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Lithium Combustion: A Review

by

Robert A. Rhein
Ordnance Systems Department

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NAVAL WEAPONS CENTER
CHINA LAKE, CA 93555-6001

Naval Weapons Center

FOREWORD

The work described in this report was initiated in February 1990 under the title "Lithium Fire Safety Study." Funding was provided under Program Element 06203262N by the Naval Air Systems Command, AIR-8032. The work was funded under Airtask A931931P/008C/W18190000.

Since lithium reacts vigorously with water and other common fire extinguishing agents, there was a concern about extinguishing a fire resulting from a lithium spill aboard a ship.This report is a review of lithium combustion and the extinction of lithium fires. It is intended as a guide to an experimental program to extinguish lithium shipboard fires.

This report has been reviewed for technical accuracy by Dr. James C. Baldwin.

Approved by
D. A. GOSS, *Acting Head*
Ordnance Systems Department
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Under authority of
D. W. COOK
Capt., USN
Commander

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(U) This review deals with the chemical reactions, ignition, and combustion of lithium combustion in air and in the components of air, including oxygen, nitrogen, water, and carbon dioxide. It was found that lithium reacts vigorously with these substances. In addition, a review of extinguishing lithium fires is included. Of the extinguishing agents, carbon has been found to be the most effective.

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INTRODUCTION

Metallic lithium has found a number of applications, particularly in fusion reactors, where it is useful as a tritium breeder blanket and as a coolant (Reference 1). In naval applications, it is used as an ingredient in batteries (Reference 2) and as a fuel in torpedoes (Reference 3). Lithium fires can be a serious problem in the nuclear industry—in the event that a lithium spill were to occur (Reference 4), or on shipboard—in the event of crash or fire scenarios involving torpedoes or lithium batteries.

The purpose of the review described in this report was to compile known information regarding lithium reactions, including combustion reactions, with nitrogen, oxygen, water, and carbon dioxide, as well as other substances, as a guide to research regarding the extinction of lithium fires. The physical properties of lithium have been described elsewhere (Reference 1). In the process of compiling data on lithium reactions, it was found that the reaction of lithium with water greatly influences the reaction of lithium with oxygen and nitrogen, the primary constituents of air, so the lithium-water reaction is first described in this report. Next are presented the lithium-oxygen reaction, the lithium-nitrogen reaction, and then the reactions, ignition, and combustion of lithium in air. A brief discussion is then included on other lithium reactions of possible relevance to lithium fire extinction, followed by a discussion of the research that had been conducted on the extinction of lithium fires.

LITHIUM REACTION WITH WATER

REACTION RATE OF LITHIUM WITH WATER

Solid lithium reacts rather slowly with water (Reference 5),

$$Li(solid) + (infinite)\,H_2O \rightarrow LiOH\,(solution) + 1/2\,H_2\,(gas) \qquad (1)$$

producing lithium hydroxide solution and releasing hydrogen (Reference 6). The heat release from the reaction is 17.51 kcal/g or 121.5 kcal/mol. The reaction is less violent than that of the other alkali metals (Reference 7).

Bulk solid lithium at room temperature did not burn spontaneously in water, and the hydrogen formed did not ignite in air. When a pea-sized piece of lithium was dropped into a container of water, it reacted much more slowly than did sodium, and it did not splatter or evolve light. A solid piece of lithium when immersed in liquid water at room temperature retained its original shape, but decreased slowly in size as it reacted with the water. A 3/8-inch sphere of lithium immersed in 250 cm^3 of water at ambient temperature in either air or argon atmosphere became warm (98 to 103°C), and the temperature of a 3/8-inch sphere of lithium immersed in water/ice slurry in an air atmosphere, where the water volume >> lithium volume, rose to approximately 40°C. In boiling water under an argon atmosphere, solid lithium reacted without combustion. These examples demonstrate the effectiveness of the surrounding water as a heat sink. The rate of dissolution of discrete lithium spheres in water at 20°C under water is described by Eq. 2:

$$r = r_0 - kt \qquad (2)$$

where

r = radius in centimeters of the lithium at any time, t
k = specific reaction rate constant in cm/s

For lithium spheres, k = 0.0036 (Reference 8). Assuming a density of lithium of 0.5, it can be shown that the reaction rate of solid lithium with liquid water is 1.087 mol/m^2-min. It is possible that the relatively low solubility of LiOH in water (5.24 moles per liter of water at 25°C, compared to NaOH of 28.5 mol/l)may be partly responsible for the rather slow lithium/water reaction (Reference 8).

Deal and Svec (Reference 9) studied the rate of the reaction between lithium metal and water vapor from 45.0 to 75.0°C by measuring the pressure of the hydrogen evolved. Values for the weight per unit area of water vapor undergoing reaction were obtained. The reaction can be expressed by Eq. 3:

$$Li + 2H_2O = 2\,LiOH + H_2 \qquad (3)$$

The rate constant was independent of water vapor pressure over a range of 22 to 55 mm. The energy of activation for the reaction was 6.2 kcal/mol for a water pressure of 50 torr and 5.5 kcal/mol for a water pressure of 100 torr. Values of log (water absorption rate, moles/m^2-min) versus 1/T (T in kelvins), for temperatures from 45.0 to 75.0°C are shown in Figure 1.

For water pressure above 55 torr, the reaction rate (mol/m^2-min) can be correlated to temperature T (kelvins) and water pressure, P (torr) by Eq. 4:

$$Log\,(rate) = \frac{1.8951 - 1011.4}{T} + 2.092\left(log\,\frac{P}{50}\right) \qquad (4)$$

A thermogravimetric analysis (TGA) of lithium dispersion in dry argon and in argon with 50% relative humidity is shown in Figure 2 (Reference 10).

From Figure 2, the slope of the curve is 0.279 mg/°C; as the heating rate is 0.67°C/min, the slope is 0.187 mg/min. Since the reaction of lithium with water follows Eq. 3, then 1 mole of lithium reacts to form 1 mole of LiOH, with a weight gain of 17.008 g. Hence the slope of Figure 2 corresponds to 0.0164 x 10^{-3} mol/min. From the lower curve of Figure 1, the mean reaction rate of lithium with water is found to 0.188 mol/m^2-min. Therefore, the effective surface area of the lithium dispersion in Figure 2 is 8.72 x 10^{-5} m^2, or 0.872 cm^2. As subsequently noted in this report, this value of surface area is found to be relevant to rate calculations.

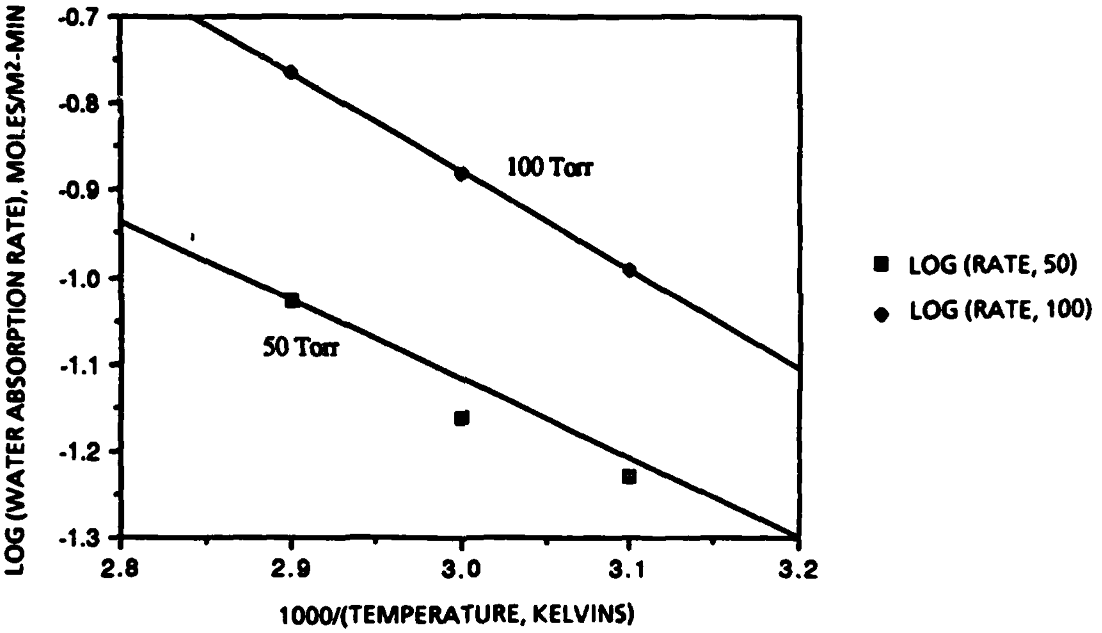


FIGURE 1. Reaction Rate of Lithium With Water Vapor: Log (Rate) Versus 1000/T (Kelvins) (Reference 9).

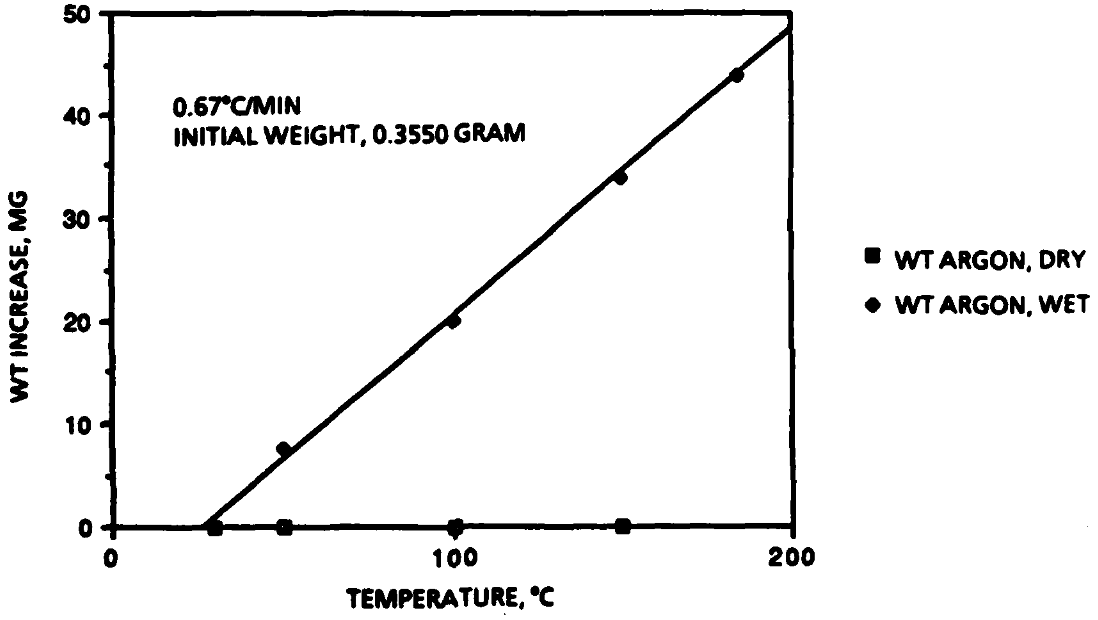


FIGURE 2. TGA of Lithium in Dry and Moist (50% RH) Argon (Reference 10).

IGNITION AND COMBUSTION OF LITHIUM WITH WATER

Lithium at 248°C was ignited by a water spray (Reference 11). Lithium reacts with water but it does not ignite unless the metal is finely divided (Reference 12). Lithium dispersions (average particle size, 22 µm) ignite when put in water, in atmospheres of either air or argon (Reference 8). When solid lithium was exposed to flowing steam, a white coating formed consisting of LiOH, $LiOH{\cdot}H_2O$ and Li_2O. In that experiment, within 5 minutes, the edges of the coating became incandescent. Lithium metal flowed through the cracks in the coating and started to burn brilliantly. The LiOH coating was initially protective; but, as it became thicker and developed cracks, it lost its protective character. The coating functioned as a thermal insulator, allowing the metal to heat to melting and ignition temperature. Beyond the ignition temperature, the reaction became quite vigorous, with hydrogen gas one of the combustion products in the lithium-steam flame (Reference 8). The rates of reaction of lithium with steam were essentially independent of temperature between 400 and 900°C and were found to be 58, 259, and 403 moles Li/m^2-min at steam concentrations in nitrogen of 5%, 15, and 30%, respectively (Reference 13).

PRODUCTS FROM THE REACTION OF LITHIUM WITH WATER

In a study of the reaction of solid lithium with water, a glassy black coat appeared on the lithium surface at the beginning of the reaction; the black coat slowly changed to a white coating of LiOH (Reference 9). In the reaction between water vapor and lithium, the primary products are LiOH and $LiOH{\cdot}H_2O$, which forms in a secondary reaction with water. Above 200°C, Li_2O forms and is practically the only product at temperatures approaching 450°C. At temperatures approaching 400°C, small quantities of LiH are also formed (Reference 14).

When lithium was reacted with water in nitrogen and in air atmospheres, no ammonia was found in solutions of the reaction product; this indicated that, under these conditions, the lithium-water reaction took complete precedence over the lithium-nitrogen reaction (Reference 8).

LITHIUM REACTION WITH OXYGEN

Lithium is highly resistant to oxidation even at elevated temperatures in pure oxygen atmospheres (Reference 1). No reaction of solid lithium in dry oxygen occurs below the melting point (References 1, 15), and lithium dispersions are inert in dry oxygen or air up to 250°C, Figure 3 (Reference 10).

The reaction of liquid lithium with oxygen in the temperature range 210 to 640°C with pressures of 1 to 130 torr showed three regimes. In the first regime, there was a nonsteady reaction. In the second regime the logarithmic rate law was operative, with activation energy of 15.3 kcal/mol. In the third regime, indicating continuous growth of the oxide film, was a linear rate relationship, with activation energy of 15.6 kcal/mol (References 1, 16).

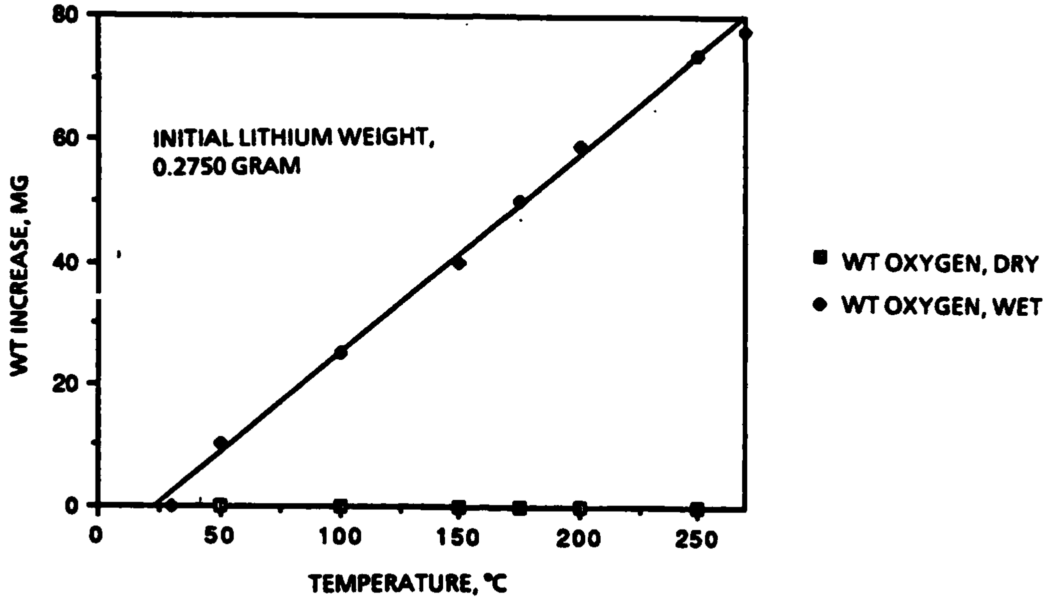


FIGURE 3. TGA of Lithium Dispersion in Dry and Moist (50%) Oxygen (Reference 10).

When solid lithium was exposed to moist oxygen (partial pressure of water, 4.6 torr) at 35°C, a white reaction product formed on the surface; when the lithium was exposed to dry oxygen, the reaction rate ceased (Reference 1). A TGA of lithium dispersion in dry oxygen versus that of oxygen containing 50% relative humidity is shown in Figure 3. As the heating rate is 0.67°C/min, the linear rate of weight increase is 0.483 mg/min. Assuming the reaction follows Eq. 5,

$$4Li + O_2 + H_2O \rightarrow 4LiOH \qquad (5)$$

and that the effective area is 0.8972 cm^2 (see the section, "Reaction Rate of Lithium With Water"), then the reaction rate is 0.232 mol/m^2-min.

The rate of oxidation of lithium is immeasureably low all the way to the ignition temperature (Reference 17); the ignition temperature of lithium in pure oxygen is uncertain; it has been cited at values as low as 190°C (Reference 18) and as high as 630°C (Reference 1). Reynolds reported that lithium ignited in oxygen above the lithium melting point (Reference 19). Grosse and Conway reported that the computed adiabatic combustion temperature of lithium in oxygen at 1 atmosphere is 2600 K (Reference 18).

Little (Reference 17) reported the ignition temperature of lithium in dry oxygen to be 607°C and independent of oxygen pressure from 1 to 300 torr, whereas Tyzak and Longton reported the ignition temperature as a function of oxygen pressure, Figure 4.

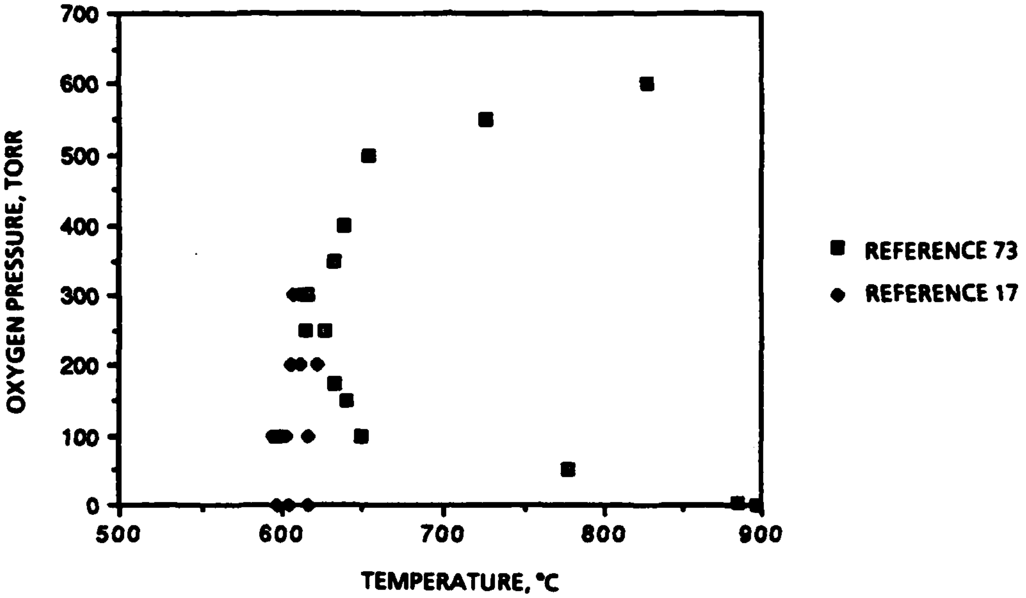


FIGURE 4. Ignition Temperature ofLithium in Oxygen Versus Pressure.

