pounds in size.(11) Almost 75 to 80% of the original lithium was present as lithium after extinguishment. Complete replacement of sodium in MET-L-X by lithium is not a requisite for successful extinguishment. Evidence exists that small amounts of metallic sodium are formed but no metallic sodium could be identified in the fire residue. During early application of the extinguishant, yellow flames were observed. Application in sufficient amounts can be performed without sinking of the agent into the molten lithium. In a 14-pound fire, MET-L-X was added to the center area of the fire with a shovel while working slowly outward to avoid bridging from the container walls.

Due to the sensitivity of the burning rate to even slight convection currents, once a lithium fire has started, attempts to ventilate the area could be detrimental to fire control. Any attempts to improve visibility through smoke removal of ventilation should be avoided. For this same reason, gas-propelled extinguishants are less effective than the same agents applied by shovel.

Application of an inert gas like argon to a well established lithium fire was completely ineffective. Direct application to the burning surface did retard the fire somewhat but removal of the argon gas source caused combustion to immediately resume.(11)

D. LITHIUM REMOVAL

Lithium spills may be transferred to buckets filled with 100 mesh powdered graphite.(1) Residual lithium contamination should be wiped clean with flameproof rags. Disposal of cold lithium residue is more difficult. The residues consist of a mixture of lithium, lithium oxide, nitride, and carbonates. Reactions of the residues with water may proceed quietly or violently. Residues in less than one pound lots should be placed in drums with wire mesh screens covering the tops.(11) If steel catch pans containing residue are included, all will sink to the bottom and the reaction will occur peacefully.(1) Burning in air or hydrolysis in natural bodies of water is not feasible due to the formation of noxious fumes and toxic acqueous waste harmful to human, animal, and vegetable life.(1)

VII. FUTURE STUDIES AND EXPERIMENTATION

The overall objective of the lithium spill studies project is to increase the state of knowledge concerning the effects of lithium spills under postulated accident conditions for the purpose of supporting magnetic fusion energy device safety assessments.

All reaction products resulting from lithium interactions should be characterized as well as their rate of formation and the temperatures involved, for all accident conditions plausible. Tests to determine reaction kinetics, the chemical nature of reaction products, heats of reaction, and aerosol properties for lithium reactions with the atmosphere, concrete, and insulating materials proposed for use in MFE facilities should be performed.

Testing under both static and dynamic conditions is suggested. The effects of radiation on the properties and interactions of lithium should be determined also. Further development and demonstration of effective materials and techniques for extinguishing small and large lithium fires resulting from pool and spray accidents is needed. Flooding with a gas to induce an inert atmosphere should be further investigated. Finally, studies should involve methods for removing lithium smoke aerosols from cells and ventilation systems. An evaluation of lithium and sodium spills to determine the applicability of existing sodium fire and spill technology to lithium hazards may provide a more efficient method for developing lithium fire and spill technology.

Supportive and additional information about the characteristics of lithium and its interactions with other compounds are contained in References 45 through 98.

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APPENDIX

LITHIUM-CONCRETE STUDIES
BY DIFFERENTIAL THERMAL ANALYSIS

Prepared By: G. C. Burrow, R. E. Witkowski, and R. G. Charles
Westinghouse Electric Corporation Research Center
Pittsburgh, PA

September 1977

APPENDIX

Westinghouse
Electric Corporation

Research and Development Center

1310 Beulah Road
Pittsburgh Pennsylvania 15235

September 7, 1977

Dr. Lewis D. Muhlestein
Westinghouse Hanford Company
P.O. Box 1970
Richland, WA 99352

Dear Lewis:

SUBJECT: Lithium-Concrete Studies by Differential Thermal Analysis, Your Requisition No. Y83259

As detailed in the above-referenced requisition, we have studied the chemical reactions between lithium and various concretes and dry Portland Cement (II) paste by Differential Thermal Analysis (DTA) over the temperature range of 25 to 800°C. Eight DTA measurements were made on five concrete samples and one cement as detailed by your test matrix. The objective of these studies was to provide preliminary base data on the effects of lithium spills, under postulated accident conditions, for the purpose of supporting your CTR Facility Safety Analysis.

The concrete samples, which were characterized under a previous contract with the Westinghouse Hanford Company (I.W.R. Order No. Y6W-S44-35602), were used in these studies. The dry Portland Cement (II) paste sample was prepared at the Westinghouse R&D Center by mixing the as-received cement with water followed by air cure for seven days. The DTA apparatus utilized in this work was that used in the sodium-concrete studies detailed in previous reports.(1,2)

Upon completion of the DTA scans, distillation to remove the excess lithium from the reaction products (625°C at 6×10^{-4} mm Hg for approximately nine hours) proved unsuccessful. Therefore, to remove the excess lithium, each DTA sample reaction product was reacted in air with distilled water in a stainless steel beaker. This procedure, for the removal of the lithium, resulted in two fractions of reaction product for each DTA sample; the water soluble and insoluble reaction products. The samples were centrifuged to separate the two fractions, the insoluble material then washed with ethanol and centrifuged again. The soluble fraction was obtained by evaporation of the distilled water on a hot plate. Both fractions were dried and loaded in appropriate XRD sample capillary tubes. The capillary tubes were sealed and readied for analysis. Characterization of the reaction products for each of the three different types of concretes and one cement sample exposed to lithium were performed by X-Ray Diffraction (XRD), see Appendix I.

The DTA results of this effort are given in Table 1 which presents the temperature(s) at which the exotherm(s) occurred, and the heat evolution for each material. The heat evolution values ($-\Delta H$, cal/gram) are based on the calibration of the DTA apparatus with a 200 mg sample of NiO which was run separately with excess lithium. The characteristic DTA curves for each run are presented in Figures 1 through 5; the NiO calibration run is shown in Figure 6. The endotherms noted in each figure at approximately 190°C represent the melting of the lithium metal.

Based on this abbreviated study, the following preliminary conclusions, related to lithium-concrete interactions, may be drawn:

A. The DTA studies of the concrete sample M1 (magnetite aggregate) yielded inconclusive results; two entirely different plots were obtained as shown in Figure 1; a large difference in heat evolution values resulted. The presence of Fe, as given in the XRD results for the insoluble reaction products, is indicative of the reduction of the magnetite component to elemental Fe. The large differences in the DTA plots may be due to (1) the separation of magnetic and non-magnetic concrete components during sample preparation or (2) preliminary interaction of the lithium with the concrete sample prior to heating.

   During previous studies involving sodium-concrete interactions, large differences in heat evolution values were also noted.(1) The funding available for this effort did not permit additional DTA runs to be made to resolve this problem.

B. The basalt aggregate concrete materials (CON-B1 and CON-B2) gave the highest apparent heat evolution values of all samples studied. The XRD results indicate the reduction of the silicates to silicides. Similar DTA plots were obtained for each sample as shown in Figure 2.

C. Concrete sample L1 (limestone aggregate) gave the most reproducible heat evolution values and exotherms, see Figure 3. The results of XRD analysis for both the water soluble and insoluble fractions of the reaction products do not offer a readily visible reaction mechanism.

D. The exotherms of the dry Portland Cement (II) paste, see Figure 4, can be attributed to the direct reduction of the silicates to silicides. The XRD analysis of the insoluble reaction products has identified silicides as a minor phase.

E. In general, these results show lithium to be, as expected, a stronger reducing agent than sodium. This is particularly evidenced by the reduction of the aggregate/cement silicates to silicides.

Dr. Lewis D. Muhlestein

September 7, 1977

We hope this preliminary study, into the interaction of lithium with concrete, fulfills your near-term requirements. If you have any questions concerning this work or if we can be of further assistance, please feel free to give us a call.

Sincerely,

G. C. Burrow

G. C. Burrow
Liquid Metal Technology

R. E. Witkowski

R. E. Witkowski
Liquid Metal Technology

R. G. Charles

R. G. Charles
Special Projects

APPROVED: ______________________
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sef

cc: J. Ballif, Westinghouse Hanford Company
W. T. Lindsay, Jr., R&D Center
R. M. Lowy, R&D Center
PIC-2-File

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TABLE I

Differential Thermal Analysis Results for the Reaction of 300 mg Samples in Excess Lithium (1000 mg). 316 SS Sample Containers with Argon Cover Gas

Sample Identification	Exotherm °C		*Heat Evolution $-\Delta H$, cal/gram	
	Run #1	Run #2	Run #1	Run #2
CON-M1	482 w 596 s	351 s 593 w 622 m	+ 218	+ 991
CON-B1	268 w 308 s 364 w	-	+ 1051	-
CON-B2	391 s 430 w	-	+ 770	-
CON-L1	695 s	702 s	+ 403	+ 536
Dry Portland Cement (II) Paste	690 s	558 s	+ 224	+ 182

---

*Based on calibration of the apparatus with a 200 mg sample of NiO with excess lithium.