Little reported that the reaction probability (that an oxygen molecule striking the lithium surface would react) is a function of pressure (torr) at 662°C), as expressed by Eq. 6,

$$\varepsilon = \frac{9.0 x 10^{-4}}{P^{0.826}} \qquad (6)$$

where

ε = reaction probability
P = oxygen pressure, in torr

From kinetic theory (Reference 20), the collision frequency of gas molecules against a wall can be expressed as Eq. 7,

$$z = 1.4 x 10^{5} P (MT)^{-0.5} \qquad (7)$$

where

z = collision frequncy, mol/m^2-min
P = pressure, torr
M = molecular weight
T = temperature, K

Little also reported an activation energy for the lithium-oxygen reaction between 880 and 935 K to be 29.5 kcal/mol (Reference 17).

LITHIUM REACTION WITH NITROGEN

RATE AND MECHANISM FOR THE REACTION OF NITROGEN WITH LITHIUM

Solid Lithium

Dispersed lithium did not react when exposed to flowing dry nitrogen at room temperature. At elevated temperatures the reaction rate between lithium and nitrogen depended on the rate of diffusion of nitrogen through the Li_3N layer (Reference 21). The rate of the reaction between solid lithium and nitrogen initially increased with the extent of nitridation, becoming constant after a critical thickness was attained. The temperature coefficient and consequently the activation energy were very small, suggesting that the rate-controlling process was the rate of passage of nitrogen through the porous nitride layer to the reactant Li/Li_3N interface by both streamline and Knudsen flow (Reference 22). An example of the reaction of solid lithium with nitrogen (100°C and 406 torr) is shown in Figure 5 (absorption of nitrogen in mol/m^2 versus time). The absorption of nitrogen is initially nonlinear, then becomes linear, with rate computed to be 0.0357 mol/m^2-min. The initial nitrogen absorption versus time was plotted in logarithmic coordinates, as shown in Figure 6.

A linear regression of the data in Figure 6 showed the relationship between nitrogen absorpsion versus time, as expressed in Eq. 8,

$$\log(N_{abs}) = -4.4583 + 2.215 \log(t) \tag{8}$$

where

N_{abs} = nitrogen absorption, mol/m^2
t = time, minutes

This relationship can be expressed as Eq. 9,

$$N_{abs} = 10^{-4.4583}(t)^{2.215} \tag{9}$$

The reaction rate can be obtained by differentiation of Eq. 9 and expressed as Eq. 10,

$$\frac{d(N_{abs})}{dt} = 7.71 x 10^{-5}(t)^{1.215} \tag{10}$$

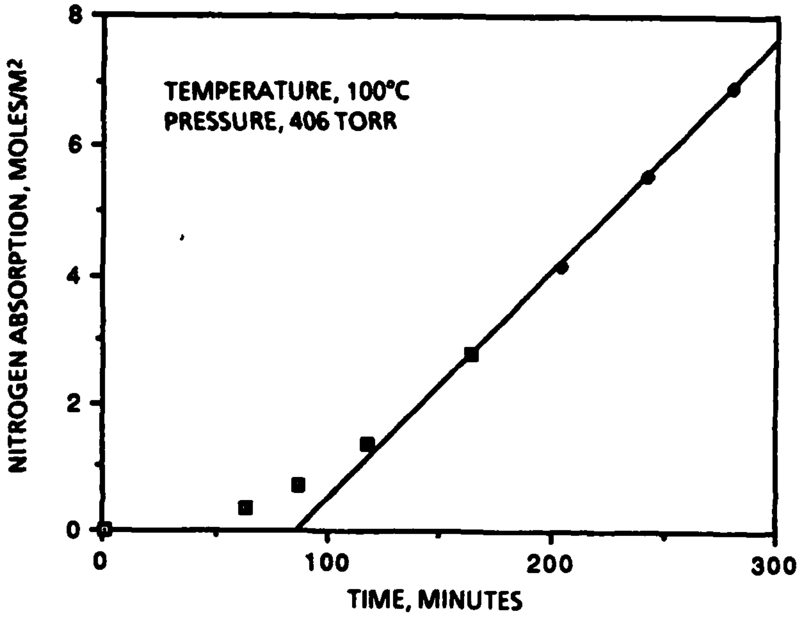


FIGURE 5. Lithium-Nitrogen Reaction: Nitrogen Absorption Versus Time (Reference 22).

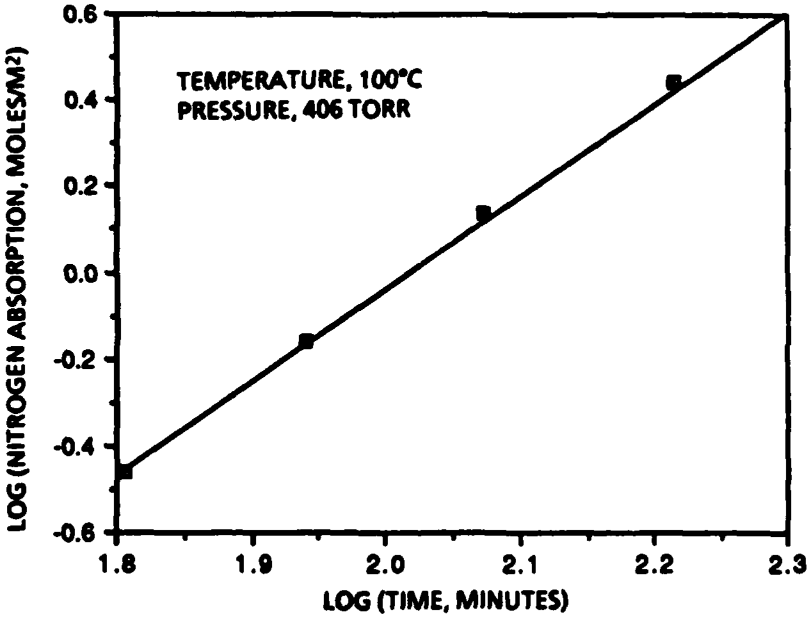


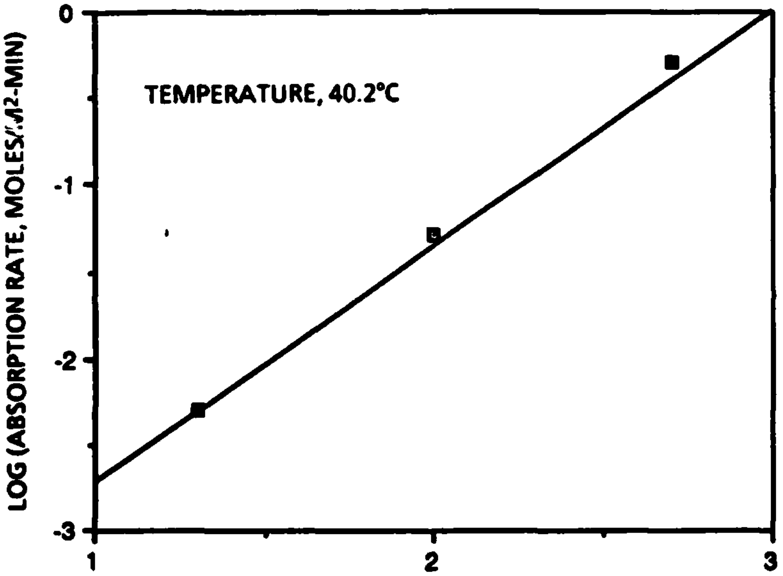
FIGURE 6. Lithium-Nitrogen Reaction: Log (Nitrogen Absorption) Versus (Log) Time (Reference 22).

During this period, a layer of nitride was formed. For the reaction of solid lithium with nitrogen, the reaction rate was essentially temperature-independent between 20 and 160°C, but was dependent upon pressure, as seen in Figure 7. A linear regression of the data of Figure 7 yielded Eq. 11,

$$\frac{d(N_{abs})}{dt} = 7.00 x 10^{-5} P^{1.4307} \tag{11}$$

where

P = pressure in torr



LOG (PRESSURE, TORR)

FIGURE 7. Reaction of Solid Lithium With Nitrogen: Log (Nitrogen Absorption) Versus (Log) Pressure (Reference 22).

Molten Lithium

The activation energy for the reaction of liquid lithium with nitrogen at 295-409°C and 5-20 torr. is Q = 23 kcal/mol (Reference 16). McFarlane and Tompkins (Reference 22) and Addison and Davies (Reference 23) each measured the reaction rate of molten lithium with nitrogen; the results are plotted in Figure 8. In both studies the reaction rate was found to be independent of pressure. The rates are expressed by Eq. 12,

$$\frac{d(N_{abs})}{dt} = 20{,}469\, x\, e^{-\frac{8094}{T}} \tag{12}$$

with an activation energy of 15.5 kcal/mol, and by Eq. 13,

$$\frac{d(N_{abs})}{dt} = 1.156\, x\, 10^{12} e^{-\frac{17{,}446}{T}} \tag{13}$$

with an activation energy of 33 kcal/mol.

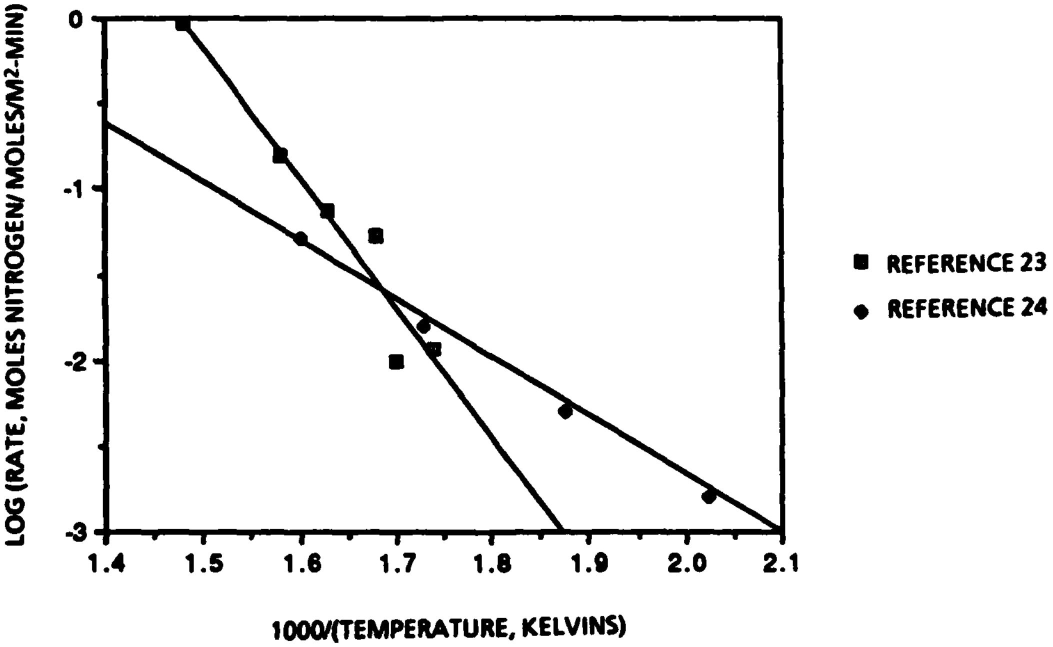


FIGURE 8. Reaction of Nitrogen with Liquid Lithium: Log (Rate) Versus 1000/T(References 23, 24).

In the study of Addison and Davies (Reference 23), the liquid lithium was studied at 400°C by following changes in gas pressure in a closed system. The liquid metal was stirred vigorously. The reaction between nitrogen and liquid lithium took place in three stages in which the rates followed the rectilinear, logarithmic, and parabolic laws successively, and were independent of pressure in the range 350-760 torr (Reference 23).

Gardner and Nishina (Reference 24) determined the reaction rate of nitrogen at the surface of molten lithium in the temperature range 400-500°C. The reaction was pseudo first-order at the surface of molten lithium and in nitrogen pressure. The reaction rate of Eq. 14 was computed from their data,

$$\frac{d(N_{abs})}{dt} = 4286Pe^{-\frac{7475}{T}} \tag{14}$$

where

P = nitrogen pressure, torr
dN_{abs}/dt = moles $(N_2)/m^2$-min

The apparent activation energy for the reaction was 14.9 kcal/mol.

Little (Reference 17) determined the probability, ε, that a nitrogen molecule striking a molten lithium surface would react, and found that

at 367°C, $\varepsilon = 1.13 \times 10^{-4}$
at 485°C, $\varepsilon = 5.23 \times 10^{-4}$
at 602°C, $\varepsilon = 1.49 \times 10^{-3}$

and that each was independent of pressure between 10 and 200 torr. Using Eq. 7 to calculate the collision frequency, the rates were found to be pressure-dependent and expressed by Eq.15,

$$\frac{d(N_{abs})}{dt} = AP \tag{15}$$

where

P = nitrogen pressure, torr
dN_{abs}/dt = moles $(N_2)/m^2$-min
A = a value that depends on temperature; for 640 K, $A = 0.118$; for 758 K, $A = 0.503$; and for 875 K, $A = 1.332$

For this reaction, the activation energy is 11.89 kcal/mol (Reference 17).

A simple model of gas-liquid reactions explained the reactivity of molten lithium with gaseous nitrogen. Chemisorption of nitrogen is followed either by conversion of nitrogen to Li_3N and the dissolving of Li_3N or by dissolving of the nitrogen in the molten lithium, where it reacts to form Li_3N. The reaction proceeds at a constant rate until the liquid lithium is saturated by the Li_3N. At this point a surface layer of Li_3N is formed, and the reaction rate is controlled by mass transport of nitrogen through the emerging crystal lattice of Li_3N (Reference 25).

Another approach assumed that the rate-determining process was the passage of lithium ions from the Li/Li_3N interface through a uniform Li_3N layer (Reference 22). For the unstirred reaction between nitrogen and lithium between 300 and 500°C, the reaction was first order and proceeded in two stages. In the first stage the speed of the reaction increased until a maximum speed was reached. This maximum speed was reached when the nitride layer that had formed on the lithium broke and permitted free passage of the nitrogen to the molten lithium. The second stage proceeded at constant speed since the surface area of lithium exposed to nitrogen remained essentially constant (Reference 26).

INFLUENCE OF MOISTURE OR OTHER MATERIALS ON THE LITHIUM/NITROGEN REACTION

A moisture content greater than 10 ppm increases the rate and extent of reaction of lithium and nitrogen (Reference 1). The presence of a lithium hydroxide film on the metal surface is necessary for lithium-nitrogen reactions (Reference 27) and explains the susceptibility of lithium to low temperature nitridation under moist conditions (Reference 1). A TGA study of lithium dispersions in both dry and moist (50% relative humidity) nitrogen is shown in Figure 9. There was essentially no reaction in dry nitrogen until the lithium melting point, whereas the moist nitrogen reacted with the lithium, beginning at ambient temperatures. Above the melting point of lithium, the moist and the dry nitrogen apparently reacted in a similar manner (Reference 10).

From Figure 9, the slope of weight increase versus temperature for moist nitrogen reaction is 0.203 mg/°C, corresponding to a weight increase of 0.303 mg/min. For the reaction between lithium and nitrogen, Eq. 16,

$$6Li + N_2 \rightarrow 2Li_3N \qquad (16)$$

the weight increase of 1 mole N_2 (28.016 grams) corresponds to its reaction with 6 moles of lithium, or a 1-gram weight increase corresponds to 0.214 mole of lithium. A weight increase of 0.303 mg/min corresponds to a reaction rate of 0.0649 millimole Li/min. As previously seen, the effective area is 0.872 cm^2; hence, the reaction rate is 0.0744 moles Li/m^2-min.

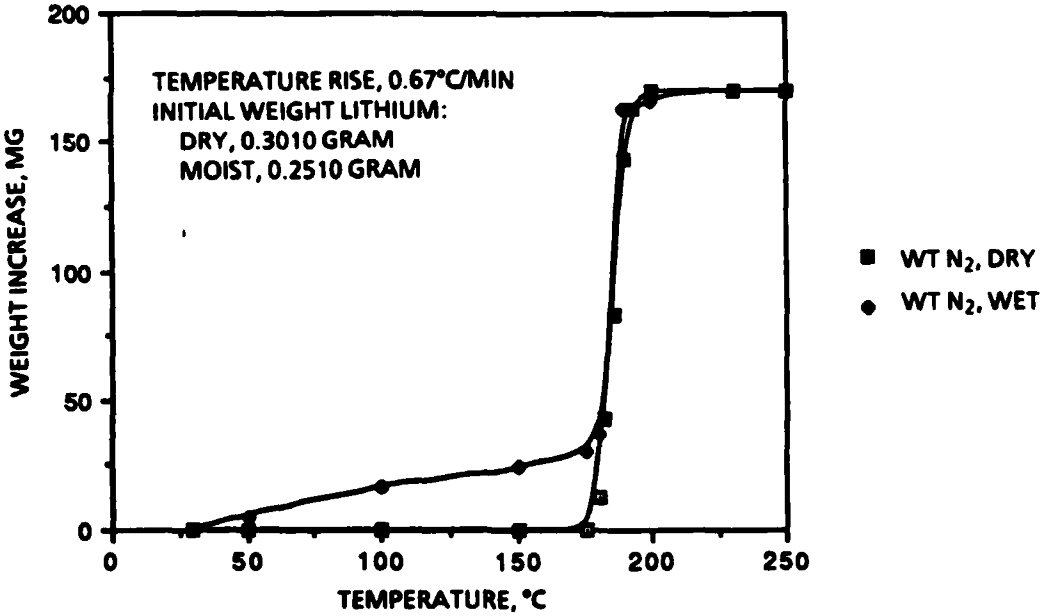


FIGURE 9. TGA of Lithium Dispersion in Dry and Moist (50% RH) Nitrogen (Reference 10).