w = weak m = moderate s = strong

Curv 691605-B

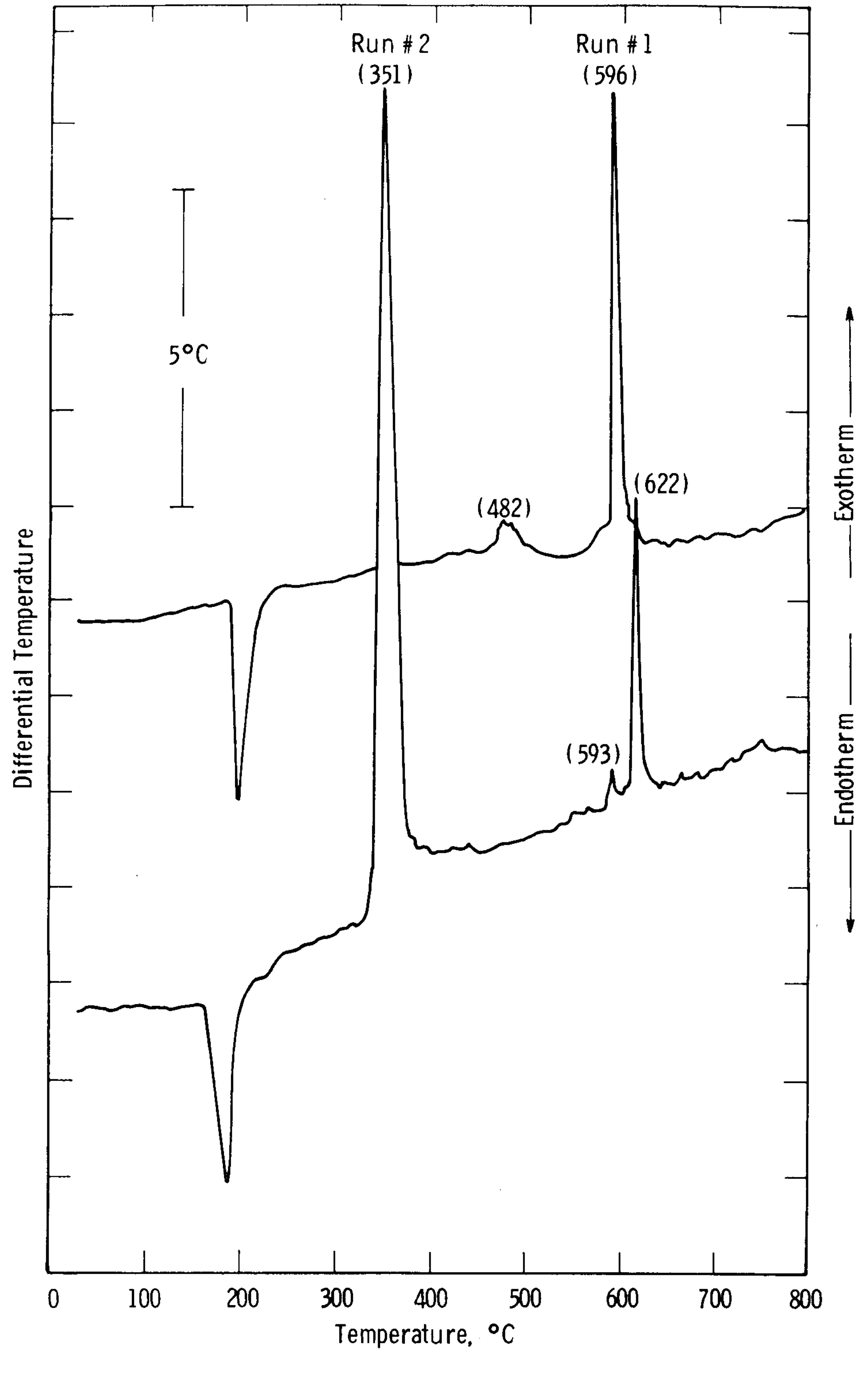

Fig. 1 — Differential thermal analysis (DTA) curves obtained for two individual 300 mg samples of Con-M1 in excess lithium (1000 mg). 316 S. S. sample container with argon cover gas