Klinaev studied the effect of impurities in lithium on the formation of its nitride at 25°C. Addition of 0.18 wt-% potassium to the lithium accelerated the reaction, while 1.13% magnesium or 0.53 wt-% retarded it. The reaction was inhibited by oxygen and hydrogen in the nitrogen, and it was completely prevented by the presence of more than 14 wt-% oxygen or more than 3.5 wt-% hydrogen in the gas (Reference 28).

IGNITION OF LITHIUM WITH NITROGEN

Ignition temperatures for lithium metal in nitrogen are quoted at between 170°C and 450°C (Reference 1). A differential thermal analysis (DTA) curve of lithium metal dispersions in dry nitrogen at a heating rate of 5°C/min shows that reaction occurred around 170°C and was rapid and exothermic (Reference 10). The TGA data of Figure 9 show a rapid rate of weight increase for lithium dispersion in both dry and moist nitrogen at about 170°C, suggesting ignition at that temperature (Reference 10).

Menzenhauer and co-workers measured ignition temperatures of 420 and 600°C of lithium in dry nitrogen, Table 1 (Reference 29).

TABLE 1. Ignition and Combustion of Lithium in Nitrogen (Reference 29).

Property	Experimental designation	
	LN1	LN2
Lithium mass, grams	103.5	113.5
Surface area, cm^2	196	196
Ignition temperature, °C	420	600
Burning duration, minutes	21	12
Burn rate, moles(Li)/m^2-min	36	67
Maximum temperature, °C	830	820
% Li reacted	75.2	55.6
% Li in aerosol	0	12
% Li in residue	100	88

Rhein found that, when lithium was heated in nitrogen, the lithium melted first, and the ignition temperatures measured were 388 and 410°C (References 30, 31).

COMBUSTION OF LITHIUM WITH NITROGEN

The combustion of lithium with nitrogen is depicted in Figure 10. The peak in the curve of the reaction rate as a function of temperature is fixed by the balance between the increasing forward reaction of Eq. 16 and the decreasing equilibrium constant with increasing temperature. Measurements of lithium-nitrogen rate, Figure 11, confirm this view.

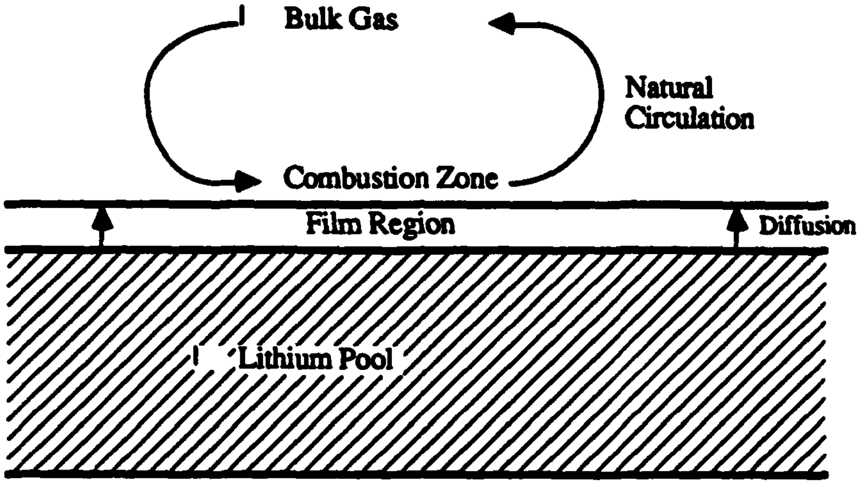


FIGURE 10. Lithium-Nitrogen Combustion Zone Geometry (Reference 32).

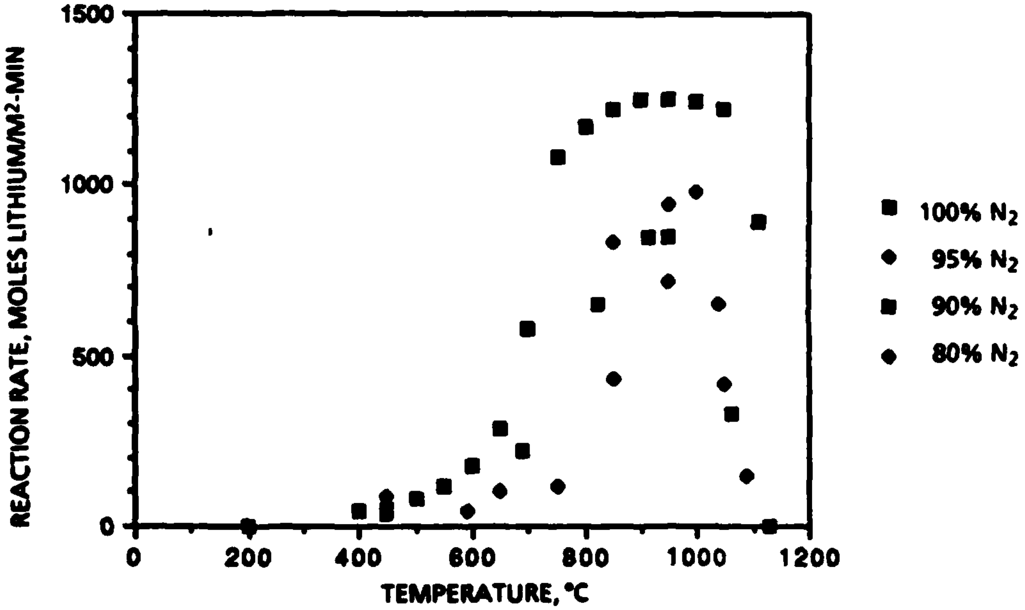


FIGURE 11. Reaction Rate of Lithium With Nitrogen in the Presence of Oxygen (Reference 13).

In the combustion zone, the composition of the film region is considered a mixture of nitrogen and lithium vapor. The thermal emissivity of the combustion zone is about 0.1. If it is assumed that the combustion zone is extremely thin, the flames may not be luminous and therefore may be opaque grey bodies, based on the existence of macroscopic product aerosols. Lithium emits primarily at its discrete rotational/vibrational lines, most of which lie between 8708 and 2302 angstroms; otherwise, the vapor is essentially transparent. If the combustion zone emits only at characteristic lines, then the pool should be strongly absorbing at those same lines, suggesting that the combustion zone should radiatively couple well with the pool, but not necessarily with the gas (Reference 32). Based on the experimental observation of violent churning in the pool, the turbulence in the combustion zone results in substantial heat and mass transfer. Since gases are being consumed in the combustion zone, mass transfer of nitrogen results from the vacuum left when nitrogen reacts to form solid Li_3N. The heat transfer in this combustion process is primarily radiation rather than convection. It was assumed that combustion is suppressed below the melting point of lithium (180.54°C) or above 1025°C, where Gibb's free energy implies a preferred reverse direction for the reaction between lithium and nitrogen (Eq. 16, Figure 12).

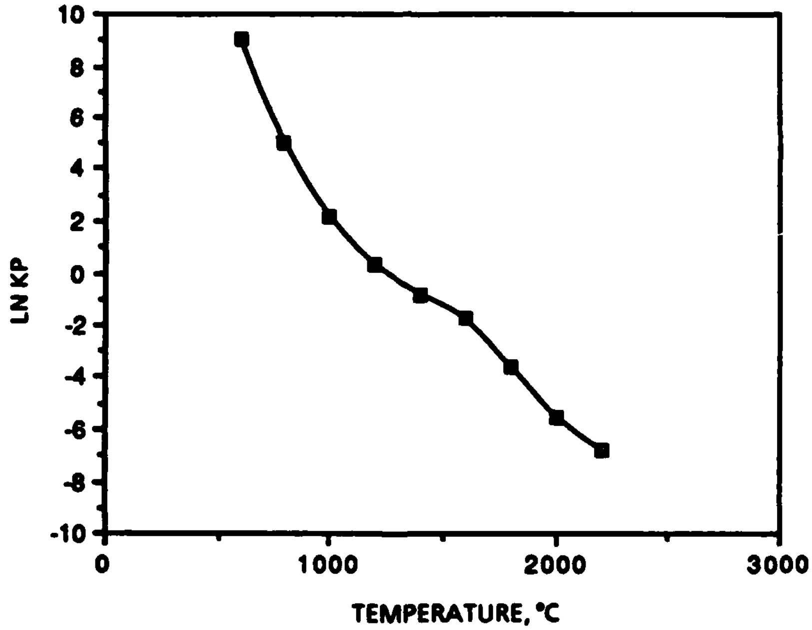


FIGURE 12. Equilibrium Constant for the Reaction: $6Li + N_2 \rightarrow 2\,Li_3N$ (Reference 32).

The reaction rate of lithium with nitrogen was determined in pure nitrogen and in nitrogen-oxygen mixtures, using a lithium pool 10.16 centimeters in diameter (0.0081 m^2), containing about 50 grams of lithium. Reactant gas velocity was calculated to be approximately 2.9 cm/s. The results are presented in Figure 11.

Upon ignition in nitrogen, temperatures around 600°C were reached in less than 1 minute with a 0.26-gram lithium dispersion sample (Reference 1). The TGA of lithium dispersion in moist (50% relative humidity) and dry nitrogen (Figure 9) shows a region of very rapid weight increase; this region can be assumed to be lithium combustion in nitrogen. For the rapid weight increase region for dry nitrogen, the slope is 10.14 mg/°C, or 3.239 m-moles Li/min, from which the reaction rate is computed to be 37.14 moles Li/m^2-min. For the rapid weight increase region in moist nitrogen, the corresponding reaction rate is 49.85 moles Li/m^2-min. Menzenhauer and co-workers studied the combustion of lithium in dry nitrogen (Table 1), and found burn rates of 36 and 67 moles Li/m^2-min and combustion temperatures of 830 and 820°C. No aerosol was produced in one experiment (LN1), and only 12% was produced in the other (LN2) (Reference 29).

In another example, 10 kg of lithium at 542°C were added to a preheated pan (0.20-m^2 surface area) in an atmosphere of $<$0.5% oxygen, 48.7% helium, and the remainder nitrogen. The lithium reacted mildly with the nitrogen in this atmosphere, producing a maximum lithium pool temperature of 565°C. The maximum lithium consumption rate was 29.8 mol/m^2-min. No flames were produced (Reference 11). The lithium-nitrogen reaction rate was hindered by the formation of a lithium nitride layer on top of the molten lithium pool. The reaction rate followed the parabolic rate law, suggesting that the reaction rate was limited by the diffusion of nitrogen through lithium nitride. The reaction rate decreased more over time, presumably as the nitride layer became thicker. The reaction products from the lithium-nitrogen experiments were observed to be a hard black ceramic lithium nitride, deposited on the bottom of the reactor, and not observed as an aerosol (Reference 13).

COMBUSTION OF LITHIUM IN NITROGEN IN THE PRESENCE OF WATER

The reaction rates of lithium with nitrogen were measured at elevated temperatures in the presence of 5, 15, and 30% steam. The lithium-nitrogen reaction rates versus lithium temperature in the presence of steam are presented in Figure 13.

It was found that at lower temperatures the water vapor acted as a catalyst and actually served to increase the lithium-nitrogen reaction rate to a level above that observed during the reaction of lithium with pure nitrogen. The catalytic effect was greatest at low temperatures and was relatively independent of the concentration of the water vapor, indicating that only a very small amount of steam is needed to cause this catalytic increase in reaction rate. The catalytic factor (i.e., the ratio of the reaction rate of lithium with nitrogen in the presence of steam to the reaction rate of lithium with pure nitrogen) is shown in Figure 14.

The curve fit to the plot showed a decrease in the catalytic effect with increasing temperature, until the reaction was controlled only by the flow rate. The steam reaction rates were relatively constant with temperature, as they were not subject to kinetics limits but were limited only by the the flow rate of the incoming steam. The chief reaction product was lithium nitride, but the secondary reaction product was a white aerosol, believed to be either lithium oxide or lithium hydroxide. (Reference 13).

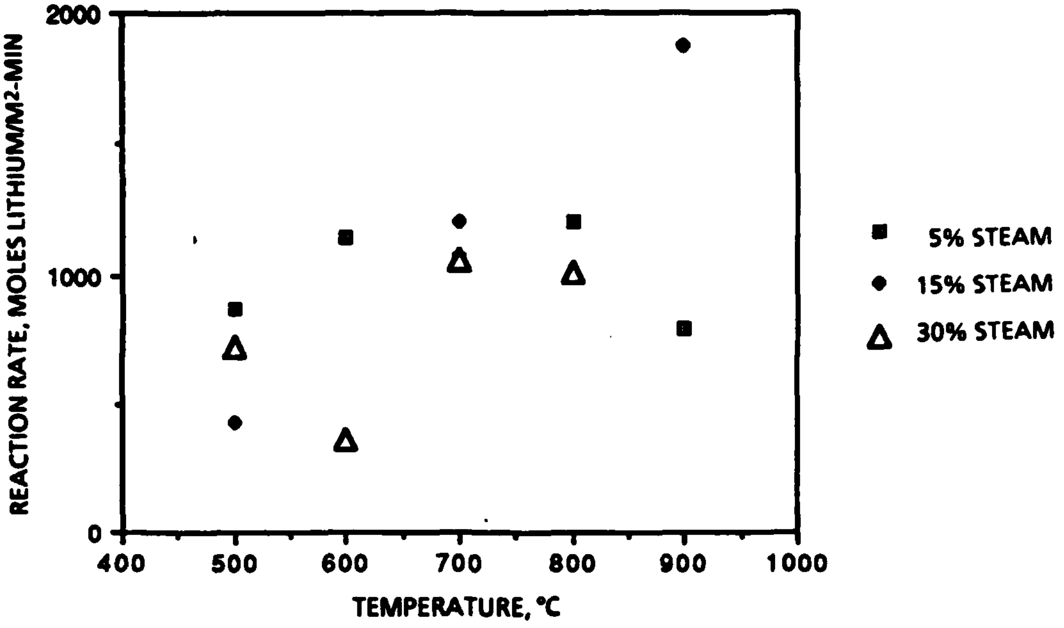


FIGURE 13. Lithium-Nitrogen Reaction Rate in the Presence of Steam (Reference 13).

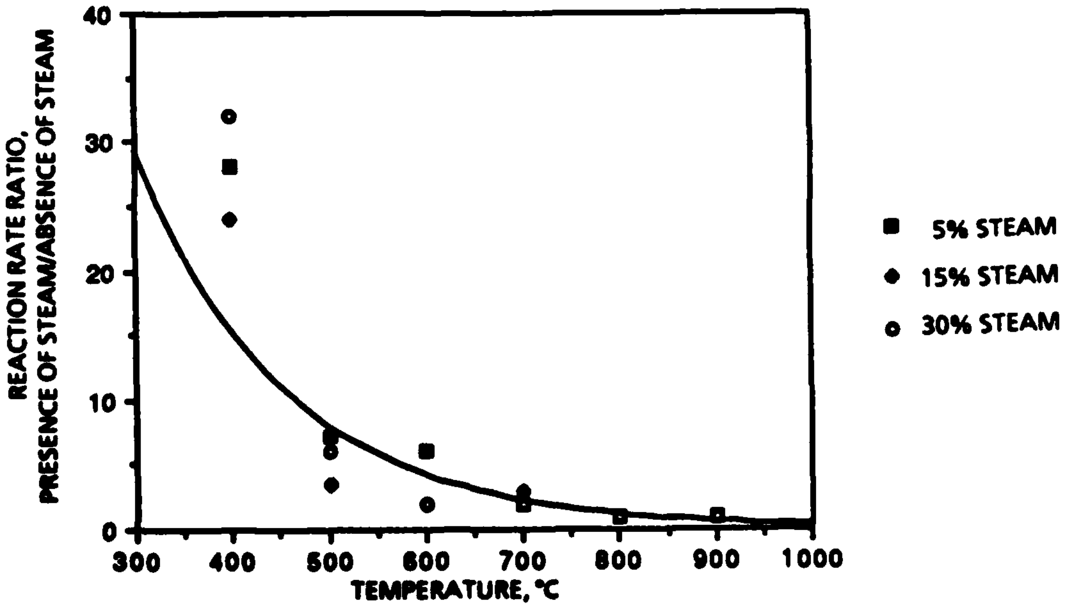


FIGURE 14. Ratio of Lithium-Nitrogen Reaction Rate in the Presence of Steam/Absence of Steam (Reference 13).

LITHIUM REACTION WITH OXYGEN-NITROGEN MIXTURES, INCLUDING AIR

OXIDATION IN AIR

Lithium tarnishes on exposure to air, but at the slowest tarnish rate of the alkali metals (Reference 15), particularly in dry air (Reference 5). The rate of reaction of lithium with air increases in the presence of additives (sodium, potassium, aluminum) (Reference 33). Lithium is highly resistant to oxidation even at elevated temperatures in dry air atmospheres (References 1, 15). Markowitz and Boryta reported that 0.2 gram of lithium dispersion, 100-150 mesh, did not gain weight when exposed to flowing dry air at room temperature for a week or when heated to 200°C, Figure 15 (Reference 10).

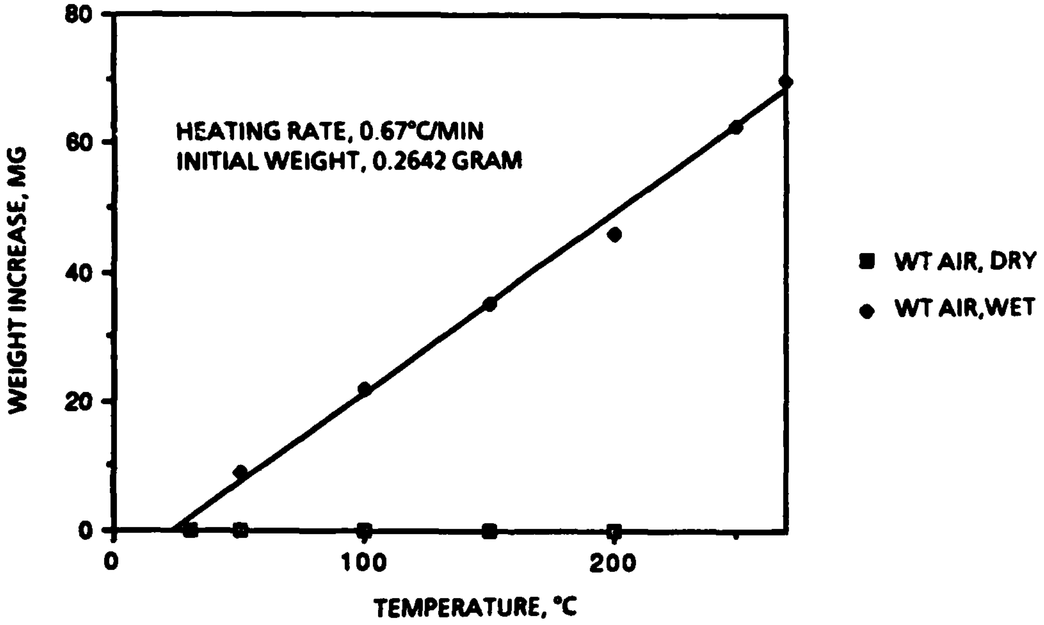


FIGURE 15. TGA of Lithium Dispersion in Dry and Humid (50% RH) Air (Reference 10).