Curve 691604-B

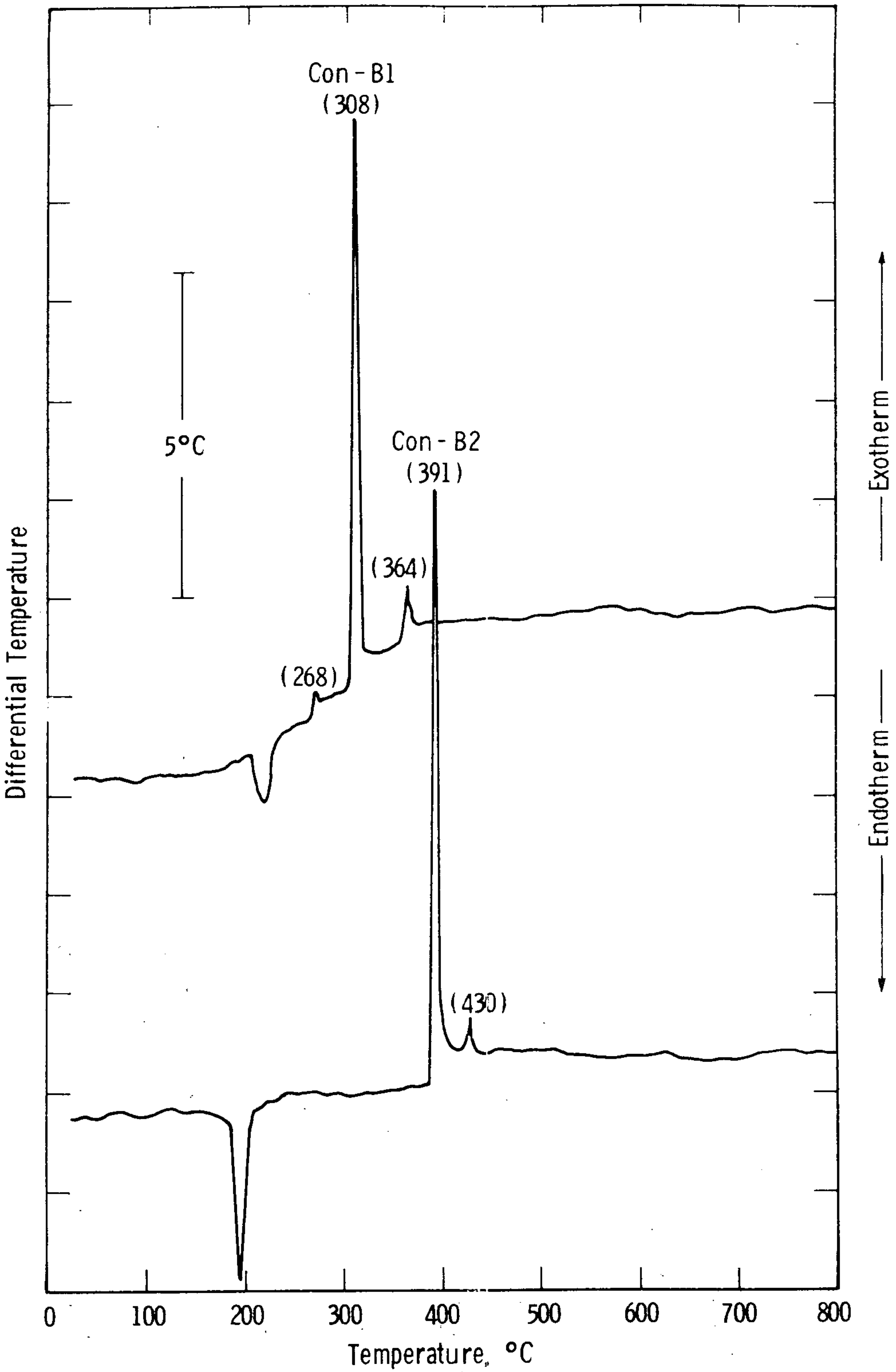

Fig. 2 – DTA curves obtained for 300 mg samples of Con-B1 and Con-B2 in excess lithium (1000 mg). 316 S. S. sample container with argon cover gas

Curve 691602-B

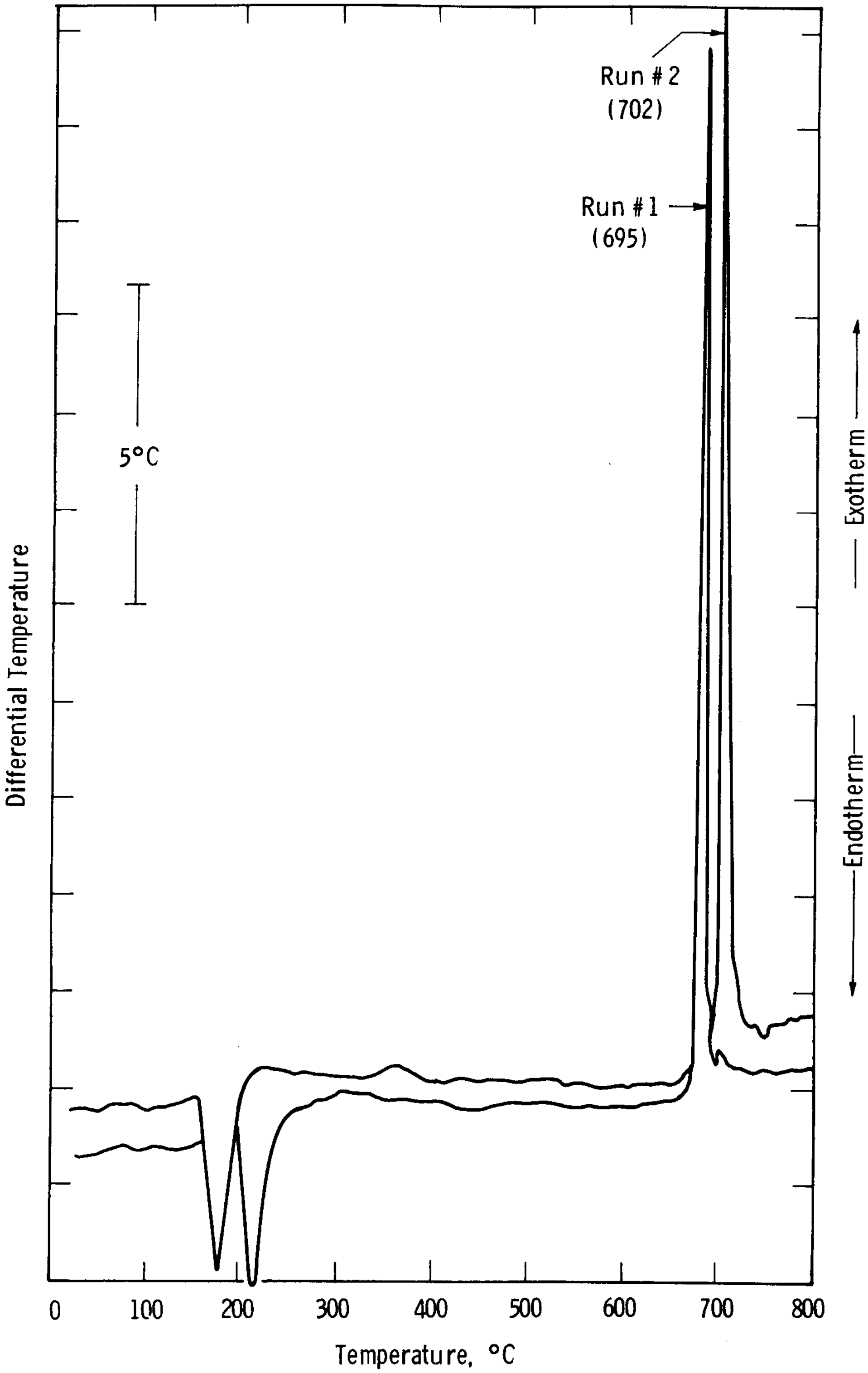

Fig. 3 — DTA curves obtained for two individual 300 mg samples of Con - Ll in excess lithium (1000 mg). 316 S. S. sample container with argon cover gas