Lithium in contact with water is a very strong reducing agent (Reference 5). The reaction of lithium with air is intensified by raising the humidity of air (Reference 33). Freshly prepared lithium surfaces exposed to 50-70% humidity in either air or argon darkened 10-30 times as fast as similar surfaces that were kept several hours in air of about 1% humidity at 20°C (Reference 34). In the presence of moisture, lithium hydroxide and carbonate are formed from the reaction of lithium with air. At a relative humidity <80%, primarily lithium nitride is formed (Reference 33). Besson and Muller stated that the black layer formed on lithium on exposure to air is the hydroxide arising from atmospheric humidity (Reference 27). In dry air, lithium remains untarnished, but in moist air its surface becomes coated with a mixture of LiOH, $LiOH \cdot H_2O$, Li_2CO_3, and Li_3N (Reference 12). Although liquid lithium will not react with oxygen in air at its melting point in the absence of water, trace amounts of moisture (10 to 15 ppm) will cause lithium to react with air at room temperature (Reference 10). The TGA of lithium dispersion in dry air (showing no reaction) versus the TGA in air with 50% relative humidity is shown in Figure 15. The rate of weight increase was 0.416 mg/min.

IGNITION IN AIR

There is much disagreement in the literature as to the ignition temperature of lithium in air, and values between 180°C and 640°C have been reported. 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. Solid lithium is not easy to ignite; even a small piece must be heated for some time before a sustained reaction takes place (Reference 1).

A wide variety of values have been reported for the ignition temperature of lithium in air. Bulk solid lithium at room temperature does not burn spontaneously in air; it can be heated to the melting point in air without inflammation (Reference 1). However, it was also reported (Reference 15) that, if lithium is heated above 180°C, it burns brilliantly in air and that the lithium ignition temperature is 200°C (Reference 33). Reported in one study was that molten lithium did not spontaneously ignite in dry air at temperatures up to 400°C, and that spontaneous ignition took place with pure metallic lithium (Reference 1) at temperatures over 600°C (around 640°C). Rogers and Everson reported that lithium exposed to normal atmospheric conditions did not ignite at 282°C, but also reported that a 450-gram lithium fire ignited at 260°C and that 100 grams of lithium ignited at 316°C (References 35, 36). Spilled lithium at 80 psig and 550°C caught fire immediately (Reference 4). Rhein measured the ignition temperature of lithium in air as 355 and 393°C (Reference 37). Menzenhauer and Sonntag measured the ignition temperature of lithium in air (Table 2); ignition occurred slightly above 400°C, and the mean ignition temperature was 450 ± 88°C (Reference 29). In air at 0.1 atmosphere pressure, in a mixture of 50% Ar/50% air, and in 90% Ar/10% air at atmospheric pressure, lithium did not ignite even when heated to 427°C (References 34, 36).

The ignition is often determined by the character of the reaction product crust formed by the oxidizing reaction. Malet and co-workers reported an ignition temperature of lithium in air of 445°C. In this study, nodulation appeared at temperatures above 445°C, and the surface of the metal transformed slowly, appearing warped and displaying yellow spots. Ignition appeared at these spots on the surface and spread to the whole mass of metal. A very hard residue in the form of cauliflower remained (Reference 38). Combustion began promptly if a piece of cold, coral-like residue was dropped into molten lithium at temperatures as low as 200°C. Other materials (asbestos, sand, iron oxide) did not initiate combustion likewise. Without the coral-like compound, hot liquid lithium may be stirred, poured, and handled in air without igniting (Reference 1).

TABLE 2. Ignition and Combustion of Lithium in Air (Reference 29).

Property	Experimental designation						
	LL1,2[a]	LL3	LL4	LL7	LL8	LL9, 10[a]	LL5,6[a]
Lithium mass, grams	103.1	102.8	104.4	51.4	49	102.2	101.9
Surface area, cm^2	196	196	196	196	196	81	196
Ignition temperature, °C	405	640	480	400	400	420	405
Relative humidity, %	81	85	78	88	79	86	23
Burning duration, minutes	11.5	8	9	9	11	15	12
Burn rate, moles(Li)/m^2-min	66	94	70	101	79	126	64
Maximum temperature, °C	1060	1080	1060	1070	1020	1065	1060
% Li in aerosol	22	27	18	25	—	23	70
Aerosol composition, wt-%							
Li_3N	1	1	1	1	1	1	1
Li_2O_3	1	1	1	1	1	1	1
Li_2O	20	31	53	11	19	8	62
LiOH	78	67	45	87	79	90	36
% Li in residue	78	73	82	75	—	77	30
Residue composition, wt-%							
Upper layer							
Li_3N	1	1	1	1	1	1	1
Li_2O_3	1	1	1	1	1	1	1
Li_2O	75	72	84	41	56	64	81
LiOH	11	7	8	39	31	16	8
Middle layer							
Undetermined	6	7	3	2	7	12	11
Li_3N	8	6	1	15	5	23	6
Li_2O_3	1	1	1	1	1	1	1
Li_2O	79	84	93	43	85	63	72
LiOH	6	9	2	2	39	1	1
Lower layer							
Undetermined	12	7	12	5	22	12	9
Li_3N	66	16	6	6	3	22	9
Li_2O_3	1	1	1	1	1	1	1
Li_2O	67	73	80	87	90	53	80
LiOH	4	3	1	1	1	1	1

[a] Average of two experiments.

Ignition of Streams of Liquid Lithium

Molten lithium at either 370°C or 675°C was ejected through a 1/4-inch nozzle into a heated chamber and a heated catch pan. There was no ignition of the stream, and the metal did not ignite in the catch pan. A dark grey to black coating formed on the stream during ejection. In another test, about 4.5 kg of lithium at 540°C was ejected under normal atmospheric conditions. The surface of the stream turned black during the run, but there was no ignition of the stream. This is probably due to a protective coating of oxides and nitrides that forms on the surface upon exposure to the atmosphere. However, when the stream hits a surface and is spread into a thin layer, ignition may occur (Reference 36). Maroni and co-workers described a lithium leak in the Lithium Processing Test Loop, where the lithium was at 80 psig and 550°C. This leak spilled about 20 gallons of lithium; the spilled lithium caught fire immediately (Reference 4).

Effect of Moisture on Ignition of Lithium in Air

When a sufficiently large mass of lithium is exposed to humid air for an extended time, it can catch fire; such accidents have been observed in industry (Reference 7). For example, 45 kg of lithium, surface area 0.55 m^2, did not ignite at 232°C. However, when water was sprayed on the surface, it spontaneously ignited and burned. A pool of 10 kg of liquid lithium with exposed area 0.20 m^2 at 248°C did not react spontaneously in air containing 0.008 gram water per gram air. A lithium pool of the same size at 539°C did react spontaneously with moist air of higher humidity (0.025 gram water per gram air), and burned with a yellow-red flame (Reference 11).

TEMPERATURES RESULTING FROM THE COMBUSTION OF LITHIUM IN AIR

Dry Air

When a 40-gram sample of lithium was ignited, it attained a flame temperature of 1350°C (Reference 67). In a study of the combustion of about 50 and 100 grams of lithium in air, presented in Table 2, the maximum temperature ranged from 1020 to 1070°C, and the mean burning temperature was 1059 ± 19°C (Reference 29). When a 100-gram sample of lithium was heated, it ignited and gave a maximum flame temperature, above the combustion vessel, of 771°C; and the flame temperature of a 450-gram lithium fire reached 970°C (References 35, 36). Lithium, 22.7 kg, preheated to 232°C, added to a pan of surface area 0.55 m^2, spontaneously ignited and burned; a maximum pool temperature of 1040°C (Reference 11) and flame temperatures of 1260°C were measured (Reference 4). A lithium leak spilled about 20 gallons of lithium, which caught fire immediately; the temperatures in the burning pool were estimated to be in excess of 1000°C (Reference 4).

It was found that experimental results from an 45-gram lithium fire could not be extrapolated to larger fires since the fire could be self-extinguishing and the flame temperature could be 316 to 427°C lower than that of a large fire. Fires of 450 grams of lithium were not self-extinguishing, but the flame temperatures were 150 to 200°C lower than those of the larger fires. Flame temperatures were the same for 4.5- and 45-kg lithium fires (Reference 36).

Moist Air

The combustion reaction of liquid lithium in air is inhibited by the presence of moisture. When 10 kg of lithium in a liquid pool (with an exposed surface area of 0.20 m^2) burned in the presence of moist air (0.008 gram water per gram air), the pool temperature increased to 1060°C and the peak flame temperature was 1150°C at a point 1.5 cm above the pool surface. When a lithium pool of the same size burned in moist air of higher humidity (0.025 gram water per gram air), the pool temperature increased to 1100°C, but the flame temperature peaked at only 890°C, measured 1.5 cm above the pool surface (Reference 11).

Barnett and Kazimi modified the LITFIRE code to model lithium chemical reactions with steam-air mixtures, and found that the effect of adding steam was to raise the emissivity of the combustion gas (and thus the gas temperature and pressure), while reducing somewhat the temperatures of both the lithium combustion zone above the pool of molten lithium and the temperature of the pool itself (Reference 39).

DESCRIPTION OF THE COMBUSTION OF LITHIUM IN AIR

In a study of lithium combustion, the lithium melted first, and the combustion appeared to be in the vapor phase (Reference 37). The combustion of lithium in air was seen to be irregular, with combustion intensity bursts superimposed on a steadily increasing combustion intensity (Reference 30). In lithium combustion, the flame or fire zone is usually confined to a porous, coral-like growth of lithium nitride/oxide which floats on the liquid metal and acts as a catalyst and a wick. Free metal is drawn into the lithium nitride/oxide by a wicking action for the combustion reaction. This wicking action of the lithium nitride/oxide is an important mechanism in lithium combustion (Reference 35). Once initiated, combustion slowly spreads across the molten metal surface through a lateral growth until the entire exposed surface is taken up by the combustion process.

In one study, expansion from a pea-sized fire to a burning area of 2 to 3 ft^2 took 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 rose to an asymptote around 400°C. A large temperature gradient existed across the burning layer, since surface temperatures around 800°C were observed (Reference 1). The rate of reaction of lithium with oxygen in air to form lithium oxide appeared to be controlled by diffusion through the nitrogen, and it can be presumed that the combustion zone is an oxygen-poor environment compared to ambient air. Very slight drafts of air greatly accelerated the rate of combustion, but a stream of nitrogen directed onto a burning surface did not accelerate the combustion rate appreciably.

The proportion of oxide to nitride 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 (Reference 1). The spread of flame across the liquid metal is normally not rapid (References 1, 4). A large temperature gradient exists between the combustion zone and the ambient air, and also between the combustion zone and the liquid lithium pool. If some combustion occurs outside the boundary of an idealized, infinitely thin combustion zone, then the true temperature at the reaction site would not be as high as predicted (Reference 32).

Explosive oxidation of lithium can occur if lithium is burned in air of high humidity (>90% RH). When a small cube (1 to 6 mm^3) of lithium was heated with a bunsen flame, either "normal" or "explosive" oxidation was observed. In the case of "normal" oxidation, the lithium melts and catches fire, burning with a scarlet flame. The mass of burning metal may become white hot as the reaction proceeds, and the scarlet flame may not be seen, but no sputtering or explosion occurs. In the case of "explosive" oxidation, the metal melts and catches fire (scarlet flame) and begins to glow red-hot, and if glowing white hot spots within the mass of burning metal are seen, an explosion takes place within about 3 seconds. The molten, burning metal behaves as if there were a sudden evolution of gas within the melt, and white-hot, burning droplets of material are flung over a wide area. The explosions may well have been caused by the formation of a very tough, thermally insulative shell of LiOH or $LiOH \cdot H_2O$ when the lithium is heated in a very humid atmosphere. Extremely high temperatures are reached inside the thermally insulated shell; and, if the temperature and pressure rise sufficiently, an explosive sputtering reaction can occur (Reference 40).

Dube and co-workers developed a lithium combustion model (LITFIRE) to describe the physical and chemical processes that occur during a hypothetical lithium fire (Reference 41). It was determined using LITFIRE that the reaction rate is limited not by lithium vapor diffusion to the combustion zone, but by convection of reactive species in the gas to that zone (Reference 32).

Lithium imparts a crimson color to a flame. When the metal burns strongly, the flame is dazzling white (References 1, 15, 29), and the reaction of lithium vapor with air forms an intense white flame (Reference 42) that is brighter than any of the other alkali metal fires (Reference 36). Combustion of lithium is accompanied by emission of dense, white, opaque fumes, which tend to mask the seat of the fire (References 1, 29).

Consumption of Lithium

In a study of the combustion of lithium (approximately 50 to 100 grams) in air, presented in Table 2, the burn rate varied from 64 to 126 moles Li/m^2-min; the mean burning rate was 74 ± 26 moles Li/m^2-min, with the lowest burn rate in the low-humidity experiments (Reference 29). Lithium (45 kg) was reacted with a large quantity of air (340 m^3) in a pan of surface area 0.55 m^2. Air was ventilated through at the rate of 175 m^3/min. The maximum consumption rate of lithium over an 0.5-hour period was approximately 100 mol/m^2-min (Reference 11).

Consumption of Oxygen

A 10-kg quantity of lithium was burned in a pool with an exposed surface area of 0.20 m^2 in air, with a humidity of 0.008 gram water per gram air. The oxygen consumption versus time is shown in Figure 16.

The initial consumption rate for oxygen was 13.1 mol/m^2-min (Reference 11). The combustion of lithium was studied in air having a humidity of 0.025 gram water per gram air. The consumption of oxygen versus time is shown in Figure 17. The initial rate of consumption of oxygen was 15.2 mol/m^2-min (Reference 11). The reaction rates of lithium with oxygen in air

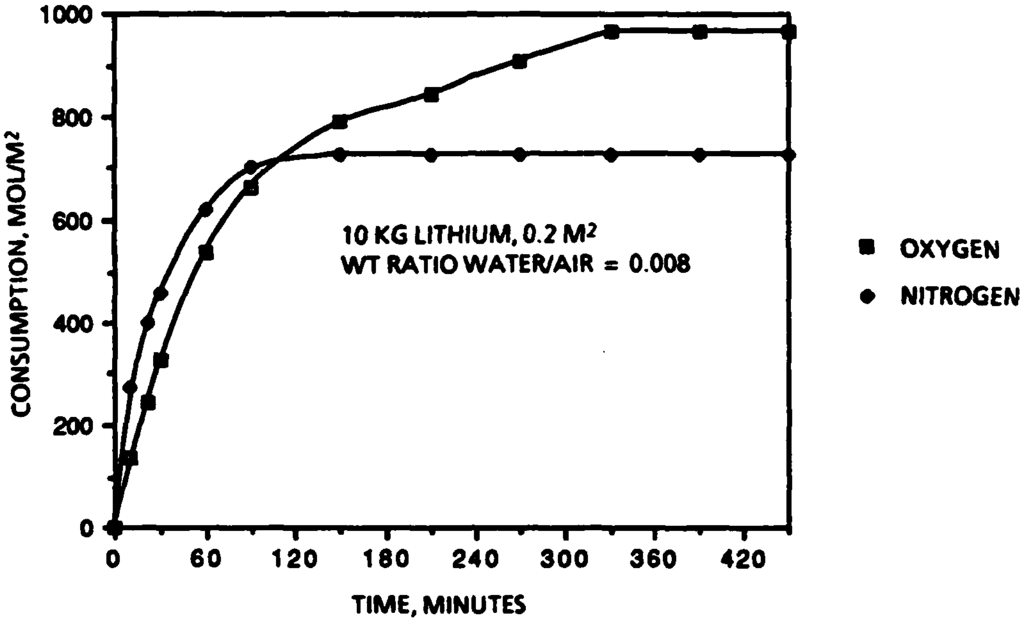


FIGURE 16. Lithium Combustion in Air: Nitrogen and Oxygen Consumption Versus Time (Reference 11).

containing steam were found to be fairly constant between 400 and 800°C, with average values shown in Table 3.

Consumption of Nitrogen

A 10-kg quantity of lithium was burned in a pool with an exposed surface area of 0.20 m^2 in air with humidity of 0.008 gram water per gram air. The nitrogen consumption versus time is shown in Figure 16. The initial consumption rate for nitrogen was 26.8 mol/m^2-min (Reference 11). The combustion of lithium was studied in air with a humidity of 0.025 gram water per gram air. The consumption of nitrogen versus time is shown in Figure 17. The initial rate of consumption of nitrogen was 5.02 mol/m^2-min. (Reference 11).

As seen in Figure 11, the presence of oxygen in nitrogen hindered the rate of reaction between lithium and nitrogen. As the oxygen content increased, the lithium-nitrogen reaction rate decreased relative to the reaction rate of lithium in pure nitrogen. The effect was not as great at temperatures below about 700°C, as the rate of reaction of lithium with oxygen is relatively low at temperatures below 700°C. At temperatures above 800°C, the lithium-nitrogen reaction was quite vigorous and competed with the lithium-oxygen reaction rate.

Experiments were performed with air-steam mixtures with 5% and 15% steam to determine the effect of the presence of both oxygen and steam on the rate of the lithium-

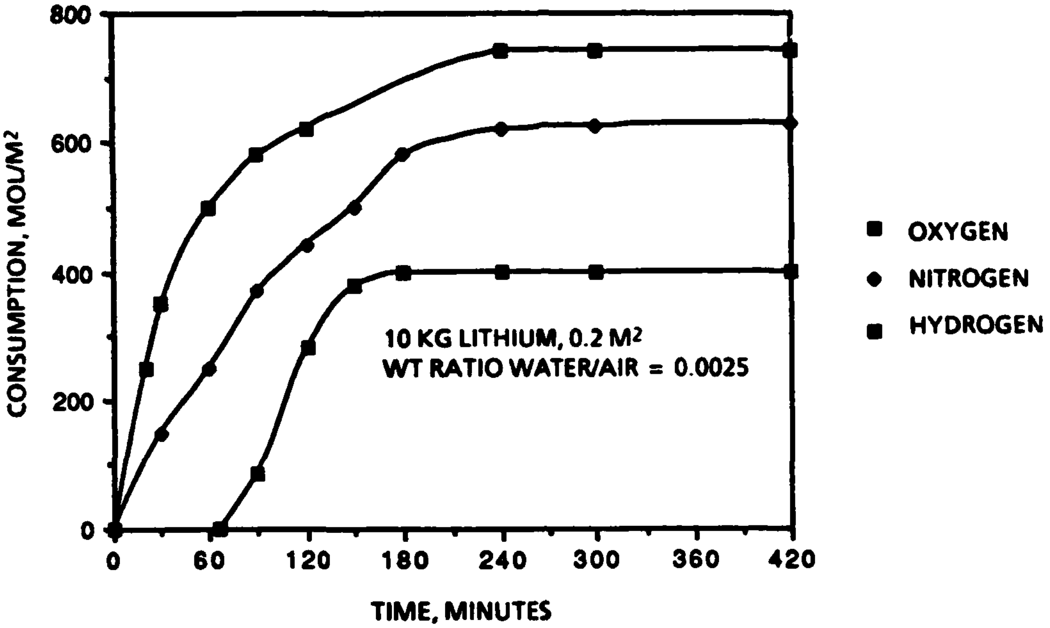


FIGURE 17. Lithium Combustion in Moist Air; Nitrogen and Oxygen Consumption, Hydrogen Production Versus Time (Reference 11).

TABLE 3. Reaction Rates of Lithium with Steam and With Oxygen (moles Li/m^2-min) (Reference 13).

Steam content, %	Reaction rate of lithium with steam	Reaction rate of lithium with oxygen
5	17.3	251
15	173	203

nitrogen reaction. The results are shown in Figure 18. It was observed that the presence of water vapor tended to negate the hindering effect of the oxygen—the reaction rates at low temperatures were slightly higher than the pure nitrogen reaction rates, yet they were lower than the reaction rates measured in the absence of oxygen. In these experiments, the lithium-nitrogen rates in the presence of oxygen and water were higher than these rates in pure nitrogen, but lower than those in the nitrogen-steam systems. Figure 19 is a plot of the ratio of the reaction rate of lithium and nitrogen in the air-steam system to the reaction rate of lithium with pure nitrogen.

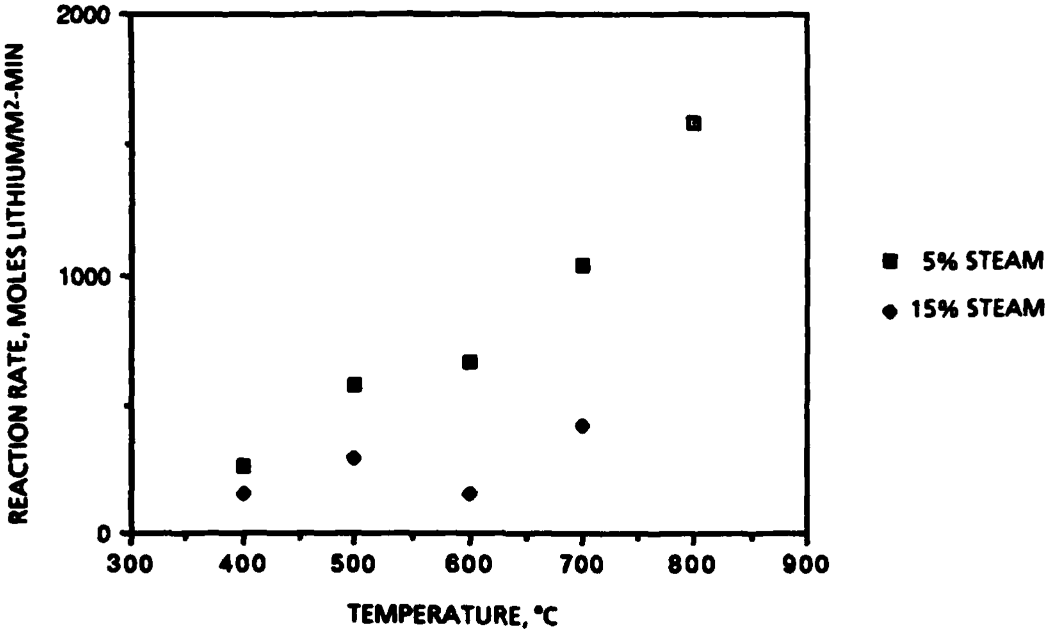


FIGURE 18. Rate of the Li-N_2 Reaction in the Presence of Air and Steam (Reference 13).

Observed in this system was that the catalytic factor decreased exponentially with increasing temperature. As the steam content increased, the lithium-nitrogen reaction rate decreased, possibly indicating that, in addition to catalyzing the nitrogen reaction, the steam was also competing with the nitrogen for the available lithium.

Consumption of Water

The combustion of lithium was studied in air with a humidity of 0.025 gram water per gram air. In this experiment, hydrogen was produced from water consumption. The production of hydrogen versus time is shown in Figure 17. The rate of production of hydrogen at 66 minutes into the run was 3.005 mol/m^2-min (Reference 11). The reaction rates of lithium with steam in air containing steam were found to be fairly constant between 400 and 800°C, with average values shown in Table 3.

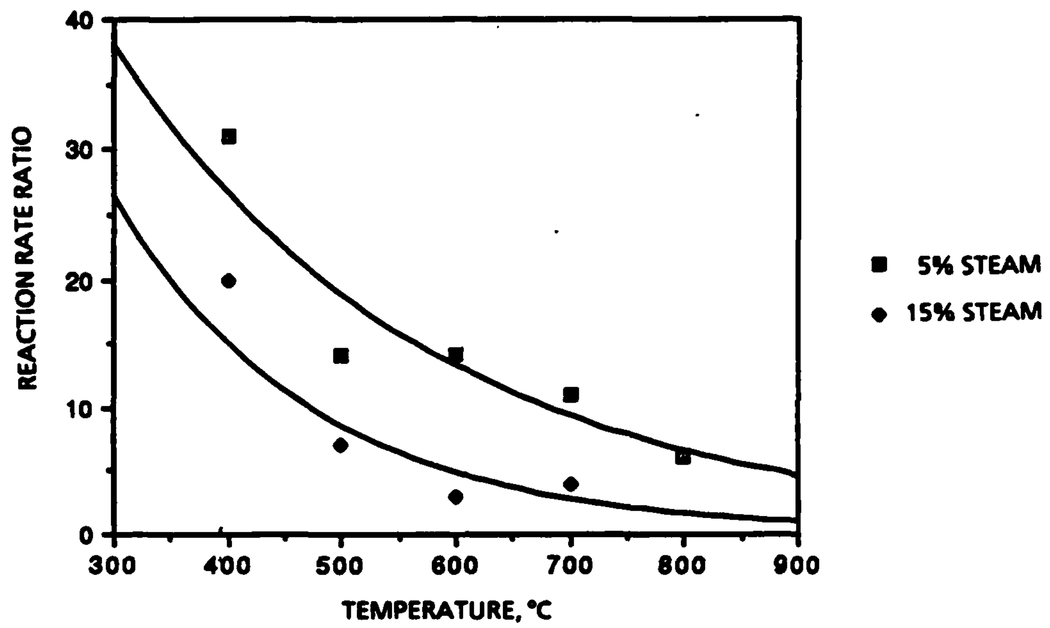


FIGURE 19. Ratio of the Reaction Rate of Lithium With N_2 in the Presence/Absence of Air and Steam (Reference 13).

REACTION PRODUCTS FROM COMBUSTION IN AIR

The reaction products from lithium combustion in a pool fire generally consist of a residue and an aerosol smoke. In this presentation, the composition of the residue is considered first, followed by a discussion of the aerosol composition.

Combustion Residue

Liquid lithium is found to react exothermically both with constituents of air (oxygen and nitrogen) and with moisture. The reaction products that remain at the reaction site are usually found to consist of equal parts lithium nitride and lithium oxide (Reference 4). In the combustion residue of lithium are found small quantities of peroxide, with monoxide primarily present (Reference 43). The residue is often colored, resulting from the presence of colloidal metal in the solid reaction products (Reference 44).

The reaction products from the lithium-nitrogen-oxygen experiments included a hard black ceramic lithium nitride, deposited on the bottom of the reactor, and not observed as an aerosol. At high temperature and with high oxygen content, the nitride was porous and cracked. The other reaction product was lithium oxide, a white powdery substance found on the top of the nitride or as an aerosol. At lithium reaction temperatures greater than 900°C, the oxide was nearly absent on the lithium pool, but deposited in the upper portions of the reactor; hence, lithium oxide tends to be generated as an aerosol at high temperatures (Reference 13).

Rhein (Reference 45) torch-heated lithium powder open to the atmosphere until the lithium ignited. The reaction product after the combustion was completed was analyzed and compared to the lithium metal prior to ignition, as shown in Table 4 (Reference 45).

TABLE 4. Analysis of Lithium Before and After Combustion in Air (Reference 45).

Substance	Quantity before combustion, millimoles		Quantity after combustion, millimoles	
	Experiment 1	Experiment 2	Experiment 1	Experiment 2
Lithium metal	7.58	14.56	0.79	0.23
Lithium oxide	0.75	0.55	2.75	3.86
Lithium nitride	—	—	0.93	2.57

Menzenhauer and Sonntag studied the combustion of lithium in air. Analyses of the residue in the lower, middle, and upper layers are presented in Table 2.

In a test performed in a vessel with a volume of 14.1 m^3, a 10-kg lithium pool with an exposed surface area of 0.20 m^2 was burned in air having a humidity of 0.008 gram water per gram air. The solid reaction products were of three types: a finely divided aerosol and, in the pan, a top layer and a dense lower layer. No lithium metal was detected in any of the samples, indicating that all of the lithium had reacted. The chemical analysis of the solid reaction products is shown in Table 5 (Reference 11).

TABLE 5. Chemical Analysis of Solid Reaction Products of Lithium Combustion in Low-Humidity Air (Reference 11).

Sample	Mass, kg	Product, wt-%				
		Li_3N	Li_2O	LiOH	$LiOH \cdot H_2O$	Li_2CO_3
Aerosol	0.61	0.1	3-8	30-50	30-50	5-15
Top layer	6.17	0.1	85-95	5-10	<1	<1
Lower layer	17.4	39	60-90	<1	<1	<1

The reaction products from the combustion of lithium with air and steam consisted of the black lithium nitride in the reactor and white aerosols consisting of lithium oxide and/or lithium hydroxide. The reaction products in the bottom of the reactor consisted of coral-like formations (Reference 13).

Combustion Aerosol

The smoke generated during lithium-air combustion is mostly Li_2O, some LiOH, and virtually no Li_3N (Reference 32). Experiments with molten lithium pools exposed to an unlimited air supply (so that the CO_2 concentration would not be depleted) produced an aerosol composed of 50% Li_2O, 20% LiOH, and 29% Li_2CO_3 (Reference 42). In a study of the combustion of lithium in air, presented in Table 2, Li_3N was essentially absent in the aerosol in all cases, but present in the residue after combustion. Low-humidity experiments produced the greatest amount of aerosol, consisting primarily of Li_2O; the aerosol produced in higher humidity experiments consisted primarily of LiOH (Reference 29).

Jeppson and Barreca characterized the aerosol that was generated by burning lithium in an unlimited air atmosphere (Reference 46). Molten lithium metal reacts exothermically with the major constituents of air, including O_2, H_2O, CO_2, and N_2, and forms an intense flame at the lithium surface that results in dense concentrations of aerosol composed primarily of lithium monoxide, lithium hydroxide, and lithium carbonate. Jeppson found that a lithium pool at a temperature initially above the melting point reacted exothermically with air of normal humidity to form an aerosol from the combustion consisting of 70% Li_2O, 15% LiOH, 3% Li_2CO_3, and 0.2%Li_2O_2 (Reference 42). Jeppson studied the behavior of lithium pool fires in a moist air environment and found that aerosol from the fire was composed of greater than 90% $LiOH \cdot H_2O$ (Reference 42). Rebar and co-workers generated lithium combustion aerosols by sweeping lithium vapor into air atmospheres with controlled carbon dioxide and water concentrations. The chemical form of the aerosols depended upon the relative humidity and carbon dioxide concentrations. Under conditions of low carbon dioxide concentration and low relative humidity (<25%), the aerosol was predominantly Li_2O with some LiOH. Under conditions of high relative humidity (>75%), the aerosol was primarily LiOH with about 23% Li_2CO_3 (Reference 47).

In Allen's work, ultrapure argon (99.999% pure), heated to 650°C, was passed over lithium heated to temperatures up to 1300°C. The reaction of lithium vapors generated with air formed an intense white flame that produced branched-chain condensation aerosol particles, of concentrations <2500 mg/m^3 (Reference 42). The aerosol from this combustion was composed of Li_2O, LiOH, or Li_2CO_3 depending upon the water or CO_2 concentration in the air. In one of the experiments, where the aerosol was about 80% Li_2CO_3, the average mass median aerodynamic diameter was 0.66 ± µ. In an experiment where the CO_2 concentration was <10 ppm and the relative humidity was <20%, the aerosol was greater than 96% Li_2O and LiOH. In an experiment where the CO_2 concentration was about 60 ppm and the relative humidity was about 74%, the aerosol was more than 98% $LiOH \cdot H_2O$. In an experiment where the CO_2 concentration was about 2%, the aerosol was more than 97% Li_2CO_3. In an atmospheric release, lithium combustion aerosols would react with the unlimited supply of CO_2 in air at moderate humidities to eventually form an aerosol that would be predominantly Li_2CO_3. Of interest in these studies was the absence of Li_3N (Reference 42). Scanning electron microscopy showed that the oxide particles formed during the combustion in the region near the flame appear in a fairly well organized crystalline structure for lithium; the average particle size is about 500 angstroms (Reference 43).

Eidson and co-workers generated chain-aggregate lithium combustion aerosols in dry, CO_2-free air prior to reaction with 0, 0.10, 0.50, 1.0, 1.75, or 5.0% CO_2 in air at a relative humidity of 52% and a temperature of 38°C. There was no conversion of aerosols to Li_2CO_3 in CO_2-free air, but there was conversion within 3 seconds after mixing of aerosols with CO_2-

enriched atmospheres. Thc extent of conversion to Li_2CO_3 depended on the molar CO_2/LiOH ratio in the range from 0 (0.0% CO_2) to 17 (1.0% CO_2), but was 77% at higher molar ratios. Incomplete conversion to Li_2CO_3 indicates that the reaction rate was not controlled solely by gas-phase CO_2 and H_2O diffusion (Reference 48).

LITHIUM REACTION WITH CARBON DIOXIDE

No reaction was observed when lithium was exposed to carbon dioxide for 5 minutes (Reference 49). TGA studies of lithium dispersions in carbon dioxide, with temperature increasing at the rate of 0.67°C/min, showed that dry carbon dioxide up to 250°C appears inert with respect to lithium metal dispersions; however, in carbon dioxide with 50% relative humidity, weight gain, indicating reaction, started at around 50°C, as shown in Figure 20 (Reference 10). The curve in Figure 20 can be expressed as Eq. 17,

$$w = -12.419 + 10.176 \log(t) \tag{17}$$

where

w = weight, milligrams
t = time, minutes

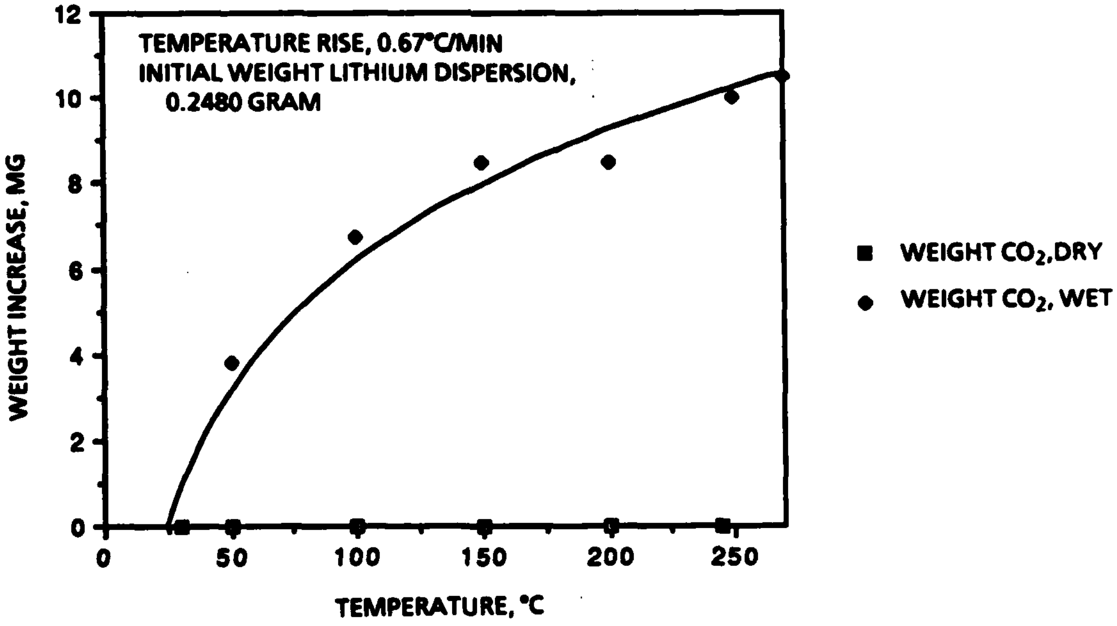


FIGURE 20. TGA of Lithium Dispersion in Dry and Moist (50% RH) Carbon Dioxide (Reference 10).

Rhein determined the ignition temperature of lithium powder ($<$100-µm size) in carbon dioxide, in a sealed combustion tube, by first evacuating and then passing the gas at 100 ml/min over approximately 0.3-0.5 gram of lithium and heating until ignition, determined by a sudden temperature rise, occurred. The lithium melted first, and the ignition temperature was found to be 330°C (References 30, 31). For the reaction with carbon dioxide, the lithium melted first; the combustion appeared to be in the vapor phase (References 30, 31), and combustion was vigorous (Reference 50).

Yuasa and Isoda found (Reference 72) that the ignition of lithium in a carbon dioxide stream had two steps, first a surface reaction and then a gas-phase reaction; this was different from the ignition of lithium in an air stream. The spontaneous ignition temperature of lithium in the carbon dioxide stream was much lower than that in the air stream. Lithium burned first in the vapor phase, then at the metal surface.