Curve 691601-B

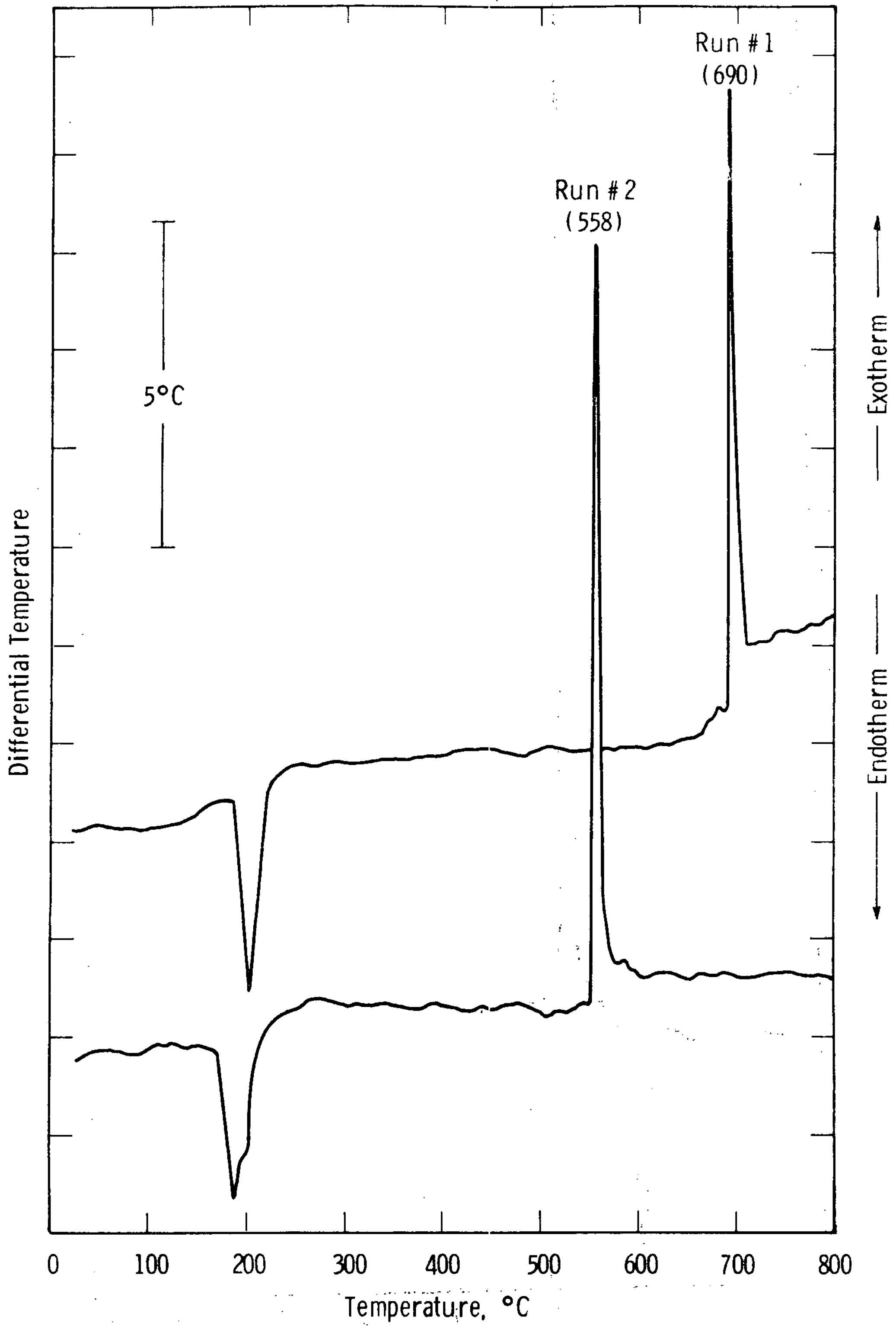

Fig. 4 – DTA curves obtained for two individual 300 mg samples of air cured (7 days) dry portland cement (II) paste in excess lithium (1000 mg). 316 S. S. sample sample container with argon cover gas