A 10-kg quantity of lithium at 540°C was added to carbon dioxide in a vessel at a pressure of 0.18 atmosphere. The lithium ignited, and the lithium pool temperature reached the lithium boiling point (1347°C), due to the reaction between the lithium and carbon dioxide. Based on the first 3 minutes of reaction, the consumption of lithium versus time was correlated by Eq. 18,

$$m = 19.8\,(1 - e^{-0.55t}) \tag{18}$$

where

m = consumption of lithium, kg
t = time, minutes

The computed maximum lithium consumption rate was 994 mol/m^2-min. A bright white intense flame was observed during the lithium transfer. Temperatures above 1400°C were observed, and a peak temperature of about 1800°C was observed 3 minutes after lithium transfer. In the reaction with carbon dioxide, about 1% of the lithium formed an aerosol, consisting of about 90% lithium carbonate. The major product of the reaction was Li_2O; all but 3% of the lithium reacted, and some free carbon and some lithium acetylide (Li_2C_2) were produced.

Rhein determined the ignition temperature of lithium powder ($<$100-µm size) in nitrogen-carbon dioxide mixtures, in a sealed combustion tube, by first evacuating and then passing the gas at 100 ml/min over approximately 0.3-0.5 gram of lithium and heating until ignition, determined by a sudden temperature rise, occurred. In each case, the lithium melted first, and the combustion appeared to be in the vapor phase. In a simulated Venus atmosphere, assumed to consist of 5% argon, 10% nitrogen, and 85% carbon dioxide, the ignition temperatures were measured to be 310, 367, and 414°C. In a simulated Mars atmosphere, consisting of 2.16% argon, 11.21% carbon dioxide, and the remainder nitrogen, the measured ignition temperatures were 386, 405, and 433°C (References 30, 37). In each experiment the lithium first melted and then apparently vaporized so that it was, in fact, the lithium vapor that was burning.

In these experiments, the powdered lithium was found by chemical analysis to contain 95.17 mol-% lithium and 4.83 mol-% Li_2O. The analysis of the combustion products of lithium in the simulated Venus and Mars atmospheres is shown in Table 6 (Reference 37).

TABLE 6. Product Composition from the Combustion of Powdered Lithium in Simulated Venus and Mars Atmospheres (Reference 37).

Atmosphere	Combustion products, mol-%						
	Li	Li_2O	Li_3N	Li_2C_2	Li_2CO_3	CO	C
Venus	2.57	56.85	0.66	1.51	8.68	0.00	29.73
Mars	15.63	44.32	13.91	1.06	0.78	15.06	9.22

LITHIUM COMBUSTION WITH OTHER SUBSTANCES

LITHIUM COMBUSTION WITH SULFUR HEXAFLUORIDE

The reaction between SF_6 and Li yields no gaseous products, as shown in Eq. 19, and releases 6530 Btu/lb. The reaction can be started by water, acid, or oxygen (Reference 32).

$$8Li + SF_6 \rightarrow Li_2S + 6LiF \tag{19}$$

The reaction of SF_6 with molten lithium is immeasureably slow at temperatures below the ignition temperature of 790°C. At temperatures in the range 790-795°C, the probability of reaction when SF_6 molecules strike a molten lithium surface is approximately 0.053 and is independent of pressure over the range 1-100 torr (Reference 17). Using Eq. 7 for the collision frequency, the reaction rate of SF_6 with lithium at 790°C is expressed by Eq. 20,

$$\frac{d(SF_6)}{dt} = 18.83P \tag{20}$$

where

$d(SF_6)/dt$ = reaction rate of SF_6, mol/m^2-min

P = pressure, torr

Engineering designs using this reaction for heat generation have been described (References 53, 54, 55, 56). The fundamental chemical, thermodynamic, and hydrodynamic processes occurring during the confined combustion of liquid lithium fuel as Rankine cycle heat sources for undersea vehicle propulsion systems were studied, using X-ray radiography (Reference 3).

REACTIONS OF LITHIUM WITH HALOGENS AND INTERHALOGENS

Upon contact with fluorine, lithium ignites at ambient temperatures (Reference 7). Lithium reacts vigorously with the halogens, emitting light (Reference 12). In order to burn in gaseous chlorine or in bromine or iodine vapor, lithium needs to be heated. With iodine vapor, the reaction is accompanied by chemoluminescence (Reference 7). With its high ionization potential, lithium reacts rather slowly with liquid bromine (Reference 5). Rhein found that the reaction of lithium powder, 100 µm size, was hypergolic with ClF_3 and ClF_5 in either the gas or liquid state (Reference 57).

REACTIONS OF LITHIUM WITH HALOCARBONS

Mixtures of lithium and some of the halogenated organic compounds (in particular, the chlorides, bromides, or iodides of the form CH_2X_2, CHX_3, and CX_4) can detonate under the influence of shock. The explosions are not violent. The derivatives of bromine and iodine appear to be a little more shock-sensitive (Reference 7). The reaction of molten lithium with halocarbon gases has been studied (Reference 17); some of the explosive or vigorous reactions of lithium with halogenated hydrocarbons were documented (Reference 58), and the lithium reactivity with a variety of organic solvents was determined, using differential thermal analysis (DTA) (Reference 59). A one-shot heating device containing a reactive charge of lithium surrounding a central core of Teflon powder was described (Reference 60).

Little (Reference 17) determined the *reaction probability as a function of* pressure for the reaction between lithium and CF_2Cl_2 and perfluorocyclobutane, C_4F_8. He expressed the reaction probability in the form of Eq. 21,

$$\varepsilon = A(T)\,P^{B(T)} \tag{21}$$

where

ε = the reaction probability

A(T) and B(T) are temperature dependent

Values of A(T) and B(T) for CF_2Cl_2 and C_4F_8 versus temperature, in kelvins, are listed in Table 7.

TABLE 7. Reaction Probability Parameters Versus Temperature for CF_2Cl_2 and C_4F_8.

Temperature, K	CF_2Cl_2		C_4F_8	
	A	B	A	B
640	0.00121	-0.91	0.00187	-0.98
758	0.00587	-1.09	0.00406	-0.55
875	0.0344	-1.00	0.0105	-0.49
994	0.098	-1.14	0.0144	-0.47

From the use of Eq. 7 for the collision frequency, the reaction rate of CF_2Cl_2 and C_4F_8 can be expressed in the forms of Eqs. 22 and 23, with rates in mol/m^2-min and pressure, P, in torr,

$$\frac{d}{dt}(CF_2Cl_2) = \alpha P^{\beta} \tag{22}$$

$$\frac{d}{dt}(C_4F_8) = \delta P^{\gamma} \tag{23}$$

In Eqs. 22 and 23, α, β, δ, and γ are functions of temperature. These parameters are shown versus temperature in Table 8.

TABLE 8. Rate Parameters for the Reaction of Lithium With CF_2Cl_2 and C_4F_8.

Temperature, K	α	β	δ	γ
640	0.609	0.09	0.732	0.02
758	2.71	-0.09	1.460	0.45
875	14.8	0	3.52	0.51
994	39.6	-0.14	4.52	0.53

REACTIONS OF LITHIUM WITH CARBON AND HYDROCARBONS

Lithium reacts with carbon, forming the carbide, at temperatures above 800°C (Reference 12). When ethylene is passed over heated lithium, an incandescent reaction results, with products that are a mixture of lithium hydride and lithium carbide (Reference 7). In the presence of an inert atmosphere of paraffin vapor, lithium can be handled at temperatures up to 200°C (Reference 1)

REACTIONS OF LITHIUM WITH POLYMERS AND ORGANIC MATERIALS

Plastics are attacked by molten lithium near the melting point (Reference 1). Various materials were subjected to a 1/16-inch-diameter stream of lithium at 590°C and 60 psig for 30 seconds. The materials were positioned 6 feet from the orifice and were sprayed with 3.2 kg of lithium. The results are listed in Table 9.

TABLE 9. Lithium Reactions With Polymers and Organic Materials (Reference 36).

Material	Results
Chrome leather	Charred and glowed almost instantly, shrank; but some remained as coke.
Chamois leather	Disappeared quickly and completely.
Greylite	Disappeared quickly and completely.
1/8-Inch-thick plexiglass	Disappeared quickly and completely.
1/2-Inch-thick plexiglass	Ignited and eventually burned after jet was removed.
G.E. Multilayer protective cloth metal	Disappeared.
1/8-Inch-thick steel backing plate	Severe buckling occurred; no penetration, bright cherry red spot 18 inches in diameter with almost white hot center spot.

REACTIONS OF LITHIUM WITH NONMETALLIC OXIDES

Lithium reacts violently with most inorganic acids, but cold concentrated sulfuric acid attacks it slowly (Reference 12).

REACTIONS OF LITHIUM WITH SILICA, CERAMICS, AND OTHER OXIDES

Barker described the high reducing power of liquid lithium with transition metal oxides (Reference 61). The attack of lithium on vitreous silica at 250°C was very rapid, with the product assumed to be the metasilicate (Reference 62), even though high-purity molten lithium may be held in quartz containers up to 285°C (Reference 1). Commercial lithium readily attacks glass (Reference 5), quartz, porcelain and other silicate materials (Reference 1). Molten lithium reacts vigorously with concrete and other materials containing moisture and rapidly with ceramic insulating materials (Reference 1). Severe attack is believed to be due to the formation of relatively stable but highly corrosive lithium oxide, nitride, and carbide (Reference 1).

Liquid lithium reacted exothermically with concretes, including magnetite and basalt concretes, under an argon atmosphere. The rate of reaction with both magnetite and basalt concretes depended upon the initial lithium temperature; at about 320°C, the reaction proceeded very slowly for several hours and then increased sharply; at an initial lithium temperature of 870°C, the reaction proceeded very fast and was completed in 2 minutes (Reference 1) The amount of available chemical energy between lithium and concrete, estimated at 150 kcal/mol lithium, may be larger than that for lithium-atmosphere reactions (Reference 32).

REACTIONS OF LITHIUM WITH METALS AND ALLOYS

Armco steel shows good resistance to temperature up to 600°C. It is generally resistant to attack up to 1000°C and higher. Austenitic and ferritic stainless steel with less than 0.12 wt-% carbon exhibit good resistance to lithium attack. Stainless steels, Types 302, 303, 304, 316, and 346, 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. Nickel shows good resistance at 225°C, limited at 300°C, and poor at 600°C. Aluminum, barium, bismuth, calcium, cadmium, lead, magnesium, platinum, silicon, silver, strontium, thorium, tin, zinc, and their alloys all react with molten lithium. Copper and its alloys show poor resistance (Reference 1).

EXTINGUISHMENT OF LITHIUM FIRES

GENERAL OBSERVATIONS REGARDING LITHIUM FIRE EXTINGUISHANTS

In general, liquid extinguishants are best suited for quiescent pools of burning metal while powders are best suited for spills that are not contained (Reference 36). The extinguishing mechanism for the liquid extinguishants were attributed to cooling, smothering, charring, or saponification or a combination of these phenomena. Secondary fires occurred frequently, but the addition of a halogenated hydrocarbon inhibited these secondary fires (Reference 36). Owing to the sensitivity of the burning rate to even slight convection currents, once a lithium fire started, attempts to ventilate the area were detrimental to fire control (Reference 1). It was found that there was no difficulty in keeping extinguishants from sinking below the molten lithium surface despite the low density of liquid lithium. This was due to the relatively high surface tension of liquid lithium and low apparent density of the solid lithium reaction products (Reference 1).

INERT GAS BLANKETING FOR LITHIUM FIRE EXTINGUISHMENT

The flame or fire zone of a lithium fire is usually confined to a porous, coral-like growth of lithium nitride that floats on the liquid metal and acts as a catalyst and a wick. To expeditiously extinguish a lithium fire, the fire zone present at the lithium nitride wick should be coated with an inert blanket of extinguishant. The bulk molten metal should be cooled as quickly as possible to prevent further outbreaks of fire.

Some investigators believe that inert gas flooding is considered most effective in controlling medium-to-large spills (Reference 4). Gas blanketing or reduction of oxygen partial pressure can be effective in controlling lithium fires; at an oxygen partial pressure of 0.1 atmosphere, lithium did not ignite (References 35, 36, 63).

However, others have found that inert gases are not suitable for extinguishing alkali metal fires (Reference 64). Application of an inert gas such as argon to a well-established lithium fire was found to be completely ineffective, in that direct application to the burning surface did retard the fire somewhat but removal of the argon gas source caused combustion to immediately resume (Reference 1).

INORGANIC LIQUIDS (WATER OR WATER FOAM) FOR LITHIUM FIRE EXTINGUISHMENT

Water

Under no conditions must water extinguishers be used against alkali metal fires (References 1, 64); water reacts with explosive violence with alkali metals (References 35, 36).

In an attempt to extinguish a 14.5-pound lithium fire, water, passing through a 1.5-inch fog spray nozzle was applied; when 2 liters of water had impacted the fire, there were two explosions producing a gas cloud; particles were thrown 50 feet in the air, 45 feet from the lithium container. It was estimated that 11-12 pounds of lithium were dispersed during these explosions; the maximum particle distance was 75 feet (Reference 65).

When a large amount of water in a high-pressure jet was directed to a 4-pound lithium fire, a fireball 4-5 feet in diameter erupted. Small particles of lithium scattered from the center. Water was deemed to be hazardous (Reference 66). In another experiment, when 55 gallons of water (deluge) were put on a 4-pound lithium fire, a fireball 4-5 feet in diameter erupted upon application. Small particles of lithium scattered from center. A water deluge was deemed to be hazardous (Reference 66).

Aqueous Foam Extinguisher

Under no conditions must foam extinguishers be used against alkali metal fires (Reference 64), since lithium readily reacts with aqueous foams found in these agents (Reference 1). Aqueous Film Forming Foam (AFFF), 6% concentration, was applied through a 1.5-inch fog spray nozzle against a 14.2-pound lithium fire. When 2 liters had been directed to the fire, a first reaction was observed, followed by a violent reaction, resulting in a 10-foot-diameter gas cloud and 2.5 psig overpressure shockwave. The particle fallout was 5 to 75 feet from the lithium container (Reference 65).

Aqueous Film Forming Foam, 6% Concentration

When 2.5 gallons of AFFF, 6% concentration, were applied against a 1-pound lithium fire, there were two large eruptions 2-4 seconds after application, throwing material more than 5 feet. Upon continued application, the fire gradually decreased and flame disappeared. Under this condition, the agent was determined to be effective. However, when 2.5 gallons of AFFF (6%) were directed onto a 4-pound lithium fire, the lithium flames increased, with particles ejected from the pan. After the agent application ceased, the fire burned steadily. In this test, the agent was deemed to be ineffective (Reference 66).

Aqueous Film Forming Foam, 3% Concentration

When 2.5 gallons of AFFF (3%) were applied against a 3-pound lithium fire, there were three violent eruptions, scattering material 4-5 feet, followed by an explosion throwing material 10 feet from center. The agent was deemed to be ineffective (Reference 66).

INORGANIC SOLIDS FOR LITHIUM FIRE EXTINGUISHMENT

Graphites

Solid Carbon. Rodgers and Everson stated that graphite is recommended for lithium fires (References 35, 63). Graphite appeared to be more effective than TEC powder or NaCl (References 35, 36). When applied to a small lithium fire, graphite did not appear to react, and it extinguished the fire if the entire surface of the fire was covered (Reference 1). Friedrich stated that graphite powder is most effective against lithium fires of ≤100 gram. The powder can be applied to the burning metal either by hand from a shovel or scoop or from an extinguisher using argon at low pressure (≤ 5 atmospheres) as propellant. A 39-gram quantity of graphite was required to extinguish a 10-gram lithium fire, and 430 grams of graphite were required to extinguish a 100-gram lithium fire (Reference 64).

In several experiments, graphite was used as an extinguishant for a 10-kg lithium fire with an area of 0.2 m^2 in 23 minutes. In one experiment (lithium pool temperature, 1100°C), 40 kg of graphite were spread on the fire; the lithium cooled to 600°C in 3.0 hours. In another experiment, 38.2 kg of graphite were sprayed over the lithium fire (lithium pool temperature 1110°C); the lithium cooled to 600°C in 1.5 hours (Reference 11).

As an extinguishant, graphite has limitations. Forty grams of lithium were ignited in a porcelain dish and allowed to burn for 2 minutes, attaining a flame temperature of 1350°C (Reference 67). When the commercial 86/14 graphite/granite blend was used as the extinguishing agent, the fire came through the layer of powder until a great excess of agent was applied. When the layer was disturbed after 15 minutes, the fire reflashed violently (Reference 67).

Warnock Patent. Warnock described a graphite-based extinguisher for lithium metal fires in which 5-15% anticaking agent and 0.25-5.0% water-repelling agent were used. Thus, an extinguishing agent was prepared by mixing the following:

> 93 wt-% graphite (a synthetic high-density electric-furnace graphite with an apparent density of 1.62) having a screen analysis of: trace on 40-mesh, 46% on 10-mesh, 23% on 200-mesh, and 11% on 325-mesh
>
> 5% Attapulgus clay having a screen analysis of 4% on 80-mesh, 11% on 100-mesh, 55% on 200-mesh, 16% on 325-mesh, and 12% through 325-mesh
>
> 2% "bulky" magnesium stearate having an apparent density of 110 g/l

In an example, a 2.25-ft^2 pan was filled with 0.25 inch of molten lithium. Heat was applied for 15 minutes, 30 seconds to ignite the lithium, and at 15 minutes, 50 seconds, the graphite-based extinguishing agent was applied from a dry chemical type fire extinguisher. The fire was well under control by 17 minutes, 15 seconds, (i.e., after 1 minute, 25 seconds). Fire broke through the graphite at 19 minutes, but was immediately re-covered to extinguish the flames (Reference 68).

G1 Powder. G1 powder is the trade name of a product of the Fyr-Fyter Company. It is composed of granular graphite to which is added phosphorus-containing compounds. When added to a fire, graphite and phosphorus decomposition compounds blanket the fire and cool the alkali metal to below the ignition point. G1 powder is suitable for both lithium spill fires and lithium fires in depth (Reference 36). In a test against a small lithium fire, Pyrene G-1 powder underwent essentially no reaction and extinguished the fire if the fire was completely covered. For (weight G-1)/(weight lithium) (in lithium fire) of 3.5 pounds/0.75 pound and 4.2 pounds/1.0 pound, there was smoke, secondary flames, and slow aftercooling. The carbon glowed after lithium fire extinguishment (Reference 1). In another effort, however, Pyrene G-1 performed poorly against a 1-pound lithium fire. When 3 pounds of Pyrene G-1 were added over a 6-minute interval, or 5 pounds were added over a 2-minute interval, to a 1-pound lithium fire, there was much black smoke during and after application (Reference 4).

LITH-X. LITH-X, a graphite-base powder with a bulk density of 0.9 g/cm^3, has been developed for lithium fires. (Reference 36). When applied to a small lithium fire, LITH-X underwent essentially no reaction and extinguished the fire if the fire was completely covered. When 2.5 pounds of LITH-X were applied to an 0.5-pound lithium fire, or 6.0 pounds were applied to a 1-pound lithium fire, there was smoke and secondary flames, and a relatively large amount of LITH-X was required for extinguishment (Reference 1). When 3.3 pounds of LITH-X were added over a 4-minute interval to a 1-pound lithium fire, extinguishment was accompanied by slow solidification. When 3.0 pounds of LITH-X were added over a 13-minute interval to a 1-pound lithium fire, extinguishment was accompanied by rapid solidification (Reference 4).

In a lithium pool fire 3 feet in diameter. the temperatures were estimated to be in excess of 1000°C. To the fire was applied LITH-X bulk extinguishant. (Reference 4).

In another application, 10 kg of lithium was added to a heated pan of surface area 0.2 m^2, and the lithium was allowed to burn until the pool temperature increased to >800°C. In one set of tests, the extinguishing agent was applied evenly to the surface; in another set of tests, the extinguishing agent was applied with a pressurized extinguisher (Ansul Model PS-MX-150-C, using argon at 2500 psi as the propelling gas). LITH-X was effective in extinguishing the lithium fire, but required 43 kg of agent, applied during a 23-minute period. The temperature decreased from about 1010°C to 900°C as the first load of agent was applied during a 4-minute period. The temperature then increased to about 1100°C and then decreased to about 950°C when the remainder of the agent was added to the fire. The pool temperature then dropped to about 700°C during the next hour. Some of the graphite base agent became airborne while being added to the fire. In a test using the pressurized extinguisher, 51.8 kg of graphite were blown through the extinguisher during an 8-minute period and 32.8 kg were applied to the fire (the remainder became airborne). The pool temperature increased to 1100°C as the agent was applied, then decreased rapidly to 600°C by 90 minutes later (Reference 11).

Graphite Microspheres. Graphite microspheres, bulk density of 1.2 g/cm^3, 86% retention on a 35 μm screen, having a particle diameter from 100 to 500 μm, appeared to be superior to other carbon formulations as a fire suppressant in that (1) little or no smoke evolved during or after their application, and (2) less material was required to achieve levels of extinguishment comparable to those of the other suppressants tested (Reference 69). The effectiveness of these microspheres in extinguishing lithium fires was compared to that of various extinguishing agents; e.g., petroleum coke, graphite flour, commercial NaCl, and commercial $(NH_4)_3PO_4$ (Reference 70). When 1.0 pound of graphite microspheres was added over a 2-minute interval or 1.5 pounds were added over a 1-minute interval to a 1-pound lithium fire, extinguishment was accompanied by very little smoke during and after application (Reference 4).

In a set of experiments, carbon microspheres were added to a 10-kg lithium fire of area 0.2 m^2. In one experiment (lithium pool temperature 1010°C), 37.0 kg of carbon microspheres were spread on the fire over a 15-minute interval; the lithium cooled to 600°C in 7.0 hours. In another experiment (lithium pool temperature, 1000°C), 32.0 kg of carbon microspheres were sprayed over the lithium fire in 9 minutes; the lithium also cooled to 600°C in 7 hours (Reference 11). In another series of tests, the lithium pool reached a temperature of 800°C before the extinguishing agent was applied. Carbon microspheres extinguished the fire, with the smallest amount of agent (3.7 kg agent per kg lithium), but required considerable time for cooling. The graphite base agent required 4.3 kg agent per kg lithium, but had a short cooling time (Reference 1).

In a further series of tests, 10 kg of lithium were added to a heated pan of surface area 0.2 m^2, and the lithium was allowed to burn until the pool temperature increased to >800°C (generally 20 to 30 minutes after ignition). In one set of tests, the extinguishing agent was applied evenly to the surface; in another set of tests, the extinguishing agent was applied with a pressurized extinguisher (Ansul Model PS-MX-150-C, using argon at 2500 psi as the propelling gas). Carbon microspheres extinguished the fire after 3.7 kg extinguishant per kg lithium had been applied during a 15-minute period. The lithium pool temperature had increased from 880 to 1010°C during the period the agent was added, then had decreased slowly to 600°C by 7 hours later. During addition, the agent would collect on the pool surface to a thickness of about 1 cm and would then sink to the bottom of the pool. The exposed lithium pool surface started burning again, and the sequence was repeated. To extinguish the fire, it was necessary to saturate the entire pool and then cover the surface with agent. In another test, 35.2 kg of carbon microspheres were sent to the fire by the argon-pressurized extinguisher, and 32 kg actually hit the fire. The agent was applied during a 9-minute period. The pool temperature remained at about 1000°C during the agent-adding period, then cooled to 600°C by 7 hours later. The carbon microspheres flowed from the extinguisher through the hose with no difficulty. They did not become airborne during the addition to the fire (Reference 11).

To examine the interaction of hot lithium with the carbon microspheres, about 7 kg of lithium at 650°C were added during a 1.5-minute period to a pan (surface area 0.20 m^2) containing 31.8 kg of carbon microspheres. The lithium reacted with the carbon to form a red reaction product. The reaction pan temperature rose to 920°C in 5 minutes, then cooled slowly over the next 20 hours. The pre-add test indicated that the maximum temperature of the lithium pool was about the same as that of a burning lithium pool with no agent.

Exfoliated Graphite. Alkali or light metal fires were extinguished by isolating the fire from the ambient atmosphere with a covering blanket of exfoliated graphite derived from graphite intercalation compounds. For example, 25 grams of a $FeCl_3$-NH_3-graphite intercalation compound were added to 1 kg of burning sodium; the compound expanded to form a blanket of exfoliated graphite over the surface, and the fire was completely extinguished in about 10 seconds. The process was accompanied by the release of NH_4Cl fumes (Reference 71).

Metals and Alloys

Lead (Shot). When applied to a small lithium fire, lead shot underwent no reaction, but resulted in incomplete extinguishing (Reference 1).

Lead (Powder). When applied to a small lithium fire, lead powder underwent a vigorous reaction, possibly because of a contaminant (Reference 1).

Lead and Tin Alloy. When applied to a small lithium fire, lead and tin alloy underwent no reaction, had good flow properties and fairly good smothering action on the fire, and was regarded as a fair extinguishing agent (Reference 1).

Brass (Granular). When applied to a small lithium fire, granular brass underwent no reaction, quenching the fire and extinguishing if the fire was completely blanketed (Reference 1).

Halides

Lithium Fluoride. When 5-10 grams of LiF were applied to a 1-gram lithium fire, the LiF did not react, although a portion of it melted; the lithium fire did not continue to burn (Reference 64). A 10-pound quantity of LiF was applied to a 4-pound lithium fire, resulting in substantial smoke; no violent event events were observed, and LiF was deemed to be effective. However, storage is prohibited aboard ships (Reference 66).

Lithium Chloride. An extinguishant possibly effective in extinguishing lithium fires is lithium chloride; there was little or no reaction when LiCl was applied to a small lithium fire; however, LiCl is quite hygroscopic and poses storage problems (Reference 1). When 5-10 grams of LiCl were sprinkled on a 1-gram lithium fire, the LiCl partly melted but did not react. The fire was extinguished when the LiCl completely covered the lithium (Reference 64).

Lithium Bromide. A 5-10 gram quantity of LiBr, when sprinkled on a 1-gram lithium fire, partly melted and underwent a mild reaction (Reference 64).

Sodium Fluoride. A 5-10 gram quantity of NaF, when sprinkled on a 1-gram lithium fire, reacted, forming dazzling sparks and a yellow smoke (Reference 64).

Sodium Chloride. Powdered sodium chloride (the primary ingredient in MET-L-X) was found by many investigators to be effective in extinguishing lithium fires. When 0.8 pound of MET-L-X was applied to an 0.75-pound lithium fire, it was regarding as very effective. It did not sink into the molten lithium. For ratios of MET-L-X to lithium (in the fire) of 1.5/1.0, 3.5/2.0, 5.1/5.0, and 14.0/14.0, there was some suggestion of sodium formation (Reference 1). MET-L-X was found to work well on 0.75- to 14-pound lithium fires. Sufficient quantities were applied without the agent sinking into the molten lithium. In a 14-pound lithium fire, MET-L-X was added to the center area of the fire with a shovel while slowly working outward to avoid bridging from the container walls (Reference 1). Thin-layer lithium spill fires can be fought with MET-L-X since the salt cannot sink; the resultant sodium fire (from the reaction of lithium with NaCl) is more easily extinguished than a lithium fire (Reference 36).

MET-L-X was used against a 10-kg lithium pool fire of surface area 0.2 m^2 and pool temperature >800°C. The MET-L-X was applied evenly to the surface with a shovel. The extinguishant tends to sink in lithium, but the fire was extinguished. A secondary sodium fire ensued because of the reaction of NaCl with lithium; however, this fire was controlled with additional application of extinguishant. Against an 0.45-kg lithium fire (1093°C), the application of 68 kg of NaCl resulted in the NaCl sinking into the fire, and the application of 13.6 kg of NaCl resulted in a secondary sodium fire (Reference 64). A 10-pound quantity of MET-L-X (NaCl) was applied to a 4-pound lithium fire. Upon initial application there resulted a burst of flame that cooled to a puff of smoke almost immediately. Some fine particle spray was observed. NaCl was deemed to be effective (Reference 66).

Other investigators have found that sodium chloride is not very useful as an extinguishant for lithium fires (Reference 1). MET-L-X powder was effective for extinguishing fires of sodium and potassium but was not recommended for lithium fires (Reference 63). When applied to a 1-gram lithium fire, a 5-10 gram quantity of NaCl reacted vigorously, with much sparking and poor quenching (Reference 64). A 40-gram amount of lithium was ignited in a porcelain dish and allowed to burn for 2 minutes, attaining a flame temperature of 1350°C. When the commercial stearate-treated sodium chloride granules were used as extinguishant, a violent reaction occurred immediately (Reference 67).

MET-L-X was applied by a shovel to a 1-pound lithium fire, where relative humidity ranged from 40 to 60% and wind speeds ranged from 0-30 ft/min. In each case, the maximum fire temperature was greater than 2000°F. When 13 pounds of salt were applied, the extinguishant tended to sink. When 2 pounds were applied, there was a violent reaction. When 3 pounds were applied, there were secondary sodium flames.

MET-L-X (NaCl) is not recommended for lithium fires of depth since it sinks, and lithium reacts with the salt to produce LiCl and sodium metal (Reference 36). MET-L-X, a sodium chloride based extinguishant, proved inefficient in extinguishing a well-established lithium fire. A 51.4-kg amount of NaCl was spread over a 10-kg lithium fire (lithium pool temperature, 1000°C), of area 0.2 m^2 in 79 minutes. The agent reacted with the lithium and caused some yellow flames and minor sparking. Lithium burning continued after the 51 kg of agent has been added. The reaction pan temperature decreased from about 950°C to about 850°C during the 79-minute period of addition (Reference 11).

Sodium Bromide. NaBr, 5-10 grams, when added to a 1-gram lithium fire, reacted vigorously, producing dazzling sparks and a yellow smoke (Reference 64).

Sodium Iodide. NaI, 5-10 grams, when added to a 1-gram lithium fire, reacted mildly. It partly melted, and iodine separated out (Reference 64).

Potassium Fluoride. Friedrich stated that a powder such as KF is most effective against fires ≤100 grams of lithium, sodium, and potassium. The powder can be applied to the burning metal either by hand from a shovel or scoop or from an extinguisher using argon at low pressure (≤ 5 atmospheres) as propellant. A 51-gram quantity of KF was required to extinguish a 10-gram lithium fire, and a 710-gram quantity of KF was required to extinguish a 100-gram lithium fire (Reference 64).

Potassium Chloride. An extinguishant possibly effective in extinguishing lithium fires is potassium chloride (Reference 1). When added to a 1-gram lithium fire, KCl, 5-10 grams, was very reactive, resulting in strong dazzling sparks; a pale-violet strong smoke developed (Reference 64).

KCl/LiCl (50-wt-% Each). When 50/50 KCl/LiCl was applied to a small lithium fire, there was a vigorous reaction, with moderate sparking that was more vigorous than that of KCl alone; however, there was effective cooling of the fire (Reference 1).

Potassium Bromide. When added to a 1-gram lithium fire, KBr, 5-10 grams, was rather reactive, resulting in strong dazzling sparks; a pale-violet strong smoke developed (Reference 64).

Potassium Iodide. When added to a 1-gram lithium fire, KI, 5-10 grams, was not very reactive; it partly melted and iodine separated (Reference 64).

Calcium Fluoride. Calcium fluoride, 5-10 grams, when added to a 1-gram lithium fire, partly melted but did not react; when the lithium was covered, the fire was extinguished (Reference 64). However, when CaF_2 , 7 pounds, was applied against an 0.75-pound lithium fire, it was found ineffective (Reference 1). Nevertheless, of the solids, calcium fluoride appeared to be the most effective (Reference 36).

Ammonium Halides. Ammonium fluoride, chloride, bromide, and iodide, 5-10 grams, when sprinkled on a 1-gram lithium fire, all reacted very vigorously, with an increase in flame intensity. The lithium continued to burn even after it had been completely covered (Reference 64).

Oxides

Magnesium Oxide. MgO, 5-10 grams, when sprinkled on a 1-gram lithium fire, was rather reactive, resulting in an increase of flames and the emission of yellow light (Reference 64).

Calcium Oxide. CaO, 5-10 grams, when sprinkled on a 1-gram lithium fire, reacted very mildly, producing an insignificant increase of flames (Reference 64).

Barium Oxide. BaO, 5-10 grams, when sprinkled on a 1-gram lithium fire, was rather reactive, partly melting and producing an increase of flames (Reference 64).

Boric Oxide. B_2O_3, 5-10 grams, when sprinkled on a 1-gram lithium fire, was mildly reactive, resulting in an increase of flames and the emission of yellow light (Reference 64). When sprinkled on a small lithium fire, B_2O_3 underwent a vigorous reaction, and was lacking in either flow or fire coverage. Hence, it was regarded as a poor extinguishant (Reference 1).

Boric Acid. H_3BO_3, when applied to a small lithium fire, underwent a vigorous reaction, but a short-duration secondary fire resulted; it was regarded as a good extinguishant, because the boric acid coating blanketed the lithium (Reference 1).

Aluminum Oxide. Al_2O_3, when sprinkled on a 1-gram lithium fire, was rather reactive and partly melted; it resulting in an increase of flames, the emission of yellow light, and smoke generation (Reference 64).

Sand (Silicon Dioxide). When sprinkled on a 1-gram lithium fire, SiO_2, 5-10 grams, was rather reactive, resulting in an increase of flames and the emission of yellow light and generation of smoke (Reference 64). Dry silica sand was reactive with the burning lithium, with much popping and cracking; persistent, vigorous flaring, and violent sparking after application directly to the areas of burning lithium (References 1, 4, 69). In a possible use of sand as an extinguishant, to a lithium pool fire approximately 3 feet in diameter, with temperatures estimated to be in excess of 1000°C, was first applied LITH-X bulk extinguishant, then MET-L-X, then dry silica sand. More sand was applied until the fire was completely under control (Reference 4).

Glass Microballoons. Leeper and Dierssen patented an extinguishant for liquid metal fires that consisted of mixtures of glass bubbles and a minor amount of finely divided graphite, SiC, or ZrB_2. In the example, the extinguishant consisted of 28 grams of an 80/20 (by weight) mixture (97.7/2.3 calculated volume ratio) of 100-250 μm glass bubbles (density, 0.298) and 0.1-0.5 μm silicon carbide. A 40-gram quantity of lithium was ignited, attaining a flame temperature of 1350°C. When the glass bubble/SiC mixture was applied, the fire was immediately contained. A hard crust formed in 5 minutes, and the fire was considered extinguished after 15 minutes (Reference 67).

Titanium Dioxide. TiO_2, 5-10 grams, when sprinkled on a 1-gram lithium fire, was explosively reactive and produced dazzling sparks (Reference 64).

Carbonates and Bicarbonates

Lithium Carbonate. When 5-10 grams of Li_2CO_3 were added to a 1-gram lithium fire, a mild reaction was observed, with little increasing of flaming (Reference 64). Li_2CO_3 appeared in another instance to be reactive; when 2 pounds of Li_2CO_3 were added to a 1-pound lithium fire there were yellow flames that indicated reaction. The fire was not suppressed; hence Li_2CO_3 performed poorly. (Reference 4).

When 10 pounds of Li_2CO_3 were applied to a 1-pound lithium fire, the reaction was fairly quiet during agent application, followed by 1 minute of frequent eruptions. The activity gradually subsided; Li_2CO_3 was deemed ineffective (Reference 66).

Sodium Carbonate. An extinguishing agent with a sodium carbonate base was unacceptable for well-established lithium fires (References 1, 11), since lithium readily reacts with sodium carbonate found in these agents (Reference 1). When 5-10 grams of sodium carbonate were added to a 1-gram lithium fire, a yellow spray of sparks was observed, but the fire did not burn further (Reference 64). Against a 10-kg lithium fire (lithium pool temperature, 1020°C), of area 0.2 m^2, 1.9 kg of Na_2CO_3 were spread in 1.3 minutes; lithium inflamed (Reference 11). In another test against a 10-kg lithium fire, pool temperature >800°C, 1.9 kg of agent Na-X, a sodium carbonate based agent, was applied during a 78-second period; it reacted vigorously with the lithium, causing yellow flames and showers of sparks shooting about 2 meters above the pool surface; an increase in pool temperature from 960 to 1010°C was measured when the sodium carbonate was added (Reference 11).

Sodium Bicarbonate. Under no conditions must dry powders containing $NaHCO_3$ be used against alkali metal fires (References 35, 36, 64). There was a vigorous reaction when $NaHCO_3$ was applied to a small lithium fire, where the $NaHCO_3$ acted as a fuel rather than as an extinguishant (Reference 1).

Potassium Carbonate. Potassium carbonate, 5-10 grams, when sprinkled on a 1-gram lithium fire, reacted vigorously, producing dazzling sparks and a pale-violet color (Reference 64).

Potassium Bicarbonate (Purple K). Purple K ($KHCO_3$) in two 15-pound extinguishers, or 30 pounds total, was used against a 14.2-pound lithium fire in a crucible. The reaction was moderately vigorous; molten lithium ejected was 5 feet from the crucible (Reference 65)

Calcium Carbonate. Calcium carbonate powder produced flaring and sputtering when applied to a lithium fire (Reference 69). Calcium carbonate, 5-10 grams, when sprinkled on a 1-gram lithium fire, reacted mildly, producing weakly increasing flames with emission of bright yellow light; smoke was generated (Reference 64).