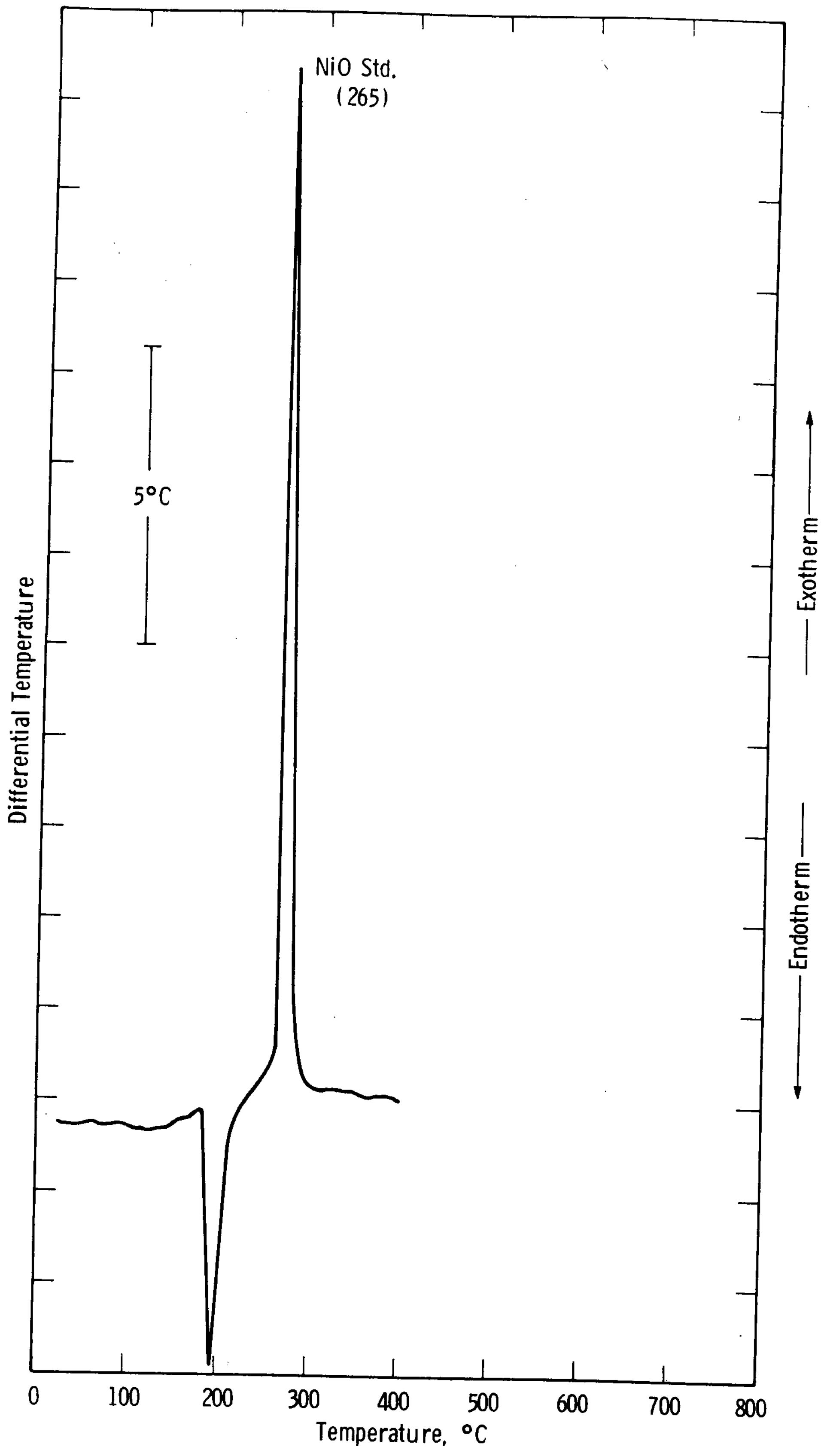

Fig. 5 — DTA curve obtained for a 200 mg sample of NiO standard in excess lithium (1000 mg). 316 S. S. sample container with argon cover gas

APPENDIX I

X-Ray Diffraction and Energy Dispersive Analysis by X-Ray of Lithium-Concrete Reaction Products

From : R&D CENTER
WIN :
Date August 31, 1977
Subject:

R. E. Witkowski
R&D 303

cc: G. C. Burrow, R&D 303-2

Six samples of concrete (capillaries) treated with lithium were submitted to the x-ray diffraction laboratory and SEM laboratory for identification of the reaction phases.

Listed below are sample designations:

GCB #1	CON-M1 + Li (water insoluble fraction)
GCB #2	CON-L1 + Li (water insoluble fraction)
GCB #3	CON-B1 + Li (water insoluble fraction)
GCB #4	CMT-1 + Li (water insoluble fraction)
GCB #5	CON-L1 + Li (water soluble fraction)
GCB #7	CON-M1 + Li (water soluble fraction)

XRD

Sealed capillaries of the reaction products were exposed in a Debye Scherrer powder camera (114.6 mm). Both chromium and copper radiation were used because certain elements cause fluorescence with copper radiation (e.g., Fe) while other elements cause fluorescence with chromium radiation (e.g., Ca). In addition, chromium radiation has a longer wavelength (2.29 Å) which permits better resolution of lines. This facilitates the analysis of samples with multiple phases. The XRD results are presented in Table 1.*

SEM and EDAX

The reaction products were removed from the capillary tubes and mounted on a standard aluminum sample mount. This mounting was done by using a small piece of double-stick tape. The powders were gently pressed on the top surface of the tape and the entire mount was then coated with approximately 300 Å of carbon to provide a conductive surface.

The samples were then examined in the SEM using an accelerating voltage of 20 KeV. The Energy Dispersive X-Ray Analyzer (EDAX) was used to detect and record the resulting X-rays produced from the electron bombardment. All elements with atomic numbers greater than 10 (Neon) are detected simultaneously with the EDAX unit.