Strontium Carbonate. Strontium carbonate, 5-10 grams, when sprinkled on a 1-gram lithium fire, reacted vigorously, producing increasing flames under emission of red light, dazzling sparks, and smoke (Reference 64).

Barium Carbonate. Barium carbonate, 5-10 grams, when sprinkled on a 1-gram lithium fire, reacted vigorously, producing increasing flames under emission of bright yellow light, dazzling sparks, and smoke (Reference 64).

Alkali Metal Oxalates

Against a 1-gram lithium fire, lithium, sodium, and potassium oxalates all reacted vigorously (Reference 64).

Alkali Metal Sulfates

When sodium sulfate (Na_2SO_4) or potassium sulfate (K_2SO_4) was sprinkled on a 1-gram lithium fire, there was violent spattering with burning lithium (Reference 64).

Inorganic Compositions and Mixtures

ABC Powder. A dry chemical marketed by Ansul Co., ABC Powder, reacted explosively with lithium. In an example, 9.1 kg of ABC powder were applied to a 0.45-kg lithium fire (1093°C), producing a violent reaction (Reference 36).

LITH-3. LITH-3 is a mixture of NH_4Cl, SiO_2 and vermiculite. LITH-3 performed poorly against a lithium fire and appeared to be reactive with the burning lithium. When 1 pound of LITH-3 was added over a 3-minute interval, or 2.7 pounds were added rapidly to a 1-pound lithium fire, there were numerous burnthroughs and reactions (Reference 4).

TEC Powder. A possibly effective substance for extinguishing lithium fires is a ternary inorganic eutectic, consisting of barium chloride (25 wt-%), sodium chloride (35 wt-%), and potassium chloride (40 wt-%); this mixture melts at 640°C. When applied against a small lithium fire, it underwent essentially no reaction and was a very effective extinguishant, forming a liquid crust over the fire. For larger fires, where the ratios of TEC/Li (in fire) were 2.5/0.5, 2.5/0.75, 2.2/2.0, and 1.5/5.0, the TEC was regarded as very effective; sinking into the lithium fire was prevented by the formation of the "coral" lithium combustion product (Reference 1).

Other investigators have found that, although TEC powder was effective for extinguishing sodium and potassium fires, it was not recommended for lithium fires (Reference 63) and was found ineffective when applied from a pressurized extinguisher (Reference 1). When TEC powder was added to a 4.5-kg lithium fire (1093°C), it did not extinguish the fire because the excessively high temperature (1093 + °C) caused this powder to melt (References 35, 36).

Sodium Stearate

When 27 kg of sodium stearate was applied to a 4.5-kg lithium fire (870°C), it did not extinguish the fire, and molten lithium came through the surface crust (Reference 35).

Refractory Compounds, Ceramics, and Minerals

Silicon Carbide. SiC, applied to a 1-gram lithium fire, was unreactive; it extinguished the fire when it covered the burning lithium. A 78-gram amount of SiC was found to extinguish a 10-gram lithium fire (Reference 64).

Zirconium Silicate. Although zirconium silicate has been considered as an extinguishant that may be effective in extinguishing lithium fires (Reference 1), zirconium silicate powder produced flaring and sputtering when applied to a lithium fire (Reference 69).

Celite 545. When applied to a small lithium fire, Celite 545 (a diatomaceous earth) underwent a vigorous reaction and appeared combustible (Reference 1).

Talcum. Talcum, applied to a 1-gram lithium fire, was mildly reactive, producing a trivial increase in flaming (Reference 64).

Pumice. When applied to a 1-gram lithium fire, pumice was very reactive, resulting in a strong increase in flaming (Reference 64).

Concrete. When applied to a 1-gram lithium fire, concrete was very reactive, resulting in a strong increase in flaming (Reference 64).

Boron Carbide. When applied to a 1-gram lithium fire, B_4C was very reactive, resulting in a buildup of flames and smoke generation (Reference 64).

Boron Nitride. When applied to a 1-gram lithium fire, BN was reactive, resulting in increasing flames and smoke generation under emission of yellow light (Reference 64).

Vermiculite. When applied to a 1-gram lithium fire, vermiculite was very reactive, resulting in a strong increase in flaming and emission of sparks (Reference 64).

Trimethoxyboroxine. When trimethoxyboroxine was applied to a small lithium fire, there was a secondary fire that burned with a green flame for only a short period; hence, it was considered as a good extinguishant. However, when used against 0.5-pound lithium fires, the following was found: for 1.6 pounds of trimethoxyboroxine, the extinguishant was not effective; for 2.8 pounds, there were secondary flames, and for 3.0 pounds, dangerous fumes were emitted (Reference 1).

ORGANIC COMPOUNDS FOR LITHIUM FIRE EXTINGUISHMENT

Hydrocarbons

Dibenzyltoluene. Of the liquid extinguishants, dibenzyltoluene appeared to be effective against lithium fires of ≤ 100 grams (Reference 36). Against a 1-gram lithium fire, 16.5 ml of dibenzyltoluene, applied at 2 cm^3/s, extinguished the fire, as did the addition of 4.2 ml of a solution of 20% chlorobromoethane in dibenzyltoluene. Against a 10-gram lithium fire, dibenzyltoluene did not extinguish the fire when applied at the rate of 6 cm^3/s, although 30 ml of a mixture of dibenzyltoluene and 20% chlorobromobenzene did extinguish the fire, generating smoke. However, at a flow rate of 20 cm^3/s, 450 ml extinguished the fire, and at a flow rate of 60 cm^3/s, 165 ml extinguished the fire. Against a 100-gram lithium fire, dibenzyltoluene did not extinguish the fire, but rather produced secondary burning when applied at the rate of 60 or 120 cm^3/s; However, 175 ml of a mixture of dibenzyltoluene and 20% chlorobromoethane, applied at the rate of 120 cm^3/s, did extinguish the fire (Reference 64).

Isopropyl Biphenyl. Isopropyl biphenyl was rapidly and completely consumed when applied to a 4.5-kg lithium fire at 870°C (References 35, 36).

Spindle Oil. Spindle oil, applied at 2 cm^3/s against a 1-gram lithium fire, did not extinguish the fire, and secondary burning resulted; however, the fire was extinguished by the addition of 8 ml of a solution of 20% chlorobromoethane in spindle oil. Against a 10-gram lithium fire, spindle oil applied at the rate of 6 cm^3/s resulted in a secondary fire but not extinguishment, although 49 ml of a mixture of spindle oil and 20% chlorobromoethane did extinguish the fire. Applied at the rate of 20 or 60 ml/min, spindle oil did not extinguish the fire, but rather produced a secondary fire Against a 100-gram lithium fire, spindle oil did not extinguish the fire, but rather produced secondary burning when applied at the rate of 60 or 120 cm^3/s. However, 155 ml of a mixture of spindle oil and 20% chlorobromoethane, applied at the rate of 120 cm^3/s, did extinguish the fire (Reference 64).

Paraffin Oil. Paraffin oil, applied at 2 cm^3/s against a 1-gram lithium fire, did not extinguish the fire, and secondary burning resulted; however, the fire was extinguished by the addition of 5.0 ml of a solution of 20% chlorobromoethane in paraffin oil (Reference 64).

Petroleum Oil. When applied to a small lithium fire, petroleum oil burned; it lost viscosity upon application to the fire, and resulted in an oil fire. This mixture was regarded as a fair extinguishant (Reference 1).

Petroleum Oil (Five Parts) + Unicel ND (One Part). When applied to a small lithium fire, petroleum oil/Unicel ND (5/1) burned vigorously, and resulted in an oil fire. This mixture was regarded as a poor extinguishant (Reference 1).

Motor Oil No.30 with Graphite. When applied to a small lithium fire, a No. 30 motor oil-graphite mixture reacted vigorously and burned; it thinned out upon application to the fire, and ultimately resulted in but a small oil fire. This mixture was regarded as a reasonably good extinguishant (Reference 1).

Motor Oil No. 30 with Pyrene G-1. When applied to a small lithium fire, a No. 30 motor oil-Pyrene G-1 mixture reacted vigorously and burned, producing an oil fire. This mixture was regarded as a poor extinguishant (Reference 1).

Motor Oil No. 30 with Celite. When applied to a small lithium fire, a No. 30 motor oil-Celite mixture reacted vigorously and burned; it thinned out upon application to the fire, and ultimately resulted in but a small oil fire. This mixture was regarded as a fair extinguishant (Reference 1).

Glycol Derivatives

Diglycol, triglycol, ethyl triglycol, and butyl triglycol, and their mixtures with 20% chlorobromoethane, applied at 2 cm^3/s against a 1-gram lithium fire, did not extinguish the fire, and violent secondary burning resulted in each case (Reference 64).

Phthalate Esters

The results from the use of a variety of phthalate esters against a 1-gram lithium fire are presented in Table 10 (Reference 64).

Adipate and Sebacate Esters

Benzylbutyl Adipate. Benzylbutyl adipate, applied at 2 cm^3/s against a 1-gram lithium fire, did not extinguish the fire, and secondary burning resulted; however, the fire was extinguished by the addition of 8.2 ml of a solution of 20% chlorobromoethane in benzylbutyl adipate (Reference 64).

Benzyloctyl Adipate. Benzyloctyl adipate, 13.7 ml, applied at 2 cm^3/s against a 1-gram lithium fire, extinguished the fire; in addition, the fire was extinguished by the addition of 5.8 ml of a solution of 20% chlorobromoethane in benzyloctyl adipate (Reference 64).

Dioctyl Sebacate. Dioctyl sebacate, 10.1 ml, applied at 2 cm^3/s against a 1-gram lithium fire, extinguished the fire; in addition, the fire was extinguished by the addition of 3.2 ml of a solution of 20% chlorobromoethane in dioctyl sebacate (Reference 64).

TABLE 10. Extinguishing Results of Liquids Against 1-Gram Lithium Fires (Reference

Fluid extinguishant	Flash point, °C	Volume of extinguishant used, cm^3 (flow rate, 2 cm^3/s)	Remarks
Didecyl phthalate	216	Not extinguished	Secondary burning
Didecyl phthalate + 20% CB		7.5	Strong smoke developed
Bis-2-ethylhexyl-phthalate	190	Not extinguished	Secondary burning
Bis-2-ethylhexyl-phthalate + 20% CB		10.0	Strong smoke developed
Diethyl phthalate	156	Not extinguished	Secondary burning
Diethyl phthalate + 20% CB		16.5	Strong smoke generated
Dibutyl phthalate	170	Not extinguished	Secondary burning
Dibutyl phthalate + 20% CB		12.2	Strong smoke generated
Dimethyl phthalate	132	Not extinguished	Secondary burning
Dimethyl phthalate + 20% CB		9.4	Strong smoke developed
Butylbenzylphthalate	190	Not extinguished	Secondary burning
Butylbenzylphthalate + 20% CB		9.8	Strong smoke developed
Dimethylglycolphthalate	174	Not extinguished	Secondary burning
Dimethylglycolphthalate + 20% CB		6.5	Strong smoke developed
Dioctyl phthalate	204	Not extinguished	Secondary burning
Dioctyl phthalate + 20% CB		6.0	Strong smoke developed
Dinonyl phthalate	210	Not extinguished	Secondary burning
Dinonyl phthalate + 20% CB		4.6	Strong smoke developed

CB is chlorobromoethane.

Dibutyl Sebacate. Dibutyl sebacate, applied at 2 cm^3/s against a 1-gram lithium fire, did not extinguish the fire, and secondary burning resulted; however, the fire was extinguished by 7.0 ml of a solution of 20% chlorobromoethane in dibutyl sebacate (Reference 64).

Fatty Acid Esters

A number of fatty acid esters were applied against a 1-gram lithium fire. The results are shown in Table 11.

Sunflower Oil. Friedrich stated that a liquid such as sunflower oil is effective against fires of ≤100 grams of lithium (Reference 64). As seen in Table 11, sunflower oil, 12.5 ml, applied at 2 cm^3/s against a 1-gram lithium fire, extinguished the fire; in addition, the fire was extinguished by the addition of 4.0 ml of a solution of 20% chlorobromoethane in sunflower oil. Against a 10-gram lithium fire, sunflower oil did not extinguish the fire when applied at the rate of 6 cm^3/s, although 26 ml of a mixture of sunflower oil and 20% chlorobromobenzene did extinguish the fire, generating smoke. However, at a flow rate of 20 cm^3/s, 225 ml extinguished the fire; and, at a rate of 60 cm^3/s, 65 ml extinguished the fire. Against a 100-gram lithium fire, 1125 ml of sunflower oil at the rate of 60 ml/s, and 715 ml at the rate of 120 ml/s, did extinguish the fire. Saponification was observed in all of these extinguishant experiments (Reference 64).

TABLE 11. Extinguishing Results of Liquids Against 1-Gram Lithium Fires (Reference 64).

Fluid extinguishant	Flash point, °C	Volume of extinguishant used, cm^3 (flow rate, 2 cm^3/s)	Remarks
Castor oil	229	8.6	Saponification
Castor oil + 20% CB		4.5	Strong smoke developed; saponification
Sunflower oil	230	12.5	Saponification
Sunflower oil + 20% CB		4.0	Strong smoke developed; saponification
Linseed oil	205	17.5	Saponification
Linseed oil + 20% CB		3.2	Extreme strong smoke generated; saponification
Olive oil	225	8.2	Saponification
Olive oil + 20% CB		4.1	Strong smoke developed; saponification
Peanut oil	282	6.2	Saponification
Peanut oil + 20% CB		2.1	Strong smoke developed; saponification
Cod-liver oil	230	12.5	Saponification
Cod-liver oil + 20% CB		3.1	Saponification; strong smoke developed
Neat's-foot oil	243	8.5	Saponification
Neat's-foot oil + 20% CB		3.5	Strong smoke developed; saponification
Bone oil	232	6.5	Saponification
Bone oil + 20% CB		3.0	Strong smoke developed; saponification

CB is chlorobromoethane.

Octyl Stearate. Octyl stearate, 11.6 ml total applied at 2 cm^3/s against a 1-gram lithium fire, extinguished the fire, as did the addition of 5.6 ml of a solution of 20% chlorobromoethane in dibenzyltoluene. Against a 10-gram lithium fire, octyl stearate did not extinguish the fire when applied at the rate of 6 cm^3/s, although 55 ml of a mixture of octyl stearate and 20% chlorobromobenzene did extinguish the fire, generating smoke. At a flow rate of 20 cm^3/s, 225 ml extinguished the fire; applied at the rate of 60 cm^3/s, 150 ml extinguished the fire (Reference 64).

Phosphate Esters

Diphenylxylenyl Phosphate. When applied at 2 cm^3/s against a 1-gram lithium fire, diphenylxylenyl phosphate did not extinguish the fire; secondary burning resulted and strong smoke developed. However, the fire was extinguished by the addition of 5.0 ml of a solution of 20% chlorobromoethane in diphenylxylenyl phosphate (Reference 64).

Trichloroethyl Phosphate. When 15.6 ml (total) of trichloroethyl phosphate was applied at 2 cm^3/s against a 1-gram lithium fire, it extinguished the fire (Reference 64).

Tricresyl Phosphate. Tricresyl phosphate, 21.5 ml total applied at 2 cm^3/s against a 1-gram lithium fire, extinguished the fire, as did the addition of 4.8 ml of a solution of 20% chlorobromoethane in tricresyl phosphate (Reference 64).

Halogenated Organic Compounds

Carbon tetrachloride must never be used as an alkali metal fire extinguishant; carbon tetrachloride reacts with explosive violence with alkali metals (References 1, 35, 36). Also, halogenated hydrocarbons cannot be used against alkali metal fires (Reference 64). For example, Halon 1211, in two 15-pound extinguishers (30 lb. total) was used against a 14.2-pound lithium fire. There was a severe, vigorous reaction; a rapid succession of explosions expelled particles 20 feet from the lithium container, with two overpressure shockwaves at 0.12 and 0.25 psig. It was estimated that 10-15% of the lithium mass was ejected (Reference 65).

Carbon Dioxide

Lithium readily reacts with carbon dioxide and, therefore, CO_2 must never be used as an alkali metal fire extinguishant (References 1, 35, 36). For example, CO_2, in two 17-pound extinguishers, or 34 pounds total, was used against a 14.2-pound lithium fire. A small amount of lithium was expelled from the crucible, and there was no extinguishing effect on the fire (Reference 65).

Polymers

Polyurethane. Lithium fires at 540°C were not extinguished with polyurethane foam (References 35, 36).

Silicone Oil. Silicone oil (AK 250), applied at 2 cm^3/s against a 1-gram lithium fire, did not extinguish the fire, and secondary burning resulted; however, the fire was extinguished by the addition of 6.3 ml of a solution of 20% chlorobromoethane in this silicone oil (Reference 64). When mixed with graphite, silicone oil (GE 9996-1000) underwent little reaction when applied to a small lithium fire. The viscosity was not substantially lowered when this mixture contacted the fire. There was very little secondary fire, and this mixture was regarded as a good extinguishant (Reference 1).

Organic Compositions

Saf (Fire Retardant Paint). Saf, when applied to a small lithium fire, reacted vigorously and burned, giving off heavy black smoke (Reference 1).

Unicel ND (Blowing Agent). Unicel ND, when applied to a small lithium fire, underwent very little reaction, although some frothing was observed. It was regarded as a fair extinguishant (Reference 1).

Celogen (Blowing Agent). Celogen, when applied to a small lithium fire, underwent very little reaction. Excellent frothing was observed, smothering the fire rapidly. Celogen thus is regarded as a good extinguishant. However, when 2.8 pounds of celogen were applied against a 1-pound lithium fire, there was secondary fire and black smoke (Reference 1).

Celogen (20%)/NaCl (80%). When 4.7 pounds of a mixture of celogen (20%) and NaCl (80%) were applied to a 1-pound lithium fire, no foaming or flotation effect was observed. This material did not appear to offer any advantage over straight NaCl (Reference 1).

CONCLUSIONS

The combustion of lithium in air involves the reactions of lithium with both oxygen and nitrogen, and these reactions are influenced by the presence of moisture. This review described the known information regarding these reactions. A lithium fire in air burns brilliantly white and emits substantial aerosol consisting primarily of lithium oxide, hydroxide, and carbonate, while the combustion residue consists of lithium oxide, nitride, and hydroxide.

Many substances were tried as extinguishants for lithium fires; the most effective ones appear to be various forms of carbon.

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