Results of the EDAX identifications were correlated with the X-ray diffraction patterns to eliminate or confirm possible compound formations present. Table 2 summarizes the elements and relative amounts present in each of the six concrete samples.

---

*XRD patterns are referenced against standards as presented in "Joint Committee on Powder Diffraction Standards, 1976 Edition".

TABLE 1: XRD Results

Log No.	Sample	Results
630-77	GCB #1	Fe
631-77		
632-77	GCB #2	$Ca(OH)_2$ major
633-77		$Ca(CO_3)$ high minor
		Fe minor
634-77	GCB #3	Fe major
635-77		Silicide phase major[*1]
636-77	GCB #4[*3]	$Ca(OH)_2$ major
637-77		$Ca(CO_3)$ high minor (higher than GCB #2)
662-77		CaO trace
664-77		Silicide phase, minor phase [*2]
638-77	GCB #5[*4]	$Li(OH)$ major
639-77		$Li(OH)\cdot H_2O$ major
		$Li_2(CO_3)$ high minor
		(smooth lines indicate fine grain size)
640-77	GCB #7[*4]	$Li(OH)\cdot H_2O$ major
641-77		Li_2CO_3 major
		$Li(OH)$ high minor
		Fe minor
		(Lines are spotty indicating coarse grain size)

---

[*] See following pages for explanation.

*1 A Comparison of d-spacings and Relative Line Intensities for GCB #3, Fe, Fe_3Si, and Fe_2Si Reference Patterns

GCB #3		Fe		Fe_3Si		Fe_2Si	
d	Intensity	d	Intensity	d	Intensity	d	Intensity
				3.26	40		
				2.80	40	2.80	40
2.03	S	2.03	100				
1.98	S			1.97	100	1.99	100
				1.70	40		
				1.62	20	1.62	10
1.43	W	1.43	20				
1.41	W			1.41	100	1.406	60
						1.256	20
1.178	W						
1.17	W	1.17	30				
1.15	S			1.45	100	1.15	100
1.01	W	1.01	10				
1.00	W			.995	100	.995	100
.90	W	.906	12				
.894	W						

The extra lines strongly resemble the Fe_3Si and/or Fe_2Si. Fe_3Si is F.C.C. (L.P. 5.64) [NaCl structure] and Fe_2Si is B.C.C. (L.P. 2.81) and Fe is B.C.C. (L.P. 2187). A search of literature produced no information on the (LiSi), (FeLi), or (FeLiSi) systems.

*2 Three Major d-Spacings for the Silicide Phase of GCB #4

d spaces 2.00 S
1.42 W
1.16 W+

Lattice parameter of 2.84 Å, similar to Fe, however, the lattice parameter is contracted.

*3 Possible Assignments of Unidentified XRD Line for Sample GCB #4

There was some concern over GCB #2 and GCB #4 due to the similarity of both XRD and EDAX results. Another sample of GCB #4 was prepared and analyzed - the results were identical with previous results of GCB #4. All the lines (d spaces) of the X-ray pattern generated by GCB #4 were identified with the exception of one - d space 7.30 Å. A positive identification is difficult with only one line, however, by using other lines coincidental with the other phases, the following compounds were possible.

$Ca(SO_4)\cdot 2H_2O$	(ASTM 6-46)
$Mg_3(OH)_5Cl\cdot 4H_2O$	7-420
$KMg(SO_4)Cl\cdot 2.75H_2O$	25-1237
$LiH(AlO_2)\cdot 5H_2O$	24-617
$Li_2Al_2O_4\cdot 4H_2O$	20-618

*4 Possible Presence of Li_2C_2

Li_2C_2 is possibly present in samples GCB #5 and GCB #7 primarily because the d spaces are superimposed on the three (3) previously identified phases Li(OH), $Li(OH)\cdot H_2O$, and Li_2CO_3.
Is it possible that this phase can exist under these conditions?

Table 2: EDAX Results

Sample	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe
GCB #1	T	--	S	S	T	--	T	S	S	M
#2	--	T	T	W	--	--	W	M	T	T
#3	--	W	W	M	T	T	T	M	T	W
#4	T	T	W	W	W	T	T	M	--	--
#5	T	T	W	M	T	--	T	W	--	--
#7	T	W	T	M	T	T	T	M	T	--

M = major.   S = strong.   W = weak.   T = trace.

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PM McConnell	W/A-11
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GT McDonald	W/221The
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GE Meadows	W/C-53
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